

Development of Advanced Electrolytes and Electrocatalysts for Electrochemical Energy Storage and Conversion Devices

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Kurzzusammenfassung

Die Entwicklung flexibler, skalierbarer und tragbarer elektrochemischer Energiespeichertechnologien ist entscheidend, um in verschiedenen Szenarien eine stabile Energieversorgung zu erreichen. Dabei wurde die Entwicklung fortschrittlicher Materialien für eine nachhaltige und effiziente Energiegewinnung, -umwandlung, -speicherung und -nutzung als Schlüsselpunkt erkannt. Diese Arbeit konzentriert sich auf das Design, die Synthese, die Charakterisierung und die Anwendung neuartiger aktiver Materialien für mehrere EES-Systeme. Die relevanten wissenschaftlich-technischen Hintergründe, die Funktionsprinzipien, der aktuelle Fortschritt und die bestehenden Herausforderungen werden ebenfalls ausführlich erörtert.

Das erste Projekt präsentiert Forschungsarbeiten zu nicht-wasserhaltigen Redox-Flow-Batterien (NRFBs), die als die vielversprechende stationäre EES-Technologie für das modulare, groß angelegte Stromnetz gelten. Ein neuartiger Elektrolyt auf Basis von $(n\text{Bu}_4\text{N})_4[\text{MV}_{13}\text{O}_{33}\text{Cl}]$ ($\text{M} = \text{V}=\text{O}^{2+} \{\text{V}_{14}\}$ or $\text{MgOH}^+ \{\text{MgV}_{13}\} \{\text{MV}_{13}\}$) in Acetonitril wurde auf seine Anwendung als Ladungsträger für nicht-wasserhaltige elektrochemische Energiespeicherung untersucht. Dieses Projekt beschreibt die ersten Untersuchungen der elektrochemischen Eigenschaften des gemischtvalenten $\{\text{MV}_{13}\}$ Clusters und zeigt die Eignung dieser Verbindung als Mehrelektronen-Ladungsträger in symmetrischen NRFBs. Dank ihrer hervorragenden physikochemischen Eigenschaften (hohe Löslichkeit, Stabilität und Nanogröße) zeigten die vorgeschlagenen NRFBs auf Basis des $\{\text{MV}_{13}\}$ Clusters eine bemerkenswerte Batterieleistung. Der zweite Teil untersucht sichere, umweltfreundliche Zink-Luft-Batterien (ZABs), die eine hohe Energiedichte, eine kostengünstige Herstellung und eine Möglichkeit zur Skalierung aufweisen. Die träge Sauerstoffreduktionsreaktion (ORR) und Sauerstoffentwicklungsreaktion (OER) stellen für ZABs in der praktischen Anwendung große Herausforderungen dar. Daher ist die Entwicklung effizienter und wirtschaftlicher bifunktionaler ORR/OER-Elektrokatalysatoren für wiederaufladbare ZABs dringend erforderlich. In diesem Zusammenhang wurde in diesem Abschnitt über atomar dispergierte FeNi-Doppelmetallpaare auf einer stickstoffdotierten Kohlenstoffmatrix mit einer hierarchischen Struktur, die von mehrwandigen Kohlenstoffnanoröhren umhüllt ist, berichtet. Insbesondere wurden Röntgenabsorptionsspektroskopie und hochauflösende Transmissionselektronenmikroskopie eingesetzt, um die atomaren aktiven FeNi-Stellen zu untersuchen. Die elektrochemischen Eigenschaften sowie die Leistung dieses Katalysators in wiederaufladbaren ZABs wurden

systematisch bewertet. Zudem wurde ein neuartiger ultradünner Pd-Metallen-Sauerstoff-Reduktions-Katalysator, dotiert mit atomarem WO_x/MoO_x (bezeichnet als D-Pd M), synthetisiert und charakterisiert. Diese Arbeit zeigt, wie Defekt-Engineering zur Verbesserung der Reaktivität der Elektrokatalysatoren eingesetzt werden kann. Die elektrochemischen Eigenschaften und die praktische Leistung dieses D-Pd M-Katalysators in primären und wiederaufladbaren ZABs wurden detailliert untersucht.

Der dritte Teil untersucht die Entwicklung von Elektrokatalysatoren für trifunktionale Zinknitrat/Nitrit-Batterien (ZNBs), die gleichzeitig eine nachhaltige Energieversorgung, die Elektrosynthese von grünem Ammoniak und den Abbau der $\text{NO}_3^-/\text{NO}_2^-$ Schadstoffe im Abwasser ermöglichen. Im Vergleich zu herkömmlichen Haber-Bosch-Anlagen zeichnet sich dieses ZNBs-Gerät durch eine schnelle dynamische Reaktion und eine dezentrale Herstellung auf Basis lokaler Produktion aus, wodurch das System leichter steuerbar ist, und die Transportkosten und Umweltauswirkungen reduziert werden. In diesem Teil wurde eine selbsttragende, bimetallische, NiCu-modifizierte, 3D-gedruckte Katalysatorelektrode auf Basis von Acrylnitril-Butadien-Styrol für Zinknitrat-Batterien durch ein stromloses Beschichtungsverfahren hergestellt. Die Morphologie, Struktur und Zusammensetzung dieser Elektrode wurden durch eine Reihe von Technologien charakterisiert, darunter Röntgenbeugung, Röntgen-Photoelektronenspektroskopie und Elektronenmikroskopie. Darüber hinaus wurden die katalytische Aktivität, Selektivität und Stabilität der hergestellten Elektrode sowie die Batterieleistung der ZNBs sorgfältig untersucht. Die Ergebnisse zeigten, dass die hergestellten ZNBs eine zuverlässige Energieversorgung und kontinuierliche Ammoniakproduktion ermöglichten. Darüber hinaus wurde ein weiterer Katalysator für die selektive elektrokatalytische Reduktion von Nitrit zu Ammoniak hergestellt. In einem dreistufigen Syntheseverfahren wurden die Rutheniumatome in eine Kupfernanodrahtstruktur eingebaut, die eine beeindruckende elektrokatalytische Aktivität und Selektivität zeigte. Die Integration dieses Katalysators in eine wässrige Zinknitritbatterie bestätigte auch den technologischen Nutzen des Elektrodensystems.

Im Rahmen dieser Studien wurden eine Reihe verschiedener fortschrittlicher Materialien und Methoden diskutiert, wobei die Bedeutung rationalen Designs, gezielter Synthese, modernster Charakterisierung sowie praktischer Anwendungen hervorgehoben wurde. Auf diese Weise wird diese Arbeit dazu beitragen, das aktuelle Verständnis der EES-Technologien zu fördern und ihre weitere universelle Anwendung voranzutreiben.

Abstract

Development of flexible, scalable and portable electrochemical energy storage (EES) technologies is crucial to achieve a stable energy supply in various scenarios, and the innovation in the advanced materials for sustainable and efficient energy harvesting, conversion, storage, and utilization has been recognized as the key points. This thesis focuses on the design, synthesis, characterization and application of novel active materials for selected EES devices. The related background, operating principle, current progress, and existing challenges are comprehensively discussed.

The first project presents research work on non-aqueous redox flow batteries (NRFBs), which is considered as the most promising EES technology for the modular, large-scale electrical grid. A novel electrolyte based on $(n\text{Bu}_4\text{N})_4[\text{MV}_{13}\text{O}_{33}\text{Cl}]$ ($\text{M} = \text{V}=\text{O}^{2+}$ **{V₁₄}** or MgOH^+ **{MgV₁₃}** **{MV₁₃}**) in acetonitrile was explored for application as charge carrier for nonaqueous electrochemical energy storage. This project describes initial investigations into the electrochemical properties of the mixed-valent **{MV₁₃}** cluster, revealing the viability of this compound to serve as multi-electron charge carrier in symmetric NRFBs. Benefiting from its excellent physicochemical properties (high solubility, stability and nano-size), the proposed NRFBs based on **{MV₁₃}** cluster demonstrated remarkable battery performance.

The second part investigates the safe, environmentally friendly zinc-air batteries (ZABs), which have high energy density, low-cost manufacturing and feasibility of scaling up. The sluggish oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) pose great challenges for ZABs in practical application. Thus, developing efficient and economic bifunctional ORR/OER electrocatalysts for rechargeable ZABs is urgently required. In this regard, atomically dispersed FeNi dual-metal pairs on the nitrogen-doped carbon matrix with a hierarchical structure wrapped by multi-walled carbon nanotubes is reported in this section. X-ray absorption spectroscopy and transmission electron microscopy were utilized to identify the FeNi dual atomic active sites. The electrochemical properties as well as rechargeable ZABs performance of this catalyst were systematically evaluated. Furthermore, a novel ultrathin Pd metallene doped with atomic WO_x/MoO_x ORR catalyst was also synthesized and characterized, demonstrating how defects engineering can be used to enhance electrocatalytic activity of the electrocatalysts. The electrochemical properties and practical performance of this catalyst in both primary and rechargeable ZABs were investigated in detail.

The third part explores the development of electrocatalysts for trifunctional zinc-nitrate/nitrite

batteries (ZNBs), which can achieve sustainable energy supply, electrosynthesis of green ammonia and degradation of the $\text{NO}_3^-/\text{NO}_2^-$ pollutant in wastewater simultaneously. Compared with traditional Haber-Bosch plants, this ZNBs device features fast dynamic response and decentralized manufacturing based on local production, making the system easier to control as well as reducing the transport costs and environmental impacts. In this part, a self-supported catalyst bimetallic NiCu modified 3D printed electrode based on acrylonitrile butadiene styrene was fabricated for zinc-nitrate batteries through typical electroless plating. The morphology, structure and compositions of this electrode were characterized by a series of technologies including X-ray diffraction, X-ray photoelectron spectroscopy and electron microscopy. Besides, the catalytic activity, selectivity and stability of the as-prepared electrode and the battery performance of the ZNBs were carefully investigated. The results demonstrated that the as constructed ZNBs enabled reliable energy supply and continuous ammonia production. Furthermore, another catalyst was prepared for selective electrocatalytic reduction of nitrite to ammonia. Through a three-step synthetic route, the ruthenium atoms were incorporated into a copper nanowire structure, which demonstrated impressive electrocatalytic activity and selectivity. The integration of this catalyst into an aqueous zinc-nitrite battery also verified the technological utility of the electrode system.

Through these studies, a range of advanced materials and methods have been discussed, highlighting the significance of rational design, targeted synthesis, state-of-the-art characterization as well as practical applications. In doing so, this thesis will serve to promote the current understanding of EES technologies and push their further universal application.

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List of abbreviations and units

Ah	Ampere hour
°C	Degree Celsius
CE	Columbic efficiency
COFs	Covalent organic frameworks
DACs	Dual-atom catalysts
DFT	Density functional theory
DTPA	Diethylenetriaminepentaacetic acid
EDTA	Ethylenediaminetetraacetate
EE	Energy efficiency
EES	Electrochemical energy storage
ESSs	Energy storage systems
EVs	Electric vehicles
FE	Faradaic efficiency
FT-IR	Fourier transform-infrared
FT-XANES	Fourier-transformed X-ray absorption near edge structure
GDL	Gas diffusion layer
h	Hour
HAADF-STEM	High-angle annular dark-field scanning TEM
HER	Hydrogen evolution reaction
IEMs	Ion exchange membranes
kg	Kilogram
kJ	Kilojoule
L	Liter
LDHs	Layered double hydroxides
M	Molar
mA	Milliampere
MABs	Metal-air batteries
{MV₁₃}	$(n\text{Bu}_4\text{N})_4[\text{MV}_{13}\text{O}_{33}\text{Cl}]$ (M= V=O ₂ ⁺ {V₁₄} or MgOH ⁺ {MgV₁₃})
MOFs	Metal-organic frameworks
NO ₂ ⁻ RR	Nitrite reduction reaction
NO ₃ ⁻ RR	Nitrate reduction reaction

NO _x -RR	Nitrate/nitrite reduction reaction
NRFBs	Non-aqueous redox flow batteries
NRR	Nitrogen reduction reaction
OCP	Open circuit potential
OER	Oxygen evolution reaction
ORR	Oxygen reduction reaction
PGMs	Platinum group metals
POMs	Polyoxometalates
RFBs	Redox flow batteries
RHE	Reversible hydrogen electrode
S	Siemens
SACs	Single-atom catalysts
SEM	Scanning electron microscopy
SOC	State of charge
TEM	Transmission electron microscopy
TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy
TMCs	Transition metal carbides
TMHs	Transition metal hydroxides
TMOs	Transition metal oxides
UV-Vis	Ultraviolet-visible
V	Volt
V _{cell}	Cell voltage
VE	Voltage efficiency
VRFBs	All-vanadium redox flow batteries
Wh	Watt hour
WT-XANES	Wavelet-transformed X-ray absorption near edge structure
XANES	X-ray absorption near edge structure
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
ZABs	Zinc-air batteries
ZNBs	Zinc-nitrate/nitrite batteries

1. Introduction

1.1 Energy storage and conversion technologies

In recent decades, the worldwide demand for energy has risen exponentially along with social and economic development, and the security of energy is regarded as one of the most essential pillars for ensuring basic social welfare and sustainable economic growth across the globe.^[1,2] Presently, the majority of energy supplies (more than 85%) is generated from non-renewable energy sources such as petroleum, natural gas, and coal.^[3] The overreliance on these conventional fossil fuels for energy generation has had devastating impacts, including air pollution, climate change, water/soil contamination and CO₂ emissions. It is worth mentioning that the finite fossil fuels cannot be replenished after consumption, indicating the exhaustion of nonrenewable energy sources is possible.^[4] Concerning the ever-increasing energy demand coupled with environmental threats and the eventual depletion of fossil fuels, the deployment of more sustainable and renewable energy sources with low/free-carbon emissions is essential. Currently, the implementation of renewable geothermal, tidal, wind and solar energies are considered as clean and green alternatives for fossil fuels. However, the harvesting of these renewable energy sources is inherently tricky as solar and wind energy are dependent on light intensity and wind speed respectively, which also require huge space for the devices' installation and operation. Furthermore, there is a large energy loss during the transportation over far-away places through the electricity grid. Undesirable intermittent availability and poor flexibility of these renewable energy sources are posing critical challenges for their direct integration into the power system. Thus, the deployment of efficient energy storage systems (ESSs) is of great importance to reducing the gap between energy generation and consumption, improving the efficiency of the power supply system, and ultimately managing fluctuations and mismatches in energy demands and supply.^[5]

There is a broad range of energy storage and conversion technologies available including mechanical, electrical, chemical, thermochemical and electrochemical storage systems. Basically, energy storage devices cope with two important missions: 1) production of clean and stable power, enabling high power-density supercapacitors or high energy-density batteries. 2) transmission of bulky energy from renewable generation to energy demand in real-time.^[6] However, major challenges related to their technical operability, durability, efficiency and high cost must be overcome to meet the requirements of low-carbon economics. Electrochemical energy storage (EES) systems are arguably the most desirable energy storage

and conversion technologies, owing to their continuous energy conversion processing without limitations in integrated devices, high manufacturing flexibility, adaptable miniaturization and portability, minimal environmental effects, as well as easier to scale up. EES technologies are generally categorized into batteries, fuel cells and supercapacitors. Specifically, the batteries and fuel cells are characterized as high specific energy devices, while the supercapacitors have relatively high specific power. Albeit considerable efforts have been dedicated to developing EES devices which hold both high energy- and power-densities then hopefully achieve the poised promise of EES technology,^[7] but the traditional battery systems are still suffering from limited energy density, poor rate capacity, worrying safety and undesirable durability, such as lithium-ion batteries. Generally, it is still a long-standing challenge to fulfill the variable energy demands in different conditions, particularly in the large-scale storage and portable electronics practice.^[8]

A landscape of research shifting from conventional EES devices to next-generation storage systems including their active materials innovations are meticulously happening with aims to find the competent EES devices that can achieve the universal utilization of renewable energy sources. Despite significant progresses have been made in the development of next-generation EES technologies in recent years, there is no single ideal device that can satisfy all possible energy demands.^[9] Thus, identifying the distinctive properties and technical characteristics of specific next generation EES devices are of great importance to leverage their advantages to be targeted for specific applications. Redox flow batteries (RFBs) are generally recognized as a desirable candidate for large-scale storage electricity grid, benefiting from the unique virtue of decoupling power and density. Metal-air batteries such as zinc-air batteries (ZABs) possess inherent safety and high energy density with theoretical specific energy, granting ZABs exciting potential for electric vehicles (EVs). Besides, zinc-nitrate/nitrite batteries (ZNBs) as a trifunctional device are considered as promising portable plants to produce value-added green ammonia from nitrate/nitrite in wastewater with sustainable energy supply. Nonetheless, the practical application of these EES devices all require advanced engineering, a revolutionary development of active materials, and a fundamental understanding of the working principles and technical characteristics of the EES devices.

1.2 Redox flow batteries

Among all the EES systems, redox flow batteries (RFBs) are one of the most distinctive devices, since RFBs store energy in redox-active, soluble, charged molecules dissolved in liquid electrolyte, and the electrochemical conversion reactions normally do not involve structural change of the active species. This unique configuration grants RFBs several merits over traditional EES devices, including long durability, fast responsiveness, low cost, and minimal environmental impacts. Most notably, RFBs have the advantage of decoupled power and capacity delivery which means that the battery power is dependent on the surface area of the electrode, while the battery capacity is determined by the volume of the energy-carrying electrolyte. In addition, RFBs also possess the special ability to be fully charged to 100% state of charge (SOC) and completely discharged to 0% SOC without ill side effects, which is impossible for other EES technologies.^[10] These distinctive properties make RFBs a highly powerful EES technology for large-scale stationary energy storage, and can be flexibly constructed to achieve any desired power and capacity output through rational modular design. Hence, the RFBs are considered among the most promising devices due to their lack of location limitations and the ease of being scaled to customized sizes, making them well-suited for large-scale stationary energy storage.

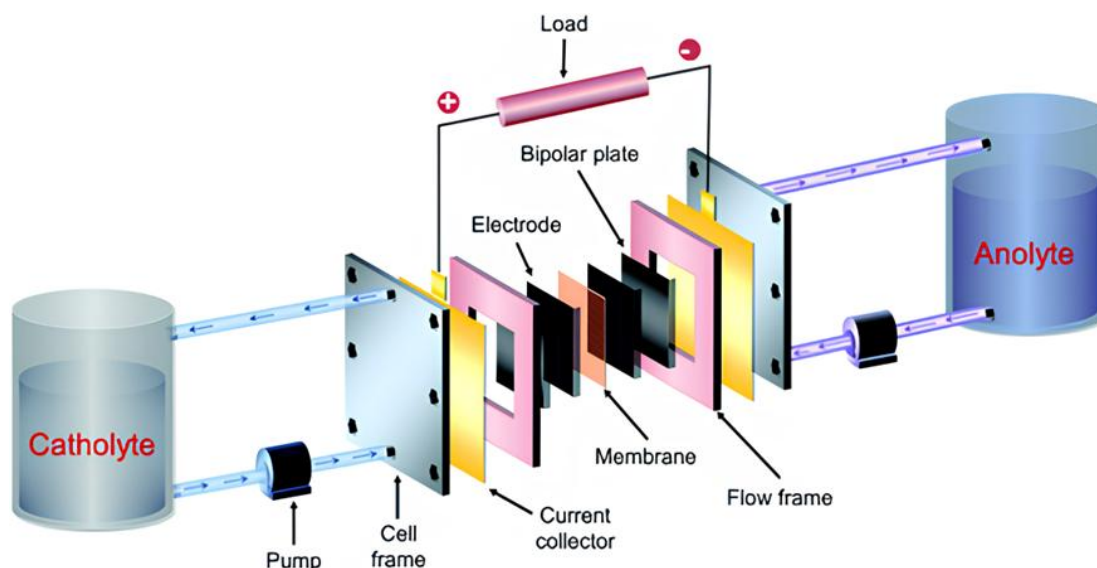


Figure 1. Schematic illustration of a typical redox flow battery.^[11] Reprinted with permission. Copyright 2015, Royal Society of Chemistry.

A simplified schematic structure of an RFB is shown in Figure 1, the generic components of the RFBs are two electrolyte reservoirs for anolyte and catholyte respectively, membrane, electrodes, and pumps. Electrolyte reservoirs are tanks where the electrolyte is stored. Membranes serve as separators to avoid the self-discharge resulting from the mixture of anolyte

and catholyte during the operation. The electrochemical energy conversion reactions take place on the surface of the electrodes (anode and cathode), and pumps are required to circulate the electrolyte flowing through the electrodes. During the charging process, the catholyte is reduced and the anolyte is oxidized, electrical energy is converted into chemical energy and stored in the electrolyte; the catholyte is oxidized and the anolyte is reduced during the discharging process while chemical energy is converted into electric energy.^[12]

Basically, achieving low-cost, high efficiency and long cycling life is of great importance for the large-scale application of RFBs. There are three essential components of RFBs system: membrane, electrode and active species in electrolyte, all of which have significant impacts on the performances of RFBs system. The following sector provides a comprehensive overview of these crucial components, their development and challenges in the realm of RFBs are also summarized.

1.2.1 Essential components of RFBs

1.2.1.1 Membrane

The membrane is a vital part of the RFBs system, its primary function is to separate the anolyte and catholyte inside the reaction chamber, avoiding electrolyte crossover contamination as well as preventing short circuits of the battery. The properties of the membrane can greatly affect the RFBs' performance in many aspects.^[13,14] Firstly, the membranes should enable the transfer of supporting electrolyte ions, maintaining the basic charge balance between the anolyte and catholyte. Simultaneously, the crossover of active species through the membrane could result in unexpected self-discharge, capacity degradation and coulombic efficiency loss, which should be forbidden. Secondly, the resistance for charge carrier ions across the membranes also impacts voltage efficiency (VE, the ratio of discharge voltage to charge voltage) in the RFBs system. Thus, membranes with high ionic conductivity are required to achieve higher power densities and optimal performances of RFBs. Thirdly, the membranes must possess good chemical stability to withstand the electro-oxidization and electro-reduction during long-term cycling operations. Moreover, membranes are supposed to be resistant against all reactions with the electrolytes (organic, highly acidic or basic electrolyte) since the membrane is thoroughly exposed to the electrolyte. Fourthly, the membranes should have good mechanical properties, such as excellent tensile and puncture strengths and low swellability, which are also critical to ensuring the longevity of RFBs during the practical operation. Lastly, the cost of membranes is

still a significant challenge in RFBs design. For many RFB systems, the membrane is the most expensive single component, comprising 30–40% of the whole reactor's cost. In summary, the desirable membranes for RFBs should have high selectivity for charge carriers and high ionic conductivity, excellent chemical and mechanical stability, and low cost (as shown in Figure 2).

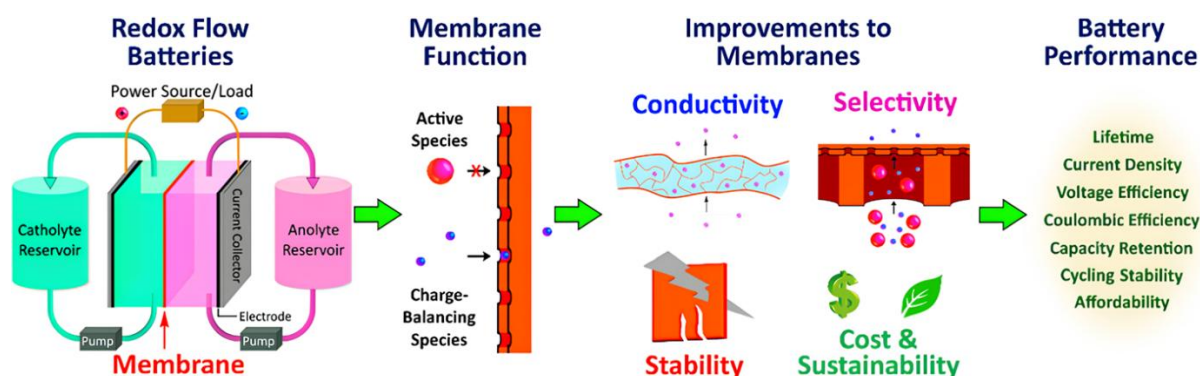


Figure 2. Function and requirements of membrane for RFBs.^[14] Reprinted with permission. Copyright 2021, American Chemical Society.

There are two main categories of membranes for RFBs: porous membranes and dense membranes. Porous membranes have been widely investigated for RFB applications since they were first reported by Li and co-workers in 2011.^[15] Porous membranes consist of numerous micropores that serve as ion transport channels, which serve for the exchanges of small particles between the anolyte and catholyte compartments. Since active species are usually larger than the supporting electrolyte ions, the selectivity is mainly controlled via the size sieving mechanism. Basically, an ideal porous membrane for RFBs should exhibit high ion conductivity and selectivity by meeting the following criteria: 1) an appropriate pore size with a narrow distribution to selectively transport supporting electrolyte ions while preventing crossover of active species; 2) an interconnected pore structure and high porosity to create numerous ion transport channels, thereby reducing resistance; and 3) high chemical and mechanical stabilities along with low cost, to ensure a long-lasting and cost-effective RFBs membrane. Additionally, the performance of porous membrane is highly dependent on their morphology and pore chemistry. Based on the origin of the pores, porous membranes for RFBs can be classified as either artificial or intrinsic.^[13] The former one is generally fabricated with flexible or linear polymers, of which the molecular chains are usually densely packed in the solid state. Therefore, specialized membrane fabrication techniques are necessary to create pores, with the nonsolvent-induced phase separation method being the most well-known. Moreover, it is important to note that porous membranes do not rely on fluoride ion exchange membrane, thereby avoiding

concerns related to chemical stability. In contrast, the dense membrane materials comprise intrinsic pores (e.g., metal-organic frameworks (MOFs) and polymers with intrinsic microporosity), with the nature of these pores being determined by the materials themselves. However, it should be realized that liquid electrolytes require dense membranes ironically conductive as they have a highly dense microstructure. Besides, the crossover contamination of active species in the electrolyte would result in the RFBs capacity degradation and coulombic efficiency losses during the cycling operation. On the other hand, dense membranes rely on ion hopping or migration to transport supporting electrolyte ions and achieve charge balance.^[16] According to whether the dense membrane materials contain fixed ion exchange groups (covalently bonded charged groups) or not, ion transport channels in dense membranes are divided into the charged channels and the uncharged ones. These dense membranes incorporate functional ion exchange groups within their structure and can be composed of dense ceramics or ion exchange membranes (IEMs).

In general, most IEMs for RFBs are homogeneous membranes made of polymers consisting of hydrophobic backbones and hydrophilic sidechains bearing fixed ion exchange groups.^[17] For IEMs with such molecular structures, microphase-separated structures can form spontaneously due to the polarity difference between the backbones and the sidechains. Reverse micelles formed by the aggregation of ion exchange groups could also prompt the formation of charged channels, particularly their size and selectivity. More specifically, larger channel dimensions enhance ionic conductivity but may compromise selectivity. A typical example of this is the fact that vanadium ions are more effectively blocked by anion exchange membranes than by cation exchange membranes, due to the Donnan repulsion effect caused by fixed cations in IEMs. Furthermore, the properties of the charged channels also strongly affect the chemical stability and mechanical strength of IEMs. For instance, when the channel size and selectivity allow active species to easily enter, the chemically vulnerable sites become more accessible and are more likely to be attacked by active material ions, resulting in chemical degradation. Besides, the ion deposition and dissolution in the channels can weaken the mechanical strength of IEMs. In addition, since homogenous IEMs are generally dense with uniform morphology, the ion transport channels are predominantly controlled by the molecular structure of polymers. In recent years, there has been an increasing focus on regulating charged channels through molecular design. Several IEMs that have been employed in RFBs, with the most common being the Nafion membrane,^[18] a perfluorosulfonic acid membrane that includes both hopping

and vehicular modalities for the conduction mechanism. Benefiting from its high ion conductivity and stability, Nafion membrane has been widely used for many RFBs systems in the industry. However, reducing its relatively high cost remains a significant challenge.

1.2.1.2 Electrode

Electrode design is essential to achieving high performance and efficient RFBs, primarily because the electrode is the battery component where the energy conversion reactions occur (as shown in Figure 3). Chemical composition, surface area and morphology of porous electrodes are crucial to exposing more active sites for electrode reactions of the electrolyte. In addition, the electrode contributes to the system polarization through not only the ohmic polarization, but also through activation polarization and concentration polarization, all of which affect the RFBs' overall performance. Typically, the desirable porous electrodes for high-power RFBs should possess the following properties: 1) high surface activity and high specific surface area for electrochemical reactions to minimize the activation loss; 2) large hydraulic permeability and wettability for efficient electrolyte transportation to minimize the concentration loss and pumping work; 3) excellent electronic conductivity to minimize the ohmic loss. Currently, the most commonly used materials for RFB electrodes are carbon fiber-based materials (graphite felts, carbon felts, and carbon papers) for their high electronic conductivity, high hydraulic permeability, chemical and electrochemical stability, as well as economic costs.^[19] However, challenges associated with the application of these materials include low specific surface area and poor electrochemical activity, limiting the RFBs to operate at a relatively low current density ($\sim 50 \text{ mA cm}^{-2}$ for aqueous all-vanadium RFBs).^[20]

Therefore, it is of great importance to appropriately design and modify the electrode materials for RFBs system. Significant efforts have been made to minimize energy losses from the electrode, including activation losses, ohmic losses, and other associated losses. One strategy is to introduce functional groups onto the carbon fiber surfaces to create abundant active sites and increase its hydrophilicity. It was found that the oxygen functional groups introduced by simple acid or thermal treatment can effectively catalyze the oxidization and reduction reactions on the electrode. Secondly, increasing the specific surface area of the electrode is also an important method to decrease the mass transfer losses. For the conventional carbon fiber-based electrodes, the voids between the fibers are several tens of micrometers in diameter, which construct efficient transport pathways for active species and facilitate high hydraulic permeability, which in turn reduces concentration losses. However, the specific surface area of

such electrodes is extremely low ($0.1\text{--}3\text{ m}^2\text{ g}^{-1}$) because of the large pore sizes.^[21] The straightforward approach to fabricating the carbon fiber electrode with smaller pores doesn't really work since it would heavily decrease its hydraulic permeability, resulting in concentration polarization and extra pump work. Hence, coating high-area materials (such as carbon blacks, carbon nanotubes, and graphene) onto carbon fiber materials is a common strategy to increase the specific surface area without sacrificing too much permeability of the electrodes.

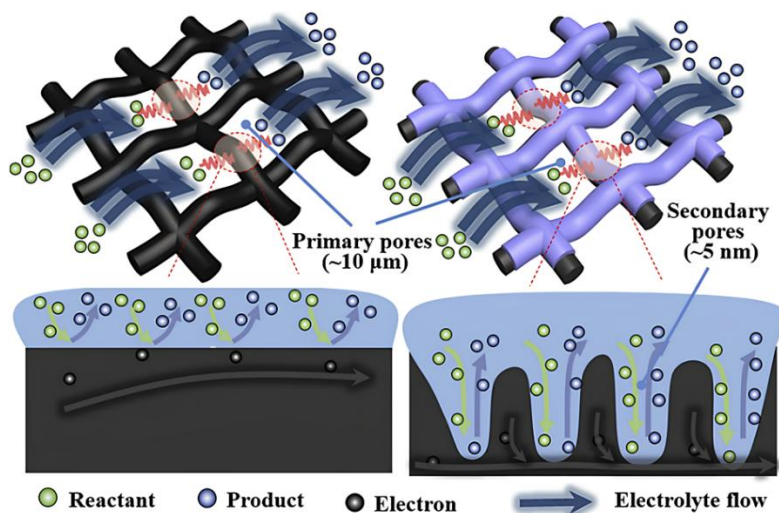


Figure 3. The schematic of the conventional carbon-fiber-based electrode and the proposed dual-scale porous carbon electrode.^[21] Reprinted with permission. Copyright 2016, Elsevier.

Additionally, another strategy to reduce the polarization and enhance the kinetics is to modify electrodes with electrocatalysts. Nobel transition metal-based catalysts, such as Pt, Au, Ir, and Pd have been investigated as efficient electrocatalysts for RFBs. However, the commercial application of these precious metal catalysts is limited due to their scarcity, high cost, as well as their unspecific catalytic activity.^[22] In contrast, non-precious transition metal-based materials show great promise as electrocatalysts for RFBs because of their excellent activity and relatively low cost. With unique electron structure, the transition metal is easier to accept or lose electrons, making it more accessible to interact with the reactants. Consequently, the non-precious transition metal-based catalysts with abundance, low cost, and impressive catalytic effect are highly promising as future electrocatalysis for RFBs. Over the past few decades, significant efforts have been devoted to the development of these electrocatalysts, such as TiO_2 , Mn_3O_4 , MoO_2 , CeO_2 , WO_3 , etc.^[20] Nevertheless, there are several challenges of non-precious transition metal-based electrocatalysts. The main problems are the frustrating conductivity and limited exposed active sites. Meanwhile, nanostructured, non-precious

transition metal-based electrocatalysts tend to agglomerate due to their high surface energy, which can significantly reduce the exposed active specific surface area. Furthermore, the weak binding force between the catalysts and the electrode cannot effectively resist the erosion of the flowing electrolyte, impairing the stability and lifetime of the battery. Therefore, rational designing of stable, high performance non-precious transition metal-based electrocatalysts is urgently needed to improve the performance of RFBs.

1.2.1.3 Electrolyte

The electrolyte is the most crucial component of RFBs, consisting of active species, supporting electrolyte and solvent media, which influence the battery's overall performance (Figure 4).^[23] The theoretical battery voltage is determined by the equilibrium potentials of active species in the cathodic and anodic half-cells, while the actual open-circuit overpotential is also affected by the inner resistance of a RFB and the electrochemical kinetics of redox-active materials. It is worth noting that the energy density of RFBs is dependent on the number of electrons transferred in the electrode reactions, the concentration of active species in the electrolyte, and the potential difference between the cathodic and anodic active molecules. Meanwhile, the physical properties of the solvent, such as the electrochemical window, pH value, viscosity, polarity, and dielectric constant, all have huge impacts on the RFBs' performance. Another key requirement for the commercialization of RFBs is minimizing cost. It is important to note that grid-scale application of the RFBs face challenges due to high manufacturing costs and volatile price of raw materials. Besides, the operating maintenance always involves expensive procedures.^[24] Generally, the active species, solvent, and supporting electrolyte should be taken into account together to develop an RFB with high energy efficiency and coulombic efficiency.

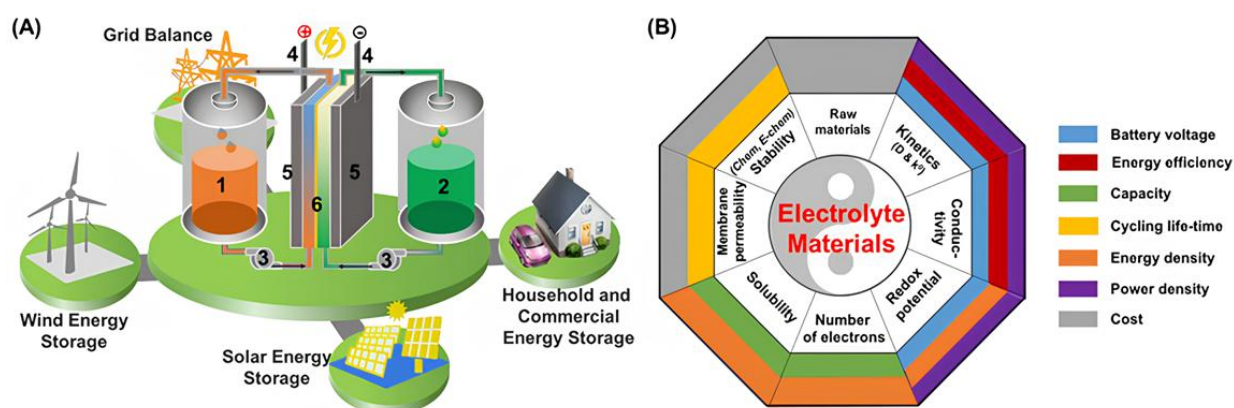


Figure 4. (A) Graphic representation of diverse applications and cell components of RFBs. (B) Correlation diagram of physicochemical properties of electrolyte materials and performance metrics of RFBs.^[23] Reprinted with permission. Copyright 2019, American Chemical Society.

The early research on the RFBs mainly focused on metal ions and halogen ions.^[25] Benefiting from the simple chemistry and high solubility, metal ions are considered as the most popular anodic candidates for aqueous RFBs. On the other hand, halogens are intensively researched as cathodic active species due to their highly reversible redox reactions and relatively low molecular weight. The most studied halogens are bromine and iodine, both of which exhibit redox potentials within the electrochemical window of water. The recent development of aqueous RFBs involves a wider range of redox species and most of which still fall in the category of transition metal ions and halogen ions, such as $\text{VCl}_3/\text{VCl}_2$, $\text{Br}^-/\text{ClBr}_2^-$, $\text{Ce}^{3+}/\text{Ce}^{4+}$ and others.^[26] Among them, all-vanadium redox flow batteries (VRFBs) are the most widely researched RFB systems to date. In the VRFBs, related vanadium couples ($\text{V}^{2+}/\text{V}^{3+}$ and $\text{VO}^{2+}/\text{VO}_2^+$) are used as the redox-active species to comprise anolyte and catholyte which dissolved in an acidic aqueous solvent (as shown in Figure 5). During the charging of the VRFB, VO^{2+} is oxidized to VO_2^+ in the catholyte, whereas V^{3+} is reduced to V^{2+} in the anolyte. The discharge reactions occur in the opposite direction, the redox reactions of the $\text{VO}_2^+/\text{VO}^{2+}$ and $\text{V}^{2+}/\text{V}^{3+}$ redox couples can be described as follows.

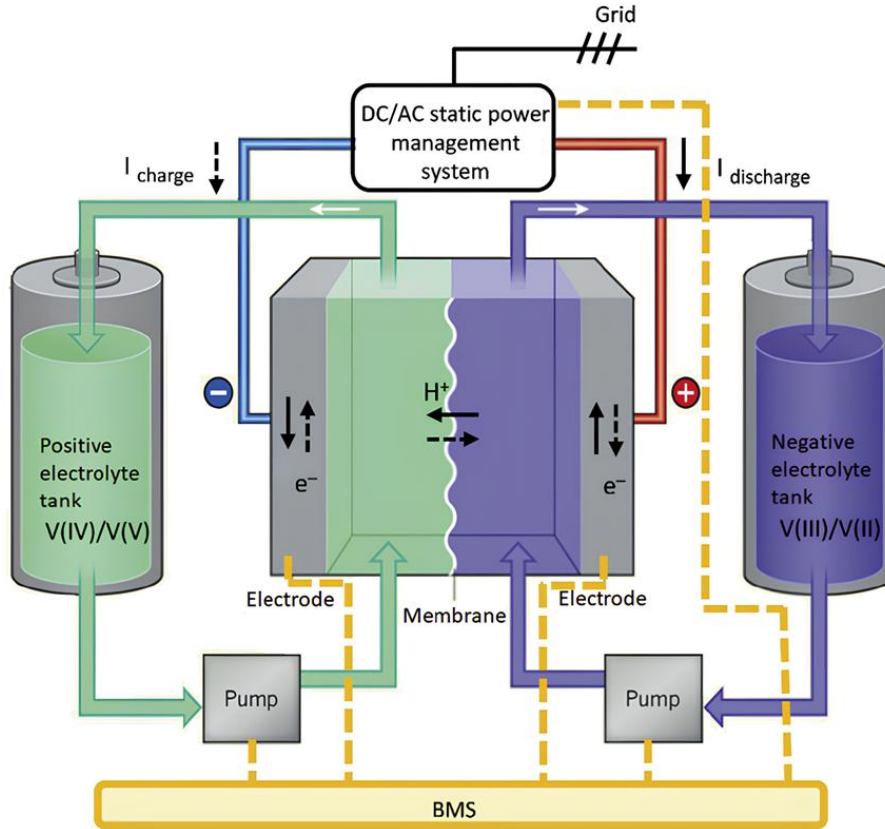
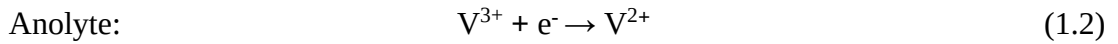
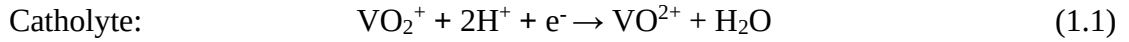


Figure 5. (A) VRFB and main components scheme.^[27] Reprinted with permission. Copyright 2020, Elsevier.

These VRFBs have demonstrated high solubilities up to 3 M and the energy density is around 30 Wh L⁻¹ with a long system life of about 15-20 years.^[28] Despite these merits, the VRFBs still face several challenges. For example, the cost of a VRFB system is \$500-\$600 per KWh which makes it less attractive when compared to other EES devices. Meanwhile, the toxicity of soluble vanadium and the strong corrosiveness of VO²⁺/VO₂⁺ redox couple further impede the widespread adoption of VRFB.^[29]

Another category of redox-active species with excellent promise for achieving high energy density and long lifetime RFBs includes metal coordination complexes,^[30] which possess the properties of both metal ions and organic ligands. For metal coordination complexes, the transition metal ion usually acts as the charge transfer center, while the redox potential can be tuned with different ligands. Particularly, charges can also be stored in ligands besides the metal center in complexes with “redox-non-innocent ligands”.^[31] By rational designing organic ligand scaffolds and metals, it is feasible to tune the properties of these complexes, such as the solubility, stability, kinetics and redox potential. Additionally, the metal coordination complexes can undergo multielectron transfer redox reactions owing to the various oxidation states of the metal center.^[32] Compared with transition metal ions, the crossover contamination through the membrane is inhibited due to the larger molecular size of metal complexes. The early research of metal coordination complexes for RFBs can be dated back to the 1980s.^[30] Recently, metal complexes of iron, cobalt, vanadium, cerium, chromium, and ruthenium with various ligands, such as ethylenediaminetetraacetate (EDTA), phenanthroline, triethanolamine and diethylenetriaminepentaacetic acid (DTPA), have been investigated as active species for RFBs application.^[32] According to the ligand types, metal coordination complexes are commonly classified into metal-ligand complexes and metallocene, both of which can be categorized into aqueous and nonaqueous RFBs depending on the solvent media of the electrolytes.

On the other hand, the large-scale deployment of inorganic species or their coordination complexes for RFBs is potentially limited by the scarcity of metal elements. Besides, the toxicity and environmental risks of some metals (such as cobalt and chromium) also raise concerns during long-term RFBs operation. In contrast, metal-free redox-active compounds with abundant sources in nature, offer a promising direction for reducing cost for RFB systems. These organic redox-active compounds also capitalize on the advantages of structural diversity,

good tunability of redox potential and solubility, as well as eco-friendliness. The first successful RFB based on organic molecules was reported by Li *et al.* in 2011,^[33] using combination of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and N-methyl-phthalimide as catholyte and anolyte respectively with acetonitrile as solvent. Over the last decade, a series of active species in anolytes have been researched, such as anthraquinone and phenothiazine. For the active species in catholyte, molecular frameworks like viologen have garnered significant attention as potential candidates for RFB applications.^[31] Even though their impressive properties hold great promise for RFBs, the organic redox-active materials still suffer from multiple challenges including: 1) low solubility; 2) poor electrochemical stability of radicals; 3) low redox potential; and 4) low ionic conductivity, all of which prevent these organic redox-active materials from being used in commercial applications. To overcome these limitations, significant efforts in molecular engineering have been dedicated to the rational design and targeted synthesis of derivatives based on these core structures. These modifications aim at enhancing the solubility and the chemical and electrochemical stability of redox-active species, paving the way for the development of high-energy-density RFBs.

Apart from the above-discussed materials, there is a wide range of family members of active species for the RFB systems. The redox-active macromolecules, polymers as well as ionic liquids with high molecular weights and large sizes, are emerging as promising candidates as active species for RFB systems.^[34,35] Their unique structures and properties significantly reduce crossover contamination, potentially eliminating the need for specific membranes and thereby lowering manufacturing costs. However, the high viscosity of macromolecule/polymer/ionic liquids-containing solution slows down the mass transport of redox species and decreases the ionic conductivity of electrolytes, hindering further advances in the cell performance of RFBs. Furthermore, polysulfide/sulfur also draws considerable attention for its high theoretical capacity, non-toxicity and low cost.^[36] The aqueous polysulfide/bromine RFBs utilize Na₂S in the anolyte, coupled with NaBr as an active species in the catholyte. Na₂S is abundant and cost-effective which also exhibits high solubility in aqueous solvents.^[37] However, despite the high solubility of polysulfide in solvent media, the solid precipitation from the insoluble short-chained polysulfides formed during long-term operation still poses a critical issue for this RFB.

Overall, the development of robust active species with excellent electrochemical properties that are derived from cheap, commercially available raw materials through simple synthetic

processes, remains a long-standing challenge for the practical application of RFB systems.

1.2.2 Key performance merits for RFBs

The unique configuration of RFBs makes them distinctive from both conventional and unconventional EES technologies, it requires different standards for assessment of the practical performance and electrochemical behaviors of RFBs^[38]. Generally, several figures of merit are utilized to quantify the practical performance of the RFBs, which makes the comparison between RFBs and other EES devices plausible. The most important performance merits include open circuit potential (OCP), specific capacity, energy density, columbic efficiency (CE), voltage efficiency (VE), energy efficiency (EE), capacity retention as well as rate capacity. Notably, all the performance merits should always be referred to the state of charge (SOC), which represents the fraction of active materials converted to their charged form.

Firstly, as the crucial components, the active species in electrolytes fundamentally determine the OCP of RFBs, the larger potential difference between cathode and anode redox couples contributes to a higher OCP for RFB systems. Since the charge carrier of the RFBs are dissolved or suspended in the electrolyte, their theoretical capacity in coulombs is related to the number of electrons stored or released by the charge carrier (n) as well as the concentration (C_{active}) and volume (Vol_{active}) of either the anolyte or catholyte at a 50% SOC. In this context, the theoretical capacity of RFBs can be calculated according to:

$$capacity = nFC_{active}Vol_{active} \quad (1.3)$$

Where F is Faraday's constant ($9.648 \times 10^4 \text{ C mol}^{-1}$).

The energy density (E) of the RFB device can be determined by integrating the cell voltage (V_{cell}) versus capacity by volume or weight, the cell voltage can be considered as a constant at a certain SOC. In this case, the theoretical energy can be calculated according to the following equations:

$$E = V_{cell}capacity \quad (1.4)$$

$$E = nV_{cell}FC_{active}Vol_{active} \quad (1.5)$$

The ratio of the total output of the electrical charge during discharge versus the charge stored after charge is defined as coulombic efficiency (CE), as shown below:

$$CE = Q_{Dchg}/Q_{Chg} \quad (1.6)$$

Here, the Q_{Dchg} and Q_{Chg} represent the total electrical charge (in C or Ah) during the discharge and charge processes, respectively. There are multiple contributors to coulombic efficiency losses including crossover contamination of active species and side electrode reactions. The coulombic losses can be reversible or irreversible depending on the electrode reaction mechanisms and the nature of the electroactive species.

The ratio of cell voltage during discharge and charge processes is defined as the voltage efficiency (VE), shown in equation 1.5.

$$VE = V_{Dchg}/V_{Chg} \quad (1.7)$$

Where the V_{Dchg} and V_{Chg} mean the average cell voltage during discharge and charge processes, respectively at a certain time or specific SOC. For the VE determination, the current density is typically set as a constant parameter. At any fixed current density, there are multiple sources of overvoltage including kinetic, ohmic, and mass transport losses, all of which can result in decreased voltage efficiency. All three sources of losses increase along with increasing current density, but not with the same dependence.

The voltage and coulombic efficiencies reflect the losses resulting from the key composites at the single-cell level, including kinetic, ohmic, mass transport, crossover contamination, and side reaction losses. However, there are other contributors of energy losses in the context of the overall RFB systems. For example, parasitic losses (temperature control, pumping losses, and other auxiliary equipment) are generally recognized as important reasons for energy losses and extra expenses. It introduces additional energy consumption such as shunt currents, irregular voltage distribution, and uneven electrolyte distribution among electrodes for the stacks of multi-cell RFB systems. Generally, the EE can be calculated according to the following equation:

$$EE = CE \times VE \quad (1.8)$$

Here, CE represents coulombic efficiency, VE represents voltage efficiency.

In addition, the specific capacity retention is an important metric in evaluating the stability and robustness of a particular RFB systems in delivering the desired energy output at a constant current density. One long-standing challenge for RFB systems is the relatively rapid capacity degradation during long-term cycling operation. The major reasons for specific capacity fading include the undesired crossover of solvent and/or active species through the membrane,

degradation of crucial cell components, undesired side reactions as well as the precipitation of active species. Moreover, rate capability is also a very important figure to assess the performance of RFB system. It is crucial to achieve stable performance at different current densities and meet the various requirements in different scenarios. Generally, the rate capability is highly dependent on the active materials, supporting electrolytes and their kinetics and mass transport at the electrodes.

1.2.3 Classification of RFBs

According to different battery configurations, RFBs can be classified into different categories. Regarding the RFBs that are constructed based on the metal-free organic redox active species or metal ions/complexes redox active species in electrolytes, RFBs can be divided into organic and inorganic RFBs, respectively. Apart from the conventional all-soluble liquid RFBs, the semi-solid RFBs indicate that RFBs can also utilize the solid and/or suspended active species (for example, Li metal as the negative electrode and a suspension electrolyte-electrode).^[39] For the semi-solid RFBs, the electrode reactions always involve the phase changes of active species. The following section focuses on the two major categories, symmetric and non-aqueous RFBs, examples and their merits/demerits are discussed as well.

Symmetric RFBs are based on the same redox active species in both anolyte and catholyte, which undergo different redox processes for electrode reactions.^[40] Thus, the active species for symmetric RFBs should possess multiple redox states and the corresponding redox potentials should be accessible in a wide electrochemical window, enabling efficient and continuous RFB operation. Generally, symmetric RFB systems are regarded as a better alternative to asymmetric RFBs, because the symmetric ones can greatly mitigate crossover contamination issues during the long-term cycling operation. Besides, the capacity degradation of symmetric RFBs could be recovered by refreshing the anolyte and catholyte. Up to now, most of the reported symmetric RFBs mainly are based on the organic redox active compounds due to their excellent electrochemical tunability and high solubility. Chen and coworkers reported a symmetric RFBs based on 5,10,15,20-tetraphenyl porphyrin as a bipolar redox-active material, which demonstrated a high volumetric capacity of 8.72 AhL⁻¹ with a high voltage of 2.83 V and excellent cycling stability.^[41] Aziz *et al.* presented a symmetric all-quinone aqueous RFB based entirely on earth-abundant elements which exhibit an OCP of 1.04 V with a high capacity of 163 mAh g⁻¹.^[42] However, it has been found that the synthesis procedure of these organic

materials must be performed under an inert atmosphere or even in an argon or nitrogen-purged glovebox to avoid side reactions with oxygen from the ambient atmosphere. The need for such stringent synthesis conditions combined with the use of noble metal catalysts adds to the complexity of the synthetic process. Thus, some special organic redox active species such as radicals still cost much more than common inorganic electroactive species, which is not a cost-effective strategy to achieve cost-effective RFBs.^[31]

In contrast, the asymmetric RFBs use two different redox active species in anolyte and catholyte, respectively, possessing the potential to maximize the battery voltage by employing appropriate redox couples in the electrolyte.^[43] These asymmetric RFBs allow for independent engineering of the two different redox active materials to attain suitable properties for either the anolyte or catholyte, while facing the major hindrance of the crossover contamination problem. There is a broad range of reported asymmetric RFBs, including metal ions, and metal coordination complexes, to organic redox active compounds as discussed above.

Moreover, RFBs generally fall into two categories with different solvent media, distinguished as aqueous RFBs and non-aqueous RFBs.^[44] Selection of the solvent for electrolyte is very crucial in the battery performance as the solubility of the electroactive material in the solvent directly influences the energy density of the RFBs. Besides, the physicochemical properties of the solvents should be considered when selecting the appropriate solvent media for active species and supporting electrolytes. Additionally, the supporting electrolyte also determines the type of membrane/separator to be used, to ensure compatibility between the solvent and supporting electrolyte. Aqueous flow batteries were discovered initially as vanadium redox flow batteries, using an aqueous concentrated acid electrolyte. The aqueous RFB systems use water as the main solvent and a highly soluble salt (for example, NaCl, NaOH and HCl) as a supporting electrolyte. Utilizing aqueous electrolytes for RFBs is propitious in many ways including 1) guaranteed safety due to their non-flammability; 2) cost-effectiveness; 3) environmental friendliness; and 4) high conductivity and rapid ion transport rates. Based on the above merits, aqueous RFBs are regarded as the most promising, cost-efficient and durable RFB technology for practical application.^[45] On the flip side, the battery voltage of aqueous RFBs is limited by the narrow electrochemical stability window of water, which is below 1.5 V. In addition, aqueous RFBs only operate under a limited range of temperatures, hindering the implementation in specific scenarios. Furthermore, the incompatibility of water with

hydrophobic organic compounds also impacts the electrochemical performance of the RFB systems.

Alternatively, by operating in a non-aqueous regime, many organic solvents possess larger electrochemical windows (up to 4 V), which provide great opportunities for active species to realize high-voltage applications in RFB systems. Moreover, organic solvents are great choices for the redox active compounds which are insoluble in water. Furthermore, organic solvents also enable non-aqueous RFBs (NRFBs) capable of operating at low temperatures.^[46] The original concept of NRFBs was first proposed by Singh in 1984.^[47] Then Matsuda *et al.* demonstrated an experimental NRFB based on tris(bipyridine) ruthenium (II) tetrafluoroborate complex $[\text{Ru}(\text{bpy})_3(\text{BF}_4)_2]$ in acetonitrile (CH_3CN) with tetraethylammonium tetrafluoroborate (TEABF_4) as the supporting electrolyte in 1988.^[48] The expected OCP of this system is approximately 2.6 V, which is higher than those of most aqueous RFBs. During the past few decades, significant advances have been achieved in developing NRFBs for attaining high energy density and power density applications with a huge number of redox-active species being investigated. However, the state-of-the-art NRFBs still have significantly high internal resistance, resulting from the low ionic conductivity of both the electrolyte and the membrane.^[49] Hence, it is of great importance to lower the electrolyte resistance through advanced electrode design and accelerate the reaction kinetics. Additionally, improving the ionic conductivity and reducing the thickness of the membrane also make sense to reduce the internal resistance of NRFBs. On the other hand, the cyclability and durability of NRFBs are still suffering from the poor electrochemical reversibility and stability of the active species in electrolytes. Thus, developing inexpensive redox active species for symmetric NRFB devices can enhance the overall performance of RFBs, paving the way for safer, more affordable, stable, and flexible practical applications in the future.

1.2.4 Polyoxometalates (POMs) as active species for RFBs

Polyoxometalates (POMs) are anionic molecular metal oxides based on high-valent transition metals (e.g., V, Mo, W), which possess great potential to meet the demands of several cutting-edge technologies. The POMs frameworks can be presented by the general formula: $[\text{M}_m\text{O}_y]^{n-}$ for isopolyanions and $[\text{X}_x\text{M}_m\text{O}_y]^{n-}$ for heteropolyanions, where X is a hetero atom, usually a main group element (P, Si, Ge, As), and M is an addenda atom, usually a d-block element with high oxidation state (V^{V} , Mo^{VI} or W^{VI}).^[50] POMs are always negatively charged, and the

negative density mainly depends on the elemental composition and the molecular structure. Generally, POMs consist of three or more transition metal oxyanions with shared oxygen atoms, forming a large closed three-dimensional framework. The metal atoms that make up the framework are called addenda atoms, usually group V or VI transition metals (such as V, Nb, Ta, Mo, W, etc.) in high oxidation states. One or more heteroatoms (such as P, Si, Ge, etc.) are enclosed in the center of the framework, and these heteroatoms share adjacent oxygen atoms with transition metal atoms. Following the development of POMs chemistry, several types of structures have been found, and there are six fundamental POMs structures which are most widely used in research 1) Anderson; 2) Lindqvist; 3) Waugh; 4) Wells-Dawson; 5) Keggin; and 6) Silverton, which are the most representative and important compounds in the POMs family (as shown in Figure 6). These structures can be distinguished by the ratio of the addenda atoms to the hetero atoms as follows: Keggin and Silverton structures have a 1:12 ratio, Dawson and Waugh have a 1:9 ratio, and Anderson has a 1:6 ratio and Lindqvist has a 6:19 ratio. Apart from these abovementioned plenary structures, the lacunary POMs species can be obtained through the hydrolytic removal of one or more metal sites from Keggin or Dawson anions, resulting in so-called lacunary POMs (such as $[\text{SiW}_{12}\text{O}_{40}]^{4-} \rightarrow [\text{SiW}_{11}\text{O}_{39}]^{8-} + \text{“WO}^{4+}\text{”}$), in which empty vacancy sites are available for further functionalization with the addition of new metal ions.^[51]

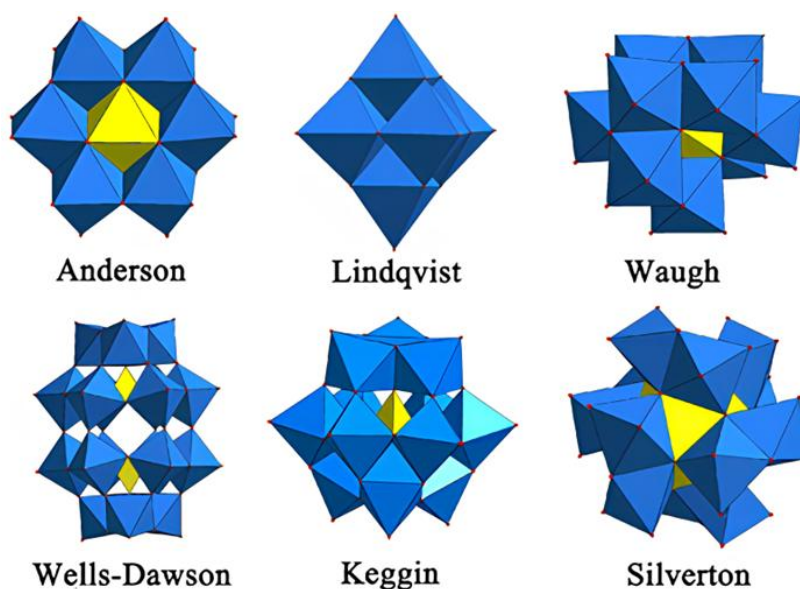


Figure 6. Six typical structures of POMs: Anderson, Lindqvist, Waugh, Wells-Dawson, Keggin, and Silverton.^[52] Reprinted with permission. Copyright 2023, Royal Society of Chemistry.

POMs can achieve metal and/or counter-cation exchange without structure decomposition, the derivatives not only expand the overall structural versatility of POMs, but also enhance their

physicochemical properties.^[53] Due to the uniqueness and versatility of special structures, POMs possess a wealth of physicochemical characteristics, including: 1) good thermal stabilities, large molecular sizes (around 1 nm), and relatively high molecular weights; 2) highly concentrated, often non-toxic (Mo, W), non-volatile, and soluble in various solvents such as water, ethanol, acetone, acetonitrile; 3) superior redox properties. Benefiting from its multiple metal centers, POMs are capable of reversibly accepting and releasing multi-electron through redox reactions. By adjusting the structure and composition of POMs, the redox properties can be easily tuned; 4) possibly functionalized by organic ligands to obtain various organic/inorganic hybrid materials and effectively improve physicochemical properties. Notably, POM clusters have been used as active materials in numerous fields, ranging from catalysis to clinical medicine. In particular, POMs exhibit enormous promise for practical applications in the energy-related realm, including electrocatalysis, photocatalysis and energy storage/conversion devices (such as supercapacitors, fuel cells and RFBs). The multi-electron redox properties, excellent stability, high solubility, tunable redox potential, and customizable structure make POMs highly promising for RFB application, as well as exhibiting significant potential in addressing challenges related to renewable energy storage.^[54] Over the past few years, RFBs based on POMs have emerged as one of the hotspots in research, and a series of advanced RFBs have been reported (as shown in Figure 7).^[55]

The earliest research work on RFBs based on POMs was conducted by Sun and colleagues in 1997, they studied an asymmetric aqueous RFB with Keggin POM $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ as anolyte active species and $\text{Fe}^{3+}/\text{Fe}^{2+}$ as catholyte active species.^[56] Later, Xiang and coworkers reported an aqueous RFB utilizing $\text{H}_6[\text{CoW}_{12}\text{O}_{40}]$, which demonstrated reversible transfer of three electrons per cluster species, and enabled a symmetric RFB operation.^[57] Subsequently, the Lu group changed the counter cations ($\text{Li}^+/\text{Na}^+/\text{K}^+/\text{H}^+$) of heteropoly acid cluster and found $\text{H}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$ exhibited high solubility of 0.74 M, the number of electrons transferred and the respective redox potentials were tuned by substituting the heteroatom template in the Keggin-type POM cluster, which endows two one-electron redox process and enables this clusters a promising application in RFBs.^[58] Furthermore, Matson et al. investigated a series of NRFBs based on Lindqvist POMs $[\text{V}_6\text{O}_7(\text{OR})_{12}]$ ($\text{R}=\text{CH}_3, \text{CH}_5$) as well as their derivatives with different heteroatoms and alkoxide ligands.^[59] Very recently, Chen and coworkers investigated a symmetric RFB based on $[(\text{CoO}_4)\text{W}_{12}\text{O}_{36}]^{6-}$ ($\{\text{CoW}_{12}\}$) cluster with the pH-controlled operating voltage output. They utilized DFT calculation to disclose the proton-coupled electron

transfer process of the $\{W_{12}O_{36}\}$ shell in thermodynamically and kinetically, explaining the negative shift of the redox potential of $\{W_{12}O_{36}\}$ shell as the pH increased from 1 to 4. Notably, the stable redox potential of $\{CoW_{12}\}$ cluster leads to an extension of the voltage window from 1.31 to 1.56 V. Consequently, the cycling measurement of the symmetrical RFB shows a low specific capacity degradation rate.^[60]

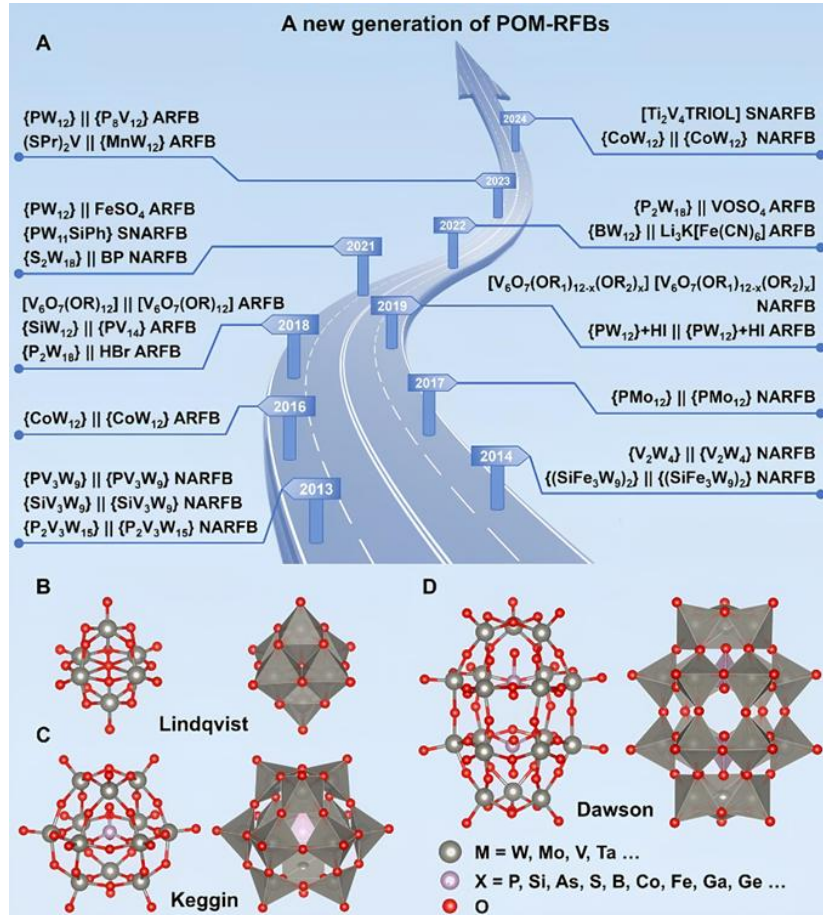


Figure 7. Fig. 1. (A) Development history of POM-RFBs. (||: Separator symbol for the anode and cathode of RFB. ARFB, A: Aqueous. NARFB, NA: Non-aqueous.) Ball-and-stick representation for POM structures of (B) Lindqvist type, (C) Keggin type, and (D) Dawson type.^[55] Reprinted with permission. Copyright 2024, Elsevier.

However, these previously reported POMs-based RFBs (both aqueous ones and non-aqueous ones) only allow no more than four-electron transfers over different oxidation states, requiring asymmetric configuration and/or different concentrations of electrolyte to handle charge imbalances. Thus, it is still challenging to develop POMs for RFBs to enable multi-electron storage and release in symmetric systems with high operation voltage. In addition, developing the redox POMs species with high solubility, good electrochemical reversibility and stability, are vital for future research to enhance the overall performance of RFBs for their large-scale implementation to enable our society's sustainable future.

1.3 Zinc-air batteries

1.3.1 Metal-air batteries

Metal-air batteries (MABs) have received ever-increasing research interest as an emerging EES technology for the practice of portable electronics, electric vehicles, and stationary power plants, particularly owing to their high energy density, availability, safety, and low cost.^[61] Unlike other conventional EES batteries where the reagents are stored within the isolated cells, MABs utilize oxygen from the atmosphere at the cathode, thus they are consequently considered as a hybrid of fuel cells and batteries integrated into an open cell system. Due to the air-breathing structure without the bulky cathode chamber, MABs have high theoretical energy densities (energy per unit weight) in the range of 1353-11429 Wh kg⁻¹ (calculated by the common Zn-, Al-, Mg- and Li-air batteries), which are about 3-30 times higher than that of lithium-ion battery.^[62] In general, a MAB consists of a metal anode saturated in an appropriate electrolyte (aqueous or nonaqueous), a porous air cathode absorbing the surrounding air, as well as a proper separator mechanically disconnecting the anode and cathode (as shown in Figure 8). The metal anode can be alkali metals (e.g., Li), alkaline earth metals (e.g., Mg), earth-abundant metals (e.g., Al), or first-row transition metals (e.g., Zn) with good electrochemical equivalence.^[63]

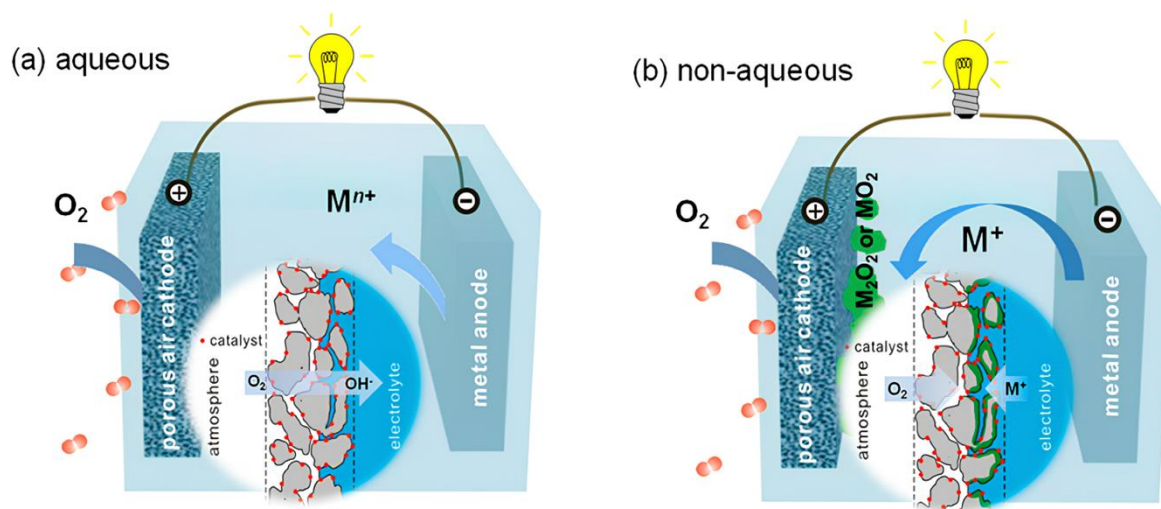
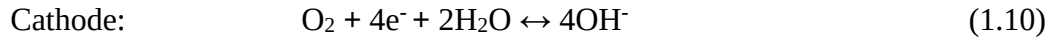
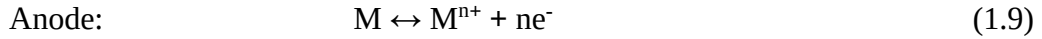


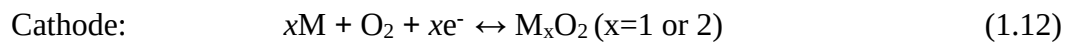
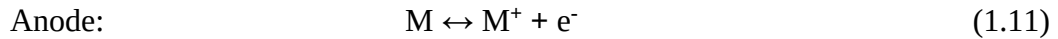
Figure 8. Schematic configuration and operation principle for (a) aqueous and (b) nonaqueous metal–air batteries.^[62] Reprinted with permission. Copyright 2017, American Chemical Society

Regarding the electrolyte of MABs, there are two categories of aqueous and nonaqueous systems that undergo different electrochemical reactions.^[64] The aqueous electrolyte is of particular interest in terms of high operation safety, great ionic conductivity of approximately 1 S cm⁻¹, low cost, and environmental benignity.^[65] The working principle of aqueous metal-air batteries is illustrated as following equations:



Notably, Li, Na, and K in the metallic form are highly sensitive to water and oxygen, which are incompatible with aqueous electrolytes. In contrast, Mg, Fe, Zn and Al-based MABs are, to some extent, compatible with aqueous electrolytes since their surfaces can be passivated by the corresponding metal oxides and hydroxides.^[66] However, due to the low reduction potentials (e.g., -2.372 V for Mg and -1.662 V for Al), they have the problems of fast self-discharge via hydrogen evolution reaction (HER), resulting in severe parasitic corrosion on Mg and Al electrode surfaces.^[67] Moreover, Mg and Al electrodeposition in aqueous electrolytes is thermodynamically impossible, which limits their broad application. Furthermore, Fe-air batteries present a very low practical energy density of about 60-80 Wh kg⁻¹ and therefore cannot be utilized for high-energy demanding applications. Zn-air batteries (ZABs), on the other hand, are rechargeable and have great stability in an aqueous media. Benefiting from its greater volumetric energy density (6136 Wh L⁻¹) and cell voltage (1.66 V), ZABs appear to be more viable for large-scale practical applications than other MABs.^[68]

Because metallic Li, Na, and K are plagued by their inherent instability with water in the aqueous electrolyte, the MABs based on these metals must utilize non-aqueous electrolytes to enable stable operations.^[69] The corresponding working principle is depicted as below:



Compared to aqueous MABs, nonaqueous MABs involve more complicated fabrication processes and face even more serious challenges including: 1) the inherent safety issue attributed to the flammable organic electrolytes; 2) the low ionic conductivity of around 1-10 mS cm⁻¹; 3) the high cost due to the rigorous manufacturing requirements; and 4) the potential environmental pollution.^[70]

1.3.2 Zinc-air batteries

ZABs are well-known as one of the most ideal battery technologies for next generation EES devices because of the following merits: 1) high theoretical energy density (1086 Wh kg⁻¹); 2) abundant reserves of zinc metal (Zn is the 4th most abundant in the earth crust, which is about 300 times greater than that of Li); 3) good rechargeability (only Zn-air batteries can be electrically rechargeable in aqueous electrolyte, while the Al- and Mg-air batteries need to be

recharged via mechanically changing the metal anodes that cannot be directly reduced from metal ions to metallic form in the aqueous electrolyte); 4) low manufacturing cost and good feasibility for commercialization; 5) high safety (enables ZABs compatible with portable/wearable electronic devices and hybrid/electric vehicles); and 6) eco-friendliness. Over the past few decades, both primary and secondary ZABs have received substantial attention from academia and industry. Especially, the rechargeable ZABs are regarded as one of the most promising EES devices for future large-scale applications.^[71]

As shown in Figure 9, a typical rechargeable ZAB consists of four essential components: Zn metal anode; an alkaline aqueous electrolyte; a separator; and an air cathode. Regarding the working principle of ZABs, the discharging process of ZABs involves the coupling of the cathodic oxygen reduction reaction (ORR) and Zn anodization reaction. Typically, O_2 diffuses into the air cathode, and then is reduced to OH^- ions, the generated OH^- ions migrate to the Zn anode. Meanwhile, metal Zn is oxidized to release Zn^{2+} ions, which then combine with the migrated OH^- ions to form $[Zn(OH)_4]^{2-}$. When the concentration of $[Zn(OH)_4]^{2-}$ in the electrolyte reaches a saturated state, it will decompose into ZnO products. However, the insulating properties ZnO make it more difficult for the Zn anode to further release Zn^{2+} ions, which decreases the effective contact interface between the electrolyte and Zn anode, thereby reducing the overall efficiency of the battery.

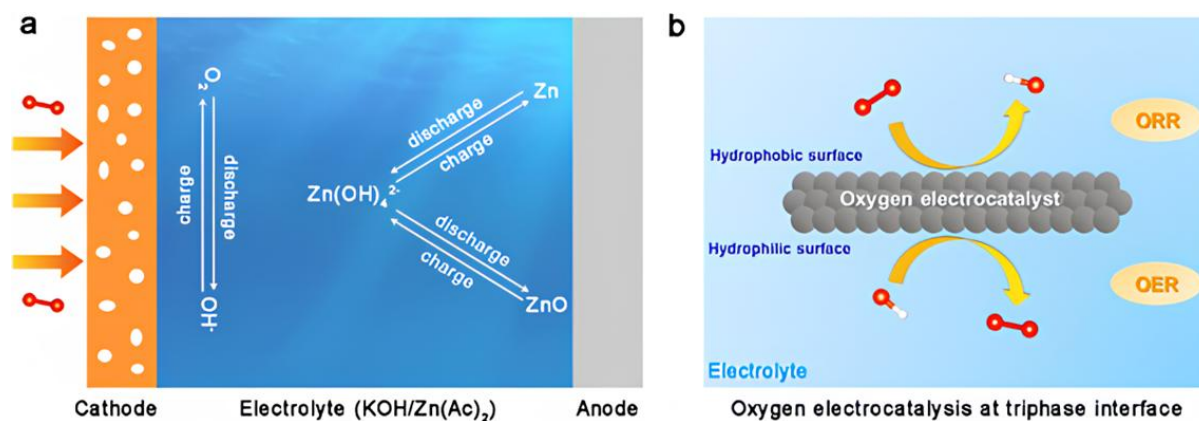
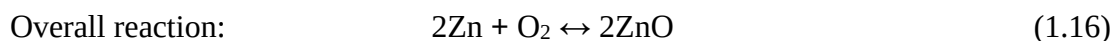
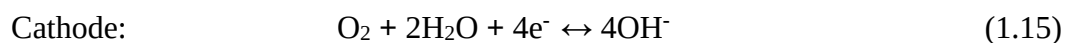
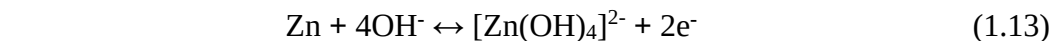


Figure 9. (a) Schematic illustration of the reaction mechanisms for alkaline ZABs. (b) Schematic operation principle of bifunctional oxygen electrocatalysis at the triphase reaction interface.^[72] Reprinted with permission. Copyright 2023, Royal Society of Chemistry.

During the charging process, it involves the oxygen evolution reaction (OER, the reverse reaction of the ORR) and its thermodynamic equilibrium potential is 1.23 V vs RHE. The corresponding charge process is as follows: OH^- ions are oxidized to O_2 at the cathode and the

Zn^{2+} ions in the electrolyte are reduced to metallic Zn and deposited on the anode surface.^[72]

The complete discharge/charge processes of ZABs can be illustrated as the below equations:



1.3.2.1 Zn anode

In the case of sufficient O_2 at the air cathode, the Zn anode is critical in determining the overall capacity of the ZABs. An ideal Zn anode should exhibit high material utilization and high efficiency, thereby giving rise to outstanding capacity and reversibility. Hence, the Zn deposition/dissolution reaction is as important as the ORR/OER performance in affecting the overall performance of rechargeable ZABs. Especially, one major reason for performance loss of ZABs during long-term cycling is the unstable interface caused by the passivation of the Zn anode.^[73] The unstable transition between Zn and ZnO in electrolytes also leads to critical issues, which seriously affect the stable operation of ZABs. In general, the Zn electrode is primarily restricted by the four following issues including 1) dendrite formation; 2) shape change; 3) surface passivation; and 4) hydrogen evolution. It is worth noting that these four factors often interact with one another and impact the battery performance over time, eventually resulting in battery failure. Up to now, the long-term reversibility of Zn in most electrolytes is still far from satisfactory. Thus, the implementation of Zn anode stabilization strategies to achieve high-rate and long-term cycling ZABs has been a hot topic in the realm of ZABs.^[74]

Zinc dendrites refer to sharp and needle-like metallic protrusions that formed under certain conditions (e.g., high current density) during the ZABs charging process. Theoretically, the dendritic morphologies result from the inhomogeneous electrodeposition of Zn during the charging process, while the Zn species in the electrolyte are reduced and subsequently redeposited on the surface of the Zn electrode. These needle-like dendrites could even puncture the separators and directly contact the air cathode, causing a short circuit. In addition, these Zn dendrites can fracture and disconnect from the Zn electrode surface, thus giving rise to losses in ZABs capacity.^[75] Several methods have been explored to solve zinc regeneration problems, including 1) designing a porous electrode to inhibit the growth of zinc dendrites; 2) adjusting the orientation of the ZABs (horizontal orientation gives better deposit quality in terms of

compactness and uniformity, which affects the deposited zinc morphology); 3) flowing electrolytes is also beneficial to obtain a more uniform zinc deposit; 4) adding alcohols and acetates into the electrolyte prevents the transformation of zincate into ZnO.^[76,77]

The improvement of the performance of ZABs has been studied by increasing the surface area of the zinc anode since finer-sized zinc particles can react more efficiently. Especially, the Zn anode with a larger surface area is favorable to increase discharge performance at high flowing rates. Increasing the Zn anode surface also inhibits the formation of the insulating layer (ZnO), enhancing the utilization efficiency of the zinc. Conventional zinc anode consists of zinc powder and polymer binder, which exhibited a limited specific discharge capacity (less than 60 % of theoretical value) resulting from the frustrating electronic conductivity of passive interface.^[73] Besides, the rechargeability of the ZABs is greatly decreased by this local dendritic growth of zinc. Therefore, the morphology engineering of porous zinc electrodes is an effective means to address these problems. For example, Long, et al. reported zinc sponge anode with a porous monolithic three-dimensional structure, demonstrating a high utilization efficiency of zinc metal of 90 % in a primary ZAB.^[78]

Moreover, the corrosion rate of zinc anode also increases along with the more exposed interface to the alkaline electrolyte. Normally, zinc corrosion rate is not fast compared with other metals used as anode in MABs. However, the reduction potential of zinc is more negative than hydrogen, which spontaneously leads to hydrogen gas evolution on the surface of the zinc anode. During the anodic discharge process of the ZABs, the side reaction of H₂ evolution is particularly problematic, causing capacity loss and eventually reducing the lifespan of the ZABs.^[79] Many strategies have been utilized to restrain the self-corrosion of Zn electrodes, such as alloy engineering, surface coating and introducing additives. It was reported that the Zn alloy with Ni and In, which have high hydrogen evolution overvoltage and effectively shifts the hydrogen evolution potentials to more negative values.^[80] Another approach is the coating of the Zn anode with other materials (e.g. Al₂O₃), the coating layer is believed to protect the zinc surface from directly contacting the alkaline electrolyte which prevents the Zn anode from side reactions in the cell.^[81] Introducing additives (e.g. zinc oxide, silicon dioxide, and surfactants) is also a solution to overcome the undesirable hydrogen evolution.^[82]

1.3.2.2 Electrolyte

As a medium of ionic migration during charge/discharge processes, the electrolyte's conductivity affects the ohmic resistance and overall performance of ZABs. The physicochemical properties of electrolytes are closely associated with the solvation and transporting behaviors of cations/anions. An ideal ZAB electrolyte should have the following features: 1) high solubility and fast diffusion capability of O_2 ; 2) wide electrochemical window; 3) low volatility and flammability; 4) stable electrolyte-electrode interface layer; and 5) good wettability.^[83] There are mainly three types of electrolytes that can be used in ZABs: aqueous alkaline solution, ionic-liquid and solid-state electrolyte. Generally, highly concentrated aqueous alkaline electrolytes (e.g., potassium hydroxide (KOH) or sodium hydroxide (NaOH)) are used for most ZABs to inhibit the anodic passivation and to increase the solubility of Zn species in the electrolyte. Aqueous KOH solutions are usually preferable to NaOH solutions due to their higher oxygen diffusion coefficients, lower viscosity and higher ionic conductivity. The solubility of Zn species in 1 mol L⁻¹ KOH is limited to ca. 1 mol L⁻¹, but the solubility increases at higher KOH concentrations. Therefore, 6 M KOH is employed in most research work on ZABs. Some additives are added to the electrolyte to solve problems associated with the Zn anode, including dendrite formation, Zn corrosion and hydrogen evolution as mentioned above. However, aqueous electrolytes can easily permeate the air cathode, causing air electrode flooding and blocking the pores for air diffusion. Besides, KOH in the electrolyte can react with CO_2 in the air and then precipitate as K_2CO_3 in the air cathode, increasing the electrolyte resistance. Moreover, the aqueous electrolyte can evaporate gradually during long-term operation, especially in low-humidity conditions, shortening the lifespan of ZABs.^[84]

As such, room-temperature ionic liquids and solid-state electrolytes have been developed as a replacement for aqueous electrolytes in ZABs. Ionic liquids are salts in a liquid state, consisting of large organic cations and anions.^[85] The wide electrochemical window and high thermal stability make ionic liquids good candidates as electrolytes in various batteries. They exhibit low vapor pressure and are, therefore, not easily vaporized in an open battery system. Zinc dendrite growth can also be suppressed by using ionic liquids as electrolytes. However, their high intrinsic viscosity and low ionic conductivity seriously limit their application in ZABs. Besides, the ORR and OER processes rely on the diffusion of oxygen and the transfer of OH^- , which cannot proceed easily in a pure aprotic ionic liquid electrolyte.

On the other hand, solid-state electrolytes, such as hydroponics gel electrolytes can increase the performance of ZABs and lifespan, as well as minimize water loss.^[86] Solid-state electrolytes normally use gel polymers as the framework to provide support for the conductive KOH solution, the ionic conductivity of these solid-state electrolytes can be as high as 0.3 S cm^{-1} at room temperature, which is close to the conductivity of 6 M KOH aqueous electrolyte. Notably, solid-state electrolytes are more compatible with portable or flexible ZABs since they can change their shapes with different battery designs and will not leak like aqueous electrolytes. In addition, they can also inhibit the dendritic growth of the Zn electrode during the charging process. So far, a series of KOH-based gel electrolytes have been fabricated to make solid-state electrolytes for ZABs. Different polymers such as polyvinyl alcohol, polyethylene glycol, polyvinylpyrrolidone, etc. served as gelling agents have been investigated.^[87] However, the disadvantages of solid-state electrolytes come from their poor interfacial interaction with electrodes, generating a high interfacial resistance and significantly reducing the reaction current. Particularly, solid-state electrolytes also serve as separators in ZABs, but their poor mechanical strength might result in an internal short circuit. Furthermore, the high intrinsic viscosity and low ionic conductivity of solid-state electrolytes also limit their application in ZABs.

1.3.2.3 Separator

Separators are essential to prevent short circuits of the ZABs cell, and selectively transport hydroxide (OH^-) ions between the air cathode and Zn anode.^[88,89] Thus, to guarantee the safety and long-term reliability of the ZABs, an ideal separator have the following properties: 1) chemically inertness in a concentrated alkaline electrolyte; 2) high ions selectivity to minimize the crossover of zincate ($[\text{Zn}(\text{OH})_4]^{2-}$) ions; 3) high ionic conductivity to reduce the ohmic loss; 4) a wide electrochemical window that exceeds the working potential range of ZABs (0.8 to 2.4 V); 5) excellent mechanical robustness to deal with the possible perforation by Zn dendrite growth; 6) cost-effectiveness in manufacturing. Most of the separators currently used in ZABs are porous membranes and anion exchange membranes, which have been adapted from Li-ion and nickel batteries.

Despite the relatively good chemical stability and low costs of these commercial porous membranes, such as Celgard 4560 and Celgard 5550 (Celgard LLC), the significant crossover of $[\text{Zn}(\text{OH})_4]^{2-}$ species from the Zn electrode to the air cathode during the discharging process

has been reported to increase cell polarization and result in capacity fading of the ZABs.^[88] This problem can be addressed by introducing an ion-selective function material to the separators, forming Zn and mixed-phase deposits in the surface layer. This ion-selective function is normally achieved by coating a commercial separator with a barrier layer. For example, an ionic liquid-induced copolymer was coated on a PP membrane, which showed a 96% reduction in zincate ion crossover.^[90]

As safer and environmentally benign OH^- conductors, anion exchange membranes (AEMs) can achieve directional and fast ion transport via nanochannels. The discharge capacity of the ZABs was increased by six times when the anion exchange membrane was used instead of Celgard separators. The A201 membrane is a mature commercial AEM, but its implementation in ZABs is severely hampered by its low water retention and poor ionic conductivity.^[91] AEMs can enhance the stability of the air cathode and make the three-phase interface more stable. Chen for the first time prepared porous alkaline AEMs with high flexibility and high conductivity, which were made of functionalized nanocellulose. Compared to the A201 membrane, these AEMs had excellent conductivity of OH^- ions, good water retention capacity in nanopore structure, and low anisotropic swelling property, which improved the discharging capability and cycling stability of ZABs. Wang and colleagues constructed hierarchically nanostructured AEMs through the nanoconfined polymerization of a dual-cation ionic liquid within a 3D porous cationic matrix.^[92] The reinforced architecture impregnated with highly conductive poly-ionic liquids in the robust networks simultaneously achieved both high ionic conductivity of 286.5 mS cm^{-1} and high mechanical robustness. The abundant OH^- on the matrix surface promoted the rapid conduction of OH^- through the Grotthus mechanism. In poly-ionic liquids, the OH^- ions are conducted by the vehicle mechanism due to their extremely high hydrophilic and water-retaining performance. The combination of the two conduction mechanisms endowed the AEMs with ultra-high ionic conductivity. However, the relatively more expensive cost of these separators is a challenge for large-scale practical applications.

1.3.2.4 Air cathode

The performance and energy efficiency of rechargeable ZABs are also greatly affected by the air cathodes, which are responsible for both ORR during discharging and OER during charging over the ZABs' operation. It is worth mentioning that, compared with the Zn electrode reactions, the air cathode reactions have a larger energy barrier that needs to be overcome.

Generally, a typical air cathode serves a variety of functions including providing O₂ diffusion channels, enhancing ion transport and electron transfer, facilitating oxygen electrochemical catalytic activity, etc.^[72,93] To achieve these purposes, four important surface/interface properties of the air electrode are required: 1) sufficient reaction area is essential for electrocatalysis. Electrocatalysts with a large specific surface area can offer enough exposed active sites for catalyzing OER/ORR, while an air electrode with sufficient reaction area can provide pore channels for efficient mass transfer and oxygen diffusion at the three-phase zone, and load enough electrocatalyst as well; 2) high electrical conductivity of the electrocatalyst and air electrode, which facilitating the charge transfer process and reducing electrochemical polarization; 3) efficient bifunctional electrocatalysts with excellent stability and activity, reducing the reaction energy barriers for ORR and OER; 4) Fast mass transfer capability of the air electrode can endow adequate oxygen and ions for oxygen electrocatalysis, reducing the concentration polarization during the reaction process.

Typically, an air electrode consists of a hydrophobic gas diffusion layer (GDL) and a hydrophilic catalyst-loaded layer. The GDL of ZABs should fulfill the following functions: 1) provide a physical substrate for catalyst loading; 2) facilitate the rapid diffusion of oxygen to the catalyst; 3) prevent electrolyte leakage; and 4) provide a conductive channel for electrons. Thus, the desirable GDL should be very porous and hydrophobic and have efficient gas diffusion capability, high electrolyte repellency, good mechanical integrity, and excellent electrical conductivity, as well as electrochemical/chemical stability in strong alkaline electrolytes in ZABs. In addition, the degree of hydrophobicity affects the polarization behavior of the ZABs in terms of conductivity (ohmic resistance) and gas permeability (mass transfer), which can be tuned by adding polymer binders (e.g., polytetrafluoroethylene (PTFE)).^[94,95] The most widely used GDL is carbon cloth due to its excellent mechanical flexibility for flexible ZABs. However, these carbon-based GDLs are prone to corrosion in alkaline media, resulting in the loss of the active surface area for oxygen electrocatalysis, uneven current distribution on the cathode surface, and serious electrolyte leakage. Furthermore, dissolved carbonate species stemming from carbon corrosion of GDLs hurt the ionic conductivity of the electrolyte. Therefore, the development of highly corrosion-resistant graphitized carbon materials or metal-based materials is necessary to achieve the stable ZABs operation. In some cases, stainless-steel mesh and nickel/copper foam are also utilized as current collectors to enhance the electrical conductivity and electrochemical stability of the GDLs.

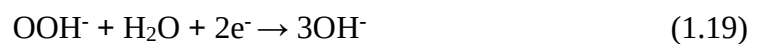
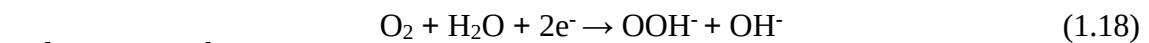
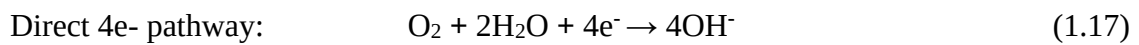
The catalyst layer is generally made up of electrocatalysts, acetylene black with high surface area and PTFE binder. Electrocatalysts directly face with the electrolyte to construct a so-called three-phase gas (O_2)/solid(catalyst)/liquid(electrolyte) interface for oxygen redox reactions.^[72] Due to the limitation of oxygen solubility in liquids, the catalyst layer should have a high specific surface area, providing enough reaction centers for oxygen reactions. Besides, favorable hydrophobicity is also required to facilitate the rapid mass transfer and oxygen diffusion. Therefore, acetylene black with high surface area can boost the hydrophilicity of the air cathode, and a PTFE binder is introduced in the active layer to get an optimal balance for hydrophilic properties. In particular, the ORR and OER are known as the kinetical-limiting reactions which greatly impact the performance of ZABs due to their high reaction energy barrier. Therefore, the rational design for air electrodes with appropriate interfacial structure and hydrophilicity, as well as strong electrical conductivity for rapid electron transport, is critical to achieve high-performance ZABs. More importantly, the development of high-performance bifunctional electrocatalysts for both ORR and the OER is urgently required to reduce overpotentials and promote oxygen electrocatalysis reactions.

1.3.3 Oxygen electrocatalysts for ZABs

It is acknowledged that the electrocatalytic ORR and OER are kinetically limiting reactions which determine the power output and cycling stability of ZABs due to their high reaction energy barriers.^[96] Thus, it is of great importance to develop appropriate bifunctional electrocatalysts to decrease the high ORR/OER overpotentials. Moreover, the improvement of ORR and OER also exerts a significant influence in the performance of other MABs, fuel cells, water splitting processes and photo-electrochemical devices.^[97] Therefore, a deeper understanding of the mechanism of ORR and OER is necessary.

1.3.3.1 Oxygen electrocatalysis in alkaline electrolyte

Generally, the ORR is a multi-electron transfer process in alkaline media that includes two different reaction pathways according to the surface properties of the catalysts: an indirect two-electron ($2e^-$) process to firstly form OOH^- which then convert to H_2O or OH^- and a direct four-electron ($4e^-$) process to generate H_2O or OH^- (as described in the equations below).^[98]



Thermodynamically, the selectivity of the $4e^-$ or $2e^-$ route mainly depends on the reactant and intermediate adsorption energies, as well as their dissociation reaction barriers on the active surface. The direct $4e^-$ process for the ORR is more efficient and desirable in practical applications than the $2e^-$ process which generates peroxide species (OOH^-), causing carbon corrosion and performance degradation. Two possible mechanisms for the $4e^-$ ORR pathway in alkaline media have been proposed: a dissociative mechanism and an associative mechanism. The dissociation mechanism can be described as the following procedure: Firstly, O_2 is adsorbed to the catalyst surface, followed by breaking the O-O bond and forming two adsorbed atomic O^* species (* represents a catalytically active site on the catalyst surface.). The resulting O^* species then reacts with hydrogen to create OH^* and eventually generates OH^- . The ORR process can alternatively be gone through the following associative mechanism: The oxygen adsorption in the active center produces O_2^* , which first combines with hydrogen to form OOH^* , and then the O-O bond is broken to produce O^* and OH^* . Finally, the products O^* and OH^* combine with hydrogen to generate the final product OH^- . In particular, whether the reaction proceeds in a dissociative or associative manner is determined by the reaction energy barrier for O-O bond breaking and the initial dissociation of O_2 .

The OER is essentially the reverse reaction of the ORR process which occurs as an anodic reaction of rechargeable ZABs.^[99] Through the OER procedure, HO^- is oxidized to generate O_2 , the reaction equation in the alkaline electrolyte is depicted below:



The OER not only involves multiple electron transfer steps but also needs to overcome substantial reaction energy barriers. In general, four O-H bonds are broken, and two O-O bonds are formed during the chemical process, resulting in extremely sluggish kinetics. Two possible pathways for OER mechanisms are proposed: 1) direct binding of two O^* to produce O_2 ; or 2) production of OOH^* , which is then transformed to O_2 .

Currently, ORR/OER electrocatalysts for the air cathode in ZABs have been intensively explored. Nevertheless, rechargeable ZABs still suffer from low output power density, limited cycling stability, and poor discharge voltage plateaus, which gravely hinder their future large-scale commercial applications. One of the major obstacles affecting the performance of rechargeable ZABs is the high overpotential at the air electrode, which is caused by the sluggish kinetics of oxygen reactions (ORR/OER).^[99,100] Therefore, the design of efficient and robust

oxygen electrocatalysts is very urgent for improving the ZABs overall performance. Based on the functions of the electrocatalyst in ORR/OER reactions, the catalyst should possess the following properties: 1) large specific surface area to expose more active sites; 2) appropriate interaction with oxygen-containing intermediates (if the binding is too weak, adsorption becomes difficult; if the binding is too strong, desorption is challenging); 3) stable during the electrochemical reaction (the catalyst should be able to resist the oxidization or reduction by reactants under the operating potentials); 4) great electronic conductivity to enable fast electron transfer. Generally, electrocatalysts for ORR/OER can be classified into three categories: noble metal catalysts, carbonaceous catalysts and transition metal catalysts, which will be discussed in the following sections.

1.3.3.2 Noble metal catalysts

Currently, platinum group metals (PGMs) have been widely investigated as oxygen electrocatalysts for application in ZABs owing to their optimal electronic structures. Nevertheless, the commercial carbon-supported PGM nanoparticles suffer from severe agglomeration or deformation during long-term operation, resulting in deactivation and inferior stability of the ZABs.^[101] In particular, the nano-sized platinum particles dispersed on the carbon matrix with high surface area, are considered as the commercial benchmark material for comparison when evaluating other oxygen catalysts due to their superior performance in ORR. However, the scarce sources of Pt make them prohibitively expensive for large-scale application in practice. Furthermore, the limited selectivity, high cost, and poor long-term durability of Pt catalyst, all posing challenges for its practical utilization in ZABs.^[102] There are two proposed strategies to reduce the cost of using Pt: One approach is to fabricate an atomically dispersed Pt-based catalyst with a high surface area, exposing more active sites and maximizing the Pt atom utilization efficiency; another method is to alloy Pt with other cheap transition metals (such as Ni, Fe or Co) to develop intermetallic compounds with good performance. Other noble metals like Pd and Ag have also been investigated as ORR catalysts because of their relatively low cost and reasonable performance. Cabrera et al. reported the bimetallic alloys with atomically precise noble metal Pd@Ag/C, which greatly enhanced the ORR reaction kinetics and electron transferred rate.^[103] However, the large-scale application of these noble-based catalysts is always limited by their scarcity and poor durability.

The benchmark for OER are Ru- and Ir-based catalysts (e.g., RuO₂ and IrO₂) in both alkaline

and acidic electrolytes. Tobias et al. assessed and compared the OER capability of Ru, Ir and Pt catalysts, revealing that their OER activities in nanoparticle form decreased in the following order: oxidized Ru > oxidized Ir > oxidized Pt.^[104] For these PGMs-based OER catalysts, the ligand effect, strain effect, and synergistic effect can adjust their interaction with the reaction intermediates, which are regarded as the main reasons for their enhanced performance. However, they also suffer from a lack of resources, high cost, as well as low durability, limiting their practical implementation. Therefore, developing cost-efficient ORR/OER electrocatalysts with high activity and outstanding durability is critical for good-performance ZABs.

1.3.3.3 Carbonaceous catalysts

Carbonaceous materials (e.g., graphene, carbon nanotubes, porous nanocarbons) are regarded as effective oxygen catalysts for ZABs due to their low cost, high surface area, excellent electrical conductivity and high stability in alkaline electrolytes.^[105] For example, graphite has excellent conductivity due to the π -bonding within the hexagonal plane with sp^2 hybridization when compared with the sp^3 hybridized carbon (such as diamond). However, the electrocatalytic activities of pure carbon materials are still unsatisfactory. Doping heteroatoms (e.g., N, P, S, F, and B) could improve their ORR/OER activities by tuning the electronic structure of the neighboring carbon atoms, and controlling the local charge density distribution as well.^[106] For example, the doping of nitrogen can introduce defects into the graphite layer and create more edge-plane sites, the nitrogen doping is normally achieved by the pyrolysis of nitrogen-containing hydrocarbons. Notably, only the pyridinic, pyrrolic, and graphitic N atoms with a planar structure can boost the catalytic activity.^[107] N-doped carbonaceous materials (like carbon nanotubes and graphene) also have received extensive attention because of their high surface area and electrical conductivity, which can either be used as electrocatalysts independently or serve as the substrate for metal-based catalysts. For example, Lopez-Salas et al. prepared a Cu^{II}/Cu^I decorated N-doped carbonaceous ORR electrocatalyst, which exhibited promising performance with a larger limiting current (-7.4 mA cm^{-2}) and faster reaction rate.^[108]

1.3.3.4 Transition metal catalysts

Transition metals, and their oxides have been revealed as promising alternatives to the precious metals-based ORR/OER catalysts due to their intrinsically high activity and sufficient stability in oxidative electrochemical environments.^[102,109] Besides, transition metal oxides (TMOs) are cheaper and easier to obtain with high abundance, making them more feasible for commercial

application.^[100] In addition to their inherent electrochemical properties, TMOs are highly attractive candidates in electrochemical and materials research due to their structural diversity and their ability to be mixed, doped, or combined with other materials (such as graphene).^[110] Among the wide range of these transition metals and metal oxides, cobalt, manganese, nickel, and iron, have been extensively explored as bifunctional catalysts, capable of simultaneously catalyzing ORR and OER for energy storage and conversion devices.

Basically, TMOs are unique in that they can form more than one cationic oxidation state, which is pertinent to their capability as electrocatalysts. Due to their variable valence states, metal oxidizes can easily transition between different oxidation states during the ORR/OER process, better tolerating the reversible oxidation and reduction, thus improving the stability of these transition metal-based catalysts. Additionally, many TMOs have a spinel lattice structure and can accommodate a large number of disordered cations and vacancies, which is beneficial for electron transfer during both OER and ORR processes. Furthermore, mixed TMOs, formed by combining TMOs with post-TMOs or mixing two low-cost TMOs, often exhibit enhanced electrocatalytic performance for ORR and significantly higher electrical conductivity than simple TMOs. For instance, Shao et al. fabricated a bifunctional catalyst with a simple chemical reaction, which combined NiO and Mn₂O₃ together via covalently bridged carbon dots. This catalyst reached a limiting current of ca. 6 mA cm⁻² during ORR and achieved a low overpotential of 298 mV at 10 mA cm⁻² for OER.^[111] As discussed above, the transition metals and metal oxides can also be combined with other materials (such as carbon-based substrates and organo-metallic frameworks), enhancing the catalytic activities of resulting catalysts owing to the synergistic effect.^[100]

In the search for efficient substitutes for noble metal catalysts, materials based on the earth-abundant transition metal hydroxides (TMHs) have attracted wide attention because of their unique structural and physicochemical features.^[112,113] Benefiting from their high-energy conversion efficiency and environmentally friendly properties, a great number of THM materials have been developed as electrocatalysts for electrochemical energy storage and conversion devices. Notably, the TMHs can be fabricated as self-supported electrodes via in-situ construction onto the conductive substrates (such as Ni foam, carbon cloth and stainless steel mesh), which exhibit several merits compared with commercial powdery-type catalysts: 1) facile fabrication (the direct utilization of conductive substrates without any complicated

process, simplifying the preparation process for electrodes); 2) the exemption of polymer binder as the adhesive reagent, ensuring fast electron transfer and avoiding the peeling issues; 3) the highly effective surface area with the 3D framework, significantly enhancing electrocatalytic performance.

Among the nanostructures of TMHs (e.g., nanoparticle, nanowire, nanotube and nanosheet), the ultrathin two-dimensional (2D) nanosheets are considered as one of the most promising electrocatalysts for ORR/OER due to the sufficient active sites, highly effective surface area and short diffusion path lengths for ions and electrons.^[114] Layered double hydroxides (LDHs) based on transition metals and their derivatives have gained increasing interest in the field of electrocatalysis, including NiFe-LDH, NiCo-LDH, and CoFe-LDH.^[99] The most striking property of LDHs is the excellent ability to exchange anions. Almost all types of anions, including anionic inorganic micro-molecules and organic macromolecules, can be intercalated into the interlayer space of the LDHs by coprecipitation or anion exchange.^[115] This property endows LDHs the variable electronic structures and adjustable interlayer distances with high surface area, which are the most important factors as catalysts or catalyst supports. Another important property is the LDHs memory effect. By calcination at high temperatures, LDHs could lose their interlayer anions and their hydrotalcite-like structure, then finally convert to layered double oxides with mixed metal oxides or spinel as the main component. Interestingly, these materials can easily restore their hydrotalcite-like structure with high intercalation capacity of anions when immersed in corresponding anion solutions. In addition, since many types of transition metals such as Fe, Ni, Co, etc., can be atomically dispersed into LDH carrier layers in a well-defined order, LDHs and layered double oxides also exhibit excellent catalytic activity towards ORR/OER processes. For examples, Wei et al. modified an organic molecule-intercalated LDHs with single atomic Co sites (Co-N or Co-S), which demonstrated excellent OER/ORR catalytic performance and enabled efficient ZABs with open circuit voltage of 1.42 V and a peak power density of 65 mW cm⁻².^[116]

Transition metal sulfides (TMSs) are regarded as very promising electrocatalysts for ORR because of their good redox reversibility, excellent mechanical and thermal stability, as well as abundant resources in nature.^[117] TMSs such as NiS₂ and CoS₂ have also been reported as promising ORR and OER electrocatalysts due to their attractive electrochemical nature. Researchers revealed that the activity of these transition metal sulfides is dependent on the

morphology and crystal structure of NiS₂. However, recent studies have shown that TMSs are usually used as pre-catalysts under alkaline conditions because they are prone to self-reconstruction or dissolution during OER.^[118] Besides, metal sulfides need to be blended with conductive substrates or supports to modify conductivity because of their electronically insulating nature.^[119]

Similarly, the transition metal carbides (TMCs) also attracted lots of attention as ORR/OER electrocatalysts due to their excellent physical and chemical properties, such as high melting points, high electronic conductivity, and chemical stability.^[120] For example, Tang et al. successfully synthesized a Mo/Co carbide electrocatalyst, which was applied to OER and displayed a low overpotential and good stability, showing the advantages of hybrid electrocatalysts over traditional ones.^[121] Very recently, the emerging nanotechnology greatly improves the practical application of TMCs in OER, since it helps to overcome the large energy loss caused by the high-temperature calcination synthesis method, and it is extremely beneficial for the construction of surface morphology. Additionally, bimetallic carbide-based materials are also potentially promising candidates as OER and ORR electrocatalysts due to the incorporation of secondary metals, which can manipulate the electronic structure and expose abundant site activities. For instance, Lan et al. reported a bimetallic as superior electrocatalyst for OER, the Co₆Mo₆C₂ composite exhibited highly electrocatalytic activity with a low overpotential of 260 mV versus RHE at 10 mA cm⁻² and a small Tafel slope of 50 mV dec⁻¹.^[122]

As for transition metal nitrides (TMNs), containing a variety of chemical bonds (metal bond, ionic bond and covalent bond) coexist, among which the ionic bond between metal atoms and nitrogen atoms can make the d-band shrink and narrow, endowing TMNs similar characteristics to precious metals in the electrocatalytic process. Thus, TMNs can be used as a substitute for precious metal catalysts for ORR and OER.^[123] Notably, compared with carbon-based materials, TMNs have stronger corrosion resistance and higher stability; compared with metal oxides/hydroxides, TMNs have better conductivity; compared with the original metal, the TMN has a larger specific surface area to expose more active sites. In addition, doping TMNs with other metals to form bimetallic nitrides, introduce synergistic effect between different metals and cause changes in electronic structure, both of which contribute to the improvement of catalytic activity, such as Ni₃FeN, Ni_{2.25}Co_{0.75}N and Ti_{0.8}Co_{0.2}N.^[98] However, it is worth noting that although transition metal nitrides have excellent catalytic activity, there is still a notable

reactivity gap with noble metal catalysts.

1.3.3.5 Transition metal-based single atom catalysts

Transition metal single-atom catalysts (SACs) have gained widespread attention across various fields due to their nearly 100% utilization efficiency of metal atoms, excellent activity and selectivity, as well as interesting versatility in a wide range of applications.^[124] Generally, SACs are materials with isolated metal atoms as active sites dispersed on a support at an atomic level. A SAC demonstrates many distinguished properties which are different from those of its nanostructured or sub-nanostructured counterparts. For instance, when the dispersion level of these metal atoms in the matrix reaches the atomic scale, there is a sharp increase in surface apparent energy, quantum size effect, unsaturated coordination environment, as well as a different interaction between the metal and the substrate, all these resulted characters endow the SACs with superior catalytic performance compared with their bulky and nanostructured counterparts.^[125] The concepts of single-atom catalysis and SACs were first reported by Zhang and co-workers in 2011. They successfully synthesized single Pt atoms on FeO_x for the catalysis of the CO oxidation reaction. Benefiting from the modified electronic structure of Pt and the charge transfer from Pt to FeO_x, this SAC exhibited exceptional catalytic activity and stability.^[126] The past few years have witnessed the progress of the construction of SACs as effective and cost-efficient catalysts for various reactions. The low-cost SACs that use diverse transition metals as active sites exhibit outstanding catalytic activity for the ORR/OER in ZABs and have been regarded as alternatives to noble metal-based catalysts. The most extensively studied and effective SACs for ZABs are M–N_x–C (M = Fe, Ni, Co, Mn, Cu, etc.; x = 2, 4, 6, etc.) supported on a carbonaceous matrix. In the M_x–N/C catalysts, the isolated active metal centers are usually dispersed on the carbon matrix and stabilized by covalent coordination or interaction of neighboring surface atoms such as nitrogen, oxygen or sulfur.^[127,128] Even though M–N_x–C moiety-based SACs lack M–M bond to break the O–O bond for ORR, SACs still achieve high performance in the ORR through a four-electron pathway. It has been proposed that the highly dispersed and coordinatively unsaturated configuration of these catalysts, as well as the enhanced charge-transfer effect due to the interaction between metal and support, remarkably improves the catalytic active sites.^[129] Their unique electronic configuration also results in the appropriate adsorption energies for oxygen-containing intermediates thus decreasing the free energies, which eventually contribute to improved intrinsic catalytic activity and the four-electron pathway for the ORR.^[130]

However, SACs also suffer from certain limitations for practical applications. Firstly, single metal atoms tend to aggregate into nanoparticles due to their high specific surface energy, so the metal loading should be controlled at a very low level (generally around 1%) to ensure the effective distribution of isolated active sites, which weakens the overall activity of the SACs.^[131] Secondly, most SACs only comprise a single configuration of a specific active site, making it challenging to break the linear scaling relationship between intermediates in complicated reactions which involve multiple reaction steps.^[132] Furthermore, the single type of active site in SACs poses challenges for developing bifunctional catalysts involving multiple active sites.^[133] To overcome these challenges, researchers have confirmed that the introduction of nonmetal elements (metal-nonmetal-atom synergies) and metal atoms (dual-metal-atom synergies) in SACs can effectively regulate the electronic coordination environment of the active sites and construct dual-atom catalysts (DACs), thus achieving improved electrocatalytic performance.^[134] As an extension of SACs, DACs not only retain all the advantages of SACs but also offer additional benefits. Particularly, DACs exhibit higher metal loading and flexible active sites that can adjust the d-band center through the electron orbitals interaction, thereby optimizing the adsorption energy of oxygen-containing intermediates on the active sites. Additionally, DACs can leverage the multiple active sites or synergistic effects to achieve more efficient catalysis. Given the tremendous potential of DACs and the requirement for developing bifunctional oxygen electrocatalysts for ZABs, considerable efforts have been dedicated to this realm.^[135]

Metal-nonmetal-atom DACs involve the substitution of coordination atoms with nonmetal elements in the first shell or beyond that shell, leading to the formation of new active sites and modifying the electronic configuration of the active sites. Alternatively, dual-metal-atom DACs refer to the construction of homonuclear or heteronuclear bimetallic catalysts. These DACs can exploit the synergistic effect between two identical or different metal atoms to surpass the theoretical limits of SACs and optimize the d-band center of the active sites. For example, Li et al. synthesized bifunctional catalyst with adjacent Fe-N₄ and Mn-N₄ sites on 2D ultrathin N-doped carbon nanosheets (FeMn-DSAC), which demonstrated remarkable catalytic activities for ORR/OER and constructed as the cathode for flexible low-temperature ZABs.^[131] Notably, the precise synthesis of these two types of dual-sites SACs with the desirable atomic configuration is essential for exploring their structure-activity relationship and promoting their

practical application, which remains challenging. Recently, several approaches have been developed for controllable synthesis of DACs, which can be categorized into bottom-up and top-down strategies.^[134] Bottom-up strategies generally involve utilizing an appropriate substrate to absorb mono- or multinuclear metal complex precursors, followed by chemical reduction to convert them into DACs. Atomic layer deposition is a typical bottom-up method, which can precisely regulate the composition and structure of the resulting catalysts via different self-limiting reactions. For instance, Yan et al. successfully obtained a homonuclear DACs with Pt₂ dimers uniformly dispersed on graphene by the atomic layer deposition strategy.^[136] Another bottom-up strategy, the ball milling technique can efficiently reconstruct the chemical bonds between metal atoms and coordination atoms. Chen et al. prepared a series of homonuclear and heteronuclear DACs using carbon black as the matrixes by ball milling method.^[137] This approach highlights its universality and scalable advantage. The top-down strategies involve the break of the metal-metal bond of the precursors to form DACs with atomic metal dual-sites or metal dimers that uniformly dispersed on the substrates. For example, pyrolyzing metal-organic frameworks (MOFs) is a common top-down strategy to synthesize DACs.^[135] Wang and coworkers pioneered the synthesis of bimetallic Fe-Co DACs via the host-guest strategy, in which bimetallic (Zn/Co)MOF was utilized as the precursor to encapsulate FeCl₃ molecules.^[138] This work used Zn species as a spacer to avoid metal aggregation during pyrolysis, the vaporization of Zn can make abundant vacancies for hosting dual active sites.

During the past few years, many researchers have successfully synthesized DACs with excellent catalytic activities through rationally designed strategies. According to the structural characteristics of active sites in DACs, they can generally be classified into three main categories: bonded, bridged, and non-bonded DACs.^[132] In addition, some catalysts could comprise two or three of the above structural characteristics, all of which might contribute to their excellent catalytic performances with different electronic configurations. Notably, DACs possess flexible architectures that enable the combination of homogeneous and/or heterogeneous active sites, making them highly attractive for improving bifunctional catalytic activity, especially for ORR and OER. Generally, we can better understand their catalytic performance and reaction mechanisms by deeply comprehending the structural characteristics of DACs, thereby offering guidance and inspiration for the synthesis of more efficient DACs.^[139] Thus, regulating the local electronic configuration and surface/interface characteristics through atomic-level modulation engineering is particularly important for

optimizing the adsorption/desorption behavior of oxygen-containing intermediates, lowering the reaction energy barrier and accelerating the ORR/OER kinetics, then effectively promoting the large-scale practical implementation of rechargeable ZABs.

1.4 Zinc-nitrate/nitrite batteries

1.4.1 Overview of the global nitrogen cycle

The nitrogen cycle is one of the most important biogeochemical cycles on earth that has existed for tens of thousands of years and greatly affected by human activities during the past centuries.^[140] Figure 10 illustrates the main forms of nitrogen and its circulation in the ecosystem. In this biochemical cycle, nitrogen fixation is the process converting atmospheric dinitrogen to usable form (such as ammonia), nitrification means oxidizing ammonia to nitrite and/or nitrate to release energy for the formation of organic materials for microorganisms. The ammonification refers to the procedure of autolysis, decay and putrefaction of biological materials to form ammonia, and denitrification is to transform nitrate to dinitrogen as the final product, by which the loss of nitrogen in the atmosphere is compensated.^[141]

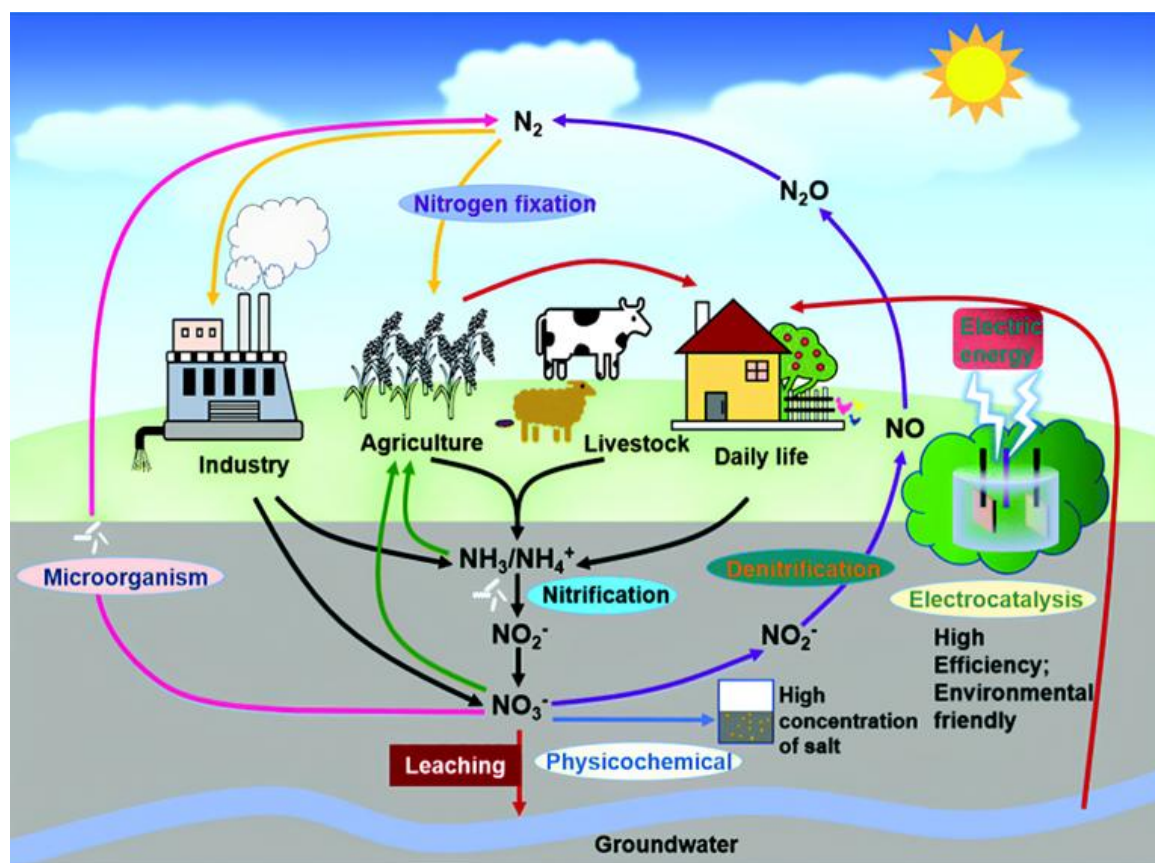


Figure 10. The main forms of nitrogen and the circulation of nitrogen in the ecosystem.^[141] Reprinted with permission. Copyright 2023, Royal Society of Chemistry.

Although nitrogen is abundant in the atmosphere in the form of gaseous dinitrogen (N_2), it is very inert and not directly usable to most life forms. For example, plants cannot directly take up nitrogen from atmosphere, N_2 must be converted into other useable forms (especially

ammonia, $\text{NH}_3/\text{NH}_4^+$) via a series of reactions. There are three main routes for N_2 conversion namely nitrogen fixation (from molecular N_2 to nitrogenous compounds), including industrial ammonia production, biological N_2 fixation (mainly referring to N-fixing microorganisms), and nitrogen activation by lightning. The natural processes deliver around 120 megatons per year of bioavailable nitrogen to the biosphere, mostly contributed by nitrogen fixation by microbes and leguminous plants, like alfalfa, clover, and beans.^[142] However, this natural process is quite limited to specific microorganisms and plants, and the recycling of organic waste into fertilizer for crops is too slow and inefficient to input enough usable nitrogen.^[143] Therefore, ammonia was regarded as the limiting nutrient element in agriculture during the pre-industrial era. The situation was changed when German chemist and engineer Fritz Haber and Carl Bosch created the industrial Haber–Bosch process,^[144] where N_2 and H_2 are converted to ammonia at high temperature and pressure, as shown in the following reaction:



The successful commercialization of large-scale production of ammonia from abundant and easily available raw resources marked a new era in human history.^[145] The Haber–Bosch process produces roughly 100 million tons of ammonia each year, almost the same amount of fixed nitrogen to the biosphere from the natural processes. According to the investigation, around 40% of the human population depends on the contribution of industrial ammonia production. However, the Haber–Bosch process is responsible for around 2-3% of global fossil fuel consumption.^[146,147]

Further, ammonia can be stepwise oxidized to nitrate (NO_3^-) in the nitrification process with hydroxylamine (NH_2OH), nitric oxide (NO) and nitrite (NO_2^-) as reactive intermediates (NO_x). Additionally, these nitrogen compounds play a very important role in both terrestrial and marine ecosystems, and widely affect the atmosphere and cryosphere.^[140,148] For the biochemical nitrogen cycle, the changes in nutrient supply can greatly influence the productivity of ecosystems and impact the competition between species and biological diversity. Besides, in the atmosphere, NO_x is essential to the photochemical production of ozone and other key oxidants as well as radical species, closely coupled to the oxidizing capacity of the atmosphere. Moreover, these nitrogen compounds are precursors of tropospheric ozone and atmospheric particulate material, which also degrades air quality.^[149] In addition, as a potent greenhouse gas and ozone-depleting agent, the emission of N_2O from denitrification also plays a key role in the chemistry of the ozone layer in the stratosphere, influencing the radiative balance of the

earth.^[150] Another great threat to ecological environments is the excessive accumulation of nitrogen pollutants, such as nitrate/nitrite in groundwater, rivers, and lakes which is detrimental to water resources.^[151] In recent decades the accumulation of nitrates/nitrites has increased dramatically owing to unrestrained human activities, including modern industrial waste disposal, and the agriculture and livestock industries.^[152] The large amount of nitrate/nitrite emission can lead to the rapid growth of algae in the water, which will make the water undergo eutrophication. Eutrophic water not only kills fish and other aquatic life but also pollutes groundwater. Significantly, if nitrate is ingested by humans over a long period, it can be converted to toxic nitrite by gastrointestinal microorganisms. Because of the deleterious impacts on human health, researchers believe that the imbalance of the nitrogen cycle and the effective processing of nitrate/nitrite in water are one of the major and urgent challenges of this century.^[153,154]

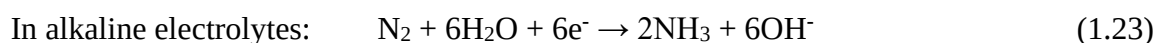
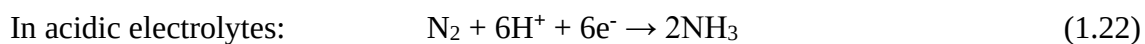
Generally, in the absence of human influences, there are significant consequences of human activities on the imbalanced global nitrogen cycle, including ever-increasing fertilizer for agriculture, climate changes, as well as biodiversity loss.^[155] Based on the abovementioned serious environmental issues related to the nitrogen cycle and the growing human population on this planet, there are many basic scientific questions surrounding the different processes in the nitrogen cycle on how to achieve human sustainable development. However, knowledge of the global nitrogen cycle is incomplete, and the development of new measurements, improved instrumentation and processing investigation, as well as sustainable nitrogen management strategies are of great importance.

1.4.2 Electrosynthesis of ammonia

Ammonia (NH_3) is an essential chemical widely used across numerous sectors, such as agriculture, pharmaceuticals, plastics, and synthetic fibers. Notably, ammonia is the second largest chemical produced in the world, about 80% of which is used for fertilizer synthesis and feeds the explosive growth of the global population.^[156] Additionally, due to the high hydrogen mass fraction (17.6 wt%), high energy density (4.25 kWh L^{-1}), and ease of storage and transportation, NH_3 has also been regarded as a promising carbon-free energy carrier and liquid transportation fuel in the future.^[157] Thus, the synthesis of ammonia is of great significance to human society and the global economy. Currently, the predominant production of ammonia still heavily relies on the traditional Haber-Bosch process, which is one of the greatest achievements

of the 20th century. However, the process requires a pure hydrogen feedstock primarily produced from strongly endothermic steam-methane reforming. Moreover, breaking the highly inert $\text{N}\equiv\text{N}$ triple bond requires large driving forces to kinetically accelerate the reaction and shift the equilibrium favorably, such as high temperatures of up to 350-450°C and high pressures of 100-200 bar. As a result, this energy-intensive ammonia production consumes 1-2% of the total energy worldwide and releases significant greenhouse gases (such as CO_2) annually because of the dependence on fossil fuels. Furthermore, the large-scale and centralized Haber-Bosch plant requires huge capital investment and can only be realized in large industrial factories, which are highly capital-intensive and result in severe regional distribution imbalances.^[158] Thus, it is urgent to develop a facile ammonia synthetic method that can be operated under mild conditions to replace the energy-intensive and unsustainable Haber-Bosch process with its complex plant facilities and unfavorable environmental impact. To this end, scientists have proposed several strategies to address this challenge, such as chemical looping, organometallic, biomimetic, photocatalytic, and (photo)electrochemical methods.^[159] Among these approaches, the electrochemical synthesis of ammonia is emerging as a compelling alternative to the Haber-Bosch process, benefiting from its mild operating conditions, zero emission of carbon dioxide, powered by renewable energy sources, capability to store renewable electricity in chemical bonds, and possibilities for distributed ammonia production.^[160] During the past few decades, research on the electrochemical synthesis of ammonia by nitrogen reduction reaction (NRR) has been extensively investigated with promising progress.

Electrochemical technologies can facilitate the thermodynamically non-spontaneous NRR with little or no limitation of thermodynamic equilibrium on the conversion rate. The general electrocatalysis process is activating absorbed N_2 molecules by supplying them with electrons and providing the electrons needed for the subsequent reduction reaction. During the process, water (H_2O in the electrolyte or even humidified air) is used as the proton source (instead of H_2 for the Haber-Bosch process) to synthesize NH_3 under room temperature and atmospheric pressure.^[159] Theoretically, electrocatalytic N_2 reduction to NH_3 is feasible under ambient conditions as long as a suitable electric potential is applied, and the reaction can be given as follows:



Generally, prior to the NRR to ammonia process, nitrogen needs to be dissolved into the electrolyte and cross the liquid interface to reach the catalyst surface. Therefore, both the inherent properties of the electrolyte and the microenvironment of the solid-liquid interface have a great influence on the NRR performance. The electrocatalytic NRR mechanism usually involves three steps: 1) the adsorption of N_2 molecules onto the catalyst surface; 2) the dissociative or associative breaking of $N\equiv N$ bond and hydrogenation; 3) the desorption of the generated ammonia. However, the direct breaking of the stable $N\equiv N$ bond (941 kJ mol^{-1}) is extremely difficult and requires a large amount of energy.^[161] Particularly, the electrochemical NRR and the catalytic process of nitrogen fixation both occur at mild conditions that do not favor the direct $N\equiv N$ bond breaking, so the activation of N_2 is usually considered as the rate-determining step. Therefore, discussions on the proposed NRR mechanisms mainly focus on the associative mechanism, in which the $N\equiv N$ bond gradually breaks as the hydrogenation of N proceeds until an ammonia molecule is released. The associative mechanism can be subdivided into distal, alternating, and enzymatic pathways.^[162] In addition, density functional theory (DFT) calculations are widely utilized in discussions on the mechanisms of electrochemical NRR.^[163] Moreover, experimental studies on the mechanisms of electrochemical NRR are also of great significance in clarifying the principles of electrochemical NRR, which is helpful to dispelling doubts about the results and provide direct evidence for the NRR process.

In recent years, continuous efforts have been dedicated to developing the NRR electrocatalysts aimed at improving catalytic selectivity and efficiency, as well as acquiring mechanistic understanding of the NRR process.^[164] However, there remains a significant limitation in the form of poor ammonia yield rate and low Faradaic efficiency (FE), which greatly hinder its practical application. The main challenges for NRR can be summarized as following: 1) the challenging adsorption and activation of N_2 resulting from their high dissociation energy and low proton affinity, as well as low solubility in water ($6.8\times 10^{-4}\text{ M}$, $1.01\times 10^5\text{ Pa}$, 298 K) hinders the reduction of N_2 both thermodynamically and kinetically, both of which result in low electrochemical performance; 2) the hydrogen evolution reaction (HER) poses a key competitive reaction to the electrochemical NRR.^[165] The NRR and HER can both occur from a thermodynamic point of view and their equilibrium potentials are close to each other. Especially, the NRR is a multi-step process that involves six electrons and six protons, suffering from sluggish kinetics. By contrast, the HER is a two-electron process, which is much more kinetically favorable. Consequently, the selectivity of electrochemical NRR is usually very low,

impeding the progression of FE and requiring high energy expenditure; 3) the catalytic performance is notably influenced by the inadequate mass transfer of N_2 in electrolyte solutions. Facing the above three urgent challenges, developing electrocatalysts with excellent activity and selectivity is essential to improve the NRR performance. In addition, innovations on the configurations of electrolytic cells are also necessary to the development of electrosynthesis of ammonia.

So far, a wide range of electrocatalysts has been reported for the electrocatalytic NRR process, including noble metal-based catalysts (such as Au, Ru, Rh, Pd, Pt, Ag, and Ir),^[166–169] non-noble metal-based catalysts (e.g., Mo, Fe, Co, Mn, Ni, Cu, W, Re, Sn, Sb, and Bi) and metal-free catalysts (B, C, N, O, F, P, S, Se, and Te).^[159] These elements can derive many categories of catalysts for electrochemical NRR, such as metals, metal alloys, transition metal carbides, nitrides, oxides, sulfides, carbon materials, black and red phosphorous, covalent organic frameworks (COFs), etc. In addition, atomic catalysts are also emerging as attractive materials for the NRR as well. Meanwhile, the electrochemical reduction of nitrogenous pollutants (such as nitrate and nitrite) to ammonia has also been explored as a promising strategy for the synthesis of green ammonia while removing pollutants from the environment at the same time.^{[170][171]}

1.4.3 Electrocatalytic nitrate/nitrite reduction

As mentioned above, the balance of the natural nitrogen cycle is disturbed because of the excessive nitrate/nitrite derived from industrial nitrogen fixation, and inefficient management of wastewater treatment, as well as the extensive emission of exhausted gas from combustion of fossil fuels (as shown in Figure 11).^[172] The imbalance between the generation and removal of nitrate/nitrite caused by human activities (especially, the over-utilization of fertilizers and industrial sewage discharge) has resulted in a serious surplus of nitrate/nitrite in the ecosystem, where the sluggish natural process of self-purification by the denitrifying bacteria is incapable of dealing with all nitrate/nitrite accumulation. As results, undesirable algal bloom and dissolved oxygen reduce in waters, both of which cause the formation of reductive toxic compounds (such as hydrogen sulfide) below the water surface, impairing the ability of local aquatic animals to survive, grow and reproduce.^[173] More worryingly, the blooming algae can generate a potent hepatotoxin called microcystin, which can cause severe damage to the liver of human beings.^[174] In addition, overconsumption of nitrate/nitrite may lead to serious health

issues by inducing methemoglobinemia and potent cancer of the digestive tract and other diseases. Therefore, offsetting the nitrogen inflow to the ecosystem and selectively removing the excessive nitrate/nitrite from waste and groundwater are the most concerning environmental issues and have attracted widespread global attention.^[175]

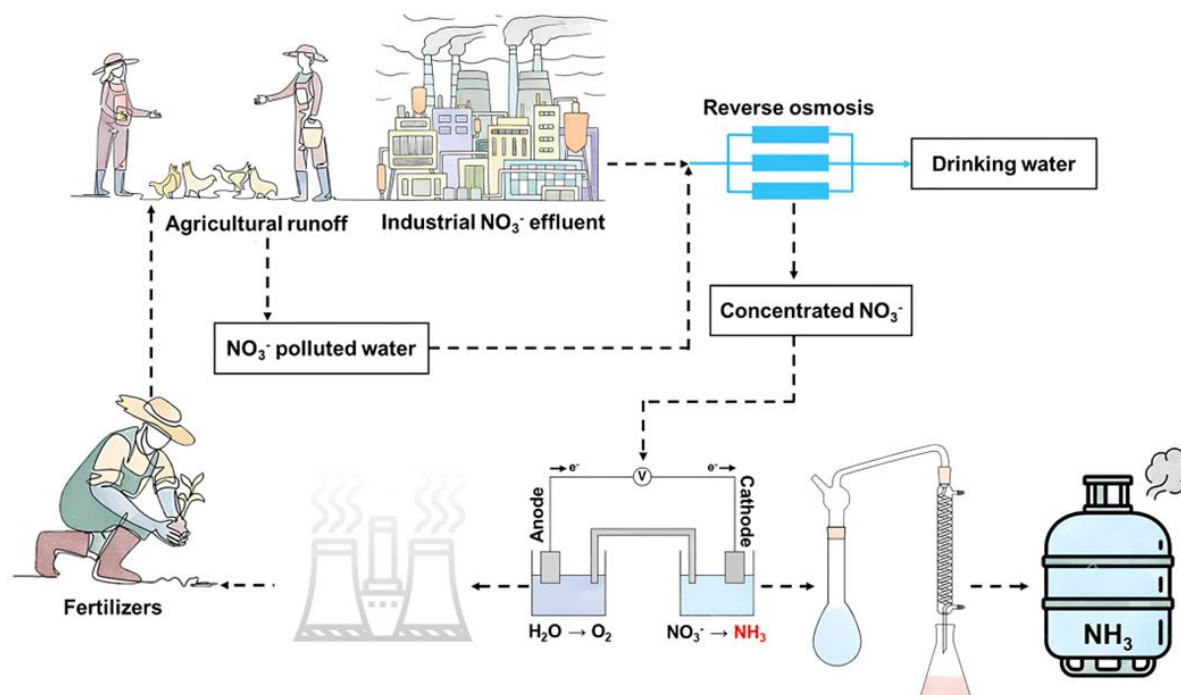


Figure 11. Schematic illustration of the eNO₃RR process integrated with existing technologies.^[172] Reprinted with permission. Copyright 2024, Elsevier.

To solve this problem, both biological and chemical technologies have been developed to reduce the nitrate/nitrite levels in water bodies.^[176] For example, utilizing denitrifying bacteria to remove excessive nitrate/nitrite is a natural pollution-free method that can stepwise convert nitrate to N₂. Chemical approaches such as reverse osmosis, ion exchange and adsorption are also explored to find out an efficient solution.^[177] However, the practical applications of these traditional techniques are limited by several drawbacks, such as a long sludge retention time, slow kinetics, as well as undesirable activity and selectivity. From an environmental perspective, the most promising nitrate/nitrite reduction technology can convert nitrate/nitrite into value-added NH₃, and features low cost, high efficiency, and environmental friendliness. Recently, electrochemical nitrate/nitrite reduction reaction (NO_xRR) has been proven as a satisfactory and environmentally friendly technology to achieve this goal.^[172]

Electroreduction is a highly efficient and eco-friendly technology that can be used to remove excess nitrate/nitrite in wastewater or polluted water and generate green NH₃, providing several

benefits. Generally, $\text{NO}_x\text{-RR}$ enables efficient and controllable NH_3 synthesis by utilizing water and nitrate/nitrite as the hydrogen and nitrogen sources, which is thermodynamically favored under ambient conditions owing to the much lower N=O bond energy (204 kJ mol^{-1}) and higher solubility of NO_3^- in aqueous solution.^[178] Importantly, NO_3^- is more stable than NO_2^- and abundant in natural waters due to the higher oxidation state. Besides, $\text{NO}_x\text{-RR}$ exhibits a remarkable FE (close to 100% at a certain electrode potential) and a higher NH_3 yield rate up to $1 \text{ mmol cm}^{-2} \text{ h}^{-1}$ than that of NRR.^[179] Therefore, $\text{NO}_x\text{-RR}$ should be much more promising in industrial practice. More appealingly, the $\text{NO}_x\text{-RR}$ process can be powered by renewable electricity (such as wind and solar energy), holding the opportunity to achieve decentralized NH_3 production and lowering the fertilizer cost in remote districts and less-developed regions.^[180] Moreover, the flexible design and controllable synthesis of ammonia from $\text{NO}_x\text{-RR}$ endow the $\text{NO}_x\text{-RR}$ device with seamless integration in existing industrial facilities, resulting in reduced investment costs and eliminating sludge production. Furthermore, this approach enables the production of high-value ammonia while effectively mitigating environmental pollutants, thereby alleviating the burden associated with the Haber-Bosch process.

The conversion of NO_3^- to NH_3 through $\text{NO}_3\text{-RR}$ is an 8-electron process that faces the competition of HER (a 2-electron process) and several by-products, including NO_2^- , NO , N_2 and N_2O .^[180,181] This complex process requires a comprehensive understanding of its underlying mechanisms, and the overall conversion can be represented by the chemical equation:



Generally, the $\text{NO}_3\text{-RR}$ process starts with the adsorption of NO_3^- onto the electrocatalyst surface which is the critical step for initiating subsequent reaction steps. As shown in Figure 12, there are two proposed primary routes for the reaction pathway: 1) direct association mechanism: NO_3^- is directly adsorbed onto the electrocatalyst surface and undergoes a series of hydrogenation steps. It begins with the formation of NO_3H , then releases H_2O to generate NO_2 . This unstable intermediate is then reduced to NO_2H and NO successively, followed by releasing another H_2O molecule. The NO continues the further hydrogenation steps to ultimately yield NH_3 ; 2) dissociation-association mechanism: after being absorbed on the electrocatalyst surface, NO_3^- is dissociated into O and NO_2 on separate active sites. These species consecutively go through the hydrogenated reduction steps and form the intermediate NO , which is then reduced further to NH_3 .^[181] Additionally, the intricate mechanisms of $\text{NO}_3\text{-RR}$ are significantly

influenced by the properties of the electrocatalyst, the composition and pH value of the electrolyte, as well as the applied potential. These factors impact the reaction pathway by affecting the adsorption energies of intermediates and the energy barriers for each reaction step, thereby influencing the overall efficiency and selectivity toward ammonia production. Particularly, the precise understanding of reaction mechanisms is critical for the rational design of electrocatalysts to improve the catalytic activity and selectivity for ammonia production.^[182,183] Similarly, DFT calculations are also extensively utilized to deepen the understanding of the NO_3^- RR mechanisms since these calculations can provide crucial insights into the adsorption energies of intermediates and the energy barriers of reaction steps, as well as elucidate the reaction pathways and the complex dynamics of the NO_3^- RR process.^[184]

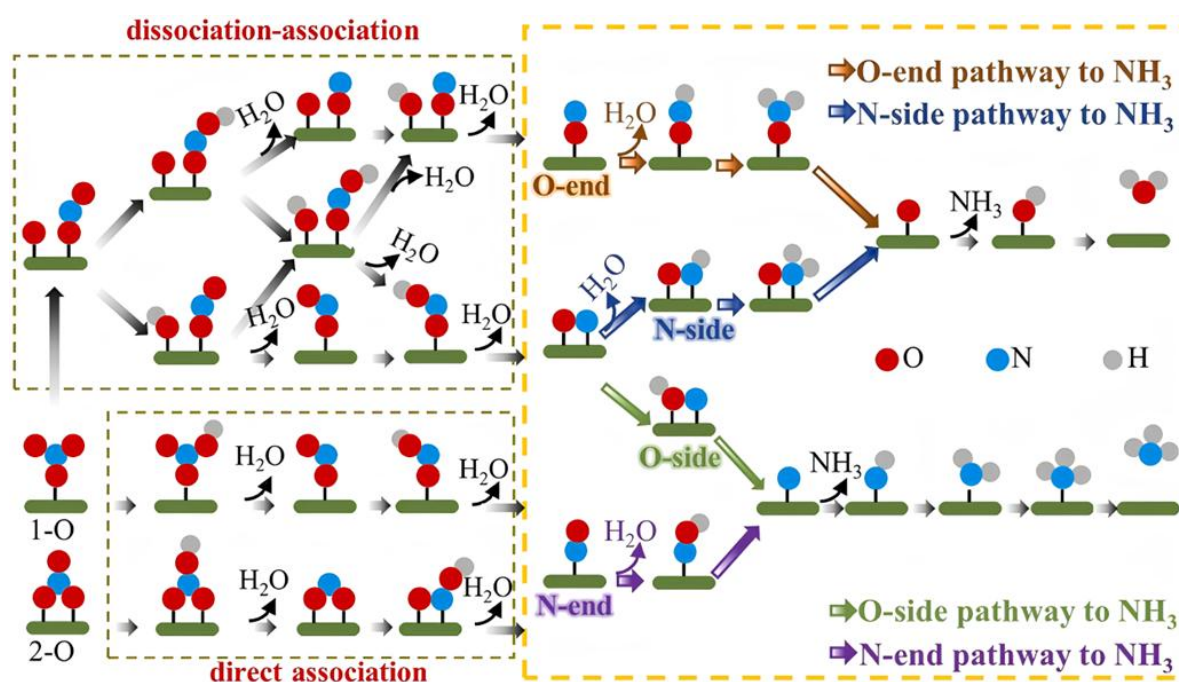


Figure 12. Schematic illustration of the dissociative-associative and directly associative mechanism for NO_3^- RR, including O-end, O-side, N-end, and N-side pathway to NH_3 .^[181] Reprinted with permission. Copyright 2022, Elsevier.

By contrast, the electroreduction reaction of NO_2^- to NH_3 follows a six-electron pathway, which also involves multiple intermediates formed at similar reduction potentials, posing a challenge to product selectivity.^[185] Thus, even though the electrochemical synthesis of ammonia from nitrogenous pollutants is a promising technology with appealing merits, several challenges need to be addressed for further practical application.^[186,187] Firstly, the detailed mechanisms for electrochemical reduction of nitrogenous pollutants are still unclear and remain to be elucidated through both computational investigation and in-situ characterization techniques. Secondly, the

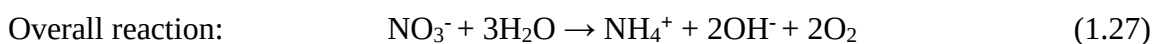
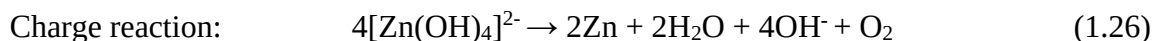
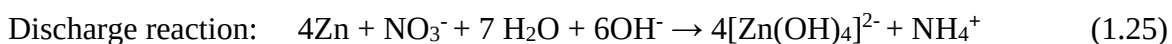
development of more advanced electrocatalysts for NO_x -RR to synthesize ammonia from nitrate/nitrite is urgently required to achieve high NH_3 yield rates and FEs, lowering the overpotential of reactions and improving the stability of catalysts. Thirdly, it is important to evaluate the NO_x -RR performance of electrocatalysts using real wastes containing nitrogenous pollutants, which helps to promote its practical application and meet industrial requirements. Developing novel electrocatalysts is critical to overcome these challenging issues. During the past few years, a variety of materials including metals, alloys, metal oxides, atomic catalysts, and non-metal materials have been systematically explored as catalysts for NO_x -RR to synthesize ammonia. For instance, Ru, Pd and Cu exhibit the highest activity and selectivity for the reduction of nitrate toward ammonia among all metallic materials. However, the corresponding ammonia yield rate is still too low to catch up with the traditional Haber-Bosch process.^[188] Typically, transition metal-based materials are highly promising for NO_x -RR because they can easily activate the $\text{N}=\text{O}$ bond through the unoccupied d orbitals, and their tunable surface morphology, electronic structure, and coordination environment can greatly affect the catalytic performance in NO_x -RR. Therefore, strategic optimization of these parameters makes great significance to enhance the catalytic activity and selectivity.^[171]

1.4.4 Zinc-nitrate/nitrite batteries

Zn-based batteries are considered as the most promising devices for large-scale energy storage applications due to the distinct advantages associated with metallic zinc.^[189,190] These merits include the high theoretical capacity (820 mAh g^{-1}), abundant reserves and lower cost of zinc ($\sim\text{US\$2 kg}^{-1}$) compared to other alkali metals (e.g., lithium $\sim\text{US\$19 kg}^{-1}$; potassium $\sim\text{US\$13 kg}^{-1}$; sodium $\sim\text{US\$3 kg}^{-1}$), high stability and reversibility in aqueous electrolytes, non-toxicity, and ease of material processing and battery fabrication. Moreover, the low anodic potential (0.763 V vs. standard hydrogen electrode) and the two-electron transfer during the battery operation contribute to the elevated energy densities of the batteries. All these additional benefits endow Zn-based batteries appealing advantages, encompassing the affordability, safety, and high ionic conductivity (up to 1 S cm^{-1}) of commonly used aqueous electrolytes (compared to the flammable organic electrolytes employed in lithium-ion batteries ($\sim 1\text{--}10 \text{ mS cm}^{-1}$)). Currently, zinc anode has been extensively utilized in diverse battery technologies, including Zn-ion batteries, Zn-air batteries (ZABs), Zn- CO_2 batteries, Zn-based flow batteries, and Zn-based flexible batteries. Among these battery devices, the aqueous Zn-based ones have attracted remarkable attention, which inherits all the abovementioned merits and include more desirable

characteristics, such as good stability and being environmentally friendly. According to different cathode active materials (e.g., metal-based oxides, redox-active compounds, and some energy-carrier gases) and corresponding electrolytes (acidic, neutral, or alkaline solution), aqueous Zn-based batteries can be divided into several distinct categories, including Zn-ion (Li/Na/K/Mg/Al), Zn-halogen (Cl_2 , Br_2 , and I_2), Zn-metal oxides ($\text{MnVO}/\text{Co}_3\text{O}_4/\text{MnO}_2$) batteries, as well as their hybrid derivatives.^[191]

In the context of NO_x^- RR to synthesize ammonia, several efficacious electrochemical techniques for NO_x^- conversion and recycling have been devised, among which Zn- $\text{NO}_3^-/\text{NO}_2^-$ batteries (ZNBs) feature prominently. By coupling NO_x^- RR with the redox reaction of Zn/Zn^{2+} to form a Zn- $\text{NO}_3^-/\text{NO}_2^-$ batteries, it is capable of producing NH_3 continuously, simultaneously generating electricity, and removing the $\text{NO}_3^-/\text{NO}_2^-$ pollutant in wastewater, achieving this promising practice of “killing three birds with one stone”.^[192–194] The schematic diagram of the aqueous rechargeable ZABs is also illustrated in Figure 12, a Zn plate was used as anode with a mixture solution containing KOH and supporting additives as anolyte, while the cathode is loaded with electrocatalysts and catholyte consisting of KOH with KNO_3 as nitrogen sources. An ion exchange membrane (such as Nafion 112) is required to effectively separate the two electrolytes and avoid cross-contamination. During the discharging process, Zn in the metallic form on the anode dissolves and releases electrons, facilitating NO_3^- RR at the cathode through electron transfer. During the charging process, water in the catholyte undergoes the OER process and produces O_2 , while $[\text{Zn}(\text{OH})_4]^{2-}$ is formed at the anode and then deposits as metallic Zn. The working principle of the rechargeable Zn- NO_3^- batteries is illustrated as the following equations:



Generally, ZNBs represent a sustainable technology with many advantages, including pollutant removal, resource recycling, carbon emissions reduction and energy saving. More importantly, compared with traditional Haber-Bosch plants, the ZNBs device features fast dynamic response and decentralized manufacturing based on local production, making the system easier to control as well as reducing transportation costs and environmental impacts. Recently, Yan and coworkers reported a ZNB using $\text{NiMoO}_4/\text{CuO}$ nanowire/CF as an electrocatalyst, which

exhibited a maximal power density of 26.2 mW cm^{-2} with high stability (more than 90 cycles).^[195] Liu et.al. also investigated a ZNB based on a hetero-structured CoO/CuO nanoarray electrocatalyst, which delivers a remarkable NH_3 yield of $60.3 \text{ } \mu\text{mol h}^{-1} \text{ cm}^{-2}$ with FE of 82.0%.^[196] Cui and colleagues studied a CuNi alloy nanoparticles (CuNi NPs) loaded on MXene as catalyst for Zn- NO_2^- batteries. The results suggested that catalytic performance was enhanced by the interaction between CuNi NPs and MXene, demonstrating excellent NH_3 yield of 10.22 mg h^{-1} and Faradaic efficiency of 95.6%. The Zn- NO_2^- battery assembled with $\text{Cu}_3\text{Ni}/\text{MXene}$ also showed an impressive power density of 8.34 mW cm^{-2} and Faradaic efficiency of 90.3%.^[197]

However, the development of ZNBs is still in the initial stage and there are several issues that need to be addressed to achieve high-performance ZNBs with good compatibility with existing industrial infrastructures. For example, the fabrication of a cost-efficient electrocatalyst with excellent catalytic activity and stability is urgently required, and optimization of the ZNBs cell configuration and electrode materials are also of significance to enhance the performance of ZNBs.^[198] In addition, feasible NH_3 extraction technology is crucial for large-scale industrial production.^[172] Hence, more efforts are required to be devoted to achieving sustainable green production of ammonia with ZNBs technology.

2. Objectives

As discussed above, the deployment of effective and efficient ESS technologies is significant to shifting away from traditional fossil fuels and making renewable energy sources universally available for daily application in modern society. The emergence of unconventional EES devices, including RFBs, ZABs and ZNBs provide a plausible solution to balance the energy demand and supply equation. Meanwhile, the growing interest in EES technologies along with the increasing demand for mature EES devices is having transformative effects in both laboratory and industrial sectors. While numerous alternative EES technologies have been developed in the past few decades with diverse configurations and technical characteristics to meet the various requirements in specific conditions, there are still several fundamental challenges need to be addressed to achieve better performance, lower cost, and longer lifetime of EES technologies, ultimately contributing to the sustainable development of human society.

The principal objective of this thesis is to develop novel advanced electrolytes and electrocatalysts and utilize them as active materials to enhance the performance of the targeted EES devices. These active materials were rationally designed and precisely fabricated to cater for specific EES devices application under technologically relevant conditions in which they are used. Furthermore, systematic investigations on the performance of these materials as well as a comprehensive understanding of the structure-property-performance relationship are presented. In the following sector, a series of electrolytes and electrocatalysts including their synthesis, characterization, and practical performance for three different next-generation EES devices will be explored:

- (a) A novel mixed-valent polyoxovanadates $\{\text{MV}_{13}\}$ cluster for use as active species in electrolytes for symmetric NRFBs.

One major challenge in RFBs research is the design of redox-active electrolyte components that combine high solubility and reversible multi-electron storage. POMs as a class of green, cheap and stable clusters have been considered as promising candidates for RFBs application. However, the utilization of traditional POMs clusters (such as molybdenum and tungsten oxidizes) in RFBs are greatly limited due to their heavy molecular mass. In addition, the conventional aqueous RFBs are suffering from the small potential window due to water oxidation/water reduction. In this part, we set out the develop a novel polyoxovanadates cluster with significantly lighter mass ($M(V) = 52 \text{ g mol}^{-1}$) and more accessible redox processes, then utilize it as active species in electrolytes for the integration in symmetric non-

aqueous RFBs.

(b) Robust and cost-efficient atomic oxygen catalysts for ZABs.

Rechargeable ZABs are amongst the most promising battery technologies, but the sluggish kinetics of the ORR and OER result in high overpotentials and unsatisfactory efficiency. Thus, the development of highly efficient, cost-effective and robust bifunctional ORR/OER electrocatalysts is of great importance to achieve the universal application of ZABs.

(1) Bifunctional DACs for OER and ORR have attracted wide attentions in the field of electrocatalysts for ZABs. However, it remains challenging to precisely control the coordination environment and fully expose the active sites. To address these concerns, structural and morphological engineering of nitrogen doped carbon matrix and multiwalled carbon nanotubes (MWCNTs) are used to construct the hierarchical structure of Fe-Ni active sites, ensuring efficient electron and mass transfer. The practical performances of this FeNi-NC@MWCNTs catalyst for OER/ORR and rechargeable ZABs are thoroughly evaluated.

(2) Catalysts based on Platinum group metals also demonstrate excellent catalytic performance towards ORR, while suffer from poor long-term stability. In this part, we employ defect-engineering to fabricate an ORR catalyst based on Pd metallene with atomically dispersed WO_x/MoO_x , this catalyst is also integrated into ZABs for practical utilization.

(c) High-performance electrocatalyst for electrosynthesis of ammonia with ZNBs.

Electrocatalytic nitrate/nitrite reduction is a promising approach to produce green ammonia in aqueous media, the conversion of $\text{NO}_3^-/\text{NO}_2^-$ to NH_3 is a complex proton-coupled multiple electron process involving a sequence of intermediates. Cu-based electrocatalysts are revealed as efficient catalysts for $\text{NO}_3^-/\text{NO}_2^-$ reduction but suffer from undesirable selectivity and stability. In this section, we prepare two bimetallic Cu alloys as self-supported electrode for $\text{NO}_3^-/\text{NO}_2^-$ electroreduction and use both of them for green NH_3 synthesis in ZNBs.

(1) A bimetallic NiCu coated electrode with sandwich structure of polymer-metal-metal oxide/hydroxide is prepared via 3D print technology (denoted as NiCu/ABS mesh) and integrated into Zn- NO_3^- batteries for realistic application.

(2) A self-supported electrode based on Cu foam incorporated with Ru atom (denoted as CuRu-3h/CF) is fabricated through electrodeposition strategy, then utilized for electrosynthesis of ammonia from nitrite in Zn- NO_2^- batteries.

3. Results and discussion

In this dissertation, the research works presented in sections 3.1, 3.3, 3.4, 3.5 and 3.6 are manuscripts which have been published in peer-reviewed journals. The research works discussed in sections 3.2 has been archived in the preprint server ChemRxiv. All manuscripts are reprinted with permission from the respective publishers.

Section 3.1 presents the research work on the synthesis and characterization of a novel polyoxovanadates **{MV₁₃}** and published in the paper titled as “Redox Self-Equilibration in Molecular Vanadium Oxide Mixtures Enables Multi-Electron Storage”. In this work, the structure and composition of this compound are clarified by single-crystal XRD and FT-IR. Besides, In-operando UV-Vis is used to reveal its structure evolution and valent characteristics. As results, this compound exhibited excellent redox properties with promise for RFB applications. Based on the findings in section 3.1, we construct a symmetric NRFB based on the **{MV₁₃}** cluster in section 3.2, the performance of this NRFB is symmetrically evaluated. In addition, in-operando UV-Vis is utilized to elucidate the reversible multi-electron storage and release of **{MV₁₃}** at different chemical states during the charging and discharging processes. The detailed results can be found in the paper “Mixed-Valent Redox-Equilibrated Polyoxovanadates for Symmetric Non-Aqueous Redox-Flow Batteries”.

Section 3.3 shows the research work on bifunctional oxygen electrocatalysts based on cheap and abundant transition metals. Here, dual atomic catalyst FeNi-NC@MWCNTs is successfully prepared via a two-step method. A series of advanced characterization techniques are employed to verify the existence of atomic FeNi dual-site, including HAADF-STEM, EXAFS, (FT)-EXAFS, and (WT)-EXAFS. Particularly, the hierarchical structure and synergistic effects greatly enhance the catalytic performance of this catalyst towards ORR/OER, and enable robust and efficient ZABs. More information can be found in the paper with title of “A Bifunctional Iron-Nickel Oxygen Reduction / Oxygen Evolution Catalyst for High-Performance Rechargeable Zinc-Air Batteries”. In section 3.4, we continue the research work on oxygen catalysts for ZABs. A defect rich Pd metallene with atomically dispersed WO_x and MoO_x (denoted as D-Pd M) is fabricated via an accessible wet chemical approach. Characterization results suggest the presence of a variety of atomic-scale defects, including pores, and concave surfaces, all of which can effectively modify the electronic configuration of the active sites and boost its catalytic activity for the ORR. The performance of the D-Pd M catalyst for ZABs

application is also evaluated. However, the rechargeability of the ZABs with the D-Pd M catalyst is undesirable, resulting from the poor OER activity of the D-Pd M. More detailed information is presented in the paper “Atomically Engineered Defect-Rich Palladium Metallene for High-Performance Alkaline Oxygen Reduction Electrocatalysis”.

Section 3.5 displays the study on the self-supported electrocatalyst for NO_3^- RR in ZNBs, a bimetallic NiCu-coated electrode is fabricated in the following three steps: 3D printing, chemical etching, and electroless plating, the obtained electrode is denoted as NiCu/ABS mesh. According to the SEM and TEM measurements, this material consists of a classic sandwich structure. The electrocatalytic performance of NiCu/ABS mesh electrode for electrosynthesis of ammonia is evaluated, demonstrating impressive results with a high Faradaic efficiency. More importantly, the Zn-nitrate batteries based on NiCu/ABS mesh electrode exhibit the promise to achieve sustainable NH_3 electrosynthesis, removal of NO_3^- pollutants from wastewater, and stable energy supply at the same time. More results and information are available in the paper “Metal Alloy-Functionalized 3D-Printed Electrodes for Nitrate-to-Ammonia Conversion in Zinc-Nitrate Batteries”. In section 3.6, we prepared an electrocatalyst CuRu-3h/CF based on Cu foam with ruthenium dispersing on the nanostructured copper surface. Through electrochemical galvanic replacement and annealing processes, the ruthenium species are incorporated into the copper foam nanowire structure, forming a self-supported electrode. The morphology, structure and composition of the CuRu-3h/CF catalyst are investigated with XRD, XPS, SEM and TEM. The performance of this catalyst for selective electrosynthesis of ammonia from nitrite is thoroughly evaluated, the Zn-nitrite battery integrated with this catalyst is assembled and studied as well. More information for this project is accessible in the paper “Ruthenium-doped Copper Nanowires for Nitrite/Nitrate to Ammonia Conversion and Their Integration in Zinc - Nitrite Batteries”.

3.1. Redox Self-Equilibration in Molecular Vanadium Oxide Mixtures Enables Multi-Electron Storage

Moritz Remmers, Boris Mashtakov, Stefan Repp, Alexandra Stefanie Jessica Rein, Ke Wang, Montaha Anjass, Zhengfan Chen, Luca M. Carrella, Eva Rentschler, Carsten Streb.



This paper described how a novel redox-equilibration driven self-assembly results in high-yield synthesis of a two-component co-crystal which contains two structurally closely related polyoxovanadates, $\{\text{MgV}_{13}\}$ and $\{\text{V}_{14}\}$. Mechanistic analyses and electrochemical studies revealed that the compound can store and release up to 16 electrons in a potential range of ca. 3.5 V, demonstrating great promise for the application in non-aqueous RFBs.

Author contributions:

Moritz Remmers: Methodology, Data curation, Investigation, Writing original draft.

Boris Mashtakov: Methodology, Data curation, Investigation, Writing original draft.

Stefan Repp: Conceptualization, Methodology, Data curation, Writing original draft.

Alexandra Stefanie Jessica Rein: Data curation, Writing original draft.

Ke Wang: Data curation, Writing original draft.

Montaha Anjass: Data curation, Writing original draft.

Zhengfan Chen: Data curation, Writing original draft.

Luca M. Carrella: Data curation, Writing original draft.

Eva Rentschler: Data curation, Writing original draft.

Carsten Streb: Project administration, Funding acquisition, Conceptualization, Supervision, Data curation, Methodology, Writing original draft.

Supporting information can be found on page 126.

“A. M. Remmers, B. Mashtakov, S. Repp, S. J. Rein, K. Wang, M. Anjass, L. M. Carrella, E. Rentschler, C. Streb, *Angew. Chem. Int. Ed* 2024, e202418864.” Reprinted with permission. Copyright, 2024, Wiley-VCH GmbH.

RESEARCH ARTICLE

Redox Self-Equilibration in Molecular Vanadium Oxide Mixtures Enables Multi-Electron Storage

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Supporting information for this article is given via a link at the end of the document.

Abstract: Polyoxometalates (POMs) are ideal components for reversible multi-electron storage in energy technologies. To-date, most redox-applications employ only single, individual POM species, which limits the number of electrons that can be stored within a given potential window. Here, we report that spontaneous redox self-equilibration during cluster synthesis leads to the formation of two structurally related polyoxovanadates which subsequently aggregate into co-crystals. This results in systems with significantly increased redox reactivity. The mixed POM system was formed by non-aqueous self-assembly of a vanadate precursor in the presence of Mg^{2+} , resulting in two mixed-valent ($\text{V}^{\text{IV/V}}$) species, $[(\text{MgOH})\text{V}_{13}\text{O}_{33}\text{Cl}]^{4-}$ ($= \{\text{MgV}_{13}\}$) and the di-vanadium-functionalized species $[\text{V}_{14}\text{O}_{34}\text{Cl}]^{4-}$ ($= \{\text{V}_{14}\}$), which co-crystallize in a 1:1 molar stoichiometry. Experimental data indicate that in the native state, $\{\text{MgV}_{13}\}$ is reduced by three electrons, and $\{\text{V}_{14}\}$ is reduced by five electrons. Electrochemical studies in solution show, that the system can reversibly undergo up to fourteen redox transitions (tentatively assigned to twelve 1-electron processes and two 2-electron processes) in the potential range between -2.15 V to +1.35 V (vs Fc^+/Fc). The study demonstrates how highly redox-active, well-defined molecular mixtures of mixed-valent molecular metal oxides can be accessed by redox-equilibration during synthesis, opening new avenues for molecular energy storage.

Molecular metal oxides, so-called polyoxometalates (POM) are unique functional molecules which have attracted immense interest due to their tunable structure and reactivity.^[1] POMs have been used in diverse areas of science and technology, ranging from biomedicine and therapeutics^[2–4] to molecular electronics,^[5,6] supramolecular assemblies^[7,8] and catalysis.^[9] One key function of POMs is their ability to reversibly store and release multiple electrons, making them ideal molecular components for energy conversion and storage technologies.^[10,11]

In general, each electron added to a POM cluster shifts the reduction potential to more negative values.^[12] The electrochemical potential difference between two reversible one-electron transitions in POMs is commonly in the range of ~0.4 V to 0.6 V (see SI, Section 2.11). In addition, the maximum overall number of electrons which can be stored per cluster unit is controlled by the cluster type (*i.e.* the number and type of metal centers present), as well as the electrochemical stabilities of the cluster, the solvent and the supporting electrolyte. For most applications in energy storage (batteries, redox-flow batteries, solar energy storage, *etc.*), increasing the number of electrons stored is a major development driver.^[13,14]

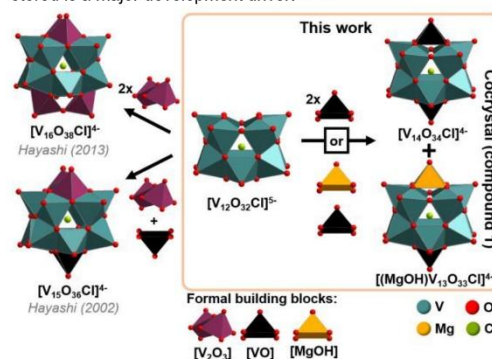


Figure 1. Formal assembly scheme and structure comparison of the mixed-cluster cocrystal 1, compared with structurally related literature-known single-cluster species $(n\text{Bu}_4)_4[\text{V}_{16}\text{O}_{38}\text{Cl}]$ and $(n\text{Bu}_4)_4[\text{V}_{15}\text{O}_{38}\text{Cl}]$.^[15,16] Note that synthetically, 1 is obtained using $[\text{V}_{10}\text{O}_{26}]^{4-}$ as vanadate precursor.

RESEARCH ARTICLE

Inspired by these challenges, ground-breaking works have focused on how to maximize electron storage in POMs. Irie, Yoshikawa, Awaga and co-workers showed that POM integration into lithium ion battery electrodes allows reversible storage of up to 24 electrons on the Keggin polyoxotungstate $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ ($n = 3-27$).^[17,18] Pioneering work on the solution redox chemistry of POMs by Symes, Poble, Nyman and Cronin showed that super-reduced Dawson polyoxotungstates $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{7-}$ ($n = 6-24$) can reversibly store up to 18 electrons per cluster in aqueous media in the presence of charge-balancing Li^+ or H^+ counterions. The system was further developed for electrochemical on-demand hydrogen generation.^[19,20]

Polyoxovanadates (POVs) have recently become a focal point for multi-electron storage due to their unique structural and electronic versatility^[21–25] combined with exceptional redox properties.^[11,26,27] In a series of outstanding reports, Matson and co-workers showed that derivatives of alkoxide-functionalized Lindqvist POVs $[\text{V}_6\text{O}_7(\text{OR})_{12}]$ ($\text{R} = \text{Me}, \text{Et}$) can undergo multiple (proton-coupled) electron transfers, enabling energy storage in non-aqueous POV-based redox-flow batteries.^[28–30] Also, some of us recently showed how metal-functionalization in dodecavanadate derivatives can be used to tune the number and position of redox-transitions.^[31–33] While these studies were primarily focused on energy technologies, it is worth noting that mixed-valent POVs have also received widespread interest from the molecular magnetism and spintronics communities as potential components for data storage systems. When considering the use of POMs in multi-electron storage and transport, one common theme is that these studies typically employ only one POM cluster species at a time. In contrast, the combined use of two or more species to maximize electron storage capacity has not been explored to date. This might be due to challenges related to incompatibilities between species including inter-cluster redox-reactions, divergent chemical stability or solubility ranges.

Here, we propose a concept to overcome these challenges by developing designer electron storage materials where two individual POV clusters are synthesized and selectively crystallized from one common reaction solution. Importantly, cluster formation and redox equilibration are achieved within the reaction solution, thereby ensuring that no chemical incompatibilities arise for the two targeted cluster species. This approach results in a 1:1 mixture of two POVs, where the combination of individual redox-processes at both clusters results in up to fourteen redox-transitions in the potential range between -2.15 V to $+1.35 \text{ V}$ (vs Fc^+/Fc). Mechanistic studies rationalize cluster formation, cluster stability and charge-storage mechanism. These insights shed light on how physical and electronic structure interact to give rise to technologically important redox properties. To develop the mixed-cluster system, we built on previous studies by some of us, where we explored the mono- or di-metal-functionalization of the dodecavanadate cluster $(\text{NMe}_2\text{H}_2)_2[\text{V}_{12}\text{O}_{32}\text{Cl}]^{3-}$ ($= \{\text{V}_{12}\}$).^[33–37] Here, we demonstrate how under non-aqueous synthesis conditions, simultaneous formation and redox equilibration of two closely related $\{\text{V}_{12}\}$ derivatives was achieved. This gave access to mixed co-crystals showing reversible multi-electron uptake and release.

The title compound **1** was synthesized by reaction of the mixed-valent precursor $(n\text{Bu}_4\text{N})_4[\text{V}^{\text{IV}}_2\text{V}^{\text{V}}_8\text{O}_{26}]$ ($= (n\text{Bu}_4\text{N})_4\{\text{V}_{10}\}$)^[38,39] with the magnesium and chloride source MgCl_2 (anhydrous) in acetonitrile at 75°C . Diffusion of diethyl ether into the green

reaction solution gave deep green crystals of **1** suitable for single-crystal X-ray diffraction (yield: 70 % based on **V**). The composition and purity of the compound were confirmed by ATR-IR-UV/Vis/NIR and EPR spectroscopies, high-resolution electrospray ionization mass spectrometry (ESI MS), thermogravimetric analysis (TGA) and single-crystal X-ray diffraction, for details see Supporting Information.

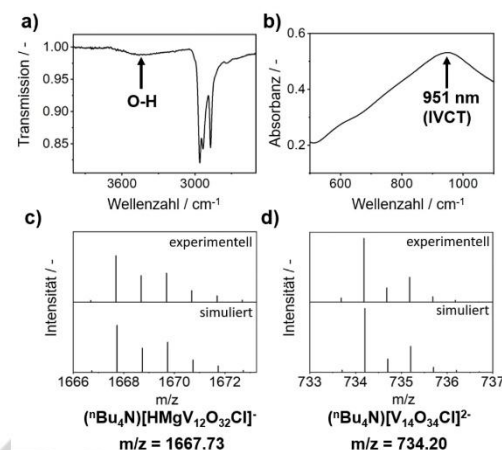


Figure 2. Characterization of **1**. a) ATR-IR spectroscopy showing the presence of O-H vibrations; b) UV/Vis/NIR spectroscopy showing characteristic V(IV)/V(V) intervalence charge-transfer (IVCT) transitions; c), d) simulated and observed isotopic patterns from high resolution ESI MS analyses, indicating the presence of $\{\text{MgV}_{13}\}$ and $\{\text{V}_{14}\}$.

Single-crystal X-ray diffraction analysis showed that **1** crystallizes in the monoclinic space group C_2 with cell axes $a = 23.189(4) \text{ \AA}$, $b = 23.197(4) \text{ \AA}$, $c = 17.660(3) \text{ \AA}$ and angles $\alpha = \gamma = 90^\circ$, $\beta = 90.089(6)$, crystallographic details see SI, Section 3.^[40] Structural analysis of the crystallographic data reveal that **1** is composed of a 1:1 mixture of two $\{\text{V}_{12}\}$ derivatives, that is the mixed magnesium and vanadium/functionalized species $[(\text{MgOH})\text{V}_{13}\text{O}_{33}\text{Cl}]^{4-}$ ($= \{\text{MgV}_{13}\}$) and the di-vanadium-functionalized species $[\text{V}_{14}\text{O}_{34}\text{Cl}]^{2-}$ ($= \{\text{V}_{14}\}$). Note that to the best of our knowledge, both clusters, $\{\text{MgV}_{13}\}$ and $\{\text{V}_{14}\}$ have not been reported previously. For charge-balance, each unit cell contains two cluster units and eight $n\text{Bu}_4\text{N}^+$ cations. The amount of $n\text{Bu}_4\text{N}^+$ cations in the bulk was verified by CHN elemental analysis and TGA (see SI, Section 2.3). The $\{\text{V}_{14}\} : \{\text{MgV}_{13}\}$ molar ratio in the bulk of **1** was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES), which gave a V : Mg atomic ratio of 1.17 : 27 (calculated: 1.0 : 27.0 for a 1:1 molar ratio of $\{\text{MgV}_{13}\}$ and $\{\text{V}_{14}\}$). The presence of the Mg-OH group in **1** was substantiated by ATR-IR spectroscopy, where a weak, characteristic signal was detected at 3460 cm^{-1} (Figure 2a).^[41] The presence of both cluster species, $\{\text{MgV}_{13}\}$ and $\{\text{V}_{14}\}$, was also observed by negative-ion mode high-resolution electrospray ionization mass spectrometry (ESI MS), see Figure 2c,d. For example, the $\{\text{MgV}_{13}\}$ -related species $(n\text{Bu}_4\text{N})[\text{HMgV}_{12}\text{O}_{32}\text{Cl}]^-$ was observed at 1667.69 m/z (calcd: 1667.73 m/z), while the

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{V₁₄} species (*n*Bu₄N)[V₁₄O₃₄Cl]²⁻ was observed at 767.15 m/z (calcd: 767.17 m/z)

In sum, these analyses suggest that **1** can be given as (*n*Bu₄N)₈[(MgOH)V₁₃O₃₃Cl][V₁₄O₃₄Cl] = (*n*Bu₄N)₈(MgV₁₃){V₁₄}. Based on this initial analysis it can be proposed that each cluster features a fourfold negative charge. This would result in three V^{IV} centers for {MgV₁₃}, and five V^{IV} centers for {V₁₄}, for details on the charge calculations see SI, Section 2.4. Since most mixed-valent POMs feature antiferromagnetic coupling,^[5, 23,42–44] it can be put forward that both, {MgV₁₃} and {V₁₄} feature one unpaired electron. Thus, the presence of unpaired electrons in **1** was probed by EPR spectroscopy (Figure 3). As a reference compound for spin counting, we utilized the mixed-valent precursor (*n*Bu₄N)₄{V₁₀}^[38,39] which features two isolated V^{IV} centers. Note that only the EPR spectrum of the reference compound shows hyperfine coupling, as electron delocalization in **1** results in a non-observable hyperfine coupling.^[45] A comparison of the spin count of both compounds at the same concentration and same sample volume, gave 1.87 unpaired electrons per formula unit of **1**. This is in line with our previous oxidation state and charge assignments which suggested that both {MgV₁₃} and {V₁₄} feature one unpaired electron each. In addition, UV/Vis/NIR spectroscopy of **1** in MeCN also supported the presence of reduced V^{IV} centers as indicated by characteristic intervalence charge transfer (IVCT) transitions in the ~500 nm – 1400 nm spectral region (Figure 2b).

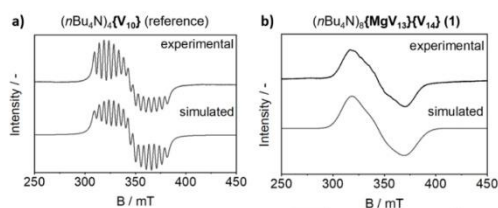


Figure 3. Simulated and experimental EPR spectra (*T* = 40 °C) of: a) the reference compound (*n*Bu₄N)₄{V₁₀}^[38] (3 mM in MeCN); b) compound **1** (3 mM in MeCN). Comparison of the spin counts gave a value of 1.87 unpaired electrons for **1**.

We were interested in the Mg²⁺-induced conversion of the mixed-valent {V₁₀} precursor into compound **1**. Note that in the absence of MgCl₂, no conversion of {V₁₀} into **1** occurs. We used UV/Vis/NIR spectroscopy to follow the changes of the characteristic signals of {V₁₀} (at λ = 500 nm) and **1** (at λ = 1000 nm), see Figure 4a. We hypothesized that the reaction might be initiated by reaction of Mg²⁺ with {V₁₀}, possibly by a Lewis-acid mechanism. Thus, we investigated the impact of {V₁₀} / Mg²⁺ molar ratios on the conversion rate by a series of [Mg²⁺]-dependent analyses. As shown in Figure 4, between 0 – 1 molar equivalents of Mg²⁺ (relative to {V₁₀}), increasing Mg²⁺ concentrations result in equilibria with decreasing {V₁₀} concentration (Figure 4b) and increasing concentrations of **1** (Figure 4c). When more than ~ 1 equivalent of Mg²⁺ is added to the reaction solution, the characteristic UV/Vis/NIR spectral signatures of {V₁₀} are lost, and no further changes of the

characteristic signatures of **1** are observed. These data suggest that the {V₁₀} conversion to **1** is driven by the presence of Mg²⁺. Previous studies have reported similar observations, where Lewis-acidic metals, such as Mg²⁺,^[36] Ca²⁺,^[32,33] Co²⁺, Ti⁴⁺ or Cu²⁺^[46] have triggered conversion processes in polyoxovanadates, particularly in organic solvents.

Thus, we determined the apparent conversion rate constant *k* at temperatures between 25 °C – 65 °C to provide initial thermochemical data for the {V₁₀} to-**1** conversion. As illustrated in Figure 4d, this allowed an Arrhenius-type plot showing linear behaviour, which gave an activation energy for the conversion of 63 kJ/mol.

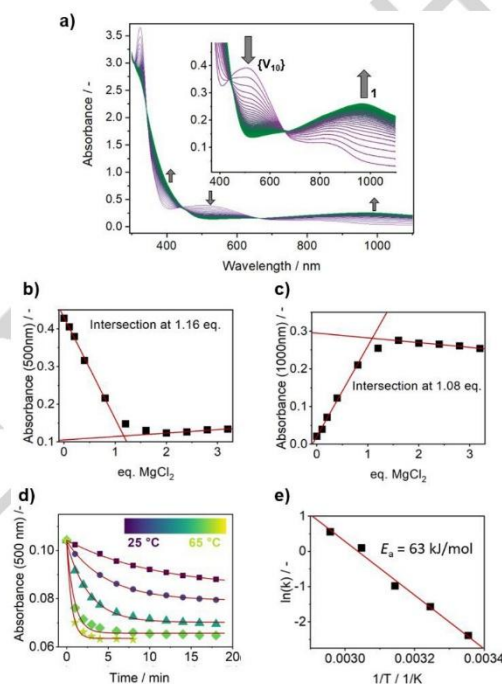


Figure 4. a) Time-lapse UV/Vis/NIR spectroscopy of the conversion of {V₁₀} to **1** at time intervals of 1 min. Three isosbestic points at λ₁ = 665 nm, λ₂ = 446 nm and λ₃ = 340 nm indicate a direct conversion process. Conditions: *T* = 35 °C, cuvette path length 10.0 mm, [{V₁₀}] : [MgCl₂ (anhydrous)] = 1 : 1.2, [{V₁₀}] = 230 μM. b) Decrease of {V₁₀} concentration as a function of [Mg²⁺] concentration, monitored by following the characteristic {V₁₀} absorbance at λ = 500 nm; samples were equilibrated for 1 h before measurement; c) Increase of the concentration of **1** as a function of Mg²⁺ concentration, monitored by following the characteristic absorbance of **1** at λ = 1000 nm; samples were equilibrated for 1 h before measurement. d) Kinetic traces and mono-exponential fits of the {V₁₀} to-**1** conversion (monitored by following the decrease of {V₁₀} concentration at λ = 500 nm) at temperatures between 25 °C to 65 °C. Conditions: Δ*T* = 10 °C, cuvette path length 2.0 mm, [{V₁₀}] : [MgCl₂ (anhydrous)] = 1 : 2.2, [{V₁₀}] = 500 μM. e) Arrhenius plot based on the kinetic traces shown in e).

Next, we explored the electrochemistry of **1**, as we hypothesized that the presence of both, {MgV₁₃} and {V₁₄} clusters in **1** could

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result in enhanced redox-reactivity and electron storage capacity. To prevent any effects of surface oxidation of the crystalline sample (which was suggested by microscopic analysis of the native crystals after storage in air), we purified **1** by recrystallization from acetonitrile under inert atmosphere and water-free conditions in an Ar-filled glovebox (see SI, Section 2.1). These samples were used for all electrochemical and EPR studies. Electrochemistry was performed in inert Ar atmosphere in a glovebox (for details see SI, Sections 2.11 and 2.12).

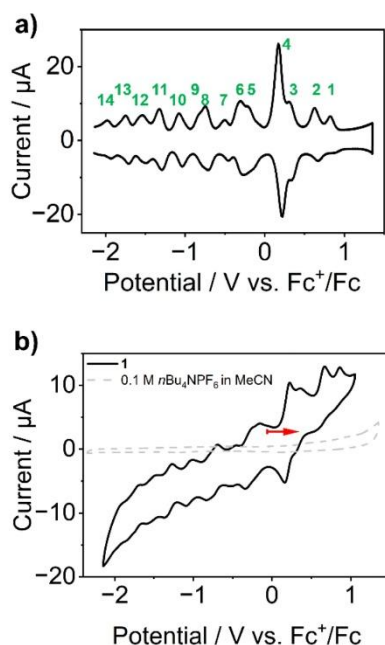


Figure 5. a) Square wave voltammogram and b) cyclic voltammogram of **1**, showing 14 pseudo-reversible redox transitions in the scan range between -2.15 V to +1.35 V vs Fc⁺/Fc, open circuit potential and scan direction are indicated by the red arrow. Conditions: anhydrous, deoxygenated acetonitrile containing *n*Bu₄NPF₆ (0.1 M) as supporting electrolyte. Scan rate 50 mV s⁻¹, [**1**]: 0.5 mM, Ar atmosphere.

Initial electrochemical analyses of **1** (0.5 mM) were performed by cyclic voltammetry (CV) and square wave voltammetry (SWV) in anhydrous, degassed acetonitrile solution containing *n*Bu₄NPF₆ (0.1 M) as supporting electrolyte (Figure 5). All electrochemical data were recorded using a silver/silver nitrate reference electrode, and the potentials were then referenced against an internal ferrocene/ferrocenium (Fc⁺/Fc) redox couple. In the potential range between -2.15 V and +1.35 V, **1** showed up fourteen redox transitions (see green labels in Figure 5). Integration of the complex SWV data results in the tentative assignment that twelve processes (processes 1, 2, 5-14) are 1-electron transfers, while two processes (processes 3, 4) are 2-electron transfers (see SI, Section 2.12). In sum, this suggests

uptake/release of 16 electrons by **1** in the given potential range. Note that initial density functional theory (DFT) computations for the first reduction of {V₁₄} and {MgV₁₃} gave theoretical redox potentials which are in close agreement ($\Delta E < 5$ mV) with the experimentally observed data (i.e., redox-transitions 8 and 9). For details see SI, Section 2.15.

To verify these findings and assess the bulk redox activity of **1**, we performed bulk electrolysis (BE) under the conditions used for CV and SWV. Under reductive BE conditions ($E_{\text{red}} = -1.45$ V), the data show that 7.86 ± 0.82 electrons can be taken up per formula unit of **1** (i.e., per one {MgV₁₃} and one {V₁₄} cluster) when starting from the native compound. Note that no significant changes of the SWV data are observed upon bulk reduction, indicating that the structural integrity of the clusters are retained (SI, Section 2.12). Also, an increase of the characteristic IVCT transitions in the VIS-NIR range are in line with the increasing number of V^{IV} centers. Under oxidative conditions ($E_{\text{ox}} = +1.22$ V), BE resulted in the release of 8.66 ± 0.86 electrons per formula unit of **1**. This is in line with a four-electron oxidation of the {MgV₁₃} and {V₁₄} species, respectively, resulting in the complete removal of all V^{IV} centers. This is supported by UV-Vis-NIR spectroscopy of the oxidized sample of **1**, where a complete loss of the IVCT transitions in the VIS-NIR range (characteristic of delocalized V^{IV} centers) was observed (SI, Section 2.12, Figure S14). Note that for the fully oxidized sample, the SWV signatures became somewhat less well defined compared to the native sample. However, upon re-reduction of the sample at the open-circuit potential OCP ($E_{\text{OCP}} = -0.06$ V vs. Fc⁺/Fc), the original SWV signals of **1** were recovered (SI, Section 2.12, Figure S15), suggesting that the structural integrity in this sample is retained or regenerated upon re-reduction. In sum BE analyses indicate that reversible uptake and release of up to 16 electrons per formula unit of **1** is possible in the potential range between -1.08 V to 1.07 V vs. Fc/Fc⁺ (for details see SI, Section 2.12). This is in line with the data observed from integration of the SWV data, where 16 electron transfers were estimated (Figure 5 and SI, Section 2.11). Note that the physical mixing of two chemically or structurally related polyoxovanadates leads to complex mixtures where redox reactions between the clusters can occur, which can lead to (partial) degradation or cluster rearrangements. Thus, redox equilibration during synthesis is an effective path to avoid this detrimental reaction (see SI, Figure Sx).

In sum, we have shown that redox-equilibration of structurally related but chemically different polyoxovanadate clusters is a new and viable synthetic route to access electroactive compounds with remarkable reversible redox-reactivity. Specifically, self-assembly and co-crystallization of two vanadium oxide clusters, {MgV₁₃} and {V₁₄} results in an unusual system where the redox-events of the two species facilitate closely aligned redox-transitions, so that up to 16 electrons can be stored in a potential range of ~ 3.5 V. In future, this new materials design approach will be used to develop high-performance electrolytes for non-aqueous redox-flow batteries.

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Supporting Information

The authors have cited additional references within the Supporting Information.^[47–65]

Acknowledgements

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Keywords: Polyoxometalate • Polyoxovanadate • Self-Assembly • Vanadium Oxide • Electrochemistry

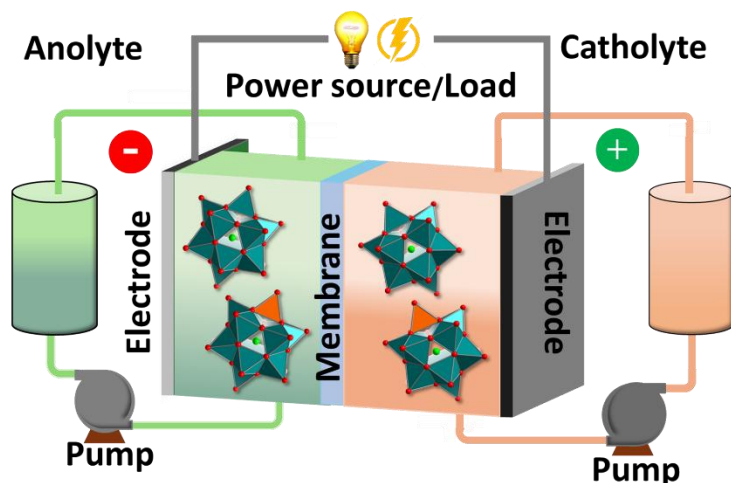
- [1] L. Cronin, A. Müller, (guest eds.), special POM themed issue, *Chem. Soc. Rev.* **2012**, *41*, 7325–7648.
- [2] L. S. Van Rompu, T. N. Parac-Vogt, *Curr. Opin. Biotechnol.* **2019**, *58*, 92–99.
- [3] F. de Azambuja, J. Moons, T. N. Parac-Vogt, *Acc. Chem. Res.* **2021**, *54*, 1673–1684.
- [4] A. Bijelic, M. Aureliano, A. Rompel, *Angew. Chem. Int. Ed.* **2019**, *58*, 2980–2999.
- [5] M. Moors, J. Warneke, X. Lopez, C. de Graaf, B. Abel, K. Y. Monakhov, *Acc. Chem. Res.* **2021**, *54*, 3377–3389.
- [6] E. Coronado, *Nat. Rev. Mater.* **2019**, *5*, 87–104.
- [7] M. Stuckart, K. Y. Monakhov, *Chem. Sci.* **2019**, *10*, 4364–4376.
- [8] A. Misra, K. Kozma, C. Streb, M. Nyman, *Angew. Chem. Int. Ed.* **2020**, *59*, 596–612.
- [9] S. Wang, G. Yang, *Chem. Rev.* **2015**, *115*, 4893–4962.
- [10] A. Sartorel, M. Bonchio, S. Campagna, F. Scandola, *Chem. Soc. Rev.* **2013**, *42*, 2262–2280.
- [11] M. Anjass, G. A. Lowe, C. Streb, *Angew. Chem. Int. Ed.* **2021**, *60*, 7522–7532.
- [12] T. Ueda, *ChemElectroChem* **2018**, *5*, 823–838.
- [13] D. G. Nocera, *J. Am. Chem. Soc.* **2022**, *144*, 1069–1081.
- [14] Z. Li, Y. C. Lu, *Adv. Mater.* **2020**, *32*, 2002132.
- [15] Y. Hayashi, N. Miyakoshi, T. Shinguchi, A. Uehara, *Chem. Lett.* **2001**, *30*, 170–171.
- [16] N. Kato, Y. Hayashi, *Dalton Trans.* **2013**, *42*, 11804–11811.
- [17] Y. Nishimoto, D. Yokogawa, H. Yoshikawa, K. Awaga, S. Irie, *J. Am. Chem. Soc.* **2014**, *136*, 9042–9052.
- [18] H. Wang, S. Hamanaka, Y. Nishimoto, S. Irie, T. Yokoyama, H. Yoshikawa, K. Awaga, *J. Am. Chem. Soc.* **2012**, *134*, 4918–4924.
- [19] J. J. Chen, M. D. Symes, L. Cronin, *Nat. Chem.* **2018**, *10*, 1042–1047.
- [20] J.-J. Chen, L. Vilà-Nadal, A. Solé-Daura, G. Chisholm, T. Minato, C. Busche, T. Zhao, B. Kandasamy, A. Y. Ganin, R. M. Smith, I. Colliard, J. J. Carbó, J. M. Poblet, M. Nyman, L. Cronin, *J. Am. Chem. Soc.* **2022**, *144*, 8951–8960.
- [21] C. Streb, "Structure and Bonding in Molecular Vanadium Oxides: From Templates via Host–Guest Chemistry to Applications." in: Polyoxometalate-Based Assemblies and Functional Materials. Structure and Bonding, Vol 176 (guest ed: Y.-F. Song). Springer, Cham, **2017**, pp. 31–47.
- [22] K. Y. Monakhov, M. Moors, P. Kögerler, "Perspectives for Polyoxometalates in Single-Molecule Electronics and Spintronics", in *Advances in Inorganic Chemistry*, Vol. 69 (Eds.: R. van Eldik, L. Cronin), Academic Press, Amsterdam, **2017**, pp. 251–286.
- [23] K. Yu. Monakhov, W. Bensch, P. Kögerler, *Chem. Soc. Rev.* **2015**, *44*, 8443–8483.
- [24] D. Gatteschi, L. Pardi, A. L. Barra, A. Müller, *Molec. Engin.* **1993**, *3*, 157–169.
- [25] W. G. Klemperer, T. A. Marquart, O. M. Yaghi, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 49–51.
- [26] S. Chakraborty, B. E. Petel, E. Schreiber, E. M. Matson, *Nanoscale Adv.* **2021**, *3*, 1293–1318.
- [27] K. R. Proe, E. Schreiber, E. M. Matson, *Acc. Chem. Res.* **2023**, *2021*, 12.
- [28] L. E. VanGelder, T. R. Cook, E. M. Matson, *Comm. Inorg. Chem.* **2019**, *39*, 51–89.
- [29] L. E. VanGelder, A. M. Kosswattaarachchi, P. L. Forrester, T. R. Cook, E. M. Matson, *Chem. Sci.* **2018**, *9*, 1692–1699.
- [30] L. E. VanGelder, E. M. Matson, *J. Mater. Chem. A* **2018**, *6*, 13874–13882.
- [31] M. H. Anjass, K. Kastner, F. Nägele, M. Ringenberg, J. F. Boas, J. Zhang, A. M. Bond, T. Jacob, C. Streb, *Angew. Chem. Int. Ed.* **2017**, *56*, 14749–14752.
- [32] S. Greiner, B. Schwarz, C. Streb, M. Anjass, *Chem. Eur. J.* **2021**, *27*, 13435–13441.
- [33] S. Greiner, B. Schwarz, M. Ringenberg, M. Dürr, I. Ivanovic-Burmazovic, M. Fichtner, M. Anjass, C. Streb, *Chem. Sci.* **2020**, *11*, 4450–4455.
- [34] K. Kastner, J. T. Margraf, T. Clark, C. Streb, *Chem. Eur. J.* **2014**, *20*, 12269–12273.
- [35] K. Kastner, J. Forster, H. Ida, G. N. Newton, H. Oshio, C. Streb, *Chemistry - A European Journal* **2015**, *21*, 7686–7689.
- [36] S. Repp, M. Remmers, A. Stefanie, J. Rein, D. Sorsche, D. Gao, M. Anjass, M. Mondeshki, L. M. Carrella, E. Rentschler, C. Streb, *Nat. Commun.* **2023**, *14*, 5563.
- [37] N. Arya, T. Philipp, S. Greiner, M. Steiner, C. Kranz, M. Anjass, *Angew. Chem. Int. Ed.* **2023**, *62*, e202306170.
- [38] A. Bino, S. Cohen, C. Heitner-Wirgin, *Inorg. Chem.* **1982**, *21*, 429–431.
- [39] K. Okaya, T. Kobayashi, Y. Koyama, Y. Hayashi, K. Isobe, *Eur. J. Inorg. Chem.* **2009**, *2009*, 5156–5163.
- [40] Deposition Number <https://www.ccdc.cam.ac.uk/services/structures?id=doi:10.1002/anie.2024XXXXX> (for 1) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe <http://www.ccdc.cam.ac.uk/structures> Access Structures service</url>
- [41] A. Kondo, R. Kurosawa, J. Ryu, M. Matsuoka, M. Takeuchi, *J. Phys. Chem. C* **2021**, *125*, 10937–10947.
- [42] P. Kögerler, B. Tsukerblat, A. Müller, *Dalton Trans.* **2010**, *39*, 21–36.
- [43] A. Müller, P. Kögerler, A. W. M. Dress, *Coord. Chem. Rev.* **2001**, *222*, 193–218.
- [44] J. Wang, C. Näther, P. Kögerler, W. Bensch, *Inorg. Chim. Acta* **2010**, *363*, 4399–4404.
- [45] O. Linnenberg, P. Kozłowski, C. Besson, J. Van Leusen, U. Englert, K. Y. Monakhov, *Cryst. Growth Des.* **2017**, *17*, 2342–2350.
- [46] T. Kobayashi, S. Kuwajima, T. Kurata, Y. Hayashi, *Inorg. Chim. Acta* **2014**, *420*, 69–74.
- [47] Y. Cao, J.-J. Chen, M. A. Barteau, *J. Energy Chem.* **2020**, *50*, 115–124.
- [48] L. E. VanGelder, A. M. Kosswattaarachchi, P. L. Forrester, T. R. Cook, E. M. Matson, *Chem. Sci.* **2018**, *9*, 1692–1699.
- [49] N. Fay, A. M. Bond, C. Baffert, J. F. Boas, J. R. Pilbrow, D.-L. Long, L. Cronin, *Inorg. Chem.* **2007**, *46*, 3502–3510.
- [50] S. Greiner, B. Schwarz, M. Ringenberg, M. Dürr, I. Ivanovic-Burmazovic, M. Fichtner, M. Anjass, C. Streb, *Chem. Sci.* **2020**, *11*, 4450–4455.
- [51] O. Linnenberg, M. Moors, A. Solé-Daura, X. López, C. Bäumer, E. Kentzinger, W. Pyckhout-Hintzen, K. Yu. Monakhov, *J. Phys. Chem. C* **2017**, *121*, 10419–10429.
- [52] G. M. Sheldrick, *Acta Crystallogr. A* **2008**, *64*, 112–122.
- [53] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
- [54] L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard, H. Puschmann, *Acta Crystallogr. A* **2015**, *71*, 59–75.
- [55] R. H. Blessing, *Acta Crystallogr. A* **1995**, *51*, 33–38.
- [56] T. Ueda, K. Kodani, H. Ota, M. Shiro, S.-X. Guo, J. F. Boas, A. M. Bond, *Inorg. Chem.* **2017**, *56*, 3990–4001.

RESEARCH ARTICLE

- [57] R. L. Belford, N. D. Chasteen, H. So, R. E. Tapscott, *J. Am. Chem. Soc.* **1969**, *91*, 4675–4680.
- [58] Q. Chen, D. P. Goshorn, C. P. Scholes, X. L. Tan, J. Zubieta, *J. Am. Chem. Soc.* **1992**, *114*, 4667–4681.
- [59] S. Stoll, A. Schweiger, *J. Magnet. Res.* **2006**, *178*, 42–55.
- [60] K. J. Laidler, *J. Chem. Educ.* **1984**, *61*, 494.
- [61] V. W. Day, W. G. Klemperer, O. M. Yaghi, *J. Am. Chem. Soc.* **1989**, *111*, 5959–5961.
- [62] V. W. Day, W. G. Klemperer, D. J. Maltbie, *J. Am. Chem. Soc.* **1987**, *109*, 2991–3002.
- [63] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378–6396.
- [64] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
- [65] Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

3.2 Mixed-Valent Redox-Equilibrated Polyoxovanadates for Symmetric Non-Aqueous Redox-Flow Batteries

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This publication reported the application of polyoxovanadates {MV₁₃} cluster in symmetric non-aqueous redox flow batteries. The {MV₁₃} clusters showed excellent electrochemical properties with fast kinetics and high solubility in acetonitrile, its nano-sized structure also guarantees its

promise for application in NRFBs. As results, the batteries showed a coulombic efficiency of 93% at 0.6 mA cm⁻² and a high stability with a capacity fading rate of 0.074% per cycle under standard operating conditions.

Author contributions:

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Mixed-Valent Redox-Equilibrated Polyoxovanadates for Symmetric Non-Aqueous Redox-Flow Batteries

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Supporting information for this article is given via a link at the end of the document.

Abstract: Redox flow batteries (RFBs) are a key technology for decentralized, scalable electrochemical energy storage. One major challenge in RFB research is the design of redox-active electrolyte components that combine high solubility and stability with reversible multi-electron storage. Here, we report the use of the two-component polyoxovanadate co-crystal $\{MV_{13}\}$ ($= (nBu_4N)_4[MV_{13}O_{33}Cl]$ ($M = V^{IV}=O^{2+}$ or $MgOH^+$)) as a highly stable and highly redox-active nonaqueous RFB component. The mixed-valent ($V^{IV/V}$) oxidation state of $\{MV_{13}\}$ enables a symmetric RFB configuration, while the organo-solubility of $\{MV_{13}\}$ allows deployment in acetonitrile. Previous electrochemical analyses have shown that $\{MV_{13}\}$ can reversibly store up to 16 electrons in the potential range of -2.2 to +1.4 V vs Fc^+/Fc . Integration of $\{MV_{13}\}$ into a symmetric RFB results in a specific capacity of 24.5 mAh, a coulombic efficiency of 93% (at a current density $j = 0.6 \text{ mA cm}^{-2}$) and high stability with a capacity fading rate of 0.074% pre cycle. *Operando* UV-Vis spectroscopy provides initial mechanistic insights into the charge-discharge behaviour and stability of $\{MV_{13}\}$. This study provides a blueprint for the design and integration of mixed-valent metal oxide clusters into non-aqueous electrochemical energy storage systems.

Introduction

Electrical energy conversion and storage technologies are crucial to achieve a carbon-neutral energy supply based on renewable energies.^[1–3] Redox-flow batteries (RFBs) are one key technology for the large-scale, stationary and decentralized storage of electrical energy.^[4] Compared with conventional secondary batteries (e.g., lithium-ion batteries), RFBs feature low cost and long service life.^[5] Their unique function allows decoupling of energy storage capacity and power density, making RFBs highly flexible and scalable.^[6]

While the energy content of RFBs can easily be increased by increasing the volume of the electrolyte, reaching higher volumetric energy density is still a major challenge: the energy density of RFBs is directly proportional to the molar concentration of the active compound in the electrolyte, the number of electrons which can be reversibly exchanged, as well as the potential range in which the system operates, see equation 1:

$$E [\text{Wh L}^{-1}] = c z F U \quad \text{eq. 1}$$

Where E = energy density, c = molar concentration of active compound, z = number of electrons exchanged, F = Faraday constant, U = operation potential.^[7]

Thus, one major thrust in RFBs research is the development of new active materials which combine high solubility, high redox-activity and high stability over a wide potential range.^[8] Moreover, active materials capable of storing and releasing multiple electrons are highly sought-after to increase RFB energy density. In addition, using identical species in both RFB half-cells is advantageous as it results in simple operation, where membrane crossover or electrochemical interference can be avoided.

Historically, aqueous RFBs have been most explored, and a variety of species have been developed, including metal ions,^[9] transition metal complexes^[10] and organic species.^[11] However, aqueous RFBs suffer from several drawback including a small potential window due to water oxidation/water reduction,^[12] also, membrane crossing can lead to self-discharging and loss of capacity.^[13] In addition, many redox-species used in aqueous RFBs offer only one-electron storage, which further limits specific energy capacity.^[14,15] Last, most aqueous RFBs utilize highly acidic or basic electrolytes to improve the solubility and stability of the redox-active materials, resulting in high maintenance cost and further diminishing the lifespan of the entire system.^[16]

To overcome these challenges, non-aqueous RFBs (NRFBs) have garnered significant attention.^[17] NRFBs utilize polar organic solvents to achieve wide potential operation windows. As an example, the prototype NRFB solvent acetonitrile has a stable potential window of up to 5 V, which enables redox-events which are not accessible in aqueous systems.^[18] Also, the use of organic solvents facilitates the use of redox-active species which are insoluble in water, thereby broadening the scope of RFBs.^[19]

Molecular metal oxides, or polyoxometalates (POMs) have received significant interest as potential multi-electron storage molecules for NRFBs.^[20] The promises of POMs clusters lie in their superior structural configuration and excellent redox properties, which facilitate the reversible storage and release of multiple electrons without structure decomposition.^[21] Notably, the solubility and redox properties of POMs clusters can be rationally tailored by introduction different counter cations and various atoms or ligands. Beyond electrochemistry, nano-sized POMs clusters offer significant advantages over smaller ionic/molecular

charge carriers, as their size and charge limits membrane crossing and prevents self-discharge.^[22]

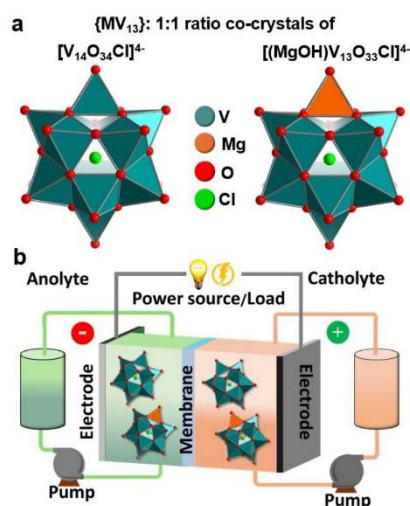


Figure 1. (a) Polyhedral representation of the two vanadate cluster species present as 1:1 molar mixture in the $\{MV_{13}\}$. (b) Schematic illustration of the symmetric $\{MV_{13}\}$ -based nonaqueous redox flow battery setup reported.

The earliest research on RFBs based on POMs was conducted by Sun and colleagues in 1997, who reported an asymmetric aqueous RFB using Keggin POM $H_3[PMo_{12}O_{40}]$ as the anolyte active species and Fe^{3+}/Fe^{2+} as the catholyte active species.^[23] Subsequently, Xiang and coworkers reported an aqueous RFB based on $H_6[CoW_{12}O_{40}]$, which demonstrated reversible transfer of three electrons and enabled symmetric RFB operation.^[24] In recent years, Matson and co-workers have reported seminal studies in the field of NRFBs based on Lindqvist POMs $[V_6O_7(OR)_{12}]$ ($R=CH_3$, C_2H_5). The group also showed how structural modifications (e.g., functionalization with heterometals or different alkoxide ligands) affects NRFB performance.^[25–28] Notably, polyoxovanadates (POVs) have attracted widespread attention as RFB active species due to their significantly lower mass ($M(V) = 52 \text{ g mol}^{-1}$) compared to more traditional molybdenum ($M(Mo) = 95 \text{ g mol}^{-1}$) and tungsten ($M(W) = 180 \text{ g mol}^{-1}$) POMs, implying that POV clusters could offer higher energy density per unit mass than heavier metal oxide clusters.^[29] To-date, most POM (N)RFBs, only allow the transfer of up to four electrons across different oxidation states, necessitating an asymmetric configuration to handle charge imbalances. Thus, it remains challenging to develop POM-based RFBs that enable multi-electron storage and release in a symmetric system with high operation voltage.^[30]

Recently, some of us reported the synthesis of mixed-valent polyoxovanadate co-crystals $\{MV_{13}\}$ ($(nBu_4N)_4[MV_{13}O_{33}Cl]$ ($M=VO^{2+}$ or $MgOH^+$) which demonstrated excellent redox properties:^[31] briefly, the $\{MV_{13}\}$ co-crystals contain 1:1 molar

mixtures of the five-electron reduced species $[V^{IV}_5V^{V}_8O_{34}Cl]^{4-}$ ($=\{V_{14}\}$) and the three-electron reduced species $[(MgOH)V^{IV}_3V^{V}_{11}O_{33}Cl]^{4-}$ ($=\{MgV_{13}\}$). Thus, $\{MV_{13}\}$ can be given as $(nBu_4N)_8[(MgOH)V_{13}O_{33}Cl][V_{14}O_{34}Cl] = (nBu_4N)_8\{MgV_{13}\}\{V_{14}\}$, see Figure 1a. $\{MV_{13}\}$ is soluble in coordinating organic solvents, e.g., acetonitrile (solubility = 10 mM), facilitating the design of multi-electron storage systems. In detail, $\{MV_{13}\}$ can reversibly store and release up to 16 electrons in the potential range of $-2.2 \text{ V} - 1.4 \text{ V}$ vs Fc^+/Fc . This is in line with previous studies on related vanadates, where increased redox-activity depending on the exact metal substitution was observed.^[32–34] Also, as the two cluster species in $\{MV_{13}\}$ form in the same reaction solution, there are no chemical incompatibilities between these components. Herein, we demonstrate that acetonitrile solution of $\{MV_{13}\}$ can be used as electrolyte for symmetric NRFB (as shown in Figure 1b). Fundamental electrochemical investigations revealed that $\{MV_{13}\}$ cluster enables reversible storage and release of 14 electrons spanning a wide electrochemical window with remarkable diffusion coefficients and excellent electron transfer rate constants in acetonitrile, ensuring promises for symmetric NRFBs applications.

Results and Discussion

$\{MV_{13}\}$ was synthesized based on the synthetic method reported recently by some of us (for synthesis and characterization, also see Supporting Information).^[31] Here, we first explored the fundamental electrochemical performance of $\{MV_{13}\}$ in acetonitrile under the targeted NRFB conditions. To this end, we utilized a three-electrode cell equipped with a glassy carbon (GC) working electrode, a platinum counter electrode, and a non-aqueous $Ag/AgNO_3$ reference electrode. The potentials were converted to the Fc^+/Fc scale using ferrocene as internal standard. For experimental details see SI.

An acetonitrile solution containing $\{MV_{13}\}$ (1 mM) as active species and $(nBu_4N)_4PF_6$ (0.1 M) as supporting electrolyte used. cyclic voltammetry (CV) and square-wave voltammetry show the general $\{MV_{13}\}$ redox processes within the potential range between -2.0 V and 1.0 V vs. Fc^+/Fc . This range was chosen based on the stability range of the carbon electrodes to be used for the final RFB setup, see below. The data shows that within this range, 12 redox transitions are observed (green labels in Figure 2a and 2b).

Based on the open circuit potential (OCP, -0.5 V), the redox processes can be separated into two parts, resulting in an anolyte (for oxidations starting from the native sample), and catholyte (for reductions, starting from the native sample), see Figure 2c. This finding is further supported by linear sweep voltammetry (LSV, Figure 2d) obtained with a rotating disk electrode (RDE). LSV analysis verifies that for each scan, multiple limiting current density plateaus are observed for anolyte and catholyte, indicating the accessibility of multiple reduced and oxidized states within the electrolyte. The initial electrochemical analysis therefore demonstrates the principal suitability of $\{MV_{13}\}$ as electrolyte for symmetric NRFB setups.

To gain initial mechanistic insights into the fundamental electrochemical performance of $\{\text{MV}_{13}\}$ relevant for NRFB operation, we analyzed charge transfer behaviour using Randles-Sevcik analyses. These data indicate that the observed redox-processes are diffusion-limited, suggesting that charge-transfer at the electrode/electrolyte interface is fast compared with diffusion. Thus, mass-transport to/from the electrode surface is considered a future limitation to be optimized for these systems. Redox-kinetics were further studied using Nicholson and Koutecký-Levich methods, to determine diffusion coefficients (D_0)

and electron transfer rate constants (k_0) for $\{\text{MV}_{13}\}$. D_0 and k_0 obtained from the two methods are generally consistent, in the order of 10^{-6} – $5 \text{ cm}^2 \text{ s}^{-1}$ (D_0) and 10^{-4} – $3 \text{ cm}^2 \text{ s}^{-1}$ (k_0), respectively (see SI, Section 2.2 and Table S1). This data is in line with previous reports on redox-active POMs in organic electrolytes.^[35,36] The data also reveal that, despite their size (diameter $\sim 1 \text{ nm}$), $\{\text{MgV}_{13}\}$ and $\{\text{V}_{14}\}$ show suitable mass transport and fast electron transfer in acetonitrile. Both features are important prerequisites for optimum NRFB operation.

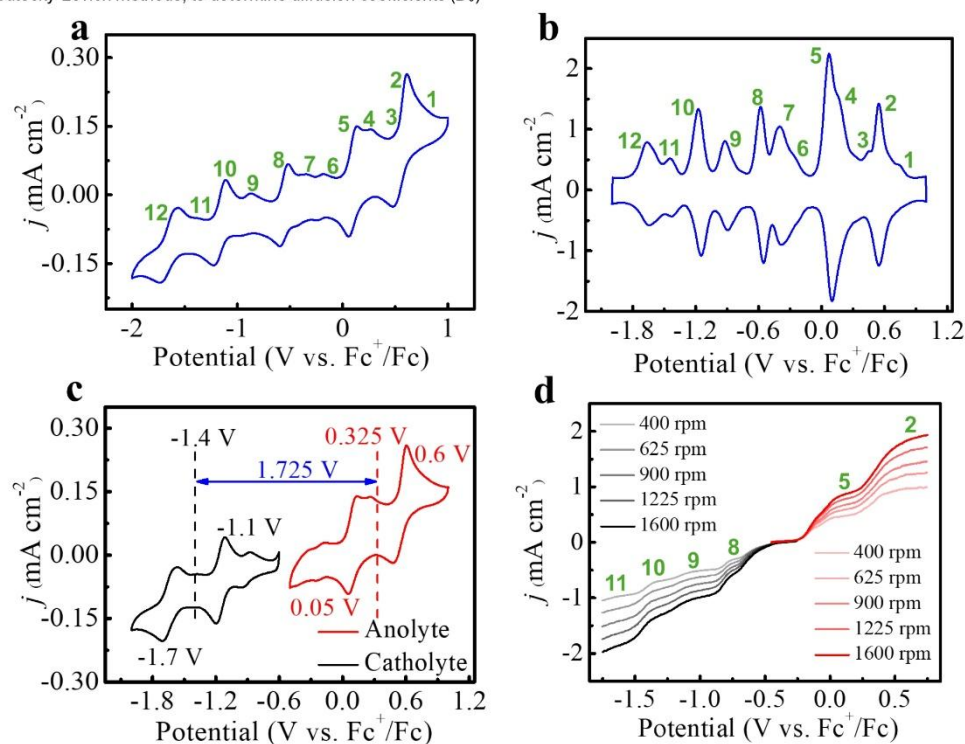


Figure 2. Electrochemical properties of the $\{\text{MV}_{13}\}$ cluster. (a) Cyclic voltammetry (CV) of 1 mM $\{\text{MV}_{13}\}$ and 0.1 M $(\text{nBu}_4\text{N})\text{PF}_6$ as supporting electrolyte in acetonitrile. (b) Square wave voltammetry (SWV) curve of the $\{\text{MV}_{13}\}$ cluster. (c) CV curves of the $\{\text{MV}_{13}\}$ cluster separated into anolyte (red curve) and catholyte (black curve) by open circuit potential (OCP) of $-0.5 \text{ V vs. Fc}^+/\text{Fc}$. (d) LSV curves of the cluster at different rotating speeds ranging from 400 rpm to 1600 rpm.

Next, we investigated the membrane crossover rate of $\{\text{MV}_{13}\}$ through a standard commercial Celgard 2400 membrane. Membrane permeability was analyzed in an electrochemical H-cell consisting of two compartments separated by the membrane. Our analyses gave a permeability of $2.35 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ and only $\sim 1.5\%$ of the active species crossed the membrane over a period of 7 days in a static diffusion test. This is significantly lower crossover compared to previous literature reports on similar species (details see SI, Section 2.3).^[28]

Given the promising features of $\{\text{MV}_{13}\}$, we designed a symmetric NRFB operated using an acetonitrile solution containing 1 mM

$\{\text{MV}_{13}\}$ and 0.1 M $(\text{nBu}_4\text{N})\text{PF}_6$. Identical solutions were used as anolyte and catholyte, and the half-cells were separated by a Celgard 2400 membrane, see Figure 1b. All NRFB tests reported in this work were performed at room temperature under N_2 atmosphere to avoid undesirable reactions with oxygen or water. The as-constructed symmetric NRFBs were tested under galvanostatic conditions at current densities ranging from 0.4 mA cm^{-2} to 1.0 mA cm^{-2} . To avoid overoxidation of the graphite electrode and possible degradation of the electrolyte components, the cutoff voltages for charging and discharging were set to 1.8 V and 0.2 V. Note that the NRFB was operated in 2-electrode

3. Results and discussion

configuration, so voltages given for the NRFB are absolute potential differences between the cathode and anode.

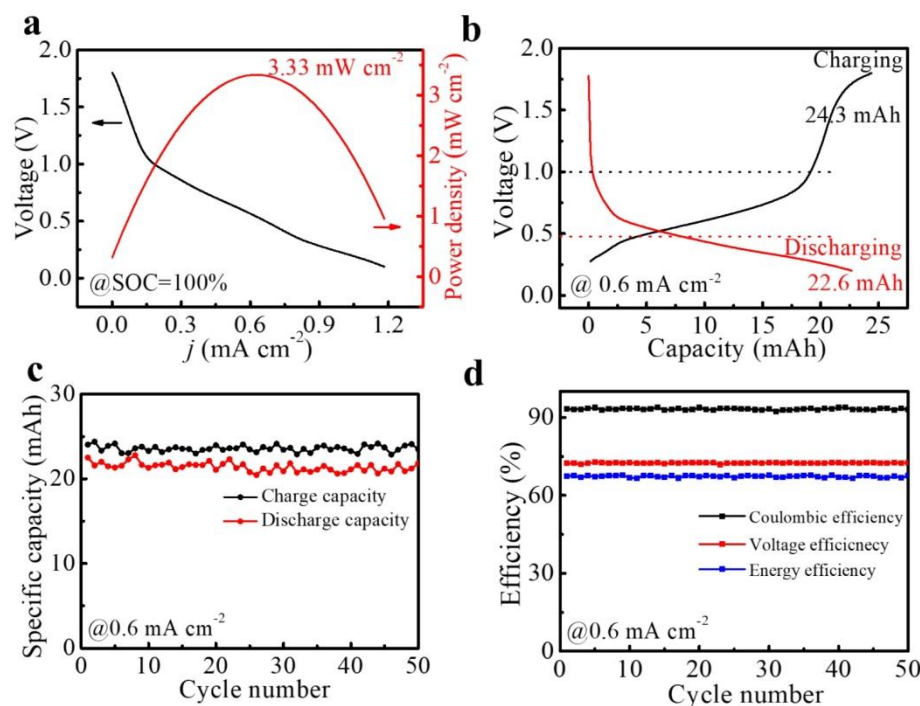


Figure 3. Symmetric non-aqueous redox flow battery performance. (a) The schematic illustration of the as-assembled {MV₁₃} based NRFBs. (b) The specific capacities of the NRFBs at current density of 0.6 mA cm⁻². (c) The specific charge discharge capacities of the NRFBs during the 50 cycles cycling test. (d) The polarization curve of the NRFBs and power density of the NRFBs at state of charge (SOC) of 100%. (e) coulombic efficiency, voltage efficiency and energy efficiency of the NRFBs during the cycling test.

According to the polarization curve shown in Figure 3a, the NRFB reaches the highest power density (3.3 mW cm⁻²) at a current density of 0.6 mA cm⁻². Notably, the polarization curve is almost linear with no obvious plateau, indicating there is no observable redox kinetic limitations for the electrode reactions of the battery. This is in line with the high kinetic rate constant k_0 for {MV₁₃} described above. As shown in Figure 3b, distinct charge and discharge plateaus were observed between 0.5 V and 1.0 V at a constant current density of 0.6 mA cm⁻². These values closely match the average potential difference of the redox processes in anolyte and catholyte. Theoretically, the average potential difference between the anolyte and catholyte based on the CV analysis in Figure 2c shows that the thermodynamic potential of the NRFB is calculated to be 1.7 V. However, for the actual full-cell, an average potential of 0.75 V at a discharge current density of 0.6 mA cm⁻² is observed. The difference between theoretical and experimental value is likely due to the overlapping faradic response for the forward electrode reaction processes and is often observed in RFBs.^[97] Under the given conditions, the system features a discharge specific capacity of 22.6 mAh and a

coulombic efficiency of 93% at 0.6 mA cm⁻². Also, stable galvanic charge (23.9 mAh) and discharge capacities (22.2 mAh) are observed during galvanostatic cycling, resulting in an excellent capacity retention of 97% after 50 cycles (reduction rate = 0.074% per cycle, see Figure 3c).

The cycling behaviour of the NRFB in constant current mode was then studied in detail: over 50 cycles (≈ 52 h), the coulombic efficiency was maintained at ~93%, confirming the excellent redox chemical and stability of {MV₁₃} (Figure 3d). The NRFB also shows good voltage efficiency of 72% and energy efficiency of 67% with negligible efficiency fading after 50 cycles. The average number of stored and released electrons per cluster unit during the charge/discharge test was calculated by integration of the dQ/dV curves (SI, Figure S9a), suggesting that ~4.1 electrons are transferred for the anolyte and ~3.8 electrons are transferred for the catholyte. The alternating current area-specific resistance (AC-ASR) of the battery was determined by high-frequency electrochemical impedance spectroscopy (EIS) at the open circuit potential (OCP). We note that the high frequency resistance curve shows no obvious polarization plateaus, indicating that the main

resistances inside the NRFB are caused by electrode and membrane resistances (SI, Figure S10).

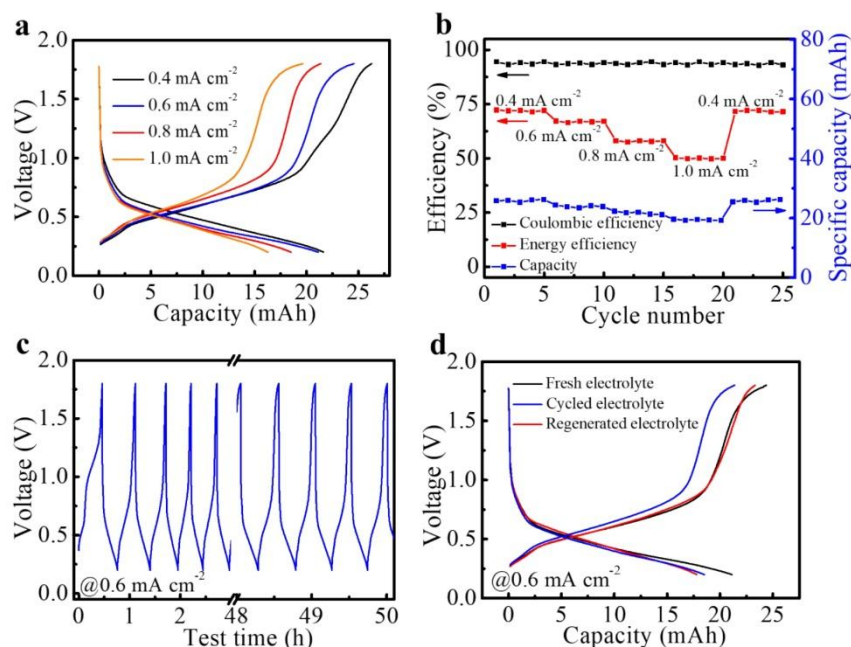


Figure 4. The battery performance of the as-constructed {MV13}-based NRFBs at different current density of 0.4, 0.6, 0.8 and 1.0 mA cm⁻². (a) The specific capacity of the NRFBs. (b) Efficiency and capacity of the NRFBs. (c) The voltage profile of the NRFBs in cyclability test at current density of 0.6 mA cm⁻². (d) The capacity of the NRFBs with fresh electrolyte, cycled electrolyte and regenerated electrolyte at current density of 0.6 mA cm⁻².

Furthermore, the rate capability of the as-assembled {MV13}-based NRFB was evaluated at current densities ranging from 0.4 mA cm⁻² to 1.0 mA cm⁻². Figure 4a shows that the highest charge capacity (25.3 mAh) and discharge capacity (23.5 mAh) are observed at a current density of 0.4 mA cm⁻², while the capacities drop with increasing current density (Figure 4b). This is most likely due to incomplete electrolyte reaction under higher current density.^[24] Coulombic efficiency and energy efficiency of the NRFBs were also investigated at varying current densities (Figure 4b). The coulombic efficiency of the NRFB remains above 93%, while the energy efficiency gradually decreases from 72% to 50% with increasing current density (SI, Figure S9b). The voltage profiles of the NRFB remain nearly identical throughout the 50 cycles test at a constant current density, indicating stable electrode reactions (Figure 4c). Minor differences on the voltage profile for the first cycle are most likely be due to an electrode/electrolyte activation process.^[38]

The ability to regenerate spent electrolytes is a key target for sustainable RFB research. To this end, the anolyte and catholyte solutions were recovered after cycling, mixed, and re-set to the original oxidation state (*i.e.*, regenerated), by bulk electrolysis at the OCP (-0.5 V). This regenerated electrolyte was then re-

deployed in the NRFB and cycled at a current density of 0.6 mA cm⁻² under our standard conditions. As shown in Figure 4d, 87.5% of the original capacity was recovered, which is a promising first demonstration of the recyclability and regeneration of the {MV13} electrolyte.

Redox stability of the active electrolyte component is crucial for the durability of the RFB. Thus, comparative CV analyses for both anolyte and catholyte were performed before and after the cycling test (see SI, Figure S11). The CVs show that all general redox features of the original anolyte and catholyte are still present. Minor shifts and a general broadening of the redox signals are observed. This indicates that overall, the system operates robustly, while the minor changes observed led us to perform further spectroscopic analyses of the system, see below.

The capacity fading observed has two likely causes: first, after prolonged cycling, we noted formation of some precipitate in the tubing. This is most likely due to crystallization of {MV13}, which effectively removes some active component from the electrolyte. Second, trace amounts of atmospheric O₂ or H₂O might have diffused into the system, *e.g.* through the tubing, resulting in undesired side reactions leading to capacity fading.^[39]

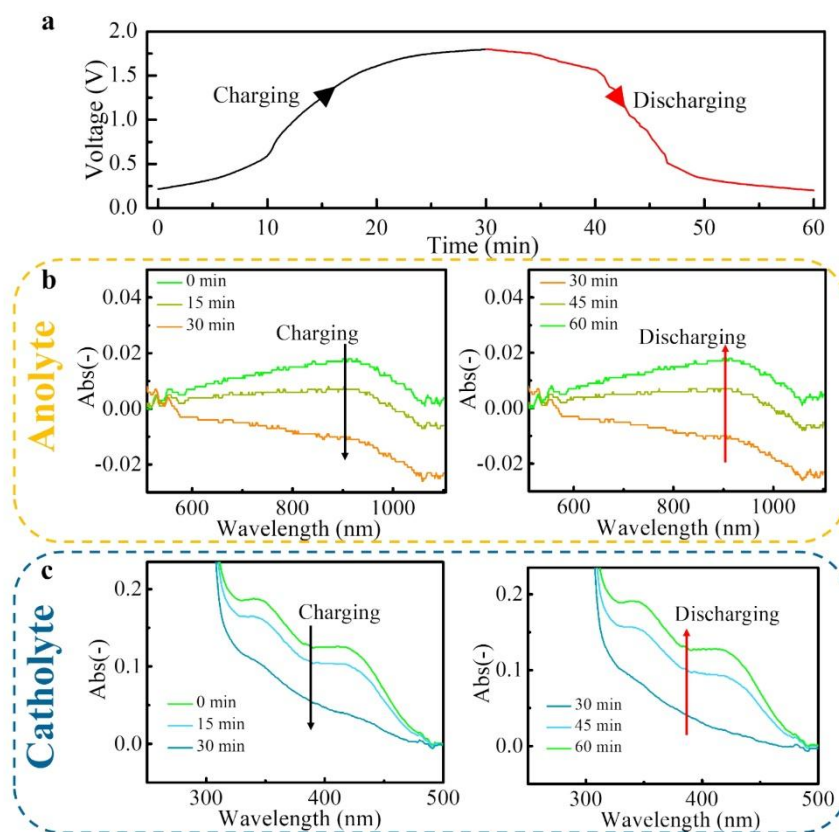


Figure 5. In-operando UV-Vis spectroscopy of the electrolytes of the **{MV₁₃}**-based NRFB with full charge-discharge at a current density of 0.6 mA cm⁻². (a) Galvanostatic charge and discharge profiles of the battery. (b) The in-operando spectrophotometric characterization of the anolyte during the charge-discharge process. (c) The in-operando spectrophotometric characterization of the catholyte during the charge-discharge process.

To gain initial mechanistic insights into the redox cycling and charge-transfer of **{MV₁₃}** during charge/discharge, we performed *operando* ultraviolet-visible (UV-vis) spectroscopy for both, anolyte and catholyte over the cycling test. UV-vis spectroscopy of **{MV₁₃}** (Figure 5 and Figure S13, SI) shows that the cluster features two prominent absorption bands, the broad V(IV/V) intervalence charge transfer (IVCT) absorption band centered at $\lambda \sim 900$ nm (Figure 5b),^[40] and the ligand to metal charge transfer (LMCT) absorption band centered at $\lambda \sim 380$ nm (Figure 5c).^[41] For the anolyte, we observed that during charging (0 min - 30 min), electro-oxidation occurs, as verified by *operando* UV-vis spectroscopy (Figure 5b and SI, Figure S13), where cluster oxidation was indicated by a loss of the characteristic IVCT transition. This indicates the oxidation of **{MV₁₃}** to an all V(V) state. This is in line with the dQ/dV analyses discussed above, which indicate the removal of approximately four electrons per **{MV₁₃}** unit. During the discharging process (30 min - 60 min), the

anolyte was electro-reduced, and the characteristic IVCT transition absorption was recovered. The IVCT spectral features before and after redox cycling are virtually identical, indicating structural integrity and identical charge-state of **{MV₁₃}**.

For the catholyte, *operando* UV-Vis spectroscopy was also used to monitor the electro-reduction during charging (Figure 5c and SI, Figure S13). Here, we observed that the characteristic absorption peak at $\lambda \sim 380$ nm decreased during charging, which is indicative of the generation of additional V(IV) centers in **{MV₁₃}**.^[31] During discharge (i.e., electro-oxidation) of the catholyte, excellent redox reversibility was observed, and the characteristic absorption at ~ 380 nm was fully recovered, and the LMCT spectral features of **{MV₁₃}** before and after redox cycling are virtually identical (Figure 5c).

To further verify the structural integrity of **{MV₁₃}**, we performed *ex-situ* Raman spectroscopy. Thus, electrolyte samples were extracted from the NRFB at different oxidation states (fresh,

oxidized, reduced and regenerated) and Raman spectra were measured under identical conditions. As shown in SI, Figure S14, the samples feature the characteristic {MV₁₃} signals, and no significant changes of the signals in terms of shifts or changes of intensity are observed at different oxidation states. This indicates that the {MV₁₃} metal oxo framework is retained during the electrochemical cycling, further emphasizing that redox-equilibrated mix-valent polyoxovanadates are promising active components for NRFBs.

Conclusion

In summary, we demonstrate how a two-component polyoxovanadate compound, {MV₁₃} (*n*Bu₄N)₄[MV₁₃O₃₃Cl] (M = V=O²⁺ {V₁₄} or MgOH⁺ {MgV₁₃}), can be used as a stable, high-performance active compound for symmetric non-aqueous redox-flow batteries. Our studies show that under NRFB conditions in acetonitrile, {MV₁₃} shows multiple reversible electrons transfer with excellent electron transfer kinetics. Under standard operating conditions, the system showed a coulombic efficiency of 93% at 0.6 mA cm⁻² and a high stability with a capacity fading rate of 0.074% per cycle. Mechanistic studies utilizing *operando* UV-Vis and Raman spectroscopies provided initial understanding of the structural stability and reversible charging/discharging of {MV₁₃} during NRFB operation. Future studies on {MV₁₃} will be focused on exploring how to improve solubility in acetonitrile or other suitable NRFB solvents. One promising approach is cation metathesis, where introduction of long-chain alkylammonium cations might be a promising route to increase solubility.^[42] In sum, this study demonstrates how symmetric NRFBs can be designed based on suitable mixed-valent V(IV/V) polyoxovanadate clusters.

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Conflict of Interest

The authors declare no conflict of interests.

Data Availability Statement

The data that support the findings of this study are openly available at Zenodo.org at 10.5281/zenodo.14191793

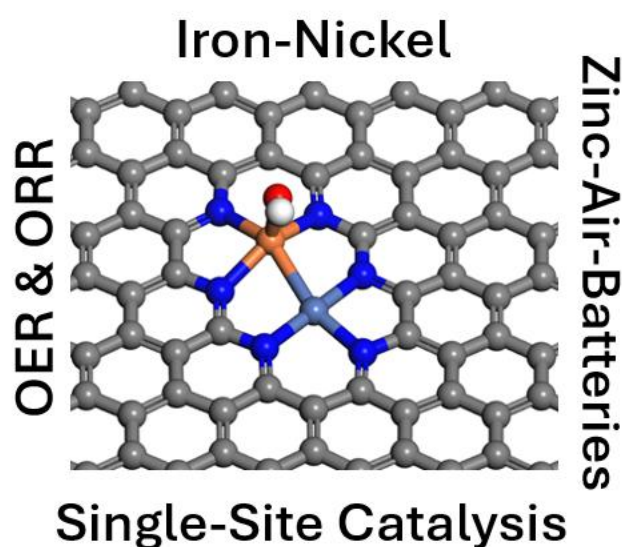
Keywords: Polyoxometalate • Polyoxovanadate • • Electrochemistry • Redox flow battery • Self-Assembly

- [1] S. Chu, A. Majumdar, *Nature* **2012**, *488*, 294–303.
- [2] B. Dunn, H. Kamath, J. M. Tarascon, *Science* **2011**, *334*, 928–935.
- [3] Z. Yang, J. Zhang, M. C. W. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon, J. Liu, *Chem. Rev.* **2011**, *111*, 3577–3613.
- [4] G. L. Soloveichik, *Chem. Rev.* **2015**, *115*, 11533–11558.
- [5] R. Yan, Q. Wang, *Adv. Mater.* **2018**, *30*, 1802406.
- [6] W. Wang, Q. Luo, B. Li, X. Wei, L. Li, Z. Yang, *Adv. Funct. Mater.* **2013**, *23*, 970–986.
- [7] M. Kapoor, R. K. Gautam, V. K. Ramani, A. Verma, *Chem. Eng. J.* **2020**, *379*, 122300.
- [8] M. Park, J. Ryu, W. Wang, J. Cho, *Nat. Rev. Mater.* **2016**, *2*, 16080.
- [9] C. Sun, H. Zhang, *ChemSusChem* **2022**, *15*, e202101798.
- [10] B. Liu, Y. Li, G. Jia, T. Zhao, *Electrochem. Energy Rev.* **2024**, *7*, 34–46.
- [11] F. Zhong, M. Yang, M. Ding, C. Jia, *Front. Chem.* **2020**, *8*, 451.
- [12] M. L. Perry, K. E. Rodby, F. R. Brushett, *ACS Energy Lett.* **2022**, *7*, 659–667.
- [13] P. Leung, X. Li, C. Ponce De León, L. Berlouis, C. T. J. Low, F. C. Walsh, *RSC Adv.* **2012**, *2*, 10125–10156.
- [14] Z. Li, Y. C. Lu, *Adv. Mater.* **2020**, *32*, 2002132.
- [15] F. Zhu, W. Guo, Y. Fu, *Chem. Soc. Rev.* **2023**, *52*, 8410–8446.
- [16] L. Yang, Y. Hao, J. Lin, K. Li, S. Luo, J. Lei, Y. Han, R. Yuan, G. Liu, B. Ren, J. Chen, *Adv. Mater.* **2022**, *34*, 2107425.
- [17] Z. Rhodes, J. R. Cabrera-Pardo, M. Li, S. D. Minteer, *Isr. J. Chem.* **2021**, *61*, 101–112.
- [18] K. Gong, Q. Fang, S. Gu, S. F. Y. Li, Y. Yan, *Energy Environ. Sci.* **2015**, *8*, 3515–3530.
- [19] S. H. Shin, S. H. Yun, S. H. Moon, *RSC Adv.* **2013**, *3*, 9095–9116.
- [20] L. Yang, J. Lei, J. M. Fan, R. M. Yuan, M. Sen Zheng, J. J. Chen, Q. F. Dong, *Adv. Mater.* **2021**, *33*, 2005019.
- [21] Q. Li, L. Zhang, J. Dai, H. Tang, Q. Li, H. Xue, H. Pang, *Chem. Eng. J.* **2018**, *351*, 441–461.
- [22] T. Ueda, *ChemElectroChem* **2018**, *5*, 823–838.
- [23] P. Sun, Y. Gu, W. You, Z. Tan, *J. Electrochem.* **1997**, *3*, 67–70.
- [24] Y. Liu, S. Lu, H. Wang, C. Yang, X. Su, Y. Xiang, *Adv. Energy Mater.* **2017**, *7*, 1601224.
- [25] L. E. VanGelder, W. W. Brennessel, E. M. Matson, *Dalt. Trans.* **2018**, *47*, 3698–3704.
- [26] L. E. VanGelder, A. M. Kossawataraachchi, P. L. Forrester, T. R. Cook, E. M. Matson, *Chem. Sci.* **2018**, *9*, 1692–1699.
- [27] L. E. VanGelder, H. D. Pratt, T. M. Anderson, E. M. Matson, *Chem. Commun.* **2019**, *55*, 12247–12250.
- [28] E. Schreiber, R. E. Garwick, M. J. Baran, M. A. Baird, B. A. Helms, E. M. Matson, *ACS Appl. Mater. Interfaces* **2022**, *14*, 22965–22972.
- [29] M. Anjass, G. A. Lowe, C. Streb, *Angew. Chem. Int. Ed.* **2021**, *60*, 7522–7532.
- [30] L. Zhang, R. Feng, W. Wang, G. Yu, *Nat. Rev. Chem.* **2022**, *6*, 524–543.
- [31] A. M. Remmers, B. Mashtakov, S. Repp, S. J. Rein, K. Wang, M.

- Anjass, L. M. Carrella, E. Rentschler, C. Streb, *Angew. Chem. Int. Ed* **2024**, e202418864.
- [32] K. Kastner, J. Forster, H. Ida, G. N. Newton, H. Oshio, C. Streb, *Chem. - A Eur. J.* **2015**, *21*, 7686–7689.
- [33] S. Greiner, B. Schwarz, M. Ringenberg, M. Dürr, I. Ivanovic-Burmazovic, M. Fichtner, M. Anjass, C. Streb, *Chem. Sci.* **2020**, *11*, 4450–4455.
- [34] S. Repp, M. Remmers, A. S. J. Rein, D. Sorsche, D. Gao, M. Anjass, M. Mondeshki, L. M. Carrella, E. Rentschler, C. Streb, *Nat. Commun.* **2023**, *14*, 5563.
- [35] C. L. Peake, A. J. Kibler, G. N. Newton, D. A. Walsh, *ACS Appl. Energy Mater.* **2021**, *4*, 8765–8773.
- [36] E. Schreiber, R. E. Garwick, M. J. Baran, M. A. Baird, B. A. Helms, E. M. Matson, *ACS Appl. Mater. Interfaces* **2022**, *14*, 22965–22972.
- [37] J. E. Jang, R. ah Kim, S. Jayasubramaniyan, C. Lee, J. Choi, Y. Lee, S. Kang, J. Ryu, S. W. Lee, J. Cho, D. W. Lee, H. K. Song, W. Choe, D. H. Seo, H. W. Lee, *Adv. Energy Mater.* **2023**, *13*, 2300707.
- [38] Y. Cao, J. J. Chen, M. A. Barteau, *J. Energy Chem.* **2020**, *50*, 115–124.
- [39] M. Li, S. A. Odorn, A. R. Pancoast, L. A. Robertson, T. P. Vaid, G. Agarwal, H. A. Doan, Y. Wang, T. M. Suduwella, S. R. Bheemireddy, R. H. Ewoldt, R. S. Assary, L. Zhang, M. S. Sigman, S. D. Minteer, *ACS Energy Lett.* **2021**, *6*, 3932–3943.
- [40] T. Yamase, *Catal. Surv. from Asia* **2003**, *7*, 203–217.
- [41] J. Tucher, C. Streb, *Beilstein J. Nanotechnol.* **2014**, *5*, 711–716.
- [42] A. Misra, K. Kozma, C. Streb, M. Nyman, *Angew. Chemie - Int. Ed.* **2020**, *59*, 596–612.

3.3 A Bifunctional Iron-Nickel Oxygen Reduction / Oxygen Evolution Catalyst for High-Performance Rechargeable Zinc-Air Batteries

Zhengfan Chen, Weiyi Cheng, Kecheng Cao, Meng Jin, Sarra Rahali, Soressa Abera Chala, Elnaz Ebrahimi, Nana Ma, Rongji Liu, Keseven Lakshmanan, Chia-Yu Chang, Chun-Chi Cheung, Haojian Luo, Yongkang Wang, Bing Joe Hwang, Carsten Streb.



This paper reported a bifunctional atomic Fe-Ni dual site composite electrocatalyst for ORR and OER, the combined experimental and theoretical (density functional theory) analyses provide in-depth understanding of the physical and electronic structure of this catalyst. The integration of the catalyst into a rechargeable zinc-air battery enabled excellent performance with specific capacity and peak power density of 782

mAhg^{-1} at (current density $j = 15 \text{ mA cm}^{-2}$) and 218 mW cm^{-2} ($j = 260 \text{ mA cm}^{-2}$), respectively.

Author contributions:

Zhengfan Chen: Conceptualization, Methodology, Investigation, Data curation, Analysis, Writing original draft.

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Supporting information can be found on page 163.

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RESEARCH ARTICLE

A Bifunctional Iron-Nickel Oxygen Reduction/Oxygen Evolution Catalyst for High-Performance Rechargeable Zinc–Air Batteries

Zhengfan Chen, Weiyi Cheng, Kecheng Cao, Meng Jin, Sarra Rahali, Soressa Abera Chala, Elnaz Ebrahimi, Nana Ma,* Rongji Liu,* Keseven Lakshmanan, Chia-Yu Chang, Chun-Chi Cheung, Haojian Luo, Yongkang Wang, Bing Joe Hwang,* and Carsten Streb*

Efficient and robust electrocatalysts for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are crucial for fuel cells, metal-air batteries, and other energy technologies. Here, a highly stable, efficient bifunctional OER/ORR electrocatalyst (FeNi-NC@MWCNTs) is reported and demonstrated its integration and robust performance in an aqueous Zinc–air battery (ZAB). The catalyst is based on neighboring iron/nickel sites (FeNi₆) which are atomically dispersed on porous nitrogen-doped carbon particles. The particles are wrapped in electrically conductive multi-walled carbon nanotubes for enhanced electrical conductivity. Electrocatalytic analyses show high OER and ORR performance (OER/ORR voltage difference = 0.69 V). Catalyst integration in a ZAB results in excellent performance metrics, including an open circuit voltage of 1.44 V, a specific capacity of 782 mAh g^{−1} (at $j = 15 \text{ mA cm}^{-2}$), a peak power density of 218 mW cm^{−2} (at $j = 260 \text{ mA cm}^{-2}$) and long-term durability over 600 charge/discharge cycles. Combined experimental and theoretical (density functional theory) analyses provide an in-depth understanding of the physical and electronic structure of the catalyst and the role of the FeNi dual atom reaction site. The study therefore provides critical insights into the structure and reactivity of high-performance bifunctional OER/ORR catalysts based on atomically dispersed non-critical metals.

1. Introduction

The development of cost-effective, sustainable, and environmental-friendly energy conversion and storage devices is a key path toward carbon neutrality.^[1–3] Rechargeable zinc–air batteries (ZABs) are amongst the most promising battery technologies as they combine high energy density (theoretical limit: 1086 Wh kg^{−1}), economic viability, and feasible scale-up.^[4–6] However, the sluggish kinetics of the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) result in high overpotentials and unsatisfactory efficiency, thereby causing major roadblocks in the development of ZABs.^[7,8] While noble metal-based catalysts might address some of these issues, their scarcity and high cost prohibit large-scale commercialization.^[9,10] Thus, the development of highly efficient and robust bifunctional ORR/OER electrocatalysts based on earth-abundant elements is a grand challenge in sustainable energy research.^[11]

Recently, single-atom catalysts (SACs) have emerged as promising alternatives to

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noble metal catalysts.^[12,13] In SACs, transition metal atoms (especially Fe, Co, Ni, and Mn) are anchored on electroactive matrices, e.g. carbon, often by coordination with dopant elements such as nitrogen, resulting in various M-N-C species.^[14,15] These materials offer unique advantages including strong metal-substrate interactions,^[16] tunable electronic structure of the active metal site as well as high electric conductivity, often resulting in excellent redox-catalytic performance.^[17–19] Also, the nearly molecular design of these materials enables optimum metal-atom utilization and -rational active site design at the atomic level.^[19,20]

However, particularly for ORR, monometallic SACs (often based on Fe, Co) are limited by unfavorable energetics for the binding of key oxygen intermediates (*O_2 and *OOH), resulting in high O_2 activation barriers.^[21] In addition, monometallic SACs often show high overpotentials for the OER reaction, as water oxidation is favored at polynuclear species.^[22]

One promising strategy to overcome these challenges is the introduction of a second metal center, resulting in dual atom catalysts (DACs).^[23] Compared with SACs, the DACs comprise adjacent hetero-metal pairs (e.g., Fe-Co, Co-Mn, Co-Ni),^[24–26] which exhibit asymmetric charge distribution at the active sites. This feature offers a promising approach to enhance the adsorption and desorption of oxygen intermediates, thereby lowering the energy barriers for O_2 activation. Moreover, synergistic effects at the dual-metal site can enhance overall catalytic performance for both ORR and OER.^[23,27] Despite major efforts in the field, the development of bifunctional DACs for use in ZABs is still in its infancy, and current challenges include control over stability and tuning of the precise coordination environment.^[28]

To date, 2D- and 3D-structured nitrogen-doped carbon matrices derived from metal-organic frameworks (MOFs) are often used for anchoring SACs. While these materials offer facile synthetic access, they often result in active sites hidden within the composite, while metal aggregation and particle migration during operation negatively affect mass transfer during operation.^[29,30] Thus, structural and morphological engineering of nitrogen-doped carbon substrates is of great significance to fully expose active sites and ensure efficient electron and mass transfer.

To overcome these challenges, SAC composites have been combined with multi-walled carbon nanotubes (MWCNTs). MWCNTs feature 1D structures with outstanding chemical and thermal stability, high specific surface area, and excellent electrical conductivity, making them ideal substrates for bifunctional ORR/OER electrocatalysts.^[31,32] In one outstanding example, Masa and co-workers reported oxygen-functionalized MWCNTs as substrate for trimetallic (Mn-Fe-Ni) oxide nanoparticles, exhibiting remarkable ORR and OER performances.^[33] Also, Streb, Liu, and coworkers used a facile one-pot assembly synthetic route to deposit nanostructured manganese vanadium oxides on nitrogen-sulfur functionalized MWCNTs, which showed excellent ORR and OER performance.^[34,35] However, establishing a chemical and electronic linkage between the reactive sites and charge transfer materials (MWCNTs) remains challenging, and often results in poor interfacial conductivity and poor long-term stability. Recently, Sun and colleagues reported an atomically dispersed Fe-N-C catalyst fabricated from a Fe modified zeolitic imidazolate framework (ZIF-8), which demonstrated im-

pressive performance for both ORR and ZABs.^[36] Liu and collaborators also employed ZIF-8 as a template and successfully prepared a bifunctional FeCo-NC catalyst for ORR and OER, enabling stable long-term ZAB operation.^[21]

Here, we build on these pioneering studies and aim at designing bifunctional ORR/OER composites where ZIF-derived DACs on conductive N-doped carbon are hierarchically integrated with MWCNTs to harness reactivity and stability synergisms. We proposed a strategy for anchoring FeNi dual-metal sites on nitrogen-doped carbon enwrapped by conductive MWCNTs via a simple two-step process (denoted as FeNi-NC@MWCNT). The resulting catalyst demonstrated excellent bifunctional OER and ORR reactivity, outperforming the benchmark Pt/C + IrO_2 and various related reference catalysts. Complementary experimental and theoretical analyses provided unique information on the reaction mode and synergism of these dual sites, offering distinct reaction pathways that are energetically not accessible by single metal site reference catalysts. The practical applicability and stability of the catalyst were demonstrated by integration in an aqueous rechargeable ZAB which showed excellent performance in long-term cycling tests.

2. Results and Discussion

2.1. Catalysts Synthesis and Structural Characterization

Figure 1a illustrates the two-step synthetic strategy for the dual-metal catalyst. First, the precursor FeNi/ZIF-8@MWCNTs was fabricated by in situ functionalization of ZIF-8 with Fe^{3+} and Ni^{2+} .^[37] The resulting dodecahedral ZIF-8 particles were anchored to the surface of MWCNTs, resulting in a self-assembled macroporous 3D structure. Calcination of this precursor at 950 °C for 3 h under Argon flow gave the target composite, hereafter referred to as FeNi-NC@MWCNT. Note that during calcination, the precursor particles were converted to 2D graphene-like nanosheets, which were mechanically stabilized by the interlinking MWCNTs. Also note that the Zn^{2+} metal present in the original ZIF-8 was removed from the sample by evaporation during pyrolysis, contributing to the formation of a highly porous N-doped carbon matrix.^[18] After pyrolysis, the composite was washed repeatedly with aqueous HCl (1.5 M) and deionized water to remove any metal salts and metal nanoparticles.^[38] To understand the impact of the dual Fe/Ni metal sites, we also synthesized the monometallic Fe-NC@MWCNTs and Ni-NC@MWCNTs as reference samples. Also, to assess the impact of the MWCNTs, we fabricated FeNi/ZIF-8 composites in the absence of MWCNTs.

The morphology and structure of the catalysts were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Figure 1b shows the SEM image of FeNi-NC@MWCNT, the structure of ZIF-8 nanoparticles was well maintained during Fe/Ni functionalization and pyrolysis. The ZIF-derived nanoparticles are interspersed within the MWCNTs, resulting in a hierarchical porous structure. Note that the MWCNT-free reference FeNi-NC shows similar particle features (Figure S1, Supporting Information), indicating the introduction of MWCNTs does not affect catalyst morphology. Also, SEM and TEM analyses do not indicate any metal or metal oxide

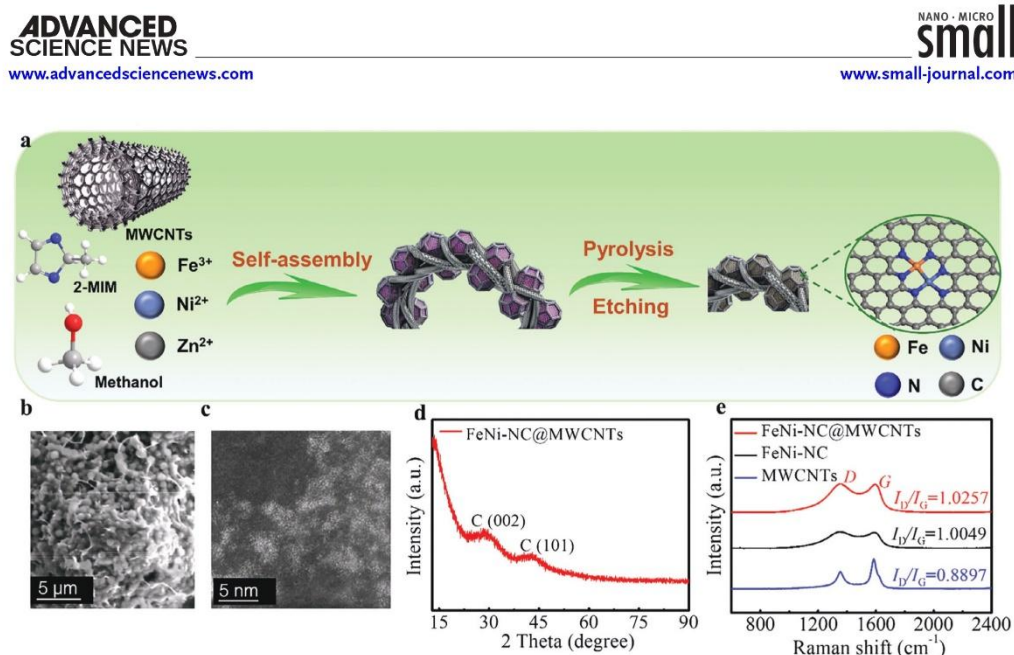


Figure 1. Synthesis, structure, and morphology of the reported catalysts. a) Illustration of the synthesis process of FeNi-NC@MWCNT. b) SEM image, c) HAADF-STEM image of FeNi-NC@MWCNT. d) Powder XRD pattern of FeNi-NC@MWCNT, and e) Raman spectra of FeNi-NC@MWCNT, FeNi-NC, and MWCNTs.

nanoparticles in both FeNi-NC@MWCNT and FeNi-NC (Figures S2, S3, Supporting Information).

To probe the dispersion of the Fe and Ni sites, we used aberration-corrected high-angle annular dark-field scanning TEM (AC-HAADF-STEM). As shown in Figure 1c, a large number of uniformly distributed bright spots are clearly identified in FeNi-NC@MWCNT, which are assigned to isolated single Fe and/or Ni atoms and/or dual single atoms sites (FeNi sites). The corresponding element mapping analysis confirms the uniform dispersion of Fe, Ni, C, and N in the carbon matrix derived from ZIF-8 (Figure S4, Supporting Information). Also, inductively coupled plasma optical emission spectroscopy (ICP OES) was used to determine the mass percentage of Fe (0.57 wt.%) and Ni (0.62 wt.%) in FeNi-NC@MWCNT (Table S1, Supporting Information). Figure 1d represents the powder X-ray diffraction (pXRD) pattern of FeNi-NC@MWCNT, the profile shows two broad diffraction peaks at $\approx 30^\circ$ and 42° attributed to the (002) and (101) lattice planes of graphitic carbon.^[20] No peaks of crystalline Fe or Ni metal-based particles were observed in FeNi-NC@MWCNT, which is in line with the microscopic analyses. The Raman spectrum of FeNi-NC@MWCNT (Figure 1e) primarily shows two characteristic bands with the D band at $\approx 1350\text{ cm}^{-1}$ and the G band at $\approx 1595\text{ cm}^{-1}$. The D band represents defects or disorders in the carbon lattice, while the G band corresponds to ordered sp^2 -hybridized graphitic carbon atoms. The ratio between the D band and G band (I_D/I_G) for FeNi-NC@MWCNT is higher than for the reference samples (see Figure S6, Supporting Information), indicating the introduction of more structural defects during synthesis. The specific surface area and pore size distribution of the catalysts were measured by N_2 sorption (Figure

S7, Supporting Information). Analysis of the data showed that the introduction of MWCNTs significantly increased the specific surface area of FeNi-NC@MWCNT. Also, FeNi-NC@MWCNT contains more micropores and mesopores than the FeNi-NC reference, which can alter mass transfer (particularly of gaseous reagents) within the composite.

X-ray photoelectron spectroscopy (XPS) measurements were performed to investigate the surface chemical states of the synthesized catalysts. XPS spectra of FeNi-NC@MWCNT and FeNi-NC both exhibit distinctive signals of C, N, and O elements, but only very weak Fe and Ni signals due to the low loading. As shown in Figure 2a, the high-resolution C 1s XPS spectrum of FeNi-NC@MWCNT is deconvoluted into three peaks at binding energies of 284.5, 285.2, and 288.7 eV, which are assigned to C–C/C=C, C=C–N, and C=O, respectively. The observation of C–N bonds indicates the successful formation of an N-doped carbon matrix. The N 1s XPS spectrum (Figure 2b) can be divided into five separate species, that is pyridinic N (398.7 eV), metal-coordinated N (399.8 eV), graphitic N (400.9 eV), pyrrolic N (402.1 eV) and oxidized N (405.5 eV). The peak located at 399.8 eV provides further evidence for the binding of Fe and/or Ni species to nitrogen centers in FeNi-NC@MWCNT.

To further identify the chemical state and coordination environment of the Fe and Ni sites in FeNi-NC@MWCNT, X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses were conducted. As shown in Figure 2c, the Fe K-edge XANES spectra reveal that the Fe energy absorption edge position of FeNi-NC@MWCNT is located between Fe foil and Fe_2O_3 , indicating the average oxidation state of Fe is between Fe(0) and Fe_2O_3 (+3). The inset graph

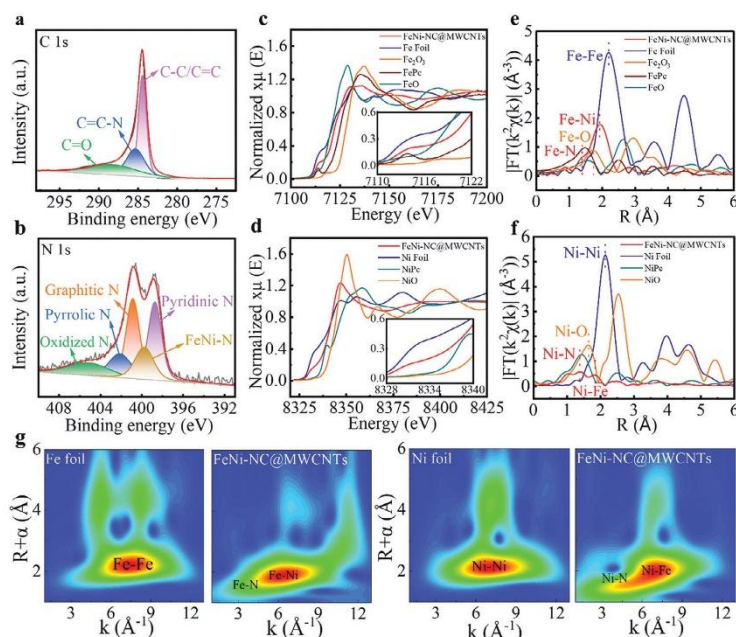


Figure 2. Chemical state and local atomic environment of FeNi-NC@MWCNT. a) Deconvoluted XPS spectrum for C 1s. b) Deconvoluted XPS spectrum of N 1s. c) Fe K-edge XANES spectra. d) Ni K-edge XANES spectra. e) Fourier-transformed k^2 -weighted EXAFS spectra of Fe K-edge. f) Fourier-transformed k^2 -weighted EXAFS spectra of Ni K-edge. g) Wavelet-transform (WT)-EXAFS plots for FeNi-NC@MWCNT, Fe foil, and Ni foil.

in Figure 2c highlights the weak pre-edge feature at ≈ 7115 eV, which is close to iron phthalocyanine (FePc) and can be assigned to the charge transfer from ligands to metal atoms and metal 1s to 3d transition in FeNi-NC@MWCNT.^[39] Similarly, the XANES spectra of the Ni K-edge for FeNi-NC@MWCNT give an average valence of Ni between Ni(0) and Ni(+2). Note that the nickel XANES data show comparable features to nickel phthalocyanine (NiPc), suggesting the existence of a Ni-N_x coordination environment in the FeNi-NC@MWCNT (Figure 2d). Notably, the pre-edge peak at ≈ 8335 eV of Ni curve in FeNi-NC@MWCNT is higher than that of NiPc, implying a distorted D_{4h} symmetry in Ni central atoms, which possibly results from Fe-Ni interactions (Figure 2d insert). Figure 2e displays the Fourier-transformed (FT) k^2 -weighted Fe K-edge EXAFS spectra in R-space. Compared with the FePc reference, a pronounced shoulder of the Fe K-edge at 1.4 Å indicates the Fe-N_x coordination structure in FeNi-NC@MWCNT. Notably, the Fe K-edge curve of FeNi-NC@MWCNT shows a major peak at 1.9 Å for Fe-Ni scattering, which is different from the peak referred to Fe-Fe interactions for Fe foil at 2.2 Å, indicating no iron metal nanoclusters in the catalyst. For the Ni K-edge FT-EXAFS, the main peak at 1.4 Å for FeNi-NC@MWCNT is comparable to the peak in the NiPc curve representing the Ni-N_x coordination structure, which is distinctive to the peaks at 1.6 Å for Ni-O (NiO) and 2.2 Å for Ni-Ni (Ni foil) (Figure 2f). Moreover, the peak at ≈ 1.8 Å for the Ni K-edge EXAFS data of FeNi-NC@MWCNT can be

assigned to Ni-Fe interactions. Besides, the formation of metal-N_x (Fe-N_x, Ni-N_x) coordination in FeNi-NC@MWCNT is further confirmed by Wavelet-transform (WT)-EXAFS spectra. Figure 2g presents the radial distance and k-space resolution to recognize the Fe and Ni at the atomic level in the FeNi-NC@MWCNT catalyst.

Compared with Fe foil, the location of the intensity maxima of FeNi-NC@MWCNT shows left-shift and down-shift in the bond length R and wave vector k respectively, suggesting the Fe atoms are atomically dispersed into the catalyst in the form of Fe-N coordination. The WT contour plot for FeNi-NC@MWCNT also exhibits a maximum intensity at 6.5 Å^{-1} in k space, considerably lower than that of Ni foil (7.5 Å^{-1}), indicating the atomic dispersion of Ni and the formation of Ni-N bonds in FeNi-NC@MWCNT. The XANES, FT-EXAFS, and WT-EXAFS results all suggest that the bulk of FeNi-NC@MWCNT features Fe-N_x, Ni-N_x, and FeNi-N_x sites. Also, nonlinear least-squares EXAFS fitting analysis was performed to quantitatively evaluate the local structural parameters for Fe species and Ni species in FeNi-NC@MWCNT. As shown in Table S2 (Supporting Information), the coordination numbers of Fe-N, Ni-N, and Fe-Ni in FeNi-NC@MWCNT are estimated to be 2.6, 3.5, and 1.5 (average value) respectively, indicating the formation of Fe-Ni interactions in FeNi-NC@MWCNT. Furthermore, FT-EXAFS k-edge curves of Fe and Ni are both in agreement with the fitting curves simulated from the proposed structural model (Figures S9, S10,

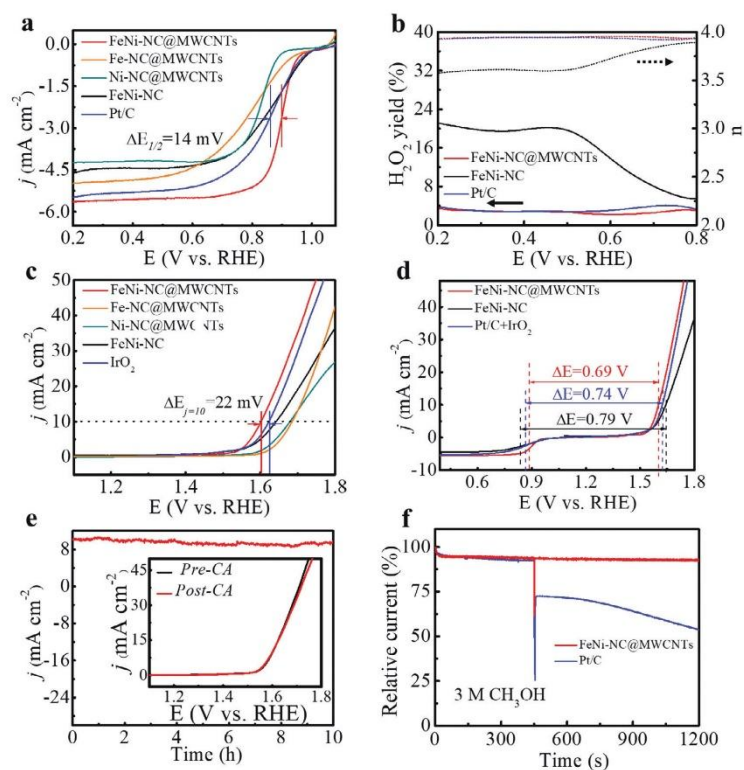


Figure 3. ORR/OER activity and stability of as-synthesized catalysts in 0.1 M KOH solution. a) ORR polarization curves at 1600 rpm of FeNi-NC@MWCNT, Fe-NC@MWCNTs, Ni-NC@MWCNTs, FeNi-NC, and commercial Pt/C. b) H_2O_2 yield and electron transfer numbers of FeNi-NC@MWCNT, FeNi-NC, and Pt/C. c) Overall polarization curves of studied catalysts. d) Overall polarization curves of FeNi-NC@MWCNT, FeNi-NC, and Pt/C+ IrO_2 for bifunctional catalytic activity tests. e) Chronoamperometry curves of FeNi-NC@MWCNT at 1.65 V (vs RHE) without iR compensation (insert: polarization curves comparison before and after 10 h stability test). f) Relative i-t curves of FeNi-NC@MWCNT and Pt/C at 0.6 V (vs RHE) and 1600 rpm with 3 M methanol was added at ca. 450 s.

Supporting Information), suggesting FeNi- N_6 sites as a dominant feature in FeNi-NC@MWCNT.

2.2. Electrocatalytic ORR and OER Performance

The bifunctional ORR/OER performance of the native FeNi-NC@MWCNT catalyst was investigated with a half-cell setup based on a typical three-electrode configuration (see Supporting Information for details). All potentials reported were referenced to reversible hydrogen electrode potentials (RHE). The performance of the reference materials Fe-NC@MWCNTs, Ni-NC@MWCNTs, FeNi-NC, and commercial Pt/C, IrO_2 were also evaluated for comparison.

The ORR tests were conducted in an O_2 -saturated 0.1 M aqueous KOH solution using a rotating disk electrode (RDE) as a working electrode. Compared with the negligible background

currents in an Ar-saturated solution, the cyclic voltammetry (CV) of FeNi-NC@MWCNT in an O_2 -saturated solution shows a major cathodic oxygen reduction peak at 0.77 V (Figure S11, Supporting Information). As shown in the linear sweep voltammetry (LSV) curves (Figure 3a), FeNi-NC@MWCNT exhibits superior ORR catalytic activity in terms of high onset potential (0.99 V), high half-wave potential ($E_{1/2}$) (0.9 V) and large limiting current density (5.63 mA cm^{-2}), which surpass these values of the references Fe-NC@MWCNTs (0.91 V, 0.88 V, 4.86 mA cm^{-2}), Ni-NC@MWCNTs (0.89 V, 0.83 V, 4.18 mA cm^{-2}), FeNi-NC (0.93 V, 0.87 V, 4.43 mA cm^{-2}), and even outperforms that of commercial Pt/C (0.95 V, 0.88 V, 5.45 mA cm^{-2}). In fact, the performance of FeNi-NC@MWCNT is superior to most currently reported SAC or DAC materials based on non-precious metals (Table S5, Supporting Information). Comparison of the title compound with the single-metal species Fe-NC@MWCNTs and Ni-NC@MWCNTs as well as the MWCNT-free sample FeNi-NC demonstrates the

impact of the dual metal sites and the carbon nanotube linkage. FeNi-NC@MWCNT also exhibits a smaller Tafel slope (48.5 mV dec^{-1}) than FeNi-NC (62.8 mV dec^{-1}) and Pt/C (58.4 mV dec^{-1}), indicating a faster ORR electrocatalytic kinetics (Figure S12, Supporting Information). Furthermore, the electron transfer number (n) and selectivity of FeNi-NC@MWCNT as well as its counterparts were evaluated by rotating ring disk electrode (RRDE) measurements. As shown in Figure 3b, the peroxide yield of FeNi-NC@MWCNT is below 3.1% and the monitored n is above 3.9 over the potential range of 0.2–0.8 V, verifying the high ORR selectivity and dominant $4e^-$ transfer mechanism. In contrast, the FeNi-NC shows a much higher peroxide yield (20%) and lower n value of 3.6 at 0.48 V versus RHE, suggesting an enhanced activity retention of FeNi-NC@MWCNT. The average n value of FeNi-NC@MWCNT was also calculated to be ≈ 3.98 (Figure S13, Supporting Information) using Koutecky-Levich (K-L) analysis of polarization curves obtained at different electrode rotation rates, further confirming a $4e^-$ transfer pathway. Moreover, the K-L plots for FeNi-NC@MWCNT at different potentials exhibit parallel linear correlation (Figure S13, Supporting Information), indicating its potential-independent electron transfer rate and the first-order reaction kinetics with O_2 concentration.

To explore the reactivity of our catalyst as bifunctional ORR/OER electrocatalysis in rechargeable Zn–air batteries, we explored both reactivities in detail. First, the OER performance of the catalysts was investigated in 0.1 M aqueous KOH. As shown in Figure 3c, FeNi-NC@MWCNT shows an OER overpotential of 370 mV at $j = 10 \text{ mA cm}^{-2}$, which is significantly lower than Fe-NC@MWCNT (473 mV), Ni-NC@MWCNT (454 mV), FeNi-NC (417 mV) and even commercial IrO_2 (390 mV). In addition, FeNi-NC@MWCNT also shows the lowest Tafel slope (63.5 mV dec^{-1}) amongst the materials tested (Figure S12b, Supporting Information). The composite also outperforms many other recently reported OER catalysts (Table S5, Supporting Information).

Electrochemical impedance spectroscopy (EIS) was performed at a potential of 1.56 V to further evaluate the OER kinetics. The diameter of the semicircle of the EIS spectrum for FeNi-NC@MWCNT is much smaller than that of the reference catalysts, revealing more efficient charge transfer and lower overall impedance, leading to faster OER kinetics (Figure S14a, Supporting Information). The potential gap ΔE (the difference between the half-wave potential ($E_{1/2}$) of ORR and the OER potential at 10 mA cm^{-2} ($E_{j=10}$)) is used as an indicator to evaluate the bifunctional activity of the studied oxygen catalysts. Note that smaller ΔE values imply high bifunctional OER/ORR performance. Figure 3d shows that FeNi-NC@MWCNT has a ΔE value of 0.69 V, which is lower than that of FeNi-NC (0.79 V) and Pt/C+ IrO_2 (0.74 V). The above analyses collectively demonstrate the high ORR and OER catalytic activity of FeNi-NC@MWCNT.

Durability is another key performance indicator for the practical applicability of bifunctional oxygen catalysts, e.g., in rechargeable ZABs. Thus, the stability of the catalysts for both ORR and OER was assessed by chronoamperometry (CA). As shown in Figure S14b (Supporting Information), after 24 h of CA for ORR at a constant potential of 0.8 V in O_2 -saturated electrolyte, FeNi-NC@MWCNT retained 93.5% of the initial current density, while significantly higher current density drops were observed for the references FeNi-NC (81.5%) and Pt/C (52.6%). The superior durability of FeNi-NC@MWCNT is further corroborated

by virtually identical LSV curves before and after the CA analysis (Figure S15a, Supporting Information).

Furthermore, its robustness was further shown by negligible loss of the chronoamperometric OER performance over 10 h polarization at 1.62 V (Figure 3e), which is further confirmed by the essentially identical LSV curves before and after CA (Insert in Figure 3e). Furthermore, the OER faradaic efficiency of FeNi-NC@MWCNT was also assessed with RRDE voltammetry. In this study, the ring potential was set as $E = 0.40 \text{ V}$ to reductively detect the oxygen generated at the disk electrode. According to the monitored ring current, disk current, and current collection efficiency (0.15), the OER faradaic efficiency of FeNi-NC@MWCNT was determined as 95.6%, which is higher than that of the reference catalysts (Figure S15b, Supporting Information). The electrochemically active surface area (ECSA) was further investigated to assess the number of accessible reactive sites, which is correlated with double-layer capacitance (C_{dl}). As shown in Figures S12c, S18 (Supporting Information), the C_{dl} of FeNi-NC@MWCNT (18.81 mF cm^{-2}) is considerably larger than that of FeNi-NC (12.35 mF cm^{-2}) and Pt/C (6.14 mF cm^{-2}), which also maintained a value of 17.96 mF cm^{-2} post OER catalysis.

Considering the high ORR activity of FeNi-NC@MWCNT, it could be used as a potential cathodic catalyst in direct-methanol fuel cells. In order to estimate the methanol tolerance of the catalysts, CA analysis for ORR at 0.8 V was studied by RDE at 1600 rpm in the presence of 3 M methanol in 0.1 M aqueous KOH electrolyte. As illustrated in Figure 3f, the relative current density of FeNi-NC@MWCNT shows minimal change over the measurement, indicating the high methanol tolerance. In sharp contrast, the current density of the Pt/C catalyst drops rapidly after injecting methanol under identical conditions.

Moreover, to reveal the structural evolution of the FeNi-NC@MWCNTs during the ORR/OER catalytic process, we collected the catalysts after a chronoamperometric test and performed HAADF-STEM measurements. These initial analyses suggest a partial loss and/or aggregation of the metal species after ORR or OER catalysis (Figures S16, S17). However, note that these structural changes did not affect the chronoamperometric performance, see above.

2.3. Primary and Rechargeable Zinc–Air Batteries Test

Considering the outstanding bifunctional catalytic activity of FeNi-NC@MWCNT, its practical performances in primary and rechargeable Zn–air batteries have been evaluated with custom-designed cells. As schematically illustrated in Figure 4a, a customized two-electrode ZAB was assembled utilizing an air cathode loaded with FeNi-NC@MWCNT as a catalyst. A zinc metal plate was used as anode. The electrolyte was 6.0 M aqueous KOH containing 0.2 M Zn(OAc)_2 . The electrolyte was continuously cycled by a peristaltic pump to prevent local concentration gradients. As references, ZABs using FeNi-NC and a mixture of commercial Pt/C + IrO_2 (with a mass ratio of 1:1) as cathode catalyst were fabricated. As shown in Figure 4b, the discharge polarization curves (at $j = 260 \text{ mA cm}^{-2}$) show that the ZAB catalyzed by FeNi-NC@MWCNT exhibits a maximum power density of 218.3 mW cm^{-2} , which is considerably higher than for Pt/C + IrO_2 (176.6 mW cm^{-2}). The ZAB based on FeNi-NC@MWCNT

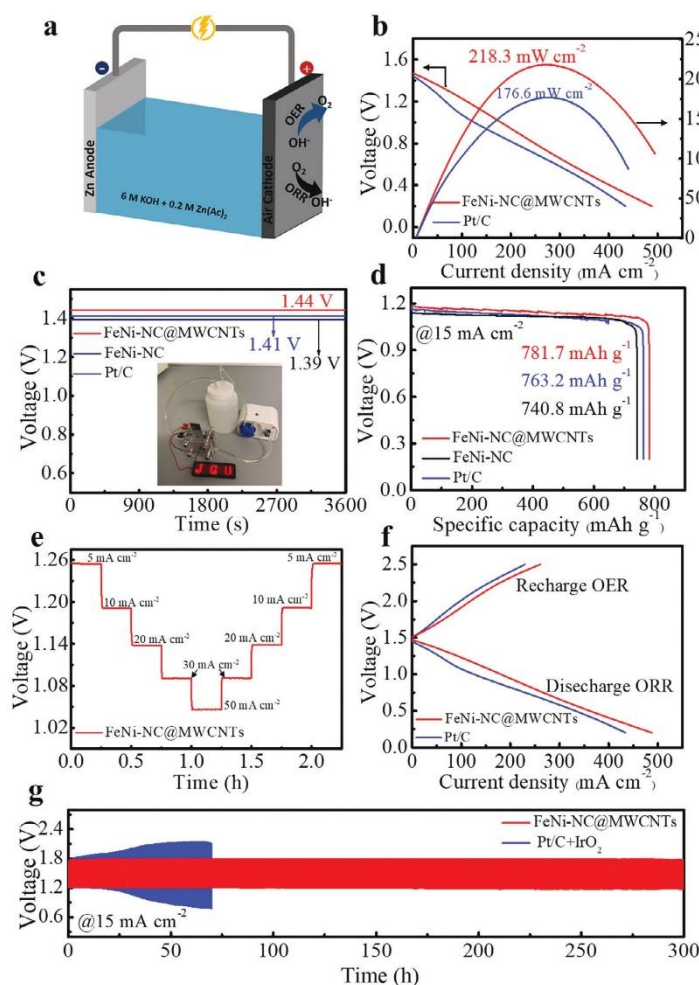


Figure 4. Zn-air batteries (ZAB) performance. a) Schematic illustration of the ZAB setup. b) Discharge polarization curves and corresponding power density curves of FeNi-NC/MWCNTs and Pt/C based ZABs. c) Open-circuit plots of FeNi-NC/MWCNT, FeNi-NC, and Pt/C based ZABs. (insert: ZAB powers the LED screen). d) Discharge plots of primary ZABs catalyzed by FeNi-NC/MWCNT, FeNi-NC, and Pt/C at a current density of 15 mA cm⁻². e) Discharge curves of FeNi-NC/MWCNT-based ZABs at different current densities of 5, 10, 20, 30, and 50 mA cm⁻². f) Polarization curves of FeNi-NC/MWCNT and Pt/C+IrO₂ catalyzed ZABs. g) Galvanostatic charge-discharge cycling performance of ZABs based on FeNi-NC/MWCNT and Pt/C+IrO₂ at a current density of 15 mA cm⁻².

also delivers a stable open-circuit voltage (OCV) of 1.44 V with no obvious changes over 1 h (Figure 4c), which is marginally higher than for FeNi-NC (1.41 V) and Pt/C + IrO₂ (1.39 V). These observations are in line with the catalytic activities in the three-electrode configuration reported above. The inserted picture in Figure 4c shows the LED display (1–5 V) was successfully lit up with the FeNi-NC/MWCNT-based ZAB, demonstrating the practical application of this catalyst. As shown in Figure 4d,

the FeNi-NC/MWCNT containing ZAB shows a specific capacity of 781.7 mAh g⁻¹ (normalized to the mass of consumed Zn), which outperforms the capacities of a Fe-NC-based ZAB (740.8 mAh g⁻¹) and Pt/C based ZAB (763.2 mAh g⁻¹). The output voltage of the FeNi-NC/MWCNT ZAB is approx. 1.18 V, which is superior to FeNi-NC (1.13 V) and Pt/C (1.16 V). Furthermore, as demonstrated in Figure S19, the primary ZAB with FeNi-NC/MWCNT catalyst was discharged under galvanostatic

conditions (15 mA cm^{-2}) for more than 21 h without a noticeable voltage drop. Figure 4e shows the remarkable discharging rate capacity and durability of FeNi-NC@MWCNT-based ZAB at various discharge current densities ranging from 5 to 50 mA cm^{-2} , no significant voltage loss was observed with increasing discharge current. Notably, the initial and final discharge voltage of the FeNi-NC@MWCNT-based ZAB at 1 mA cm^{-2} remains unchanged (1.25 V), suggesting a robust long-term discharge capacity.

To further investigate the rechargeability of the ZABs, the long-term cycling stability of the ZABs catalyzed by FeNi-NC@MWCNT was tested by continuous galvanostatic charge/discharge at a current density of 15 mA cm^{-2} . The duration of each cycle was set to 1 h (0.5 h for discharging and 0.5 h for subsequent charging) with an initial charge voltage of 1.8 V and discharge voltage of 1.15 V, respectively. The ZABs with commercial Pt/C + IrO₂ were examined under identical conditions for comparison. As shown in Figure 4f, the ZAB assembled with FeNi-NC@MWCNT exhibits a higher discharge current density and a lower charge/discharge voltage gap compared to the ZABs based on Pt/C + IrO₂. In addition, the round-trip efficiency of the ZABs was calculated based on the charge/discharge voltage gap of the second cycle. The ZAB with FeNi-NC@MWCNT exhibits a high round-trip efficiency of 73% (Figure S20, Supporting Information), surpassing that of the Pt/C + IrO₂ catalyzed ZAB (65%). For the long-term cycling test, as shown in Figure 4g, the FeNi-NC@MWCNT catalyzed ZAB demonstrates a narrower charge/discharge voltage gap and negligible voltage drop after 300 h cycling, suggesting its superior durability which outperforms most of the recently reported SAC/DAC catalyzed ZABs (Table S6, Supporting Information). In contrast, a substantial charge-discharge voltage drop was observed in the reference ZAB with Pt/C + IrO₂ mixture after 75 h. Based on the above results, the FeNi-NC@MWCNT is a promising and robust alternative to precious metal-based catalysts for both primary and rechargeable Zn-air batteries.

2.4. Density Functional Theory Calculation

To further elucidate the catalytic activity and reaction mechanism of FeNi DACs for ORR and OER, first-principles calculations were performed using density functional theory (DFT) methods. Different types of models for both heteronuclear and homonuclear sites FeNi₆, FeN₄, NiN₄ were constructed with coordination environments based on experimental XANES/EXAFS results (Figure S21, Supporting Information). Also, a model for nonadjacent FeN₄-NiN₄ sites was constructed as a reference to assess the critical role of adjacent hetero-bimetallic active sites. According to the adsorption energy of OH* (ΔG_{OH^*}) on active sites in different models (Table S3, Supporting Information), the pristine FeNi₆ site exhibits a negative adsorption energy of -0.24 V for OH*, suggesting the strong adsorption and difficult desorption of OH* on the metal sites. Thus, the OH* would be spontaneously adsorbed on the metal sites during catalysis in alkaline media, and it has been reported that OH* serves as a modifying ligand to optimize the electronic configuration of metal sites and influence their catalytic ORR/OER activity.^[40] As depicted in Figure S22 (Supporting Information), the FeNi-NC model is the

favorable configuration with OH* pre-adsorbed on the Fe site of FeNi₆, denoted as FeNi-OH-NC.

Based on EXAFS fitting, we proposed that FeNi₆ (FeNi-OH-NC) could be the main contributor to the enhanced catalytic performance of FeNi-NC@MWCNT. Therefore, the FeNi-OH-NC configuration was chosen as the key model for the subsequent ORR/OER computational investigations, and Fe-NC, Ni-NC, and nonadjacent Fe-Ni-NC were also simulated for comparative investigation. Particularly considering the possible reactive sites for the nonadjacent Fe-Ni-NC, two models of Fe@Fe-Ni-NC (on the Fe site) and Ni@Fe-Ni-NC (on the Ni site) were both calculated for the ORR/OER. Note that the optimized results for the adjacent FeNi-OH-NC model suggest that Fe is the reactive site.

Figure 5a illustrates the proposed $4e^-$ pathway for the ORR mechanism on optimized FeNi₆ sites in the FeNi-OH-NC model (other possible models and their oxygen-containing intermediates are depicted in Figures S23–S28, Supporting Information). The corresponding ORR calculated Gibbs free energy diagrams of these constructed models are evaluated at different electrode potentials (Figure S29, Supporting Information). At the potential U of 0 V, the four elementary steps are energetically downhill for all models, indicating all the involved reaction steps are exothermic in nature. When the potential is at 0.86 V, the fourth step ($\text{OH}^* + \text{OH}^- \rightarrow \text{O}^* + \text{H}_2\text{O} + e^-$) is recognized as the rate-determining step (RDS) for the FeNi-OH-NC model with a free energy difference of only 0.04 eV.

In comparison, the RDS for both Fe@Fe-Ni-NC and Fe-NC is also the fourth step with corresponding variation in free energy of 0.67 and 0.66 eV, respectively. The RDS for Ni-NC and Ni@Fe-Ni-NC is the second step ($\text{OOH}^* + e^- \rightarrow \text{O}^* + \text{OH}^-$) with corresponding variation in free energy of 0.52 and 0.51 eV, respectively. When the potential U increases up to 1.23 V, the fourth step is still recognized as the RDS for the FeNi-OH-NC model and the calculated free energy difference is determined as 0.41 eV, which is lower than those of Fe@Fe-Ni-NC (1.04 eV) and Fe-NC (1.03 eV) with the same RDS, and also lower than those of Ni-NC (0.89 eV) and Ni@Fe-Ni-NC (0.88 eV) with RDS in the second step, suggesting the FeNi-OH-NC has the lowest energy barrier for ORR. Notably, the free energies of each step for the Fe-NC and Fe@Fe-Ni-NC model are close to each other at the three investigated potentials, as are those for the Ni-NC and Ni@Fe-Ni-NC models, indicating that the nonadjacent metal sites can't leverage the synergistic effects. Figure 5b displays the proposed reaction mechanism for the OER process, the corresponding OER free energy diagrams of these constructed models are shown in Figure 5d and Figure S29c,d (Supporting Information). At the potential of 0 V (Figure S29c, Supporting Information), all the interaction steps are uphill, implying that the OER is energetically unfavorable at this potential. When U = 1.23 V, the RDS of FeNi-OH-NC is the second step ($\text{OH}^* + \text{OH}^- \rightarrow \text{O}^* + \text{H}_2\text{O} + e^-$) with a free energy difference of 0.59 eV, which is the lowest compared with those of the other four models as shown in Figure 5d. When U = 1.57 V (Figure S29d), the free energy difference for the RDS of FeNi-OH-NC towards OER is evaluated as 0.25 eV, which is also lower than those of the other four models. Similarly, the Fe-NC model exhibits comparably overlapped free energies diagrams with the nonadjacent Fe@Fe-Ni-NC model, as are

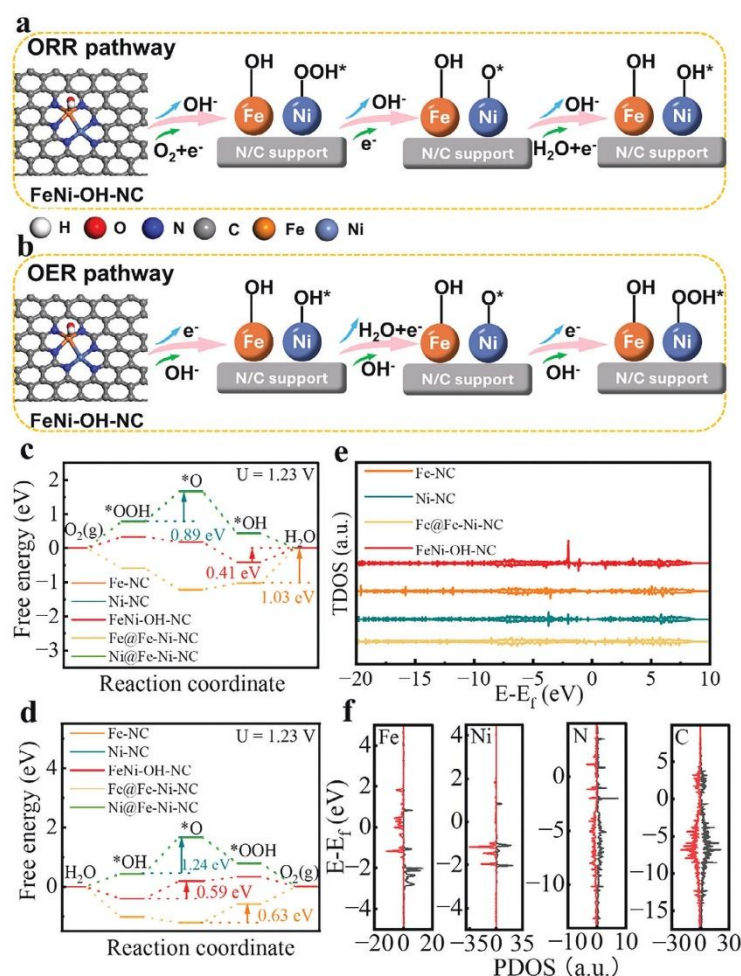


Figure 5. Density functional theory (DFT) calculations. a) Proposed mechanism for ORR and b) for OER on FeNi-OH-NC model. The grey, blue, orange, and cyan balls represent carbon, nitrogen, iron, and nickel atoms, respectively. c) Free energy diagrams of ORR intermediates on Fe-NC, Ni-NC, Fe@Fe-Ni-NC, Ni@Fe-Ni-NC, and FeNi-OH-NC models at different potentials. d) Free energy diagrams of OER intermediates on Fe-NC, Ni-NC, Fe@Fe-Ni-NC, Ni@Fe-Ni-NC, and FeNi-OH-NC models at different potentials. e) The total density of states (TDOS) of Fe-NC, Ni-NC, Fe@Fe-Ni-NC, Ni@Fe-Ni-NC, and FeNi-OH-NC models. f) Projected density of states (PDOS) of Fe, Ni, N, and C for FeNi-OH-NC model.

those for the Ni-NC and Ni@Fe-Ni-NC models. All the above results indicate that the adjacent FeNi heteroatom configuration as an active site effectively promote ORR/OER catalytic performance.

The ORR/OER catalytic activity can also be evaluated by considering the adsorption energy (ΔG_{OH^*}) and $\Delta G_{O_2} - \Delta G_{OH}$ as indicators to establish a volcano-shaped curve with ORR/OER overpotentials. Figure S30a (Supporting Information) shows the ORR overpotential η versus ΔG_{OH^*} , the FeNi-

OH-NC model is located at the top of the volcano curve with the smallest overpotential of 0.41 V, which is significantly lower than the monometallic models Fe-NC (1.03 V), Ni-NC (0.89 V) and the nonadjacent bimetallic models Fe@Fe-Ni-NC (1.04 V) and Ni@Fe-Ni-NC (0.88 V). Thus, the theoretically calculated trends of the ORR reactivity are consistent with the experimental results. Similarly, FeNi-OH-NC also exhibits the best OER catalytic activity with an overpotential of 0.59 V (Figure S30b, Supporting Information), followed by

Fe@Fe-Ni-NC (0.61 V), Fe-NC (0.63 V), Ni@Fe-Ni-NC (1.23 V) and Ni-NC (1.24 V). Here also, theory supports the experimental findings.

Furthermore, as shown in Figure S31 (Supporting Information), the charge distribution analysis reveals that N atoms in the FeNi-OH-NC model are more negatively charged compared to Fe-NC, Ni-NC, and nonadjacent Fe@Fe-Ni-NC models, suggesting the formation of metal-metal interactions of adjacent Fe-Ni sites in FeNi-OH-NC. This feature is expected to enhance the charge transfer and electron redistribution at the active sites. This modifies the electronic configuration of the Fe and Ni atoms, and facilitates the adsorption of oxygen intermediates, resulting in improved catalytic activity.

Furthermore, analysis of the total density of states (TDOS) shown in Figure 5e suggests that FeNi-OH-NC features a higher density of states across the Fermi level (followed by Ni-NC, Fe@Fe-Ni-NC, and Fe-NC), indicating the highest electronic conductivity of the FeNi-OH-NC model. This calculated finding is in agreement with the EIS experimental results described above. Figure 5f presents the detailed projected density of states (PDOS) for Fe 3d, Ni 3d, N 2p, and C 2p orbitals of the FeNi-OH-NC model. Compared with monometallic models Fe-NC, Ni-NC and nonadjacent bimetallic Fe@Fe-Ni-NC models (Figures S32–S34, Supporting Information), the adjacent bimetallic FeNi-OH-NC model demonstrates more hybrid electrons near the Fermi level, implying the existence of electronic interaction of Fe, Ni, and N on the active sites. Therefore, the DFT analysis demonstrates the adjacent diatomic FeNi-OH-NC configuration induces subtle modulation of the asymmetric electronic configuration of FeNiN₆ active sites, which facilitates the kinetics of the electrocatalytic ORR/OER process.

3. Conclusion

A dual-atom catalyst based on adjacent iron and nickel sites is reported. The catalyst shows outstanding performance for both ORR and OER, which allows the integration into high-performance rechargeable Zinc–air batteries that use the new bifunctional catalyst for both ORR and OER. Experimental and theoretical analyses rationalize the observed catalytic performance and robustness. Mechanistic studies into the nature of the catalytic site allow an initial understanding of the role and synergism of the metal centers as well as the N-doped carbon matrix and the conductive carbon nanotube support structure. The results suggest that OH* is pre-adsorbed on the Fe site of FeNiN₆, while the adjacent diatomic FeNi-OH-NC configuration induces subtle modulation of the asymmetric electronic configuration of FeNiN₆ active sites. The work provides an effective strategy to develop advanced bifunctional catalyst for critical energy conversion and storage processes.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are openly available in Zenodo.org at DOI 10.5281/zenodo.13336766, reference number 13336766.

Keywords

density functional theory, electrocatalysis, oxygen evolution reaction, oxygen reduction reaction, Zinc–Air–Battery

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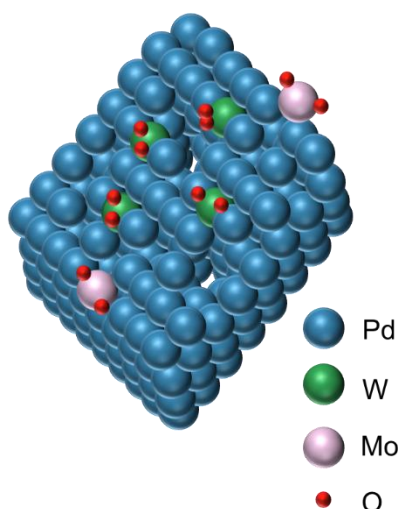
Published online:

- [1] B. Dunn, H. Kamath, J.-M. Tarascon, *Science* **2011**, 334, 928.
- [2] Z. Yang, J. Zhang, M. C. W. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon, J. Liu, *Chem. Rev.* **2011**, 111, 3577.
- [3] T. M. Gür, *Energy Environ. Sci.* **2018**, 11, 2696.
- [4] P. Gu, M. Zheng, Q. Zhao, X. Xiao, H. Xue, H. Pang, *J. Mater. Chem. A* **2017**, 5, 7651.
- [5] J. S. Lee, S. T. Kim, R. Cao, N. S. Choi, M. Liu, K. T. Lee, J. Cho, *Adv. Energy Mater.* **2011**, 1, 34.
- [6] L. Bai, D. Wang, W. Wang, W. Yan, *ChemSusChem* **2024**, 27, 202400080.
- [7] S. Ren, X. Duan, S. Liang, M. Zhang, H. Zheng, *J. Mater. Chem. A* **2020**, 8, 6144.
- [8] E. Davari, D. G. Ivey, *Sustain. Energy Fuels* **2018**, 2, 39.
- [9] Q. Shi, C. Zhu, D. Du, Y. Lin, *Chem. Soc. Rev.* **2019**, 48, 3181.
- [10] T. H. Yang, J. Ahn, S. Shi, P. Wang, R. Gao, D. Qin, *Chem. Rev.* **2021**, 121, 796.
- [11] Z. F. Huang, J. Wang, Y. Peng, C. Y. Jung, A. Fisher, X. Wang, *Adv. Energy Mater.* **2017**, 7, 1700544.
- [12] Y. Wang, F. Chu, J. Zeng, Q. Wang, T. Naren, Y. Li, Y. Cheng, Y. Lei, F. Wu, *ACS Nano* **2021**, 15, 210.
- [13] B. Singh, V. Sharma, R. P. Gaikwad, P. Fornasiero, R. Zbořil, M. B. Gawande, *Small* **2021**, 17, 2006473.
- [14] Q. Zhang, J. Guan, *Adv. Funct. Mater.* **2020**, 30, 2000768.
- [15] L. Wei, E. H. Ang, Y. Yang, Y. Qin, Y. Zhang, M. Ye, Q. Liu, C. C. Li, *J. Power Sources* **2020**, 477, 228696.
- [16] U. I. Kramm, L. Elbaz, *Nat. Catal.* **2023**, 6, 1111.
- [17] M. Xu, M. Peng, H. Tang, W. Zhou, B. Qiao, D. Ma, *J. Am. Chem. Soc.* **2024**, 146, 2290.

- [18] J. Yang, W. Li, D. Wang, Y. Li, *Adv. Mater.* **2020**, *32*, 2003300.
- [19] H. Zhang, H. T. Chung, D. A. Cullen, S. Wagner, U. I. Kramm, K. L. More, P. Zelenay, G. Wu, *Energy Environ. Sci.* **2019**, *12*, 2548.
- [20] T. Cui, Y. Wang, T. Ye, J. Wu, Z. Chen, J. Li, Y. Lei, D. Wang, Y. Li, *Angew. Chem.* **2022**, *134*, 202115219.
- [21] T. Gu, D. Zhang, Y. Yang, C. Peng, D. Xue, C. Zhi, M. Zhu, J. Liu, *Adv. Funct. Mater.* **2023**, *33*, 2212299.
- [22] D. Yu, Y. Ma, F. Hu, C. C. Lin, L. Li, H. Y. Chen, X. Han, S. Peng, *Adv. Energy Mater.* **2021**, *11*, 2101242.
- [23] S. Ajmal, Y. Zhao, G. Yasin, F. O. Boakye, M. Tabish, M. M. Alam, A. G. Al-Sehemi, W. Zhao, *ChemCatChem* **2024**, *16*, 202301392.
- [24] Y. He, X. Yang, Y. Li, L. Liu, S. Guo, C. Shu, F. Liu, Y. Liu, Q. Tan, G. Wu, *ACS Catal.* **2022**, *12*, 1216.
- [25] G. Dey, R. Jana, S. Saifi, R. Kumar, D. Bhattacharyya, A. Datta, A. S. K. Sinha, A. Aijaz, *ACS Nano* **2023**, *17*, 19155.
- [26] Z. Li, H. He, H. Cao, S. Sun, W. Diao, D. Gao, P. Lu, S. Zhang, Z. Guo, M. Li, R. Liu, D. Ren, C. Liu, Y. Zhang, Z. Yang, J. Jiang, G. Zhang, *Appl. Catal. B Environ.* **2019**, *240*, 112.
- [27] W. Zhang, Y. Chao, W. Zhang, J. Zhou, F. Lv, K. Wang, F. Lin, H. Luo, J. Li, M. Tong, E. Wang, S. Guo, *Adv. Mater.* **2021**, *33*, 2102576.
- [28] X. Han, X. Ling, D. Yu, D. Xie, L. Li, S. Peng, C. Zhong, N. Zhao, Y. Deng, W. Hu, *Adv. Mater.* **2019**, *31*, 1905622.
- [29] L. Zou, Y. S. Wei, C. C. Hou, C. Li, Q. Xu, *Small* **2021**, *17*, 2004809.
- [30] S. Ma, W. Han, W. Han, F. Dong, Z. Tang, *J. Mater. Chem. A* **2023**, *11*, 3315.
- [31] G. Lota, K. Fic, E. Frackowiak, *Energy Environ. Sci.* **2011**, *4*, 1592.
- [32] Y. Ji, L. Huang, J. Hu, C. Streb, Y.-F. Song, *Energy Environ. Sci.* **2015**, *8*, 776.
- [33] D. M. Morales, M. A. Kazakova, S. Dieckhöfer, A. G. Selyutin, G. V. Golubtsov, W. Schuhmann, J. Masa, *Adv. Funct. Mater.* **2020**, *30*, 1905992.
- [34] X. Xing, R. Liu, M. Anjass, K. Cao, U. Kaiser, G. Zhang, C. Streb, *Appl. Catal. B Environ.* **2020**, *277*, 119195.
- [35] X. Xing, R. Liu, K. Cao, U. Kaiser, C. Streb, *Chem. – A Eur. J.* **2019**, *25*, 11098.
- [36] H. Tu, H. Zhang, Y. Song, P. Liu, Y. Hou, B. Xu, T. Liao, J. Guo, Z. Sun, *Adv. Sci.* **2023**, *10*, 2305194.
- [37] Y. Song, C. Yu, D. Ma, K. Liu, *Coord. Chem. Rev.* **2024**, *499*, 215492.
- [38] K. Zhao, S. Liu, G. Ye, X. Wei, Y. Su, W. Zhu, Z. Zhou, Z. He, *ChemSusChem* **2020**, *13*, 1556.
- [39] X. Ao, W. Zhang, Z. Li, J. G. Li, L. Soule, X. Huang, W. H. Chiang, H. M. Chen, C. Wang, M. Liu, X. C. Zeng, *ACS Nano* **2019**, *13*, 11853.
- [40] X. Zhu, D. Zhang, C. J. Chen, Q. Zhang, R. S. Liu, Z. Xia, L. Dai, R. Amal, X. Lu, *Nano Energy* **2020**, *71*, 104597.

3.4 Atomically Engineered Defect-Rich Palladium Metallene for High-Performance Alkaline Oxygen Reduction Electrocatalysis

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This publication reported the fabrication of the defect rich Pd metallene with atomically dispersed WO_x and MoO_x via a facile wet chemical approach. Characterization results showed the existence of a variety of atomic-scale defects which can effectively modify the electronic configuration of the active sites and improve its catalytic activity for the ORR. This catalyst also exhibited impressive performance for practical utilization in zinc-air batteries.

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Supporting information can be found on page 190.

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RESEARCH ARTICLE

Atomically Engineered Defect-Rich Palladium Metallene for High-Performance Alkaline Oxygen Reduction Electrocatalysis

Yupeng Zhao, Zhengfan Chen, Nana Ma, Weiyi Cheng, Dong Zhang, Kecheng Cao, Fan Feng, Dandan Gao, Rongji Liu,* Shujun Li,* and Carsten Streb*

Defect engineering is a key chemical tool to modulate the electronic structure and reactivity of nanostructured catalysts. Here, it is reported how targeted introduction of defect sites in a 2D palladium metallene nanostructure results in a highly active catalyst for the alkaline oxygen reduction reaction (ORR). A defect-rich WO_x and MoO_x modified Pd metallene (denoted: D-Pd M) is synthesized by a facile and scalable approach. Detailed structural analyses reveal the presence of three distinct atomic-level defects, that are pores, concave surfaces, and surface-anchored individual WO_x and MoO_x sites. Mechanistic studies reveal that these defects result in excellent catalytic ORR activity (half-wave potential 0.93 V vs. RHE, mass activity 1.3 A mgPd^{-1} at 0.9 V vs. RHE), outperforming the commercial references Pt/C and Pd/C by factors of ≈ 7 and ≈ 4 , respectively. The practical usage of the compound is demonstrated by integration into a custom-built Zn-air battery. At low D-Pd M loading ($26 \mu\text{gPd cm}^{-2}$), the system achieves high specific capacity ($809 \text{ mAh g}_{\text{Zn}}^{-1}$) and shows excellent discharge potential stability. This study therefore provides a blueprint for the molecular design of defect sites in 2D metallene nanostructures for advanced energy technology applications.

technologies including fuel cells, metal-air batteries, and electrochemical H_2O_2 production.^[1–3] The ORR is a challenging reaction, due to the high O_2 bond dissociation energy (498 kJ mol^{-1}) and the sluggish kinetics of O_2 -related proton-coupled multi-electron processes.^[2,4] These factors significantly impede the practical application of the ORR. To overcome these challenges, numerous electrocatalysts have been developed, including those based on platinum group metals (PGMs),^[5] noble metal-free materials,^[6,7] and even metal-free catalysts.^[8] Currently, both the intrinsic activity and the long-term stability of noble metal-free and metal-free catalysts are significantly inferior to those of PGM-based electrocatalysts.^[4]

Owing to their unique electronic structure and optimum oxygen molecule adsorption energy, electrocatalysts based on PGMs have received widespread attention and are still a focal point for advanced ORR catalyst development.^[9] However, challenges remain, particularly in the case of platinum-based catalysts. While these materials demonstrate excellent catalytic performance, they often suffer from poor long-term stability.^[10–12] Importantly, highly dispersed Pt nanoparticles show a notable tendency to aggregate

1. Introduction

The oxygen reduction reaction (ORR) is one of the most important catalytic processes for energy conversion and storage

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during catalysis, resulting in the formation of larger particles with reduced reactivity.^[13] Furthermore, the high binding energy of Pt and Pd to oxygen molecules limits the generation and conversion of intermediates (such as *OH and *OOH) into H₂O/OH[•], indicating potential opportunities for enhancing the catalytic properties by modification in their electronic structure.^[14,15] Moreover, the substantial cost associated with Pt and Pd is major impediment to their broad industrial use.^[16] Thus, chemical strategies are urgently required which optimize electronic structure and reactivity of PGMs while at the same time making optimum use of all metal centers available in the catalyst.^[17–19]

These challenges have recently been targeted by the development of two-dimensional (2D) metal nanosheets, so-called metallenes, which have shown unique electronic structure and high reactivity and durability.^[20–22] Metallenes are metal or alloy materials featuring individual layers of atomic thickness.^[23,24] Metallenes offer optimum utilization of the individual metal atoms due to their high specific accessible surface area and abundance of low-coordinated reactive metal sites.^[25–27] A significant breakthrough in this realm was achieved by Guo and colleagues, who successfully synthesized PdMo bimetalene.^[28] The group discovered that strain and quantum effects within the ultrathin structure of the metallene lead to a downward shift of the d-band center, thereby lowering the oxygen molecule binding energy and enhancing electrocatalytic performance. Moreover, the electronic structure can be further modulated by doping with Mo atoms. As a result, PdMo bimetalene exhibits a lower d-band center and superior ORR catalytic activity compared to pure Pd metallene. Building on this advancement, Jin and co-workers further demonstrated that the durability of PdMo bimetalene can be significantly improved by interstitial doping with carbon. This modification results in stabilization of the Mo sites within the bimetalene structure.^[29] In addition, defect engineering has proven to be a critical tool in the advancement of Pd metallene. Wang and colleagues successfully developed a defect rich Pd metallene characterized by abundant pores, which created a multitude of highly active sites. This innovation resulted in a significant enhancement in ORR activity.^[30] Concurrently, research by Guo and coworkers revealed that the concave surfaces on Pd metallene lead to a modest downward shift in the d-band center and allow fine-tuning of oxygen molecule binding energies. This structural modification contributes to improved ORR performance, showcasing the impact of the surface geometry on catalytic efficiency.^[31]

Here, we build on these pioneering studies and report a novel ultrathin Pd metallene doped with atomic WO_x/MoO_x (referred to as **D-Pd M**) featuring by a curved defect-rich structure. Key for the synthetic access to this new compound is the use of molecular metal oxides (polyoxometalates, POMs), here reduced [H₃PMo₁₂O₄₀] • x H₂O (= PMo₁₂), N, N-dimethylformamide (DMF), and tungsten hexacarbonyl (W(CO)₆) as reducing agents. Meanwhile, W(CO)₆ was used as a structure-directing agent. PMo₁₂ and W(CO)₆ also acted as molecular precursors to deposit MoO_x and WO_x into the Pd metallene. The resulting **D-Pd M** showed excellent ORR activity, with a high half-wave potential (*E*_{1/2} = 0.93 V vs. RHE), high mass activity (1.3 A mg_{Pd}^{−1} at 0.9 V vs. RHE) and superior stability over 10,000 test cycles. Practical applicability of **D-Pd M** was demonstrated by integration into an

operational Zn-air battery at ultra-low Pd loading (26 μg_{Pd} cm^{−2}), showing high specific capacity (809 mAh g_{Zn}^{−1}), exceptional discharge performance and ultra-long cycling stability (continuous operation for 300 h over 300 charge/discharge cycles).

2. Results and Discussion

Figure 1 illustrates the synthetic procedure to access **D-Pd M**. Initially, a solution of PMo₁₂ in DMF was irradiated with ultraviolet (UV) light (*λ*_{max} = 254 nm) to reduce the POM cluster. The solution undergoes a clear transition from its initial yellow to dark blue color, and a new broad peak at 760 nm appeared in the reduced solution (Figure S1, Supporting Information), all of which suggests that the POM cluster was reduced to heteropoly blue.^[32,33] The solution containing the reduced PMo₁₂ was then combined with a DMF solution containing the metal precursors palladium (II) acetylacetonate (Pd(acac)₂) and W(CO)₆, resulting in reduction of Pd²⁺ to Pd (0) and formation of the palladene sheets.^[30] During the reaction, carbon monoxide was gradually released by thermal decomposition of W(CO)₆. CO is known to strongly adsorb on Pd (111) facet, which in turn facilitates the anisotropic lateral growth and formation of 2D ultrathin metallene.^[23,31,34] For comparison, conventional Pd metallene (**Pd M**) was prepared using a modified literature method, see Supporting Information (SI),^[34] where citric acid was used as the reducing agent instead of PMo₁₂.

The morphology and structural properties of the as-synthesized **D-Pd M** and **Pd M** were characterized by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). As shown in **Figure 2a**, **D-Pd M** exhibits an ultrathin 2D nanosheet structure with a lateral diameter of ≈1 μm. In contrast, **Pd M** exhibits a hexagonal nanosheet structure with an average diameter of 70 nm (Figure S2, Supporting Information). Selected area electron diffraction (Figure S3, Supporting Information) confirms the presence of a face-centered cubic (fcc) structure, and atomic force microscopy measurements (Figure S4, Supporting Information) give an average thickness of ≈0.9 nm, suggesting the presence of 3 to 5 Pd atom layers.^[28] TEM energy-dispersive X-ray spectroscopy (TEM-EDX; Figure S5, Supporting Information) shows the homogenous distribution of Pd, W, and Mo throughout the metallene. The atomic ratio of Pd:W:Mo was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) to be 93.8: 5.2: 1. Detailed morphological analysis of the TEM data reveals curved surface with abundant defects, including pores and concave structures (Figure S6, Supporting Information), which could be due to the oxidative etching of O₂ and PMo₁₂ in the highly acidic environment provided by PMo₁₂.^[26,31] The defects were further probed by HR-STEM. **Figure 2b** shows the presence of pores (red circle, **area 1**) and concave areas (dark blue circle, **area 2**), also see Figure S7 (Supporting Information).^[15] The brighter contrast observed in **Figure 2b** is indicative of the lower thickness in these areas compared to their surroundings. Notably, in the higher magnification of **area 1** (Figure 2c), step atoms at the inner edge can be observed. Meanwhile, in **Figure 2d**, the clear atom distribution and brighter contrast indicate the presence of a concave structure.^[15] Numerous concave structures with various diameters, typically less than 10 nm, are observed in **Figure 2e** (dark blue circles).

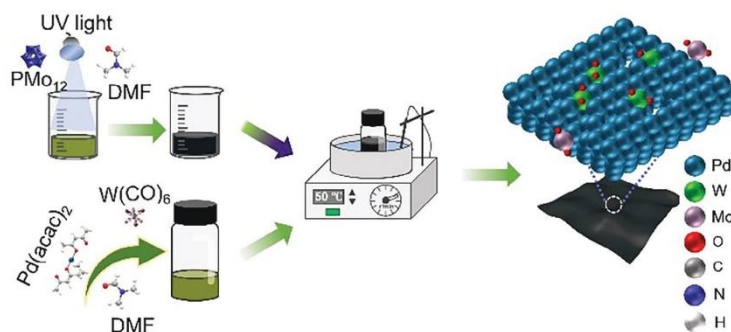


Figure 1. Schematic illustration for the fabrication of D-Pd M.

We also use a false-color mode to illustrate the thickness contrast more clearly (Figure S8a–d, Supporting Information). Additionally, curved structures are also observed in HRTEM (green rectangles in Figure 2e; Figure S8e, Supporting Information), which leads to lattice distortion. The fast Fourier transformation (FFT) pattern (Figure S8f, Supporting Information) exhibits a sixfold symmetric fcc structure, implying that the metallene is stacked dominantly along the (111) facets.^[15] TEM analyses give a lattice spacing of 0.23 nm (Figure 2f), which exceeds that of bulk Pd, suggesting the presence of intrinsic tensile strain due to its atomically thin structure.

The results are consistent with powder X-ray diffraction (pXRD) analyses shown in Figure 2g, where the peak at 39.4° is attributed to the (111) plane of the fcc structure of Pd metallene. Additionally, smaller peaks corresponding to the (200) plane at 46.7° and the (220) plane at 68.1° in D-Pd M compared to Pd M and Pd/C indicate the predominance of the (111)-exposed feature. Furthermore, the shifts to lower 2θ angles observed in D-Pd M compared to Pd M and Pd/C are attributed to strain effects and lattice distortions caused by the defect structure. Next, the oxidation states of D-Pd M were investigated by X-ray photoelectron spectroscopy (XPS). The deconvoluted spectrum of Pd 3d shows the distinct characteristic peaks centered at 335.4 and 340.7 eV, which are assigned to Pd (0) $3d_{5/2}$ and Pd (0) $3d_{3/2}$, respectively (Figure 2h). The small peaks at 336.7 and 342 eV are assigned to PdO, assigned to surface oxidation of Pd.^[25,26] The results indicate that D-Pd M is dominated by metallic Pd. The deconvoluted W 4f spectrum (Figure 2i) shows the existence of W^{5+} species.^[35] In contrast, the oxidation state of Mo cannot be assigned reliably by XPS due to the low concentration of Mo species in D-Pd M.

X-ray absorption spectroscopy (XAS) characterization was performed to further investigate the chemical states and local coordination environments of D-Pd M. The normalized Pd K-edge X-ray absorption near-edge structure (XANES) spectrum (Figure 3a) of D-Pd M is similar to the Pd foil reference, indicating its dominant metallic state,^[25,26] which coincides with the XPS result. Fourier transform extended X-ray absorption fine structures (FT-EXAFS) analysis was employed to investigate the local environment of the Pd atoms (Figure 3b). The strong peak in the D-Pd M EXAFS spectrum at 2.57 Å is assigned to the

Pd-Pd pairs.^[28] The average coordination number (CN) of elements is proportional to the intensity of $FT-\chi(k)$ peak and the corresponding fitting results of Pd K-edge FT-EXAFS (Figure S9 and Table S1, Supporting Information) give an average CN of 10.7 ± 1.0 , which is lower than that in Pd foil ($CN_{Pd\text{ foil}} = 12$), indicating the existence of unsaturated Pd sites. This is in agreement with the proposed thin-layered structure and the presence of multiple defects in the D-Pd M.^[31] The W species in D-Pd M was further investigated by analyzing its L₃-edge XANES and FT-EXAFS spectra. As shown in Figure 3c, the white-line peak intensity is between WO_2 and WO_3 , which gives an approximate oxidation state of +5.^[35,36] This finding is consistent with the results obtained from XPS analysis. In addition, the peaks in the FT-EXAFS spectrum (Figure 3d) at 1.38 and 2.43 Å can be assigned to W-O and W-Pd environments.^[36,37] The corresponding fitting results of W L₃-edge FT-EXAFS show the CN of W-Pd is 6.3 ± 0.8 . Based on these results, we propose that WO_x ($x = 2.5$) is doped on the surface of metallene. Additionally, W substitutes the position of Pd, as illustrated in Figure S12 (Supporting Information).^[38] Notably, while W-W pairs are present in bulk WO_2 and WO_3 , they are not observed in D-Pd M according to the FT-EXAFS spectrum and wavelet transform analysis (Figure 3g), which can better resolve features in K-space and radial distance. The results indicate that atomic WO_x species are doped on the surface of the metallene. Furthermore, we also investigated the chemical states and local coordination environments of Mo in D-Pd M by employing MoO_2 , MoO_3 , and Mo foil as reference materials. In Figure 3e, MoO_3 exhibits a distinct pre-edge feature at $\approx 19,995$ eV, which is not observed in MoO_2 and Mo foil. Additionally, a weak pre-edge is observed in D-Pd M, suggesting that the oxidation state of Mo in D-Pd M falls between that of MoO_2 and MoO_3 .^[39] Furthermore, the near-edge structure XANES spectra also support this conclusion. The FT-EXAFS spectrum in Figure 3f indicates the presence of Mo-O and Mo-Pd pairs, with no Mo-Mo species observed (Figure 3h), suggesting atomic dispersion of MoO_x . The fitting results of Mo K-edge FT-EXAFS for Mo-Pd give a CN of 0.9 ± 0.2 , indicating that the MoO_x are located on the surface of the Pd sheets rather than being embedded in the Pd lattice, as illustrated in Figure S12 (Supporting Information).^[39] More detailed peak assignments for FT-EXAFS of Pd, W, and Mo can be found in Table S1 (Supporting Information). The comparison of

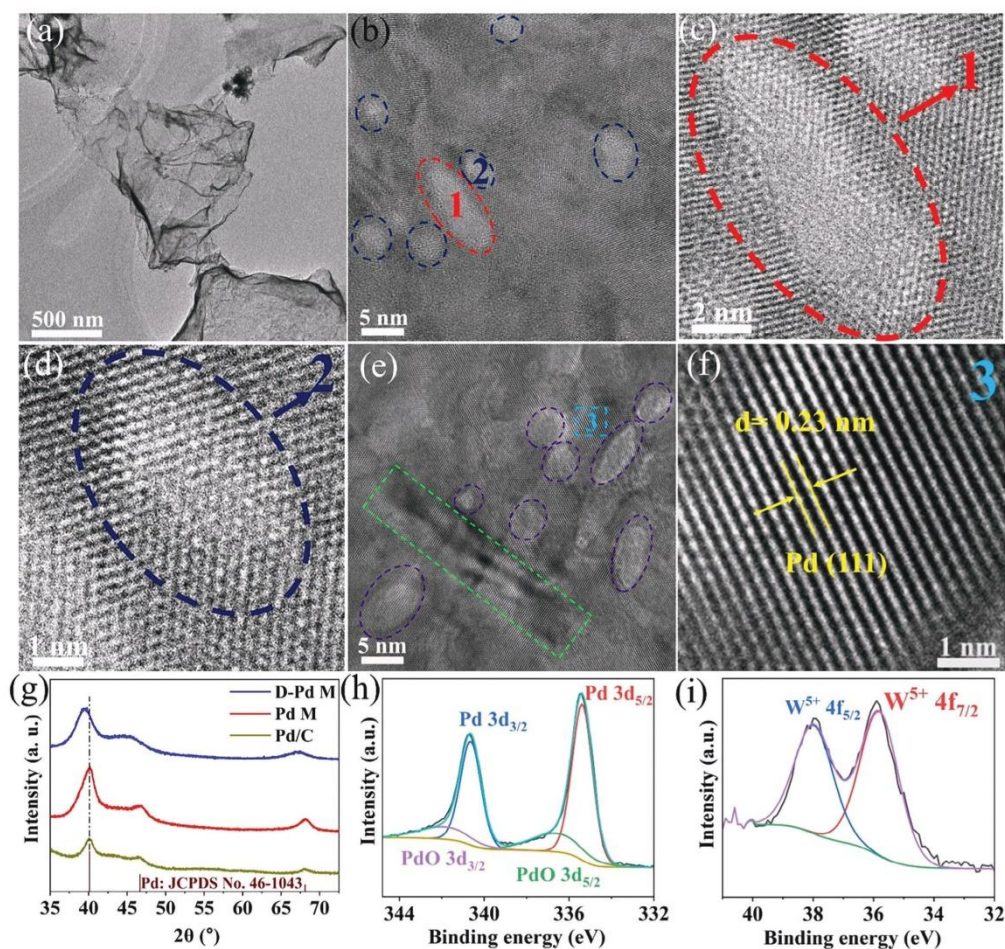


Figure 2. a) TEM image and b,e) HRTEM images of D-Pd M, with corresponding enlarged crystal details shown in c,d,f) for selected areas (area 1, area 2, and area 3, respectively). g) XRD patterns of D-Pd M, Pd M, and Pd/C. h) Deconvoluted XPS spectra of Pd 3d and i) W 4f of D-Pd M.

corresponding fitting results and the raw data can be found in Figures S9–S11 (Supporting Information).

In the next step, we evaluated the electrocatalytic performance of the D-Pd M for ORR in 0.1 M aqueous KOH using a typical three-electrode electrochemical setup. Here, the saturated calomel electrode was used as the reference electrode, and a graphite rod was employed as the counter electrode. All potentials in this study have been converted to reversible hydrogen electrode potentials (RHE, see details in the Supporting Information). Prior to the measurement, freshly prepared D-Pd M and Pd M were deposited on a VULCAN® XC-72 carbon support (See details in Supporting Information). In addition, commercial 10% Pd/C and 20% Pt/C were also used as ORR catalyst refer-

ences. The respective catalysts ink was drop-cast onto the glassy carbon rotating disk electrode, which acted as the working electrode. The metal loading on the electrode for D-Pd M/C and Pd M/C was controlled to be $10 \mu\text{g cm}^{-2}$, while that of commercial Pd/C and Pt/C was controlled to be $15 \mu\text{g cm}^{-2}$ to reach the well-defined limiting current densities. The typical cyclic voltammetry (CV) curves of all the catalysts were recorded in N_2 -saturated 0.1 M KOH at a scan rate of 50 mV s^{-1} . As shown in Figure 4a and Figure S13 (Supporting Information), the peak located at 0.74 V of D-Pd M/C is assigned to Pd oxide reduction.^[28] Notably, the reduction potential is a descriptor of the Pd-O binding energy. Compared to Pd/C (0.69 V) and Pd M/C (0.73 V), the peak of D-Pd M/C shifts positively, revealing its weaker

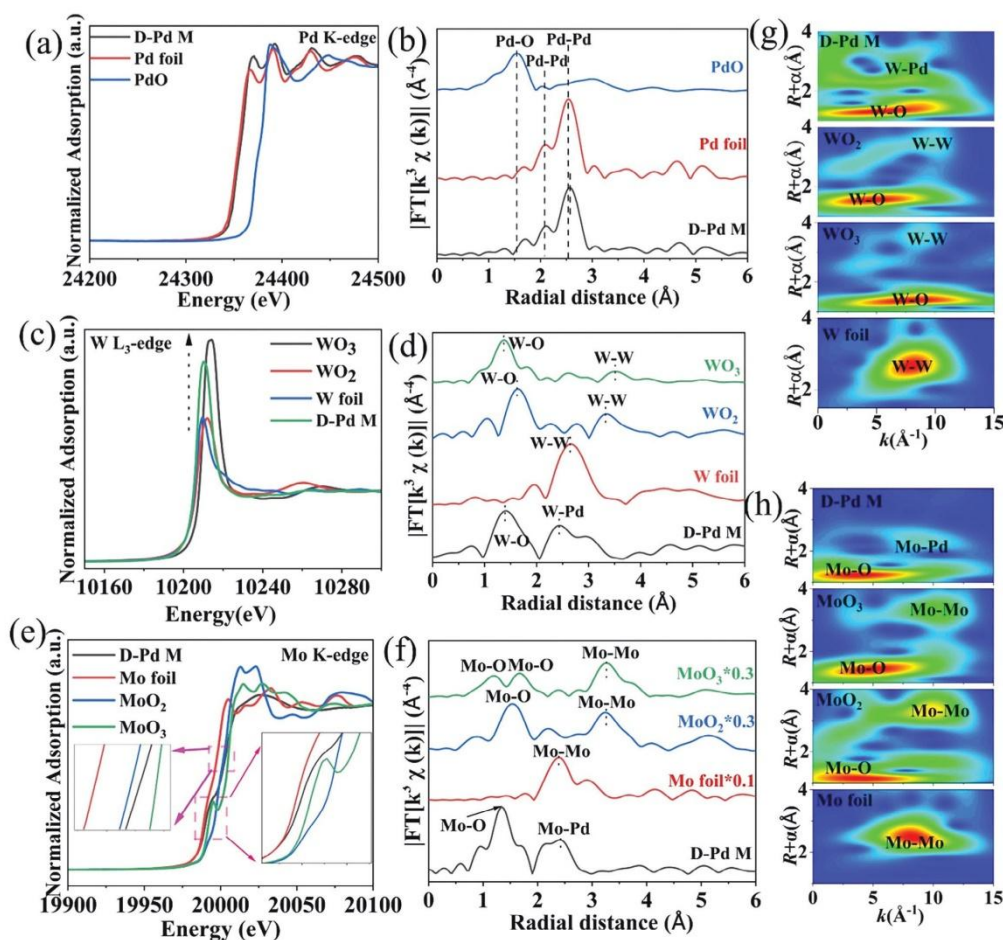


Figure 3. XAS characterizations of D-Pd M. Experimental XANES spectra a,c,e) and EXAFS spectra b,d,f) of Pd, W, and Mo, respectively. Wavelet transform profiles of W g) and Mo h).

oxygen affinity.^[27,40] Next, we determined the electrochemically active surface areas (ECSAs) of D-Pd M/C and reference catalysts by underpotentially deposited hydrogen (H_{upd}) and underpotentially depositing copper (Cu_{upd}) methods (See method details in Supporting Information). The ECSAs determined from the Cu_{upd} method were used for further analysis. The ECSA values are estimated by Cu_{upd} to be $79 \text{ m}^2 \text{ g}_{Pd}^{-1}$ for D-Pd M/C, $70.5 \text{ m}^2 \text{ g}_{Pd}^{-1}$ for Pd M/C, $40.4 \text{ m}^2 \text{ g}_{Pd}^{-1}$ for Pd/C, and $51.8 \text{ m}^2 \text{ g}_{Pt}^{-1}$ for Pt/C, respectively (Figure S14, Supporting Information). The increased active areas of D-Pd M can be attributed to its porous and curved structure. This structural characteristic ensures that more active sites are exposed to the electrolyte during the catalytic process.

The linear sweep voltammetry (LSV) curves of all the samples were determined in an O_2 -saturated 0.1 M KOH electrolyte at a scan rate of 20 mV s^{-1} to assess their ORR performance. As shown in Figure 4b, D-Pd M/C shows the most positive half-wave potential ($E_{1/2}$, 0.93 V) and onset potential (E_{onset} , 1.02 V), as compared with those of Pd M/C (0.87 and 0.99 V), Pd/C (0.87 and 1.02 V), and Pt/C (0.88 and 1.01 V), revealing that D-Pd M/C exhibited the best catalytic performance for ORR among all the catalysts. The diffusion-limiting current density (j_l) of D-Pd M/C (5.7 mA cm^{-2}) is also higher than that of Pd M/C (5.4 mA cm^{-2}), Pd/C (5.5 mA cm^{-2}), and Pt/C (5.6 mA cm^{-2}). Such high limiting current density is a benefit to the high-power densities of Zn-air batteries. Besides, D-Pd M/C has the smallest Tafel slope

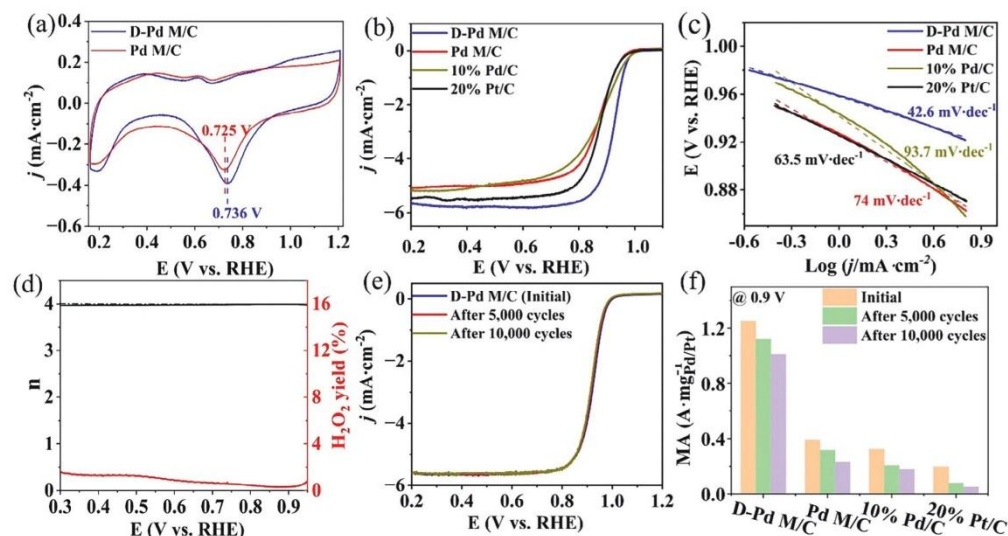


Figure 4. a) CVs of D-Pd M/C and Pd M/C, b) LSVs, and c) Tafel slopes of D-Pd M/C, Pd M/C, Pd/C, and Pt/C, d) electron transfer number and H_2O_2 yield of D-Pd M, e) LSVs of D-Pd M, and f) mass activities of D-Pd M/C, Pd M/C, Pd/C, and Pt/C at 0.9 V before and after 5,000 and 10,000 cycles.

value (Figure 4c) of 42.6 mV dec^{-1} , compared with that of Pd M/C (74 mV dec^{-1}), Pd/C (93.7 mV dec^{-1}), and Pt/C (63.5 mV dec^{-1}), which indicates faster ORR reaction kinetics on the surface of D-Pd M. To further quantify the intrinsic ORR activity, kinetic currents were calculated for all catalysts using the Koutecký-Levich (K-L) equation (see details in Supporting Information). These were then normalized based on the metal mass loading of the catalysts and the ECSA to determine the mass activity (MA) and specific activity (SA). As shown in Figure S15 (Supporting Information), D-Pd M/C achieves an MA of $1.3 \text{ A mg}_{\text{Pd}}^{-1}$ at the generally chosen potential of 0.9 V, which is 3.3, 3.9, and 6.5 times higher than that of Pd M/C, commercial Pd/C, and commercial Pt/C. Additionally, D-Pd M/C delivers an MA of $5.2 \text{ A mg}_{\text{Pd}}^{-1}$ at 0.85 V. This value is also apparently higher than that of Pd M/C ($1.4 \text{ A mg}_{\text{Pd}}^{-1}$), commercial Pd/C ($0.88 \text{ A mg}_{\text{Pd}}^{-1}$), and commercial Pt/C ($0.88 \text{ A mg}_{\text{Pt}}^{-1}$). Likewise, D-Pd M/C also has specific activities of 6.13 and 1.5 mA cm^{-2} at 0.85 and 0.9 V, respectively, which significantly outperform Pd M/C (1.86 and 0.52 mA cm^{-2}), commercial Pd/C (2.46 and 0.91 mA cm^{-2}), and commercial Pt/C (1.31 and 0.3 mA cm^{-2}). The excellent ORR catalytic performance of D-Pd M/C can be attributed to the lower Pd-O binding energy, which facilitates the generation of intermediates ($^*\text{OH}$ and $^*\text{OOH}$) and their transformation to H_2O . Furthermore, to understand the catalytic process of D-Pd M, rotating ring-disk electrode measurements were used to determine the electron transfer number (n) and hydrogen peroxide yield, see details in Supporting Information. As shown in Figure 4d and Figure S16a (Supporting Information), the electron transfer number is >3.9 between 0.3 to 0.95 V, revealing a four-electron transfer-dominated pathway, which agrees well with the results obtained from the K-L plot at rotation rates between 625 and

2025 rpm (Figure S16b,c, Supporting Information). The H_2O_2 yield is only 0–1.6% within the potential range from 0.8 to 0.3 V. Pd M/C, Pd/C, and Pt/C exhibit similar results, indicating a consistent four-electron transfer process (Figure S17, Supporting Information).

Apart from electrocatalytic activity, stability is another essential criterion for the comprehensive evaluation of the catalytic performance. Therefore, we employed accelerated durability tests by CV cycling between 0.6 and 1.0 V at a scan rate of 200 mV s^{-1} in an O_2 -saturated 0.1 M KOH electrolyte. As shown in Figure 4e, after 5,000 and 10,000 cycles, the $E_{1/2}$ of D-Pd M/C shows only negligible decay (4 and 6 mV, respectively). In contrast, an apparent negative shift was observed for Pd M/C (10 and 23 mV), commercial Pd/C (19 and 23 mV), and commercial Pt/C (25 mV and 38 mV), respectively (Figure S18, Supporting Information). In addition, the MA of D-Pd M/C at 0.9 V has decreased by 10.4% and 19.2% after 5,000 and 10,000 cycles (Figure 3f), which outperforms those of Pd M/C (18.7% and 41%), commercial Pd/C (36.6% and 44.6%), and commercial Pt/C (60.4% and 74.6%). The same scenario was also observed at 0.85 V vs. RHE in all the catalysts (Figure S19, Supporting Information). Additionally, the morphology and structure of D-Pd M have no obvious degradation after 10,000 cycles, compared to the pristine sample. In comparison, the apparent aggregation of Pt nanoparticles was observed in Pt/C (Figure S20, Supporting Information). The composition of D-Pd M was determined by ICP-OES, which shows the atomic ratio of Pd:W is 94.2:5.8. However, no Mo was determined, which indicates that MoO_x dissolved under the electrochemical tests and explained the slight catalytic degradation.

Based on the previous report from Norskov, the binding energy between catalysts and O_2 is linearly correlated with the

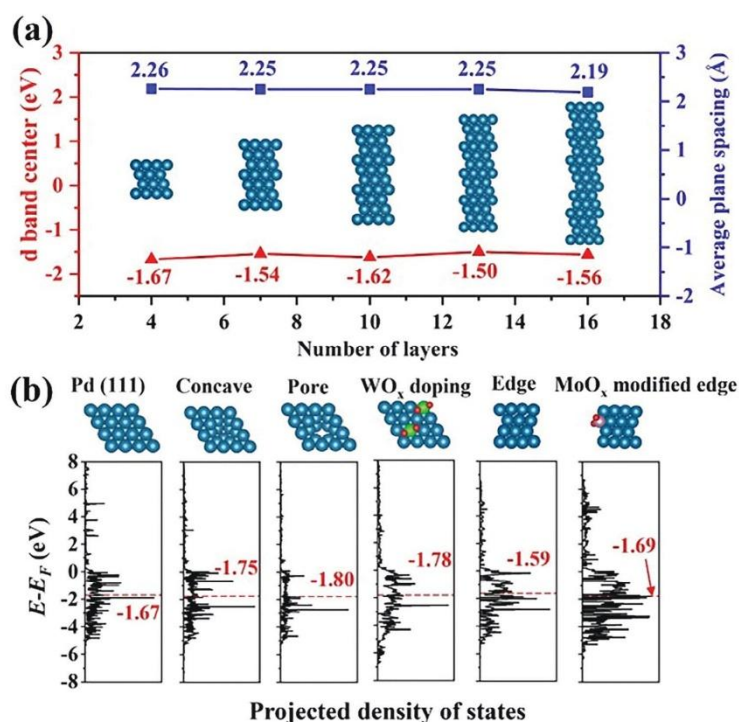


Figure 5. DFT calculations of *d*-band centers. a) The *d*-band center of surface atoms and average plane spacings of Pd nanosheets with 4, 7, 10, 13, and 16 layers. The side view of atomic models is inserted. b) From left to right, the *d* band centers of surface atoms in Pd (111), exposed sublayer atoms in concave defects, exposed sublayer atoms in pores defects, surface atoms in WO_x doping, edge atoms, and MoO_x modified edge atoms. The first four schematic illustrations are from the top view and the last two are from side view of atomic model. The navy, green, pink, and red balls represent Pd, W, Mo, and O, respectively.

energy center of the valence *d*-band density of states (*d*-band center), making it one of the most successful descriptors of ORR activity.^[41] We therefore calculated the *d*-band centers of various defects in **D-Pd M** using density functional theory (DFT) to elucidate the reasons for the superior ORR activity of **D-Pd M**. We constructed a four-atom layer model for the **D-Pd M**, incorporating WO_x doping into the surface lattice of metallene and MoO_x attachment to the edge Pd atoms. The loading of W and Mo were set to 5% and 1%, respectively, to be in line with experimental results. As shown in **Figure 5a**, the *d*-band centers of surface Pd atoms in different layer Pd sheets were calculated. A downward shift (≈ 0.11 eV) in the *d*-band center of surface atoms is observed in the four-layer Pd sheet compared to the sixteen-layer Pd sheet, which results in less strongly bound O₂ on the surface Pd atoms.^[28] We note that the average spacing between the planes in four-layer Pd metallene is 3.2% greater than in a 16-layered nanosheet, indicating a higher level of tensile strain in the four-layer structure compared to multilayer Pd sheets. The electronic structures tuned by defects were also investigated. As illustrated in **Figure 5b**, in a perfect four-layer Pd sheet, the

d-band center of the surface atoms in the (111) plane is -1.67 eV. However, when subjected to concave defects and pore defects, the sublayer layer atoms feature substantially lower *d*-band centers (-1.75 and -1.8 eV, respectively) compared to the surface atoms. This indicates a weaker binding ability to O₂, thereby facilitating the formation and conversion of intermediates (*OH and *OOH) to H₂O/OH.^[14,15] The findings confirm that concave and pore defects serve as effective means to introduce highly active sites, thereby enhancing the catalytic properties for ORR. Moreover, embedding WO_x into the surface Pd lattice also leads to a downshift of the *d*-band center by 0.11 eV. The average *d*-band center of edge Pd atoms was calculated to be -1.59 eV, significantly higher than that of surface atoms. This discrepancy reveals the less favorable catalytic features for ORR exhibited by edge atoms. After attaching MoO_x to the edge Pd atoms, the *d*-band center of these atoms shifted downward to -1.69 eV, a value similar to the *d*-band center of surface atoms in Pd (111), indicating the improved catalytic properties. These computational results suggest that size effects, pore defects, concave defects, WO_x doping, and MoO_x modification can effectively enhance the ORR activity of

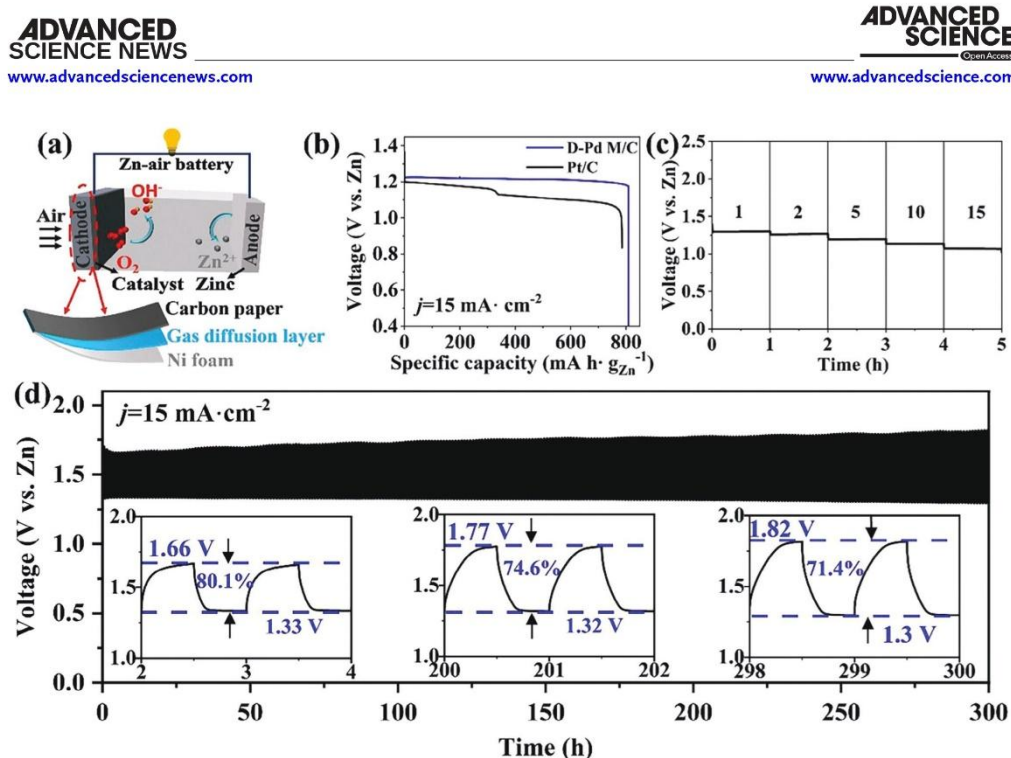


Figure 6. a) Scheme of the aqueous Zn-air battery, b) full discharge profile (voltage versus specific capacity of discharge) for a Zn-air battery using D-Pd M/C as the air cathode at a current density of 15 mA cm⁻², c) the discharge curves of Zn-air batteries at current densities of 1, 2, 5, 10, and 15 mA cm⁻², and d) the charge-discharge profiles of two Zn-air batteries worked at a current density of 15 mA cm⁻² with each cycle lasting 60 min.

D-Pd M. We note that these calculations do not consider the leaching of MoO_x species during long-term electrochemical operation (see above).

Next, the practical utility of the D-Pd M catalyst was tested by integration into an aqueous custom-built Zn-air battery (Figure S21, Supporting Information). Given the economic expense of Pd metal, we opted to test the system at an extremely low Pd loading at the cathode (26 μg_{Pd} cm⁻²). The principal structure of the Zn-air battery is shown in Figure 6a; briefly, the battery is based on a carbon paper-supported D-Pd M/C as the air cathode, a Zn plate as the anode, and 6 M aqueous KOH solution containing 0.2 M Zn(CH₃COO)₂ as the electrolyte. Initial tests show that the Zn-air battery achieves a high open-circuit potential (OCP) of 1.4 V (Figure S21, Supporting Information). The specific capacities of the D-Pd M/C-based battery at 15 mA cm⁻² is illustrated in Figure 6b. For comparison, a reference Zn-air battery using commercial Pt/C coated carbon paper (26 μg_{Pt} cm⁻²) as air cathode was tested under the same conditions. After normalizing for the weight loss of Zn, the D-Pd M/C-based battery exhibits a discharge specific capacity of 809 mAh g_{Zn}⁻¹, corresponding to an energy density of 982 Wh kg_{Zn}⁻¹, which outperforms the Pt/C-based battery (785 mAh g_{Zn}⁻¹ and 890 Wh kg_{Zn}⁻¹). In addition, during the long-term discharge test, the potential of the D-Pd M/C-based cell remained remarkably stable and only

a slight potential decrease of 0.05 V was observed. In contrast, a notable potential drop (>0.2 V) was observed for the Pt/C-based battery. The stability of the D-Pd M/C-based battery is further shown by the discharge curves at various current densities (Figure 6c). Also, the D-Pd M/C-based battery achieves a high power density (55 mW cm⁻²) compared with the Pt/C-based battery (37 mW cm⁻²), see Figure S22a (Supporting Information). The power density of the D-Pd M/C-based battery can be increased by at higher D-Pd M loadings, see Figure S22b (Supporting Information).

To assess the cycling durability, the D-Pd M/C-based Zn-air battery was further tested at a charging and discharging rate of 15 mA cm⁻² for 60 min per cycle. As illustrated in Figure 6d, D-Pd M/C-based battery exhibits a significantly longer cycling lifetime over 300 cycles (≈300 h) with a small charge/discharge voltage gap. Initially, the charge/discharge voltage efficiency reached 80.1% with a potential gap of 0.33 V. During cycling, the voltage efficiency decreased slowly, while the discharging potential remained exceptionally stable throughout the measurement. The gradual increase in charging potential resulted in a decrease in round-trip voltage efficiency, possibly attributed to imperfect oxygen evolution activity under conditions of very low palladium loading (Figure S22c, Supporting Information).

3. Conclusion

In summary, we demonstrate how molecular-level tuning of 2D metallene structures becomes possible using bottom-up materials design routes. The study shows how introduction of various defect sites impacts the oxygen reduction reaction reactivity of a 2D palladene nanostructure catalyst, leading to high reactivity and stability under harsh conditions. Combined experimental and theoretical analyses reveal the correlation between defects, change in electronic structure, and resulting reactivity. Integration of the catalyst into as cathode in a Zn-air battery demonstrated outstanding performance at very low Pd loading. This study offers valuable insights into the design of efficient ORR catalysts with reduced precious metal consumption, which can open new paths for larger-scale deployment of non-earth-abundant elements.

4. Experimental Section

The authors have cited additional references within the Supporting Information.^[31,33,42–46] A preprint of this manuscript has been deposited at <https://doi.org/10.26434/chemrxiv-2024-fkr00>.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are openly available in Zenodo.org at <https://doi.org/10.5281/zenodo.10984539>, reference number 10984539.

Keywords

defect engineering, electrocatalysis, metallene, oxygen reduction reaction, zn-air battery

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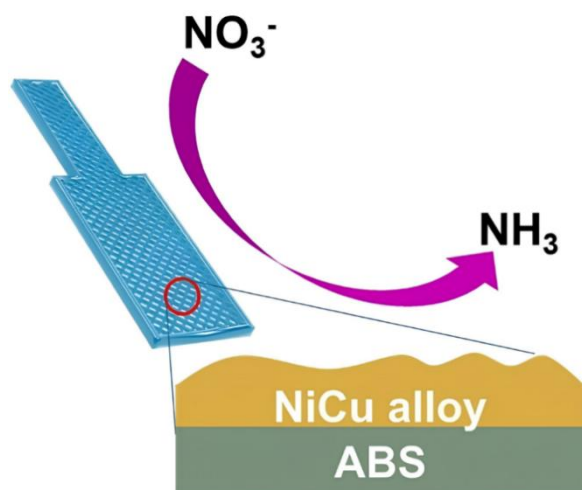
Published online:

- [1] S. Chu, A. Majumdar, *Nature* **2012**, 488, 294.
- [2] A. Han, X. Wang, K. Tang, Z. Zhang, C. Ye, K. Kong, H. Hu, L. Zheng, P. Jiang, C. Zhao, Q. Zhang, D. Wang, Y. Li, *Angew. Chem., Int. Ed.* **2021**, 60, 19262.
- [3] C. Lim, A. R. Fairhurst, B. J. Ransom, D. Haering, V. R. Stamenkovic, *ACS Catal.* **2023**, 13, 14874.
- [4] Z. Ma, Z. P. Cano, A. Yu, Z. Chen, G. Jiang, X. Fu, L. Yang, T. Wu, Z. Bai, J. Lu, *Angew. Chem., Int. Ed.* **2020**, 59, 18334.
- [5] Z. Lyu, X.-G. Zhang, Y. Wang, K. Liu, C. Qiu, X. Liao, W. Yang, Z. Xie, S. Xie, *Angew. Chem., Int. Ed.* **2021**, 60, 16093.
- [6] Q. Yang, Y. Jia, F. Wei, L. Zhuang, D. Yang, J. Liu, X. Wang, S. Lin, P. Yuan, X. Yao, *Angew. Chem., Int. Ed.* **2023**, 62, 202315752.
- [7] M. A. de Araújo, A. A. Koverga, A. M. P. Sakita, F. B. Ometto, L. G. da Trindade, E. A. Ticianelli, *ChemCatChem* **2023**, 15, 202201594.
- [8] J. Zhang, L. iangti Qu, G. Shi, J. Liu, J. Chen, L. Dai, D. Zhang, J. Liu, L. Dai, L. Qu, G. Shi, J. Chen, *Angew. Chem., Int. Ed.* **2016**, 55, 2230.
- [9] Z. Zhao, C. Chen, Z. Liu, J. Huang, M. Wu, H. Liu, Y. Li, Y. Huang, *Adv. Mater.* **2019**, 31, 1808115.
- [10] K. J. Sawant, Z. Zeng, J. P. Greeley, *Angew. Chem., Int. Ed.* **2024**, 63, 202312747.
- [11] E. Hornberger, V. Mastronardi, R. Brescia, P. P. Pompa, M. Klingenhof, F. Dionigi, M. Moglianetti, P. Strasser, *ACS Appl. Energy Mater.* **2021**, 4, 9542.
- [12] T. Đukić, L. Pavko, P. Jovanović, N. Maselj, M. Gatalo, N. Hodnik, *Chem. Commun.* **2022**, 58, 13832.
- [13] D. Y. Chung, J. M. Yoo, Y. E. Sung, *Adv. Mater.* **2018**, 30, 1704123.
- [14] S. Huang, S. Lu, S. Gong, Q. Zhang, F. Duan, H. Zhu, H. Gu, W. Dong, M. Du, *ACS Nano* **2022**, 16, 522.
- [15] F. Lin, F. Lv, Q. Zhang, H. Luo, K. Wang, J. Zhou, W. Zhang, W. Zhang, D. Wang, L. Gu, S. Guo, *Adv. Mater.* **2022**, 34, 2202084.
- [16] N. Zhang, Q. Shao, X. Xiao, X. Huang, *Adv. Funct. Mater.* **2019**, 29, 1808161.
- [17] L. Bu, N. Zhang, S. Guo, X. Zhang, J. Li, J. Yao, T. Wu, G. Lu, J. Y. Ma, D. Su, X. Huang, *Science* **2016**, 354, 1410.
- [18] X. Wang, Z. Li, Y. Qu, T. Yuan, W. Wang, Y. Wu, Y. Li, *Chem* **2019**, 5, 1486.
- [19] Y. Yang, W. Xiao, X. Feng, Y. Xiong, M. Gong, T. Shen, Y. Lu, H. D. Abruña, D. Wang, *ACS Nano* **2019**, 13, 5968.
- [20] L. Zhang, Z. Zhao, X. Fu, S. Zhu, Y. Min, Q. Xu, Q. Li, *ACS Appl. Mater. Interfaces* **2023**, 15, 5198.
- [21] Q. Yang, L. Shi, B. Yu, J. Xu, C. Wei, Y. Wang, H. Chen, *J. Mater. Chem. A* **2019**, 7, 18846.
- [22] B. R. Anne, S. Il Choi, *Curr. Opin. Electrochem.* **2023**, 39, 101303.
- [23] S. Huang, S. Lu, S. Gong, Q. Zhang, F. Duan, H. Zhu, H. Gu, W. Dong, M. Du, *ACS Nano* **2022**, 16, 522.
- [24] M. Xie, S. Tang, B. Zhang, G. Yu, *Mater. Horiz.* **2023**, 10, 407.
- [25] K. Chen, Z. Ma, X. Li, J. Kang, D. Ma, K. Chu, *Adv. Funct. Mater.* **2023**, 33, 2209890.
- [26] Y. Xiong, J. M. McLellan, J. Chen, Y. Yin, Z. Li, Y. Xia, *J. Am. Chem. Soc.* **2005**, 127, 17118.
- [27] J. Guo, L. Gao, X. Tan, Y. Yuan, J. Kim, Y. Wang, H. Wang, Y. J. Zeng, S. Il Choi, S. C. Smith, H. Huang, *Angew. Chem., Int. Ed.* **2021**, 60, 10942.
- [28] M. Luo, Z. Zhao, Y. Zhang, Y. Sun, Y. Xing, F. Lv, Y. Yang, X. Zhang, S. Hwang, Y. Qin, J. Y. Ma, F. Lin, D. Su, G. Lu, S. Guo, *Nature* **2019**, 574, 81.
- [29] K. Zhang, Y. He, R. Guo, W. Wang, Q. Zhan, R. Li, T. He, C. Wu, M. Jin, *ACS Energy Lett.* **2022**, 7, 3329.

- [30] H. Yu, T. Zhou, Z. Wang, Y. Xu, X. Li, L. Wang, H. Wang, *Angew. Chem., Int. Ed.* **2021**, *60*, 12027.
- [31] J. Ge, P. Wei, G. Wu, Y. Liu, T. Yuan, Z. Li, Y. Qu, Y. Wu, H. Li, Z. Zhuang, X. Hong, Y. Li, *Angew. Chem., Int. Ed.* **2018**, *57*, 3435.
- [32] E. A. Nagul, I. D. McKelvie, P. Worsfold, S. D. Kolev, *Anal. Chim. Acta* **2015**, *890*, 60.
- [33] J. N. Barrows, G. B. Jameson, M. T. Pope, *J. Am. Chem. Soc.* **1985**, *107*, 1771.
- [34] Y. Li, Y. Yan, Y. Li, H. Zhang, D. Li, D. Yang, *CrystEngComm* **2015**, *17*, 1833.
- [35] P. Castillero, V. Rico-Gavira, C. López-Santos, A. Barranco, V. Pérez-Dieste, C. Escudero, J. P. Espinós, A. R. González-Elipé, *J. Phys. Chem. C* **2017**, *121*, 15719.
- [36] H. Wang, H. Zheng, L. Ling, Q. Fang, L. Jiao, L. Zheng, Y. Qin, Z. Luo, W. Gu, W. Song, C. Zhu, *ACS Nano* **2022**, *16*, 21266.
- [37] K. Chen, F. Wang, X. Lu, Y. Li, K. Chu, *ACS Catal* **2023**, *13*, 9550.
- [38] K. Chen, Z. Ma, X. Li, J. Kang, D. Ma, K. Chu, *Adv. Funct. Mater.* **2023**, *33*, 2209890.
- [39] J. Wu, J. Fan, X. Zhao, Y. Wang, D. Wang, H. Liu, L. Gu, Q. Zhang, L. Zheng, D. J. Singh, X. Cui, W. Zheng, *Angew. Chem., Int. Ed.* **2022**, *61*, 202207512.
- [40] Y. Wang, D. Sun, M. Wang, Z. Feng, A. S. Hall, *J. Phys. Chem. C* **2020**, *124*, 5220.
- [41] B. Hammer, J. K. Nørskov, *Surf. Sci.* **1995**, *343*, 211.
- [42] G. Kresse, J. Furthmüller, *Comput. Mater. Sci.* **1996**, *6*, 15.
- [43] G. Kresse, J. Hafner, *Phys. Rev. B* **1994**, *49*, 14251.
- [44] G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, *59*, 1758.
- [45] K. Lee, É. D. Murray, L. Kong, B. I. Lundqvist, D. C. Langreth, *Phys. Rev. B* **2010**, *82*, 081101.
- [46] V. Wang, N. Xu, J. C. Liu, G. Tang, W. T. Geng, *Comput. Phys. Commun.* **2021**, *267*, 108033.

3.5 Metal Alloy-Functionalized 3D-Printed Electrodes for Nitrate-to-Ammonia Conversion in Zinc–Nitrate Batteries

Si Liu, Yupeng Zhao, Zhengfan Chen, Dandan Gao, Fan Feng, Tobias Rios-Studer, Joachim Bansmann, Johannes Biskupek, Ute Kaiser, Rongji Liu, Carsten Streb.



This paper reported a self-supported catalyst based on bimetallic NiCu alloy and 3D printed polymer with a sandwich structure consisting of polymer-metal-metal oxides and/or hydroxides. The composite electrode showed high performance in the green electrosynthesis ammonia from of nitrate, giving NH_3 Faradaic efficiencies of up to 83% and NH_3 yield rates up to $860 \mu\text{g}/(\text{h}\cdot\text{cm}^2)$.

Author contributions:

Si Liu, Yupeng Zhao: Conceptualization, Methodology, Investigation, Data curation, Analysis, Writing original draft.

Zhengfan Chen: Methodology, Investigation, Data curation, Writing original draft.

Danan Gao, Fan Feng: Data curation, Writing original draft.

Tobias Rios-Studer, Joachim Bansmann: Data curation, Writing original draft.

Johannes Biskupek, Ute Kaiser: Data curation, Writing original draft.

Rongji Liu: Data curation, Methodology, Writing original draft.

Carsten Streb: Project administration, Funding acquisition, Conceptualization, Supervision, Data curation, Methodology, Writing original draft.

Supporting information can be found on page 217.

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Metal Alloy-Functionalized 3D-Printed Electrodes for Nitrate-to-Ammonia Conversion in Zinc-Nitrate Batteries

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Electrocatalytic nitrate reduction is a promising approach to remove harmful nitrate and produce ammonia in aqueous media. Here, we demonstrate how 3D printed polymer electrodes can be electrodeless plated with a bimetallic NiCu alloy film suitable for sustained nitrate-to-ammonia reduction. Characterization by powder X-ray diffraction, X-ray photoelectron spectroscopy, scanning/transmission electron microscopy and energy-dispersive X-ray spectroscopy indicate that the electrode has a two-layer structure consisting of polymer/ coating layer of

metal alloys. The composite electrode shows high-performance in the nitrate-to-ammonia electroreduction, giving NH_3 Faradaic efficiencies of up to 83% and NH_3 yield rates up to $860 \mu\text{g}/(\text{h cm}^2)$ at -0.38 V vs. RHE. We show that the electrode can easily be integrated into a Zn-nitrate battery, giving a power density of 3.8 mW cm^{-2} with continuous NH_3 production. The system combines three productive outputs, that is removal of nitrate pollutants, synthesis of valuable ammonia and generation of "green" electricity.

Introduction

NH_3 is a fundamental indispensable ingredient for chemical synthesis, agriculture and pharmaceuticals industry.^[1,2] Large scale production of NH_3 was not feasible until the Haber-Bosch process was developed, which requires high temperature and pressure to drive the combination reaction of N_2 and H_2 .^[3,4] This process has dramatically improved the production of fertilizer and facilitated the manufacture of nitrogen-containing compounds in industry. However, as a result of the high energy

barrier of the reaction and the growing demand for NH_3 , Haber-Bosch cost nearly 2% of global energy and result in 400 Mt of CO_2 emission yearly.^[5–7] To address this problem, the reduction of N_2 to NH_3 (NRR) using H_2O as the proton source and powered by renewable electricity has garnered public attention due to its potential to address CO_2 emissions and offer a sustainable pathway for the future NH_3 industry. However, the high energy barrier for breaking the $\text{N}\equiv\text{N}$ triple bond and the low-efficiency mass transport at the gas-liquid-solid interface significantly impeded this approach. As an alternative, the nitrate (NO_3^-) electroreduction to NH_3 (NO_3RR) is energetically more favorable than direct NRR for NH_3 electrosynthesis, particularly since nitrate is an ubiquitous water pollutant (due to intensive agriculture), has a high water solubility and a low dissociation energy for the $\text{N}=\text{O}$ bond. Thus, ammonia generation by nitrate reduction could be an efficient path to access a valuable chemical while removing aqueous pollutants.

The conversion of NO_3^- to NH_3 is a complex proton-coupled eight electron process involving a sequence of intermediates. According to theoretical studies, Cu binds hydrogen poorly but adsorbs nitrate radicals and NO_3RR intermediates strongly, resulting in remarkable selectivity for NH_3 generation.^[8,9] In addition to metallic Cu, CuO , Cu_2O , and Cu_3P were also reported as NO_3RR catalysts with high Faradaic efficiency (FE).^[10–15] Furthermore, bimetallic or multimetallic Cu alloys exhibit higher activity and selectivity than monometallic Cu-based electrocatalysts, allowing for controllable intermediate adsorption and increased conversion efficiency by adjusting the elemental composition and electronic structure of the catalyst.^[16–22]

In addition to the activity and selectivity of the catalyst itself, the architecture, conductivity, and cost of the substrates must all be addressed in consideration of manufacturing the supporting electrodes. An ideal electrode substrate should facilitate mass transfer, possess a large specific surface area for catalyst deposition, and enable rapid release of products. Most

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recently, 3D printing has garnered much attention in fabricating electrodes owing to the simple fabricating process, flexible structure building, wide range of printed materials and low cost.^[23–26]

This work developed a general method for preparing 3D printed electrodes for the NO₃RR. The commercial thermoplastic polymer acrylonitrile butadiene styrene (ABS) was used, and 3D printed into a microstructured lattice support. Subsequent surface modification of the ABS resulted in the generation of surface carboxyl and amino groups suitable for metal coordination (focus: Ni²⁺, Cu²⁺). Then, the NiCu alloy was coated onto the polymer surface by electroless plating. The resulting electrode was tested for the NO₃RR in aqueous media and showed excellent performance. Its integration into an aqueous Zinc-nitrate battery demonstrated the technological utility of the electrode system.

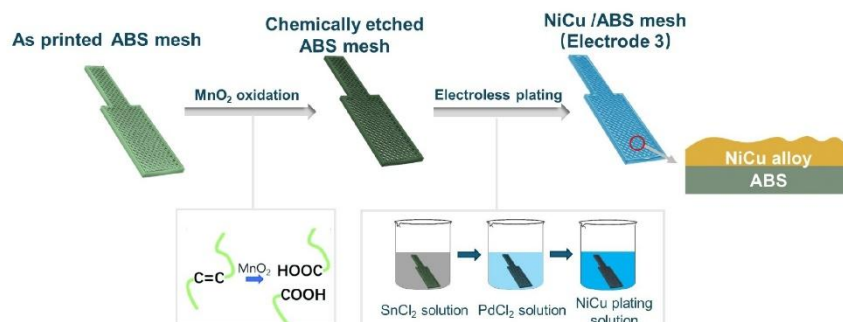
Results and Discussion

The 3D printed electrodes were fabricated in a three-step process involving 3D printing, chemical surface etching, and electroless plating (Scheme 1). The electrodes were designed and 3D printed with a microstructured lattice pattern to

increase their surface area and mass transfer properties (Scheme 1 and SI, Figure S1a) based on earlier works by some of us.^[27] Based on these reported studies, the ABS polymer surface of the electrode was then oxidized to generate carboxylate and amine binding sites for metal ion coordination (Scheme 1).

To study the impact of the metal composition, we prepared the following electrodes: pure Ni (**Electrode 1**), pure Cu (**Electrode 2**) and bimetallic NiCu alloy (**Electrode 3**). **Electrode 1** was prepared as reported recently by some of us.^[27] **Electrode 2** was prepared using a similar method using Cu²⁺ instead of Ni²⁺ for electroless plating (see SI). **Electrode 3** was fabricated by electroless plating with a NiCu alloy. This was achieved using aqueous solutions of NiSO₄·6H₂O and CuSO₄ which were reduced in a self-catalyzed reaction using NaH₂PO₂ as reductant (see SI). The plating temperature was optimized at 60 °C based on an optimum deposition rate and the low glass transition point of ABS.^[27–30] The detailed procedures of preparing three electrodes are described in the SI.

Figure 1a shows the powder X-ray diffraction pattern (pXRD) of **Electrode 1**, **2** and **3**. The broad peaks for **Electrode 1** and **Electrode 2** at ~20° are attributed to the printed ABS. This feature was not observed in **Electrode 3** due to the strong NiCu alloy signal. Following Ni electroless plating, new peaks evolve



Scheme 1. Schematic illustration of the chemical etching, electroless plating with NiCu metal on 3D printed ABS mesh electrodes.

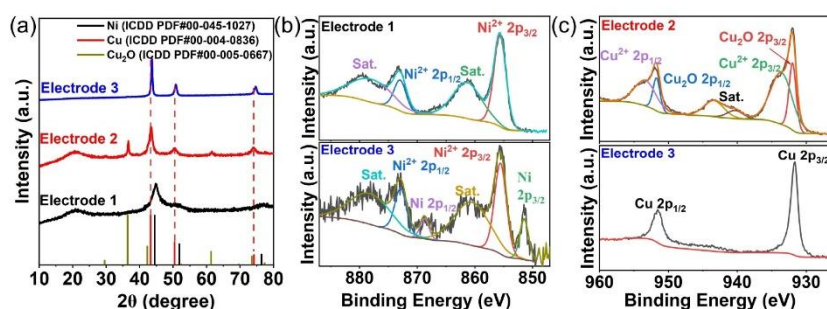


Figure 1. (a) pXRD patterns for **Electrode 1**, **2** and **3**. (b) high resolution XPS spectra of Ni 2p for **Electrode 1** and **3**. (c) high resolution XPS spectra of Cu 2p for **Electrode 2** and **3**.

at $\sim 45^\circ$, 52° and 76° correspond to metallic Ni. Similarly, due to the coating of Cu, the pXRD pattern in **Electrode 2** shows prominent metallic Cu peaks at $\sim 43.4^\circ$, 50.4° , and 74.0° . It is worth noting that the peaks at $\sim 36.6^\circ$ and 61.6° demonstrate that part of Cu^{2+} in the plating solution were only be partially reduced to Cu_2O , as previously observed.^[31] In **Electrode 3**, there is no discernible signal for Cu_2O , since NaH_2PO_3 was used as strong reducing agent (rather than HCHO used for the synthesis of **Electrodes 1/2**). The pXRD patterns in Figure 1a illustrate that **Electrode 3** shows signals consistent with a face-centered cubic lattice characteristic for Ni, Cu and their alloys. The larger lattice spacing observed for **Electrode 3** (marked with dashed lines) is due to the increased lattice constants due to the larger atomic radius of Cu compared with Ni.^[32,33]

The surface compositions of the electrodes were investigated by X-ray photoelectron spectroscopy (XPS). The survey XPS spectrum of **Electrode 3** shows no Pd was left on the electrode though we used PdCl_2 solution during the treatment of ABS substrates (Figure S1d). Figure 1b illustrates that the Ni species on the surface of **Electrode 1** and **Electrode 3** are comparable, showing a main contribution from Ni^{2+} ,^[34] which is presumably formed by surface-oxidation of the metallic nickel deposited. In addition, the signal at 851.4 eV observed for **Electrode 3** indicates the presence of metallic Ni. In contrast, no metallic Ni peak was observed in the **Electrode 1**. This might be resulted from the formation of a thick $\text{NiO}/\text{Ni}(\text{OH})_2$ surface layers, so that no XPS signal of the underlying Ni metal is observed. The Cu 2p XPS for **Electrode 2** shows the characteristic peaks for Cu(I) (peaks at 951.8 and 932 eV correspond to the $\text{Cu}(\text{I})$ $2p_{1/2}$ and $\text{Cu}(\text{I})$ $2p_{3/2}$, respectively) and Cu(II) (peaks at 953.6 and 933.8 eV correspond to the $\text{Cu}(\text{II})$ $2p_{1/2}$ and $\text{Cu}(\text{II})$ $2p_{3/2}$, respectively) species, and the satellite peaks from high-spin Cu(II) ions, indicating the co-existence of Cu_2O and $\text{CuO}/\text{Cu}(\text{OH})_2$ on the surface (Figure 1c).^[35] In comparison, mainly metallic Cu peaks (peaks at 951.6 and 931.7 eV correspond to

the $\text{Cu}(0)$ $2p_{1/2}$ and $\text{Cu}(0)$ $2p_{3/2}$, respectively) are observed for **Electrode 3**, which is consistent with the pXRD result.

The morphology of **Electrode 1** was analyzed by scanning electron microscopy (SEM), which indicates the deposited Ni layer on printed ABS substrate has a wrinkled structure composed of aggregated particles with diameters between ~ 700 nm to 1.5 μm (SI, Figure S2). In comparison to **Electrode 1**, the electroless Cu coating layer on **Electrode 2** is composed of aggregated particles with a diameter of approximately 500 nm (SI, Figure S3). According to Figure S4a, b, the Cu particles are a mixture of polycrystalline and amorphous structures, which was further confirmed by the selected area electron diffraction (SAED) pattern (SI, Figure S4c). The high-angle annular dark-field scanning-transmission electron microscopy (HAADF-STEM) and corresponding energy-dispersive X-ray spectroscopy (EDX, SI, Figure S5) mapping illustrates the distribution of the main elements, Cu and O, in the coating layers of **Electrode 2**. It is worth noting that there are also C and N with the atomic ratio of $\text{C/N}=4/1$, confirming the presence of residual EDTA (from the synthesis) on the copper surface.^[36] The SEM image of **Electrode 3** shows the NiCu coating layer on printed ABS substrate has a rough surface (Figure S1b,c) contains dense aggregates of nanoparticles with diameters around 100 nm (Figure 2a). While the TEM image of the NiCu coating layer of **Electrode 3** (Figure 2b) demonstrates that the formed NiCu layer has a thick dense stacked structure. The SAED pattern (Figure 2c) shows the randomly ring features which confirm the polycrystalline structure of the plated metal particles. The EDX mapping images of the NiCu coating layer on printed ABS substrate indicate the homogenous distribution of Ni, Cu, O, and P (Figure 2d–g).

To investigate the electrocatalytic NO_3RR performance of the as-prepared electrodes, a three-electrode system with the as-prepared electrodes as working electrode, Pt wire as counter electrode, saturated calomel electrode (SCE) as reference

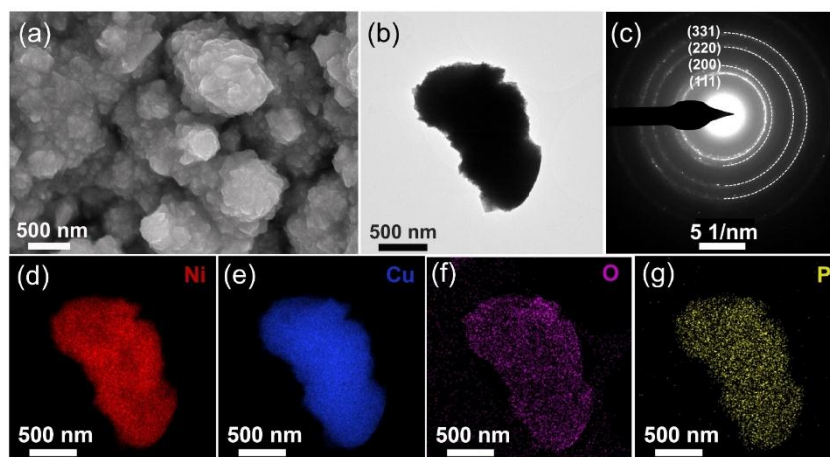


Figure 2. Microscopic characterization of **Electrode 3**. (a) SEM image, (b) TEM image, (c) SAED pattern, (d–g) EDX elemental mapping analysis.

electrode was set up in a H-cell. The anolyte and catholyte were separated by Nafion membrane. To evaluate the performance of the electrodes, linear sweep voltammetry (LSV) curves were collected from 0.4 to -0.8 V vs. RHE in 0.5 M Na_2SO_4 as electrolyte with and without 50 mM NaNO_3 . In comparison, **Electrode 1** (Figure S6) was more active for the hydrogen evolution reaction (HER) compared with NO_3RR due to the Ni coating,^[17] while both the LSV curves of **Electrode 2** (Figure S7) and **Electrode 3** (Figure 3a) show the obvious increase of current density in the presence of NO_3^- with the onset potential at around -0.21 V, indicating the efficient role of Cu based catalysts (here Cu, Cu_2O and CuO/Cu(OH)_2) for NO_3RR . Meanwhile, for both **Electrode 2** and **Electrode 3**, the current density increased sharply to its transport-limited value (from -0.4 V to -0.6 V) of ~ 50 mA/cm² for NO_3^- reduction, and then further increased as a result of the occurrence of HER (Figure 3a and SI, Figure S7). The selectivity of **Electrode 1**, **Electrode 2** and **Electrode 3** under various applied potentials was further investigated by 2 h of chronoamperometry in 0.5 M aqueous Na_2SO_4 containing 50 mM NaNO_3 (SI, Figures S8–S10). The presence of NH_4^+ and NO_2^- was quantified by UV-vis spectroscopic analyses. To create the calibration curves, a series of electrolytes with known concentrations of NH_4Cl and NaNO_2 were measured using a colorimetric approach (SI, Figure S11). Figure 3b and SI, Figure S12 show the corresponding FE of NH_4^+ for **Electrode 1**, **2** and **3**. As shown in Figure 3b, **Electrode 3** shows increasing FE for NH_4^+ within the potential range from -0.18 to -0.38 V, reaching a maximum value of 83% at -0.38 V. However, at -0.48 V and -0.58 V, the FE was slightly reduced to 82% and 70% respectively, which might be

related to the competitive undesired HER. In contrast, for **Electrode 1**, the maximum FE was obtained at -0.18 V (62%), then declined linearly to 16% at -0.58 V, indicating the increasing HER selectivity (Figure S12a) when the overpotential is increasing; while for **Electrode 2**, the FE of NH_4^+ indicates a volcano-like distribution with the peak value of 76% at -0.48 V (Figure S12b). The comparison reveals that **Electrode 3** containing Ni and Cu exhibits higher NH_4^+ efficiency than **Electrode 2** containing only Cu in all the investigated potential ranges. The above findings indicate that **Electrode 3** is the most efficient electrode for NO_3^- to NH_3 conversion, possibly owing to the synergistic effect between Ni and Cu.^[37] The NH_4^+ yield rate was further calculated to evaluate the performance of **Electrode 3** (Figure 3c). As expected, at the onset potential region of the reaction, **Electrode 3** demonstrates low NH_4^+ yield rate (111 $\mu\text{g}/(\text{h cm}^2)$) at -0.18 V and then it increases to 861 $\mu\text{g}/(\text{h cm}^2)$ at -0.38 V. However, this value remains constant even at more negative applied potentials, which is in accordance with the mass-transfer limiting platform (from -0.4 V to -0.6 V) in the LSV curves.^[17] It should be noted that **Electrode 1** and **Electrode 2** showed higher NH_4^+ yield rate at some potentials compared with **Electrode 3** (Figure S12c), which may be due to the higher current densities of these electrodes. The NiCu based **Electrode 3** also shows comparable activities with the current reported NiCu based catalysts (Table S1), however this work shows a feasible green method for the synthesis of the electrodes based on the 3D printed substrates.

Further, the effect of NO_3^- concentration on the catalytic performance of **Electrode 3** was also studied. As shown in SI, Figure S13a, the current density in the LSV curves improves as

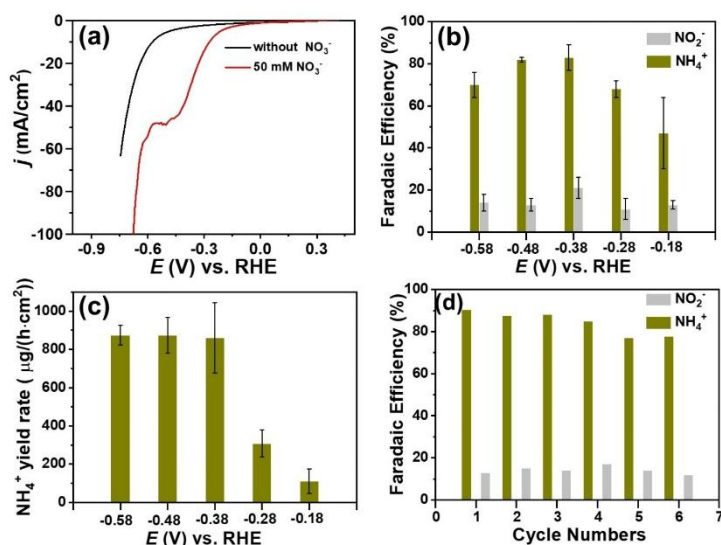


Figure 3. Electrocatalytic NO_3^- -to- NH_3 conversion by **Electrode 3**. (a) LSV curves of **Electrode 3** in 0.5 M Na_2SO_4 and 0.5 M $\text{Na}_2\text{SO}_4 + 50$ mM NaNO_3 . (b) FE of NH_4^+ and NO_2^- on the **Electrode 3** at different potentials. (c) NH_4^+ yield rate of **Electrode 3** in 0.5 M $\text{Na}_2\text{SO}_4 + 50$ mM NaNO_3 at different potentials and (d) Stability test of **Electrode 3** at -0.38 V vs. RHE.

the concentration of NaNO_3 increases. Further analyses show that both the FE and yield rate for NH_4^+ were decreased when we increased the concentration of NaNO_3 to 100 and 200 mM compared with that in 50 mM, which could be due to the higher NO_2^- selectivity in high nitrate concentration (Figure S13b,c).

The experimental results show that **Electrode 1** (containing Ni) works efficiently as a HER catalyst, while **Electrode 2** (containing Cu) works efficiently for NO_3^- conversion to NH_3 . The synergistic effect of Ni and Cu in **Electrode 3** further promotes the NO_3^- to NH_3 conversion, thus increasing the NH_3 selectivity.

It is understood that the conversion of NO_3^- to NH_3 can be separated into a number of elementary reactions. Initially, NO_3^- is adsorbed to form $^*\text{NO}_3^-$, followed by a series of deoxidation processes ($^*\text{NO}_3^- \rightarrow ^*\text{NO}_2^- \rightarrow ^*\text{NO} \rightarrow ^*\text{N}$), and subsequently, sequential hydrogenation of $^*\text{N}$ occurs ($^*\text{N} \rightarrow ^*\text{NH} \rightarrow ^*\text{NH}_2 \rightarrow ^*\text{NH}_3$).^[33,38] It has been reported that Ni alloying with Cu can induce an upshift of the Cu d-band center towards the Fermi level in CuNi alloys, thereby increasing the binding strength of NO_3RR intermediates on the catalyst surface. This enhanced binding suppresses the desorption of intermediates and promotes their further hydrogenation, ultimately leading to increased ammonia production.^[17,37]

NMR was used to confirm NH_4^+ amount in the electrolyte and exclude the possible contamination effect from the environment. Similar to the UV-vis approach, the calibration curves were obtained by preparation of reference electrolytes containing known concentrations of $^{14}\text{NH}_4\text{Cl}$ and $^{15}\text{NH}_4\text{Cl}$. The

intensity of the NMR signals increases as the concentration of $^{14}\text{NH}_4\text{Cl}$ or $^{15}\text{NH}_4\text{Cl}$ increases, as shown in SI, Figure S14 a,b, and the ^1H NMR spectra exhibit the characteristic feature of three peaks for $^{14}\text{NH}_4\text{Cl}$ and two peaks for $^{15}\text{NH}_4\text{Cl}$. The electrolytes were collected after 2 h electrocatalysis at -0.38 V vs. RHE in the electrolyte containing 50 mM $\text{Na}^{14}\text{NO}_3$ or $\text{Na}^{15}\text{NO}_3$. In the $\text{Na}^{15}\text{NO}_3$ labeled electrolytes, only two peaks emerge in ^1H NMR spectra as shown in SI, Figure S15, indicating that the NH_3 generated is from electrochemical nitrate reduction rather than contamination. The FE for $^{14}\text{NH}_4^+$ and $^{15}\text{NH}_4^+$ are 73% and 67% respectively.

Long-term stability is another critical criterion in determining the suitability of the electrode for practical application. **Electrode 3** was therefore operated at the optimum conditions (-0.38 V vs. RHE for 2 h in the electrolyte containing 50 mM NaNO_3) and recovered, washed, and reused for 6 runs, see SI, Figures S16, S17. The FE of NH_4^+ declined slightly during cycling but remained at 78% in the 6th cycle, indicating of the high stability of **Electrode 3** (Figure 3d). Furthermore, the corresponding FE of NO_2^- underwent little variations during cycling. SEM measurement was used to reveal the potential morphology change for the cycling tested electrode, which shows virtually no changes compared with the fresh samples (SI, Figure S18). In addition, pXRD analysis shows the same characteristic signals as the pre-catalytic sample (SI, Figure S19).

For practical application, we further constructed a novel Zn-nitrate battery utilizing **Electrode 3** as the cathode and zinc foil as the anode (illustrated schematically in Figure 4a).^[14,39,40] As depicted in Figure 4b, the battery maintains a constant open

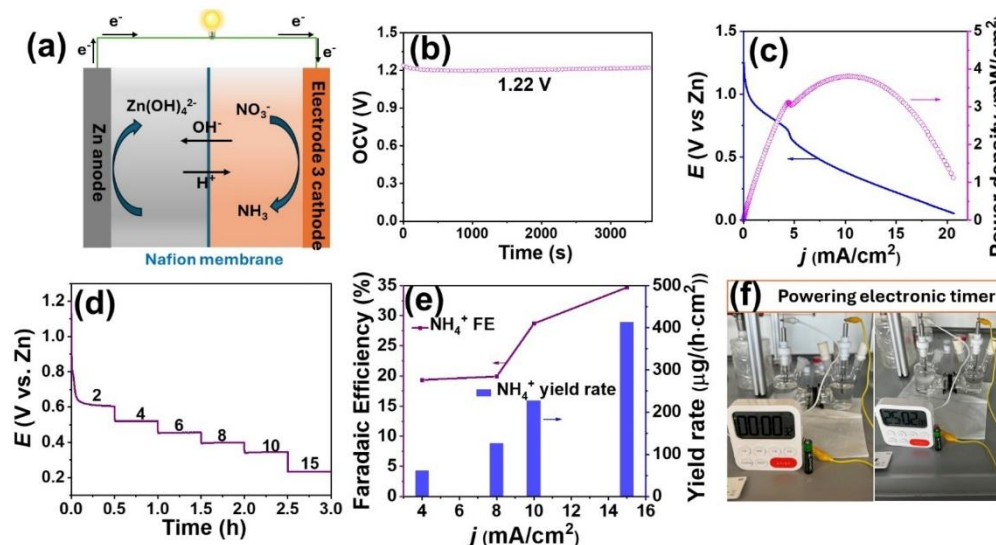


Figure 4. Electrochemical performance of hybrid aqueous Zn-nitrate batteries based on **Electrode 3**. (a) Schematic illustration of the Zn-nitrate battery with Zn anode and **Electrode 3** cathode. (b) Open-circuit voltage of Zn-nitrate battery. (c) Discharge polarization curves and corresponding power density curves of the Zn-nitrate battery. (d) Discharging curves at different current densities of 2, 4, 6, 8, 10 and 15 mA/cm^2 . (e) NH_4^+ FE and NH_4^+ yield rate of Zn-nitrate battery after 0.5 h discharging. (f) A photograph of an electronic timer powered by our **Electrode 3** based Zn-nitrate battery, operating for ~25 h.

circuit voltage (OCV) of 1.22 V for at least 1 hour. Figure 4c displays the charge-discharge LSV curves of the **Electrode 3**-based Zn-nitrate battery. The discharge curve demonstrates an increasing output current density as the cathodic potential becomes more negative. The power density of the battery peaks at 3.8 mW/cm² (Figure 4c). Figure 4d depicts the time-dependent discharge curves of the Zn-nitrate battery under different currents ranging from 2 to 15 mA/cm², indicating good long-term electrochemical stability. Figure 4e illustrates the NH₄⁺ yield and corresponding FE during discharge at various output current densities. The **Electrode 3**-based Zn-nitrate battery achieves a high NH₄⁺ formation rate of approximately 410 μg/(hcm²) and attains an FE of 35% at 15 mA/cm². Furthermore, the **Electrode 3**-based Zn-nitrate battery powers an electronic timer for at least 25 hours (Figure 4f). In summary, the Zn-nitrate battery system expands the scope of Zn-based batteries. The Zn-nitrate battery system achieves three objectives: sustainable energy supply, NH₃ electrosynthesis and degradation of the NO₃⁻ pollutant in wastewater.

Conclusions

In summary, we report the design of a 3D printed, Ni–Cu alloy functionalized electrode for efficient nitrate-to-ammonia reduction. When compared with the pure Ni and Cu coated electrodes, the mixed NiCu coated electrode exhibited higher Faradaic efficiency for electrosynthesis of NH₃ from nitrate. In addition, we report high stability and reusability of the electrode. Integration of the electrode into a Zn-nitrate demonstrated its operational capacity for combined sustainable electricity production, NH₃ electrosynthesis, and NO₃⁻ pollutant degradation. The reported approach could in future allow the facile, scalable design of (multi)functional 3D printed electrode materials.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: 3D Printing · Electroless Plating · Electrocatalysis · Ammonia synthesis · Zn–Nitrate Batteries

- [1] J. W. Erisman, M. A. Sutton, J. Galloway, Z. Klimont, W. Winiwarter, *Nat. Geosci.* **2008**, *1*, 636–639.
- [2] G. Ertl, *Angew. Chem. Int. Ed.* **2008**, *47*, 3524–3535.
- [3] H. Xu, Y. Ma, J. Chen, W. X. Zhang, J. Yang, *Chem. Soc. Rev.* **2022**, *51*, 2710–2758.
- [4] G. Soloveichik, *Nat. Catal.* **2019**, *2*, 377–380.
- [5] B. H. R. Suryanto, H.-L. Du, D. Wang, J. Chen, A. N. Simonov, D. R. MacFarlane, *Nat. Catal.* **2019**, *2*, 290–296.
- [6] Z. Y. Wu, M. Karamad, X. Yong, Q. Huang, D. A. Cullen, P. Zhu, C. Xia, Q. Xiao, M. Shakouri, F. Y. Chen, J. Y. (Timothy) Kim, Y. Xia, K. Heck, Y. Hu, M. S. Wong, Q. Li, I. Gates, S. Siahrostami, H. Wang, *Nat. Commun.* **2021**, *12*, 1–10.
- [7] C. J. M. van der Ham, M. T. M. Koper, D. G. H. Hetterscheid, *Chem. Soc. Rev.* **2014**, *43*, 5183–5191.
- [8] H. Wan, A. Bagger, J. Rossmeisl, *Angew. Chem. Int. Ed.* **2021**, *60*, 21966–21972.
- [9] T. Hu, C. Wang, M. Wang, C. M. Li, C. Guo, *ACS Catal.* **2021**, *11*, 14417–14427.
- [10] Y. Wang, W. Zhou, R. Jia, Y. Yu, B. Zhang, *Angew. Chem. Int. Ed.* **2020**, *59*, 5350–5354.
- [11] J. Liang, B. Deng, Q. Liu, G. Wen, Q. Liu, T. Li, Y. Luo, A. A. Alshehri, K. A. Alzaharani, D. Ma, X. Sun, *Green Chem.* **2021**, *23*, 5487–5493.
- [12] W. Fu, Z. Hu, Y. Zheng, P. Su, Q. Zhang, Y. Jiao, M. Zhou, *Chem. Eng. J.* **2021**, 133680.
- [13] Y. Bu, C. Wang, W. Zhang, X. Yang, J. Ding, G. Gao, *Angew. Chem. Int. Ed.* **2023**, *62*, e202217337.
- [14] H. Jiang, G. F. Chen, O. Savateev, J. Xue, L. X. Ding, Z. Liang, M. Antonietti, H. Wang, *Angew. Chem. Int. Ed.* **2023**, *62*, e202218717.
- [15] W. Qiu, S. Qin, Y. Li, N. Cao, W. Cui, Z. Zhang, Z. Zhuang, D. Wang, Y. Zhang, *Angew. Chem. Int. Ed.* **2024**, e202402684.
- [16] L. Mattarozzi, S. Cattarin, N. Comisso, A. Gambirasi, P. Guerriero, M. Musiani, L. Vázquez-Gómez, E. Verlato, *Electrochim. Acta* **2014**, *140*, 337–344.
- [17] Y. Wang, A. Xu, Z. Wang, L. Huang, J. Li, F. Li, J. Wicks, M. Luo, D. H. Nam, C. S. Tan, Y. Ding, J. Wu, Y. Lum, C. T. Dinh, D. Sinton, G. Zheng, E. H. Sargent, *J. Am. Chem. Soc.* **2020**, *142*, 5702–5708.
- [18] L. Mattarozzi, S. Cattarin, N. Comisso, R. Gerbasi, P. Guerriero, M. Musiani, E. Verlato, *Electrochim. Acta* **2017**, *230*, 365–372.
- [19] D. Reyter, D. Bélanger, L. Roué, *Electrochim. Acta* **2008**, *53*, 5977–5984.
- [20] H. Liu, X. Lang, C. Zhu, J. Timoshenko, M. Rüschler, L. Bai, N. Guijarro, H. Yin, Y. Peng, J. Li, Z. Liu, W. Wang, B. R. Cuenya, J. Luo, *Angew. Chem. Int. Ed.* **2022**, *61*, e202202556.
- [21] Q. Hu, K. Yang, O. Peng, M. Li, L. Ma, S. Huang, Y. Du, Z. X. Xu, Q. Wang, Z. Chen, M. Yang, K. P. Loh, *J. Am. Chem. Soc.* **2024**, *146*, 668–676.
- [22] F. Y. Chen, Z. Y. Wu, S. Gupta, D. J. Rivera, S. V. Lambeets, S. Pecaut, J. Y. T. Kim, P. Zhu, Y. Z. Finrock, D. M. Meira, G. King, G. Gao, W. Xu, D. A. Cullen, H. Zhou, Y. Han, D. E. Perea, C. L. Muhich, H. Wang, *Nat. Nanotechnol.* **2022**, *17*, 759–767.
- [23] J. Lölsberg, O. Starck, S. Stiefel, J. Hereijgers, T. Breugelmans, M. Wessling, *ChemElectroChem* **2017**, *4*, 3309–3313.
- [24] V. A. Beck, A. N. Ivanovskaya, S. Chandrasekaran, J. B. Forien, S. E. Baker, E. B. Duoss, M. A. Worsley, *Proc. Natl. Acad. Sci. USA* **2021**, *118*, e2025562118.
- [25] Z. Lyu, G. J. H. Lim, J. J. Koh, Y. Li, Y. Ma, J. Ding, J. Wang, Z. Hu, J. Wang, W. Chen, Y. Chen, *Joule* **2021**, *5*, 89–114.
- [26] W. Zhang, H. Liu, X. Zhang, X. Li, G. Zhang, P. Cao, *Adv. Funct. Mater.* **2021**, 2104909.

- [27] S. Liu, R. Liu, D. Gao, I. Trentin, C. Streb, *Chem. Commun.* **2020**, 56, 8476–8479.
- [28] H. S. Yu, S. F. Luo, Y. R. Wang, *Surf. Coat. Technol.* **2001**, 148, 143–148.
- [29] F. Yang, B. Yang, B. Lu, L. Huang, S. Xu, S. Zhou, *Acta Phys.-Chim. Sin.* **2006**, 22, 1317–1321.
- [30] J. Georgieva, S. Aramyanov, *J. Solid State Electrochem.* **2007**, 11, 869–876.
- [31] J. Eskhult, M. Herranen, L. Nyholm, *J. Electroanal. Chem.* **2006**, 594, 35–49.
- [32] J. Zhang, M. D. Baró, E. Pellicer, J. Sort, *Nanoscale* **2014**, 6, 12490–12499.
- [33] L. Fang, S. Wang, C. Song, X. Yang, Y. Li, H. Liu, *J. Hazard. Mater.* **2022**, 421, 126628 (1–9).
- [34] M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson, R. S. C. Smart, *Appl. Surf. Sci.* **2011**, 257, 2717–2730.
- [35] M. C. Biesinger, L. W. M. Lau, A. R. Gerson, R. S. C. Smart, *Appl. Surf. Sci.* **2010**, 257, 887–898.
- [36] J. Liu, J. Fu, Y. Zhou, W. Zhu, L. P. Jiang, Y. Lin, *Nano Lett.* **2020**, 20, 4823–4828.
- [37] Y. Liu, B. Deng, K. Li, H. Wang, Y. Sun, F. Dong, *J. Colloid Interface Sci.* **2022**, 614, 405–414.
- [38] S. Han, H. Li, T. Li, F. Chen, R. Yang, Y. Yu, B. Zhang, *Nat. Catal.* **2023**, 6, 402–414.
- [39] Y. Guo, R. Zhang, S. Zhang, Y. Zhao, Q. Yang, Z. Huang, B. Dong, C. Zhi, *Energy Environ. Sci.* **2021**, 14, 3938–3944.
- [40] Y. Liu, R. Cheng, H. Ren, T. Sun, D. Liu, *ACS Sustainable Chem. Eng.* **2024**, 12, 3780–3789.

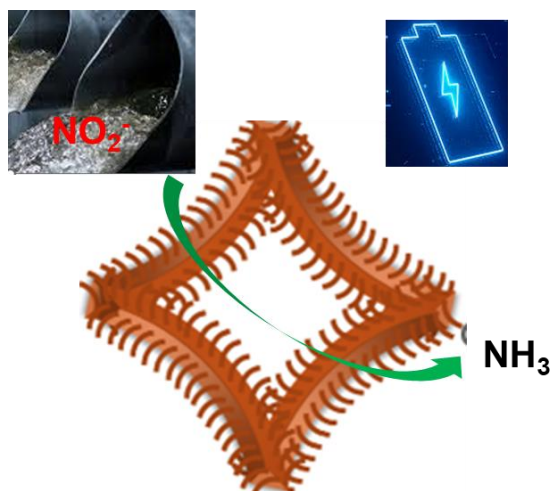
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3.6 Ruthenium-doped Copper Nanowires for Nitrite/Nitrate to Ammonia Conversion and Their Integration in Zinc - Nitrite Batteries

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This publication reported a facile route to fabricate a Cu foam-based electrode with Ru atomically incorporated into the copper nanowires. The electrochemical investigation revealed that this catalyst exhibited a high Faraday efficiency near 100 % for the reduction of nitrite with a yield rate of 33.2 mg h⁻¹ cm⁻² at a potential of -0.2 V vs. RHE. Moreover, aqueous Zinc-nitrite batteries integrated with CuRu-3h/CF

catalyst achieved a power density as high as 9 mW/cm² with a NH₃ yield rate of 2100 µg h⁻¹ cm² at a current density of 30 mA/cm².

Author contributions:

Tobias Rios-Studer, Zhengfan Chen: Conceptualization, Methodology, Investigation, Data curation, Analysis, Writing original draft.

Christean Nickel, Fan Feng: Data curation, Writing original draft.

Kevin Sowa, Ekemena O. Oseghe: Data curation, Writing original draft.

Sina Sadigh Akbari, Sarra Rahali: Data curation, Writing original draft.

Leon Prädél, Dandan Gao: Data curation, Writing original draft.

Rongji Liu: Data curation, Methodology, Writing original draft.

Carsten Streb: Project administration, Funding acquisition, Conceptualization, Supervision, Data curation, Methodology, Writing original draft.

Supporting information can be found on page 236.

T. Rios-Studer, Z. Chen, C. Nickel, F. Feng, K. Sowa, E. O. Oseghe, S. S. Akbari, S. Rahali, L. Prädél, I. Lieberwirth, G. Zhang, D. Gao, R. Liu, C. Streb. ChemCatChem 2024, e202401690.

RESEARCH ARTICLE

Ruthenium-doped Copper Nanowires for Nitrite/Nitrate to Ammonia Conversion and Their Integration in Zinc - Nitrite Batteries

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Abstract: The electrochemical reduction of nitrite (NO_2^-) and nitrate (NO_3^-) not only enables sustainable, circular routes to produce ammonia (NH_3), but also eliminates pollutants in groundwater. Here, we report a facile synthesis of Ru-doped Cu nanowires on Cu foam electrodes with low Ru (0.48 wt.%) loading. The composite electrode shows high-performance in the $\text{NO}_2^-/\text{NO}_3^-$ to NH_3 electroreduction, giving NH_3 Faradaic efficiency of up to 100% and NH_3 yield rates up to $33.2 \text{ mg h}^{-1} \text{ cm}^{-2}$ at -0.2 V vs. RHE in NO_2^- reduction. For the nitrate-to-ammonia reduction, the electrode also shows high activity with Faradaic efficiency of 88.4 % (at -0.6 V vs RHE) and a yield rate of $62.5 \text{ mg h}^{-1} \text{ cm}^{-2}$ (at -1.0 V vs. RHE). We show that the electrode can easily be integrated into a Zn–nitrite battery, giving a power density of 9.1 mW cm^{-2} , a NH_3 yield rate of $1.88 \text{ mg h}^{-1} \text{ cm}^{-2}$ and a nitrite-to-ammonia Faradaic efficiency of 88.9 % at a current density of 20 mA cm^{-2} . The system combines three productive outputs, that is removal of NO_x^- pollutants, synthesis of valuable NH_3 and generation of “green” electricity.

Introduction

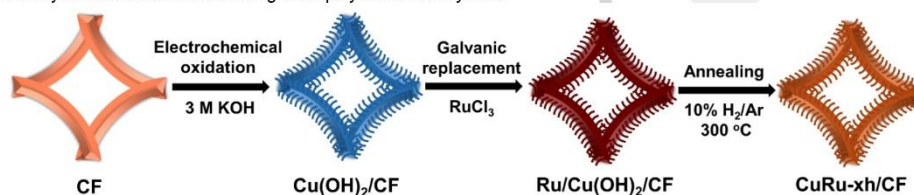
Ammonia (NH_3) is one of the most essential and important chemical feedstocks in modern society, with over 150 million tons produced annually. NH_3 plays a crucial role in the production of nitrogen fertilizers for agriculture and many chemicals for industry.^[1–3] Additionally, NH_3 is gaining increasing interest as carbon-free fuel for energy storage due to its high energy density (4.3 kWh kg^{-1}).^[4] To-date, the Haber-Bosch-process is the dominant route in the synthesis of NH_3 , where NH_3 is formed by the reaction of gaseous nitrogen (N_2) with gaseous hydrogen (H_2) under high temperature and high pressure, which results in a high energy demand and a significant impact on the global carbon

footprint. The Haber-Bosch-process consumes about 1–2% of all energy worldwide and is responsible for more than 1 % of the annual global CO_2 emissions.^[5,6] To solve this problem, electrochemical synthesis of NH_3 under ambient conditions offers an energy-efficient reaction pathway.^[7,8] However, the direct reduction of nitrogen comes with challenges, such as the low aqueous solubility and high dissociation energy. Furthermore, the potential needed to reduce nitrogen is in a region where the hydrogen evolution reaction (HER) occurs. An alternative to the reduction of nitrogen is the reduction of NO_x^- (nitrate (NO_3^-) and nitrite (NO_2^-)), which is easily dissolved in water and the dissociation energy of the N=O bond (204 kJ mol^{-1}) is only about a quarter of the dissociation energy of the N_2 triple bond (941 kJ mol^{-1}).^[9] NO_x^- is also a major water pollutant due to extensive fertilizer use and industrial processes, and its accumulation in the environment leads to serious health and ecological issues.^[10] The urgent need to eliminate NO_x^- and produce NH_3 makes the NO_x^- reduction reaction (NO_xRR) via an efficient electrocatalytic route particularly compelling.^[11,12]

Although electrocatalytic NO_xRR has garnered increasing attention from researchers as a promising pathway for NH_3 synthesis, the reaction kinetics and product selectivity in electrochemical NO_xRR are largely determined by the choice of catalyst. To date, a wide range of catalysts have been reported in recent years such as noble metals,^[13–15] transition metals,^[16,17] metal alloys,^[18–25] as well as metal oxides.^[26–28] Among them, Cu-based materials have emerged as particularly attractive candidates for NO_xRR due to their low cost, weak hydrogen evolution tendency, and high electrical conductivity.^[17,19,29–33] However, the weak adsorption of hydrogen (H_{ad}) on bare Cu limits the hydrogenation rate of N-intermediates, resulting in low Faradaic efficiency (FE) for NH_3 production. To address this issue,

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noble metals such as Rh, Ru, Pt, and Au, known for their excellent hydrogen adsorption–desorption properties, have been merged with Cu substrates to enhance the hydrogenation ability of Cu-based catalysts at more positive potentials, significantly reducing the overpotential for the NO_xRR .^[25,34] It has been proposed that the Cu site preferentially stabilizes nitrogen intermediate species, whereas the vicinal noble metals supply the activated H species required for the surface hydrogenation to proceed. Additionally, due to synergistic effects, 3d transition metals like Fe, Co, and Ni have also been used to modify Cu-based electrodes to create bimetallic composite materials with high NO_xRR performance.^[35] This report builds on pioneering work on the design of noble metal (Ru and Rh)-doped nanostructured Cu catalysts.^[25,34] Here, we used a modified method for synthesizing a Cu foam (CF) based composite electrode, where Cu nanowires were grown on the CF surface, and Ru sites were then deposited on the Cu nanowires. The resulting composite is referred to as CuRu-xh/CF, where x represents the duration of the galvanic replacement reaction. The catalyst shows high selectivity towards NH_3 formation and inertness toward HER, as well as a low NO_2^- activation barrier reported for Ru catalysts.^[34,36] The optimized electrode CuRu-3h/CF shows high performance for both, nitrite and nitrate reduction to ammonia, and integration into an aqueous Zinc-nitrite battery demonstrated the technological deployment of the system.



Scheme 1. Schematic illustration of the synthetic process of CuRu-xh/CF.

X-ray photoelectron spectroscopy (XPS) analyses reveal the presence of both Cu and Ru in CuRu-3h/CF. The high-resolution Cu 2p XPS spectrum of CuRu-3h/CF is shown in Fig. 1b. The spectrum shows strong peaks of Cu^0 $2p_{3/2}$ and Cu^0 $2p_{1/2}$ located at binding energies of 932.5 eV and 952.2 eV as well as weak peaks at higher binding energies of 934.1 eV and 954.2 eV associated with Cu^{2+} .^[38] To distinguish the chemical states between copper metal and oxides, we have also performed Cu Auger XPS analysis. The Cu LMM Auger spectrum of CuRu-3h/CF (SI, Fig. S2a) shows the peaks associated with Cu^{2+} , Cu^+ and Cu^0 ^[39–41] indicating the partial surface oxidation of metallic Cu in CuRu-3h/CF. Fig. 1c displays the high-resolution Ru 3d XPS spectrum of CuRu-3h/CF. Similarly, the peaks could be deconvoluted into separated peaks for both Ru^0 and Ru^{4+} .^[42] Besides, the high-resolution Ru 3p XPS spectrum (SI, Fig. S2b) also shows the peaks associated with both Ru^0 and Ru^{4+} ,^[43] which could also indicate the partial surface oxidation of metallic Ru in CuRu-3h/CF.

The morphology of the different electrodes was investigated using scanning electron microscopy (SEM). The surface of the pure CF is smooth (Fig. S3), while the images of $\text{Cu}(\text{OH})_2/\text{CF}$ (Fig. S4)

Results and Discussion

Scheme 1 shows the three-step synthetic process for CuRu-xh/CF (see details in the experimental procedures in Supporting Information (SI)). Briefly, the CF was firstly electrochemically oxidised to $\text{Cu}(\text{OH})_2/\text{CF}$, the obtained $\text{Cu}(\text{OH})_2/\text{CF}$ was then treated with RuCl_3 solution in a galvanic replacement reaction to obtain $\text{Ru}/\text{Cu}(\text{OH})_2/\text{CF}$. In the last step, the $\text{Ru}/\text{Cu}(\text{OH})_2/\text{CF}$ was annealed in a 10% H_2/Ar atmosphere to obtain CuRu-xh/CF. The electrodes were used as-prepared without further pre-treatment. Powder X-ray diffraction (pXRD) was used to confirm the formation of $\text{Cu}(\text{OH})_2$ during the electrochemical oxidation (Fig. S1). The pXRD patterns of pure CF, as well as the synthesized pure nanostructured CF (NCF, see experimental procedures in SI) and CuRu-xh/CF, are compared in Fig. 1a. The pure CF as well as the synthesized electrodes exhibit three distinct diffraction peaks at two theta values of 43.3° , 50.4° and 74.1° , which are attributed to the (111), (200) and (220) lattice planes of a face centred cubic (fcc) crystalline structure of Cu (PDF#70-3039). However, no diffraction peaks associated with metallic Ru were present in CuRu-xh/CF, which indicates that no crystalline Ru particles are present.^[37]

show a change of the morphology to a uniform nanowire structure during the electrochemical oxidation, where the nanowires appear smooth and straight. After galvanic replacement and annealing, the nanowires shown in the images of CuRu-xh/CF are no longer smooth and straight and instead appear elongated and curved with many particles agglomerated on the nanowires (Fig. 1d–1e and SI, Fig. S5–S7). This structural change is also present in NCF (Fig. S8), which was prepared without the galvanic replacement reaction, indicating the aggregation of metallic Cu nanoparticles on the nanowires during the thermal reduction of $\text{Cu}(\text{OH})_2$. The comparison indicates that the structural changes occur during the annealing process, not during the cation exchange process. However, it should be noted that the duration of the galvanic replacement reaction affects the morphology. By comparing the different CuRu-xh/CF electrodes, it can be observed that a shorter reaction time (CuRu-1h/CF and CuRu-3h/CF) does not lead to significant changes in morphology. However, some particle aggregation is noticeable at the ends of the nanowires (Fig. 1d–1e and SI, Fig. S5–S6). If the galvanic replacement reaction time was extended to 5h, the nanowires were no longer uniformly present on the surface, and instead were agglomerated (Fig. S7).

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SEM energy dispersive X-ray spectroscopy (SEM-EDX, Fig. 1f and SI, Fig. S9) shows that Ru is uniformly distributed on the Cu surface. The loading of Ru determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) for CuRu-xh/CF was 0.25 wt.% ($x = 1$), 0.48 wt.% ($x = 3$) and 0.92 wt.% ($x = 5$) respectively (SI, Fig. S10). This indicates prolonged galvanic replacement time can be used to control the Ru loading amount. Furthermore, we have also performed transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) to get more detailed information about the CuRu-3h/CF electrode (SI, Fig. S11). The images of the surface layer of the electrode show a polymorphic structure. The lattice spacing was determined as

0.30 nm which corresponds to the lattice spacing of Cu₂O (110) (Figure S11d, e), which further indicates partial surface oxidation of CuRu-3h/CF electrode.

The NO₂RR performance was tested in an H-cell filled with 1 M aqueous KOH as electrolyte, the two cell compartments were separated by a Nafion 117 membrane. A three-electrode system using the as-prepared CF-based electrode as the working electrode, Hg/HgO (1 M KOH) as the reference electrode and the Pt wire as the counter electrode. All potentials reported in this study were converted to reversible hydrogen electrode potentials (RHE).

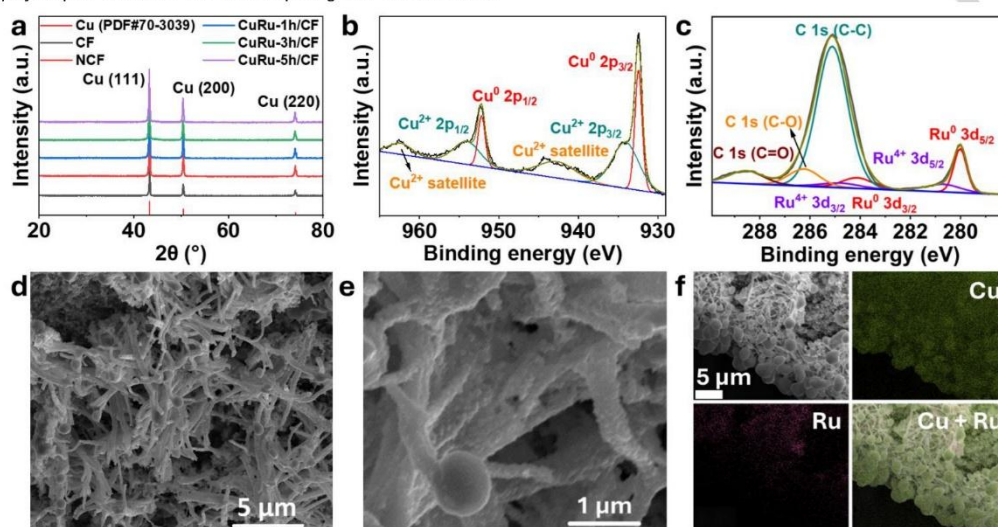


Figure 1. Structural and elemental analyses of CuRu-xh/CF. (a) pXRD pattern of the synthesized electrodes, (b) high-resolution Cu 2p XPS spectrum and (c) high-resolution Ru 3d XPS spectrum of CuRu-3h/CF, (d-e) SEM images of CuRu-3h/CF with different magnifications, and (f) SEM-EDX elemental mapping of CuRu-3h/CF.

To gain fundamental insight into the electrode reactivity, we performed linear scan voltammetry (LSV) of the pure CF, NCF and CuRu-xh/CF electrodes between 0.6 and -0.6 V vs. RHE in the presence and absence of 0.1 M NaNO₂. As shown in Fig. 2a, the current density for all electrodes increased over a wide range of potentials in the presence of NO₂⁻, compared to the LSV performed without NO₂⁻, which indicates the apparent reduction of NO₂⁻ for all these electrodes. The reduction peak at ~-0.4 V can be attributed to the reduction of Cu²⁺ to Cu⁺.^[44,45] Further comparison indicates that the presence of nanowire structure of the synthesized electrodes resulted in a higher catalytic activity compared to pure CF that was further increased in the presence of Ru (CuRu-xh/CF). CuRu-3h/CF shows the highest catalytic activity and the current density reaches 570 mA/cm² at a potential of -0.6 V vs. RHE. Additionally, CuRu-xh/CF shows a lower onset potential for NO₂⁻ reduction at 0.25 V vs. RHE, compared to pure CF (-0.05 V vs. RHE). We further performed the Tafel slope

analysis of different electrodes toward NO₂RR (SI, Fig. S12). It is shown that the Tafel slope of NCF (152 mV dec⁻¹) significantly decreased compared with that of CF (207 mV dec⁻¹) due to the formation of nanowires on the surface of NCF. While the doping of Ru on the NCF (CuRu-xh/CF electrodes) further increased the Tafel slopes that could be due to the different reaction mechanisms caused by the interaction between Ru and Cu. However, due to the potential coexistence of both HER and NO₂RR, and the complex multi-step NO₂RR process, it is not easy to investigate the kinetics of NO₂RR by using simple Tafel slope analysis.

Thereafter, chronoamperometry tests were performed at potentials between 0.2 and -0.2 V vs. RHE to determine NH₃ selectivity of the NO₂RR using pure CF, NCF and CuRu-3h/CF as catalysts (SI, Fig. S13). We used the indophenol blue method (IBM) with UV vis absorption spectroscopy as well as ¹H NMR spectroscopy to confirm and quantify the NH₃ production at

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different potentials (SI, Fig. S14).^[46] The resulting potential dependent NH_3 FE is shown in Fig. 2b. It can be seen that the FE of CuRu-3h/CF is the highest at all applied potentials and reaches ~100% even at a positive potential of 0.1 V vs. RHE. It is notable that the nanostructured NCF does not result in a higher FE than pure CF, indicating the presence of Ru in CuRu-3h/CF is the cause of the notably higher selectivity towards NH_3 formation. The corresponding NH_3 yield rates are shown in Fig. 2c. It is visible that CuRu-3h/CF also shows the highest yield rate at all applied potentials with a maximum yield rate of $33.2 \text{ mg h}^{-1} \text{ cm}^{-2}$ at a potential of -0.2 V vs. RHE, which is about four times higher than that of pure CF. It should be noted that NCF shows a notably higher yield rate than pure CF, suggesting that the Cu nanowire structure in NCF enhances catalytic activity compared to the smooth surface of pure CF, most likely due to the increased specific surface area. We also compared the calculated FE and yield rate of NH_3 measured by IBM and NMR spectroscopy. As shown in Fig. 2d, the results of the two different methods are consistent. Next, we tested the long-term stability of the CuRu-3h/CF catalyst using eight consecutive 30-min electrolysis cycles at 0.1 V vs. RHE (SI, Fig. S15). The NH_3 yield rate and FE of each cycle are shown in Fig. 2e. It is shown that the NH_3 yield rate and FE were essentially maintained over 8 cycles, indicating the CuRu-3h/CF has a high stability for the NO_2RR . Post-catalytic analysis of CuRu-3h/CF gave us further information regarding the structural stability. The pXRD patterns show that there is no change in structure and the same diffraction peaks are present after the reaction (SI, Fig. S16). Cu LMM Auger XPS analysis of Cu shows a decrease of Cu^{2+} and increase of Cu^+ after the reaction (SI, Fig. S2a,c), indicating the partial surface reduction

during NO_2RR . The high-resolution Ru 3p XPS spectrum after the reaction does not show any Ru signal (SI, Fig. S2d). However, ICP-OES was used to verify the presence of Ru, and the loading amount of Ru after reaction was ~0.29 wt.%, indicating some leakage of Ru during reaction. Encouragingly, the leaking of Ru did not reduce much of the activity of the CuRu-3h/CF electrode. SEM images (SI, Fig. S17) of CuRu-3h/CF after NO_2RR indicate that the surface structure changed from nanowires to nanosheets during the reaction. SEM-EDX analyses show that Ru is still uniformly distributed on the surface after the reaction (SI, Fig. S18-19). However, we note that this surface restructuring of CuRu-3h/CF does not have a significant effect on the NO_2RR activity of this material.

To investigate the NO_2^- removal capabilities of CuRu-3h/CF, a batch conversion test was performed at -0.2 V vs. RHE with a nitrite-N concentration of 365 ppm (Fig. 2f). NO_2^- quantification was determined using N-(1-naphthyl)ethylene diamine spectrophotometric method (SI, Fig. S20).^[47] Even at this low nitrite concentration, the nitrite-to-ammonia FE reached 92 %. After 2 h of electrolysis, only 9 % of the initial nitrite concentration (*i.e.* 33 ppm) remained in the solution. Note that the sum concentrations of nitrite-N and ammonia-N throughout the measurement remain constant and are consistent with the initial nitrite-N concentration, indicating the high NO_2^- to NH_3 conversion selectivity. Even at a positive potential of 0.1 V vs. RHE, the CuRu-3h/CF still shows efficient conversion of NO_2^- to NH_3 . The FE reached as high as 92 % after 2 h electrolysis and remained above 80% after 6 h, with only 5 % of the initial nitrite (with a nitrite-N concentration of 19 ppm) remaining in the solution at the end (Fig. S21).

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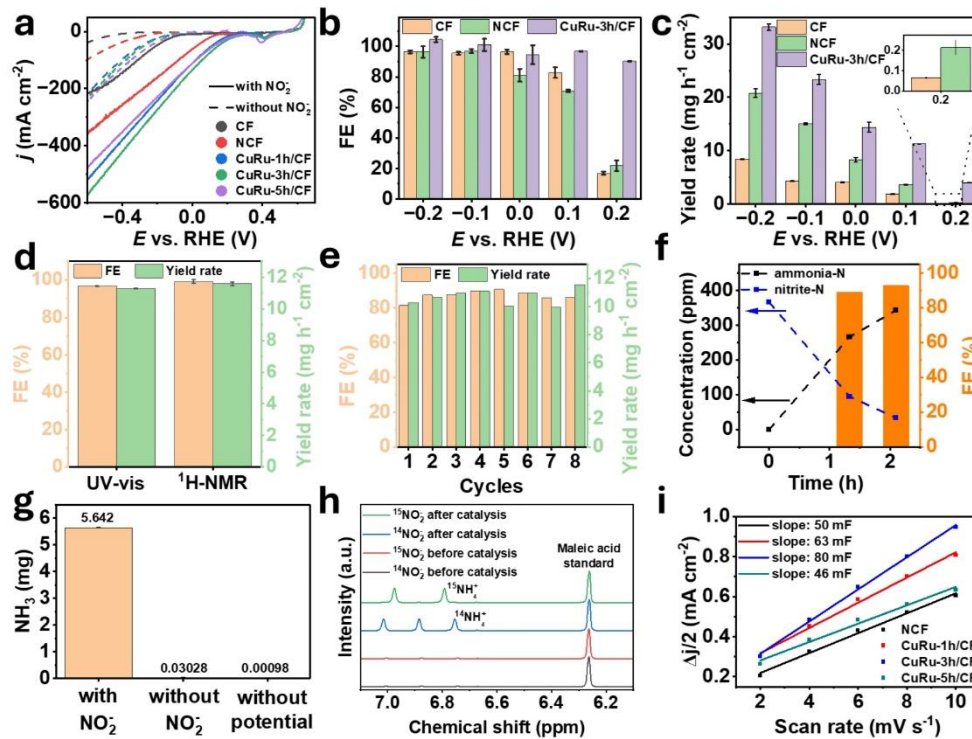


Figure 2. Electrocatalytic NO_2RR performance of different electrodes in 1 M KOH solution. (a) LSV curves of pure CF, NCF and CuRu-xh/CF in the presence and absence of NO_2^- . (b) NH_3 FE and (c) NH_3 yield rate of pure CF, NCF and CuRu-3h/CF. The error bars represent the standard deviations of three independent measurements. (d) Nitrite-to- NH_3 FE and yield rate of CuRu-3h/CF at 0.1 V vs. RHE, detected by indophenol blue method and ^1H NMR spectroscopy. (e) cycling stability tests of CuRu-3h/CF at 0.1 V vs. RHE. (f) NO_2^- removal using CuRu-3h/CF with an initial nitrite-N concentration of 365 ppm at a potential of -0.2 V vs. RHE. (g) NH_3 yield of CuRu-3h/CF with NO_2^- at 0.1 V vs. RHE, without NO_2^- at 0.1 V vs. RHE and without potential in the presence of NO_2^- . (h) ^1H NMR spectra of the electrolyte before and after electrocatalysis using $^{14}\text{NO}_2^-$ and $^{15}\text{NO}_2^-$ as nitrogen source, and (i) ECSA analysis of NCF and CuRu-xh/CF.

To confirm the origin of the nitrogen atoms incorporated in the synthesized NH_3 , several control experiments were undertaken. First, we note that virtually no NH_3 is detected when 0.1 M aqueous NO_2^- solutions were kept at the open circuit potential (OCP). Also, when a potential of 0.1 V vs. RHE was applied, no significant NH_3 formation was detected unless NO_2^- was present in the solution (Fig. 2g). These results indicate that NH_3 originated from the reduction of NO_2^- . Also, isotope labelling experiments were carried out for NO_2RR in the presence of $^{14}\text{NO}_2^-$ or $^{15}\text{NO}_2^-$ followed by product identification and quantifications via ^1H NMR. As shown in Fig. 2h, the characteristic splitting of the ^1H resonance into 3 symmetric signals when using $^{14}\text{NO}_2^-$ and the corresponding splitting into 2 symmetric signals when using $^{15}\text{NO}_2^-$ reveal the presence of $^{14}\text{NH}_4^+$ and $^{15}\text{NH}_4^+$ in the NMR spectra. The above results verify that NH_3 originates from NO_2^- reduction.

To understand the origin of the notable NO_2RR performance of CuRu-3h/CF, we measured the electrochemically active surface area (ECSA) and the charge-transfer resistance (R_{ct}) at the

electrode/electrolyte interface, as both parameters are crucial for the reactivity of heterogeneous electrocatalysts. Electrochemical double-layer capacitance (C_{dl}) tests were performed to determine the ECSA of the synthesized CF-based electrodes (SI, Figs. S22–23). Fig. 2i shows the C_{dl} of the electrodes, the resulting ECSA is shown in the SI, Fig. S24. It is noted that CuRu-3h/CF shows the highest ECSA among all the electrodes. The result shows that the addition of Ru first leads to an increase in ECSA compared to NCF, but longer reaction time in CuRu-5h/CF leads to a decrease in ECSA, which may be attributed to the agglomeration of the Cu nanowires as observed from the SEM images. Further, an electrochemical impedance study (EIS) was performed to determine the R_{ct} of the electrodes (SI, Fig. S25). It is notable that CuRu-3h/CF features more than ten times lower R_{ct} than that of NCF, which enables efficient and fast electron transfer at the solid–electrolyte interface, while all the CuRu-xh/CF electrodes have similar R_{ct} values (SI, Table S1). These specific characteristics grant CuRu-3h/CF its superior activity for NO_2RR .

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Furthermore, we also investigated the performance of CuRu-3h/CF in NO₃RR. First, we performed LSV between 0.6 V and -1.2 V vs. RHE in the presence and absence of NO₃⁻ (SI, Fig. S26). The current density increases with more negative potentials in the presence of NO₃⁻, indicating the efficient reduction of NO₃⁻. Next, we performed CA measurements at potentials between -0.1 and -1.0 V vs. RHE (SI, Fig. S27). The NH₃ production was confirmed

and quantified using the IBM, and the resulting nitrate-to-ammonia FE and yield rate are displayed in SI, Fig. S228. Highest FE (88.4 %) was detected at a potential of -0.6 V vs RHE; the highest yield rate (62.5 mg h⁻¹ cm⁻²) was observed at -1.0 V vs. RHE. The above results show that CuRu-3h/CF has high performance for the conversion of NO_x to NH₃, which is comparable to the related CF-based catalysts (SI, Table S2-S3).

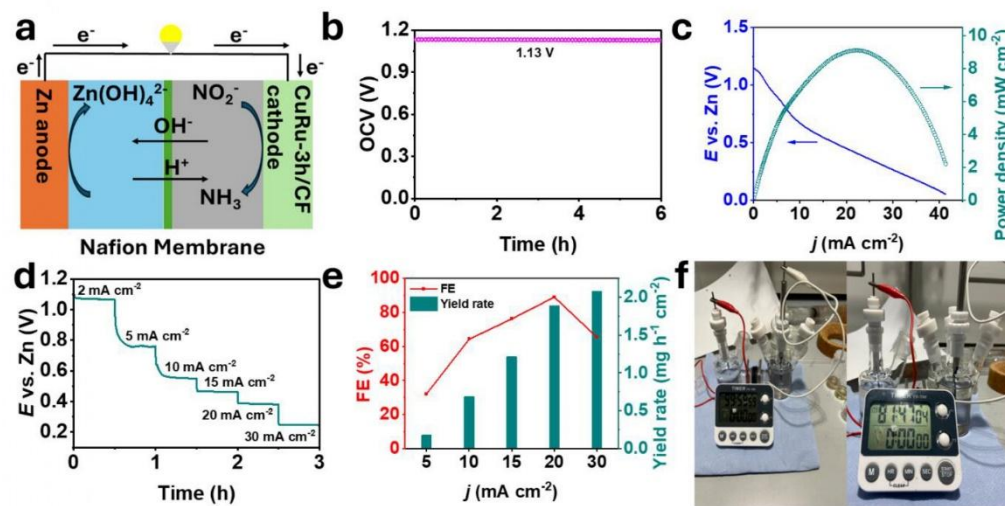


Figure 3. Zinc-nitrite battery test. (a) Schematic illustration of the zinc-nitrite battery with Zn anode and CuRu-3h/CF cathode, (b) Open-circuit voltage of the zinc-nitrite battery, (c) Discharge polarisation curve and corresponding power density curve of the zinc-nitrite battery, (d) Discharging curves at different current densities, (e) NH₃ FE and yield rate of the zinc-nitrite battery, and (f) Photograph of an electronic timer powered by our CuRu-3h/CF based zinc-nitrite battery.

For a practical application, we designed a zinc-nitrite battery using CuRu-3h/CF as cathode and zinc foil as anode (Fig. 3a). The battery maintains a constant OCP of 1.13 V for at least 6 h (Fig. 3b). Fig. 3c shows the charge-discharge LSV curves of the CuRu-3h/CF based zinc-nitrite battery. The discharge curve shows an increasing output current density with more negative cathodic potential, and the power density reaches 9.1 mW cm⁻². The time dependent discharge curves of the battery at current densities from 2 to 30 mA cm⁻², displayed in Fig. 3d, indicate a good long-term electrochemical stability. Fig. 3e displays the NH₃ yield and corresponding FE during discharge with various output current densities. The CuRu-3h/CF based zinc-nitrite battery achieves a NH₃ yield rate of 1.88 mg h⁻¹ cm⁻² and a FE of 88.9 % at a current density of 20 mA cm⁻². Lastly, the CuRu-3h/CF based zinc-nitrite battery was used to power an electronic timer for at least 18 h (Fig. 3f). In summary, the Zn-nitrite battery achieves three tasks: sustainable energy supply, NH₃ electrosynthesis and removal of NO₂⁻ pollutant in wastewater.^[48,49]

Conclusion

In summary, we report the facile synthesis of a Ru-doped Cu nanowires electrode for highly efficient NO_x to - NH₃ reduction

with high activity (with FE near 100 % and a yield rate of 33.2 mg h⁻¹ cm⁻² at a potential of -0.2 V vs. RHE) and high stability. Integration of the electrode into a Zn-nitrite battery demonstrated its operational capacity for combined sustainable electricity production, NH₃ electrosynthesis, and NO₂⁻ pollutant removal. The reported approach provides us a hint for designing high-performance transition metal-based catalysts for sustainable NH₃ synthesis.

Supporting Information

Experimental and analytical data are available as Supporting Information. The raw data reported in this manuscript is available at zenodo.org via <https://doi.org/10.5281/zenodo.13881049>

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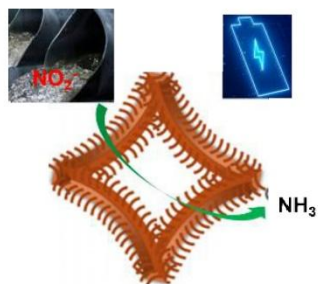
Humboldt Foundation. D.G. acknowledges the Deutsche Forschungsgemeinschaft (DFG) for a Walter Benjamin Fellowship (project no. 510966757). G.Z. and C.S. acknowledge the International CAS Partnership Project (039GJHZ202029GC). R.L., D.G., and C.S. gratefully acknowledge financial support by Johannes Gutenberg University Mainz, the Top-Level Research Initiative SusInnoScience and the Gutenberg Research College. The authors acknowledged Dr. Mihail Mondeshki for NMR measurements and discussion.

Keywords: Nitrite Reduction • Nitrate Reduction • Electrocatalysis • Ammonia synthesis • Zn–Nitrite Batteries

- [1] P. H. van Langevelde, I. Katsounaros, M. T. M. Koper, *Joule* **2021**, *5*, 290–294.
- [2] H. Xu, Y. Ma, J. Chen, W. X. Zhang, J. Yang, *Chem. Soc. Rev.* **2022**, *51*, 2710–2758.
- [3] C. J. M. Van Der Ham, M. T. M. Koper, D. G. H. Hetterscheid, *Chem. Soc. Rev.* **2014**, *43*, 5183–5191.
- [4] E. Spatolisano, L. A. Pellegrini, A. R. de Angelis, S. Cattaneo, E. Rocco, *Ind. Eng. Chem. Res.* **2023**, *62*, 10813–10827.
- [5] B. H. R. Suryanto, H. L. Du, D. Wang, J. Chen, A. N. Simonov, D. R. MacFarlane, *Nat. Catal.* **2019**, *2*, 290–296.
- [6] X. Fu, J. Zhang, Y. Kang, *Chem. Catal.* **2022**, *2*, 2590–2613.
- [7] S. Z. Andersen, V. Čolić, S. Yang, J. A. Schwalbe, A. C. Nielander, J. M. McEnaney, K. Enemark-Rasmussen, J. G. Baker, A. R. Singh, B. A. Rohr, M. J. Statt, S. J. Blair, S. Mezzavilla, J. Kibsgaard, P. C. K. Vesborg, M. Cargnello, S. F. Bent, T. F. Jaramillo, I. E. L. Stephens, J. K. Nørskov, I. Chorkendorff, *Nature* **2019**, *570*, 504–508.
- [8] K. Li, S. Z. Andersen, A. Xu, N. H. Deissler, J. Bjarke, V. Mygind, C. Wei, *Science* **2023**, *712*, 707–712.
- [9] T. Mou, J. Long, T. Frauenheim, J. Xiao, *Chempluschem* **2021**, *86*, 1211–1224.
- [10] R. Chauhan, V. C. Srivastava, *Chem. Eng. J.* **2020**, *386*, 122065.
- [11] H. Xu, Y. Ma, J. Chen, W. X. Zhang, J. Yang, *Chem. Soc. Rev.* **2022**, *51*, 2710–2758.
- [12] X. Zhang, Y. Wang, Y. Wang, Y. Guo, X. Xie, Y. Yu, B. Zhang, *Chem. Commun.* **2022**, *58*, 2777–2787.
- [13] H. Liu, J. Park, Y. Chen, Y. Qiu, Y. Cheng, K. Srivastava, S. Gu, B. H. Shanks, L. T. Roling, W. Li, *ACS Catal.* **2021**, *11*, 8431–8442.
- [14] Y. Yao, S. Zhu, H. Wang, H. Li, M. Shao, *Angew. Chem. Int. Ed.* **2020**, *59*, 10479–10483.
- [15] J. Li, G. Zhan, J. Yang, F. Quan, C. Mao, Y. Liu, B. Wang, F. Lei, L. Li, A. W. M. Chan, L. Xu, Y. Shi, Y. Du, W. Hao, P. K. Wong, J. Wang, S. X. Dou, L. Zhang, J. C. Yu, *J. Am. Chem. Soc.* **2020**, *142*, 7036–7046.
- [16] J. Yuan, Z. Xing, Y. Tang, C. Liu, *ACS Appl. Mater. Interfaces* **2021**, *13*, 52469–52478.
- [17] Y. Wang, W. Zhou, R. Jia, Y. Yu, B. Zhang, *Angew. Chem. Int. Ed.* **2020**, *59*, 5350–5354.
- [18] J. X. Liu, D. Richards, N. Singh, B. R. Goldsmith, *ACS Catal.* **2019**, *9*, 7052–7064.
- [19] Y. Bu, C. Wang, W. Zhang, X. Yang, J. Ding, G. Gao, *Angew. Chem. Int. Ed.* **2023**, *62*, e202217337.
- [20] K. H. Kim, H. Lee, X. Huang, J. H. Choi, C. Chen, J. K. Kang, D. O'Hare, *Energy Environ. Sci.* **2023**, *16*, 663–672.
- [21] B. Bi, A. Q. Dong, M. M. Shi, X. F. Sun, H. R. Li, X. Kang, R. Gao, Z. Meng, Z. Y. Chen, T. W. Xu, J. M. Yan, Q. Jiang, *Small Struct.* **2023**, *4*, 2200308.
- [22] Y. Wang, A. Xu, Z. Wang, L. Huang, J. Li, F. Li, J. Wicks, M. Luo, D. H. Nam, C. S. Tan, Y. Ding, J. Wu, Y. Lum, C. T. Dinh, D. Sinton, G. Zheng, E. H. Sargent, *J. Am. Chem. Soc.* **2020**, *142*, 5702–5708.
- [23] H. Li, C. Yan, H. Guo, K. Shin, S. M. Humphrey, C. J. Werth, G. Henkelman, *ACS Catal.* **2020**, *10*, 7915–7921.
- [24] K. Chen, Z. Ma, X. Li, J. Kang, D. Ma, K. Chu, *Adv. Funct. Mater.* **2023**, *33*, 2209890.
- [25] H. Liu, X. Lang, C. Zhu, J. Timoshenko, M. Rüschler, L. Bai, N. Guijarro, H. Yin, Y. Peng, J. Li, Z. Liu, W. Wang, B. R. Cuenya, J. Luo, *Angew. Chem. Int. Ed.* **2022**, *61*, e202202556.
- [26] X. Lu, H. Song, J. Cai, S. Lu, *Electrochem. commun.* **2021**, *129*, 107094.
- [27] D. Qin, S. Song, Y. Liu, K. Wang, B. Yang, S. Zhang, *Angew. Chem. Int. Ed.* **2023**, *62*, e202304935.
- [28] R. Daiyan, T. Tran-Phu, P. Kumar, K. Iputera, Z. Tong, J. Leverett, M. H. A. Khan, A. Asghar Esmailpour, A. Jalili, M. Lim, A. Tricoli, R. S. Liu, X. Lu, E. Lovell, R. Amal, *Energy Environ. Sci.* **2021**, *14*, 3588–3598.
- [29] J. Li, J. Gao, T. Feng, H. H. Zhang, D. Liu, C. Zhang, S. Huang, C. Wang, F. Du, C. Li, C. Guo, *J. Power Sources* **2021**, *511*, 230463.
- [30] Z. Song, Y. Liu, Y. Zhong, Q. Guo, J. Zeng, Z. Geng, *Adv. Mater.* **2022**, *34*, 2204306.
- [31] H. Jiang, G. F. Chen, O. Savateev, J. Xue, L. X. Ding, Z. Liang, M. Antonietti, H. Wang, *Angew. Chem. Int. Ed.* **2023**, *62*, e202218717.
- [32] J. Yang, H. Qi, A. Li, X. Liu, X. Yang, S. Zhang, Q. Zhao, Q. Jiang, Y. Su, L. Zhang, J. F. Li, Z. Q. Tian, W. Liu, A. Wang, T. Zhang, *J. Am. Chem. Soc.* **2022**, *144*, 12062–12071.
- [33] Q. Chen, X. An, Q. Liu, X. Wu, L. Xie, J. Zhang, W. Yao, M. S. Hamdy, Q. Kong, X. Sun, *Chem. Commun.* **2022**, *58*, 517–520.
- [34] F. Chen, Z. Wu, S. Gupta, D. J. Rivera, S. V. Lambeets, S. Pecaut, J. Yoon, T. Kim, P. Zhu, Y. Z. Finck, D. M. Meira, G. King, G. Gao, W. Xu, D. A. Cullen, H. Zhou, Y. Han, D. E. Perea, C. L. Muhich, H. Wang, *Nat. Nanotechnol.* **2022**, *17*, 759–767.
- [35] J. Y. Fang, Q. Z. Zheng, Y. Y. Lou, K. M. Zhao, S. N. Hu, G. Li, O. Akdim, X. Y. Huang, S. G. Sun, *Nat. Commun.* **2022**, *13*, 7899.
- [36] N. Q. Tran, L. T. Duy, D. C. Truong, B. T. Nguyen Le, B. T. Phan, Y. Cho, X. Liu, H. Lee, *Chem. Commun.* **2022**, *58*, 5257–5260.
- [37] R. Redón, A. Herrera-gomez, N. G. García-pe, A. L. Fernández-osorio, M. Bravo-sanchez, G. Gomez-sosa, *Appl. Surf. Sci.* **2015**, *340*, 25–34.
- [38] A. C. Miller, G. W. Simmons, *Surf. Sci. Spectra* **1993**, *2*, 55–60.
- [39] D. Li, G. Wang, L. Cheng, C. Wang, X. Mei, *ACS Omega* **2018**, *3*, 14755–14765.
- [40] Y. Liang, R. Zhang, K. Xiao, F. Ye, X. Ma, W. Liu, H. Yin, B. Mao, X. Song, C. Hu, *Chem. Commun.* **2024**, *60*, 4699–4702.
- [41] V. Hayez, A. Franquet, A. Hubin, H. Terryn, *Surf. Interface Anal.* **2004**, *36*, 876–879.
- [42] D. J. Morgan, *Surf. Interface Anal.* **2015**, *47*, 1072–1079.
- [43] M. Pang, Y. Fang, L. Chen, R. Sun, X. Li, H. Pang, S. Zhang, L. Xu, D. Sun, Y. Tang, *Nanoscale* **2024**, *16*, 17519–17526.
- [44] Y. Wang, A. Dutta, A. Iarchuk, C. Sun, S. Vesztorgom, P. Broekmann, *ACS Catal.* **2023**, *13*, 8169–8182.
- [45] A. Paliwal, C. D. Bendas, E. S. Thornburg, R. T. Haasch, A. A. Gewirth, *ACS Catal.* **2023**, *13*, 6754–6762.
- [46] H. Liu, X. Lang, C. Zhu, J. Timoshenko, M. Rüschler, L. Bai, N. Guijarro, H. Yin, Y. Peng, J. Li, Z. Liu, W. Wang, B. R. Cuenya, J. Luo, *Angew. Chem. Int. Ed.* **2022**, *61*, e202202556.
- [47] P. Nagaraja, M. Shivaswamy, H. Kumar, *Int. J. Environ. Anal. Chem.* **2001**, *80*, 39–48.
- [48] Z. Bi, J. Hu, M. Xu, H. Zhang, Y. Zhou, G. Hu, *Angew. Chem. Int. Ed.* **2024**, *63*, e202313434.
- [49] S. Liu, Y. Zhao, Z. Chen, D. Gao, F. Feng, T. Rios-Studer, J. Bannmann, J. Biskupek, U. Kaiser, R. Liu, C. Streib, *ChemElectroChem* **2024**, *11*, e202400291.

RESEARCH ARTICLE

Entry for the Table of Contents



Copper nanowires doped with small amounts of Ruthenium (250 ppm) show high performance for the electrocatalytic nitrite/nitrate-to-ammonia reduction. The nanowires can be integrated into a Zinc–nitrite battery to provide electricity, ammonia and nitrite removal.

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4. Summary and outlook

In summary, this work briefly summarizes the related background knowledge, working principle, recent progress, and current challenges toward next generation EES technologies, including RFBs, ZABs and ZNBs. A variety of novel advanced electrolytes and electrocatalysts have been successfully synthesized via several plausible and easily accessible synthetic strategies. In addition, their structure, morphology, electrochemical property, electrocatalytic activity, stability as well as practical application for corresponding EES devices were thoroughly evaluated and discussed respectively.

This thesis provides extensive experimental data and analysis, underscoring the importance of rational design and targeted synthesis in accurately predicting performance for specific applications. State-of-the art characterization techniques are vital for a deeper understanding of the structure-property-performance relationship, while systematic performance evaluation plays a crucial role in guiding the design and synthesis of materials.

(a) Electrolytes based on mixed-valent polyoxovanadates $\{\text{MV}_{13}\}$ cluster for NRFB

We synthesized a novel polyoxovanadates $\{\text{MV}_{13}\}$ cluster as active species in electrolytes and integrated them into symmetric NRFBs, the electrochemical properties of the active species and the performance of the constructed NRFBs were both systemically investigated. As results, the mixed-valent redox-equilibrated $\{\text{MV}_{13}\}$ exhibited excellent redox properties with reversible multi-electron transfer spanning a wide electrochemical window of 3.5 V. Moreover, the NRFB demonstrated a specific capacity of 24.5 mAh at current density of 0.6 mA cm⁻². The cyclic tests revealed the high stability of this NRFB with a capacity fading rate of 0.074% per cycle and negligible loss of columbic efficiency after 50 cycles. Notably, the NRFBs delivered a stable coulombic efficiency of 93% over the cycling measurements. Furthermore, in-operando UV-Vis was utilized to monitor the reversible multi-electron storage and release of $\{\text{MV}_{13}\}$ at different chemical states during the charging and discharging processes.

(b) Oxygen electrocatalysts for rechargeable ZABs

In this part, we successfully synthesized a bifunctional DAC FeNi-NC@MWCNTs based on transition metals, its morphology, structure and chemical states were carefully measured with SEM, XRD, XPS, XAS techniques, which verified the atomically dispersion of Fe and Ni atoms in the FeNi-NC@MWCNTs catalyst. Particularly, the atomic FeNi dual metal pairs were

anchored into a nitrogen-doped porous carbon matrix, which was in-situ linked by MWCNTs via a self-assembly process. The hierarchical structure and atomic dispersion of active sites both granted the catalyst highly efficient and durable catalytic performance for ORR/OER and ZABs application. Consequently, the bifunctional catalyst FeNi-NC@MWCNTs showed a voltage difference of 0.69 V between the half-wave potential of ORR (0.90 V vs. RHE) and the potential of OER at 10 mA cm⁻² (1.59 V vs. RHE). In the ZABs study, the battery with the FeNi-NC@MWCNTs achieved a high open circuit voltage of 1.44 V and an excellent peak power density of 218.3 mW cm⁻² at a current density of 260 mA cm⁻². Moreover, this rechargeable ZAB exhibited remarkable long-term durability over the charging-discharging cyclic test (600 cycles, 300 h) with negligible voltage gap increasing.

Furthermore, a defect-rich Pd metallene with atomically doped tungsten and molybdenum oxides (WO_x and MoO_x) (denoted as D-Pd M) was prepared via a straightforward wet-chemical strategy. Characterization results revealed the existence of atomic-scale defects in the catalyst, such as pores, and concave surfaces, which finely tuned the electronic structure of the active sites and contributed to the improved catalytic activity for the ORR. DFT calculations were also conducted to indicate the mechanisms of the downward shift of the *d*-band center in Pd, which resulted in reduced binding energy with O₂. As results, the D-Pd M exhibited remarkable ORR activities with a high half-wave potential (0.927 V vs. RHE). Notably, D-Pd M also demonstrated exceptional stability even after 10,000 cycles of testing, outperforming conventional Pd nanosheets and commercial Pd/C. For the ZABs application, the ZABs integrated with D-Pd M delivered a high specific capacity of 809 mAhg⁻¹ and demonstrated exceptional discharge and ultralong cycling stability, achieving continuous operation for 300 hours over 300 cycles.

(c) Electrocatalysts for electrosynthesis of ammonia from nitrite/nitrate with ZNBs

In this sector, we developed a self-supported catalyst based on the bimetallic NiCu-coated 3D printed electrode (NiCu/ABS mesh) with thermoplastic polymer as substrate. A series of characterization techniques including powder XRD, XPS, SEM and TEM were employed to clarify the morphology and compositions of the as-prepared catalyst. The results indicated that this electrode had a typical sandwich structure consisting of polymer-metal-metal oxide/hydroxide (mainly Ni and NiO/Ni(OH)₂). The electrocatalytic performance of this NiCu/ABS mesh electrode was systematically evaluated and showed high-performance for the

electrosynthesis of green ammonia from nitrate with a high Faradaic efficiency of 83% and yield rate of $860 \mu\text{g}/(\text{h}\cdot\text{cm}^2)$ at -0.38 V vs RHE. Besides, the zinc-nitrate batteries integrated with the NiCu/ABS mesh electrode demonstrated a power density of 3.8 mW cm^{-2} with continuous NH_3 production.

Lastly, we fabricated an electrocatalyst CuRu-3h/CF by dispersing atomic ruthenium on a nanostructured copper foam surface, then used it for the selective synthesis of ammonia from nitrite. Notably, the introduction of ruthenium species into the Cu foam-based electrode greatly facilitated the hydrogen adsorption-desorption process and enhanced the hydrogenation ability of this catalyst at more positive applied potentials. As results, the CuRu-3h/CF catalyst achieved high selectivity towards ammonia formation and inertness toward HER of copper with the low nitrite activation barrier of ruthenium. The electrochemical investigation revealed that this catalyst reached a high Faraday efficiency near 100 % for the reduction of nitrite with a yield rate of $33.2 \text{ mg h}^{-1} \text{ cm}^{-2}$ at a potential of -0.2 V vs. RHE. Even at low nitrite concentrations of about 400 ppm the catalyst maintained a Faraday efficiency over 89% with a high selectivity of 99% towards the formation of ammonia. Moreover, aqueous zinc-nitrite batteries integrated with CuRu-3h/CF catalyst were assembled and evaluated as devices for sustainable energy, NH_3 electrosynthesis and removal of NO_3^- pollutant in wastewaters as well. According to the results, the batteries delivered a constant open circuit voltage of 1.13 V for at least six hours and achieved a power density as high as $9 \text{ mW}/\text{cm}^2$ with a NH_3 yield rate of $2100 \mu\text{g h}^{-1} \text{ cm}^2$ at a current density of $30 \text{ mA}/\text{cm}^2$ and a FE of about 90% at a current density of $20 \text{ mA}/\text{cm}^2$, respectively.

It remains unclear which new EES technology will become the dominant leader in the future power market, but it is for sure that there will be significant improvement over current EES devices in terms of performance, availability and cost reduction over the next decades. This ongoing process not only involves the advancement of new electrochemistry but also the development of well-integrated hybrid systems which take advantage of the strength of multiple EES technologies features. Also, the opportunities and challenges of advanced active materials for next generation EES devices require further efforts.

5. References

- [1] S. Chu, A. Majumdar, *Nature* **2012**, 488, 294–303.
- [2] Z. M. Chen, G. Q. Chen, *Energy Policy* **2011**, 39, 5920–5928.
- [3] P. C. Stern, K. B. Janda, M. A. Brown, L. Steg, E. L. Vine, L. Lutzenhiser, *Nat. Energy* **2016**, 1, 16043.
- [4] M. Höök, X. Tang, *Energy Policy* **2013**, 52, 797–809.
- [5] R. Baños, F. Manzano-Agugliaro, F. G. Montoya, C. Gil, A. Alcayde, J. Gómez, *Renew. Sustain. Energy Rev.* **2011**, 15, 1753–1766.
- [6] J. Liu, J. Wang, C. Xu, H. Jiang, C. Li, L. Zhang, J. Lin, Z. X. Shen, *Adv. Sci.* **2018**, 5, 1700322.
- [7] M. De Rosa, O. Afanaseva, A. V. Fedyukhin, V. Bianco, *J. Energy Storage* **2021**, 44, 103443.
- [8] A. Vlad, N. Singh, C. Galande, P. M. Ajayan, *Adv. Energy Mater.* **2015**, 5, 1402115.
- [9] G. J. Navathe, S. R. Prasad, A. M. Mane, S. H. Barge, T. D. Dongale, V. Shaikh, M. M. Karanjkar, S. B. Teli, P. S. Patil, N. R. Prasad, *ES Energy Environ.* **2022**, 17, 11–32.
- [10] J. Noack, N. Roznyatovskaya, T. Herr, P. Fischer, *Angew. Chemie - Int. Ed.* **2015**, 54, 9776–9809.
- [11] K. J. Kim, M. S. Park, Y. J. Kim, J. H. Kim, S. X. Dou, M. Skyllas-Kazacos, *J. Mater. Chem. A* **2015**, 3, 16913–16933.
- [12] X. Ke, J. M. Prahl, I. J. D. Alexander, J. S. Wainright, T. A. Zawodzinski, R. F. Savinell, *Chem. Soc. Rev.* **2018**, 47, 8721–8743.
- [13] P. Xiong, L. Zhang, Y. Chen, S. Peng, G. Yu, *Angew. Chemie - Int. Ed.* **2021**, 60, 24770–24798.
- [14] C. A. MacHado, G. O. Brown, R. Yang, T. E. Hopkins, J. G. Pribyl, T. H. Epps, *ACS Energy Lett.* **2021**, 6, 158–176.
- [15] H. Zhang, H. Zhang, X. Li, Z. Mai, J. Zhang, *Energy Environ. Sci.* **2011**, 4, 1676–1679.
- [16] J. Yuan, Z. Z. Pan, Y. Jin, Q. Qiu, C. Zhang, Y. Zhao, Y. Li, *J. Power Sources* **2021**, 500, 229983.
- [17] L. Liu, C. Wang, Z. He, R. Das, B. Dong, X. Xie, Z. Guo, *J. Mater. Sci. Technol.* **2021**, 69, 212–227.
- [18] H. Amiri, M. Khosravi, M. Ejeian, A. Razmjou, *Adv. Mater. Technol.* **2021**, 6, 2001308.
- [19] M. Gencten, Y. Sahin, *Int. J. Energy Res.* **2020**, 44, 7903–7923.
- [20] R. Huang, J. Wang, S. Liu, Y. Yang, W. Deng, Y. Su, *J. Power Sources* **2021**, 515,

- 230640.
- [21] X. L. Zhou, Y. K. Zeng, X. B. Zhu, L. Wei, T. S. Zhao, *J. Power Sources* **2016**, 325, 329–336.
- [22] K. Amini, J. Gostick, M. D. Pritzker, *Adv. Funct. Mater.* **2020**, 30, 1910564.
- [23] J. Luo, B. Hu, M. Hu, Y. Zhao, T. L. Liu, *ACS Energy Lett.* **2019**, 4, 2220–2240.
- [24] D. G. Kwabi, Y. Ji, M. J. Aziz, *Chem. Rev.* **2020**, 120, 6467–6489.
- [25] A. Jameson, E. Gyenge, *Halogens as Positive Electrode Active Species for Flow Batteries and Regenerative Fuel Cells*, Springer Singapore, **2020**.
- [26] I. Iwakiri, T. Antunes, H. Almeida, J. P. Sousa, R. B. Figueira, A. Mendes, *Energies* **2021**, 14, 5643.
- [27] A. Trovò, *J. Power Sources* **2020**, 465, 228229.
- [28] A. Aluko, A. Knight, *IEEE Access* **2023**, 11, 13773–13793.
- [29] M. Kapoor, A. Verma, *Wiley Interdiscip. Rev. Energy Environ.* **2022**, 11, e439.
- [30] B. Liu, Y. Li, G. Jia, T. Zhao, *Electrochem. Energy Rev.* **2024**, 7, 34–46.
- [31] F. Zhong, M. Yang, M. Ding, C. Jia, *Front. Chem.* **2020**, 8, 451.
- [32] T. C. Palmer, A. Beamer, T. Pitt, I. A. Popov, C. X. Cammack, H. D. Pratt, T. M. Anderson, E. R. Batista, P. Yang, B. L. Davis, *ChemSusChem* **2021**, 14, 1214–1228.
- [33] Z. Li, S. Li, S. Liu, K. Huang, D. Fang, F. Wang, S. Peng, *Electrochem. Solid-State Lett.* **2011**, 14, A171–A173.
- [34] P. Rohland, E. Schröter, O. Nolte, G. R. Newkome, M. D. Hager, U. S. Schubert, *Prog. Polym. Sci.* **2022**, 125, 101474.
- [35] V. M. Ortiz-Martínez, L. Gómez-Coma, G. Pérez, A. Ortiz, I. Ortiz, *Sep. Purif. Technol.* **2020**, 252, 117436.
- [36] J. Lei, Y. Zhang, Y. Yao, Y. Shi, K. L. Leung, J. Fan, Y.-C. Lu, *Nat. Energy* **2023**, 8, 1355–1364.
- [37] L. Tang, W. Lu, H. Zhang, X. Li, *Energy Mater. Adv.* **2022**, 2022, 9850712.
- [38] Y. A. Gandomi, D. S. Aaron, J. R. Houser, M. C. Daugherty, J. T. Clement, A. M. Pezeshki, T. Y. Ertugrul, D. P. Moseley, M. M. Mench, *J. Electrochem. Soc.* **2018**, 165, A970–A1010.
- [39] F. Pan, Q. Wang, *Molecules* **2015**, 20, 20499–20517.
- [40] G. Sikukuu Nambafu, *Electrochem. commun.* **2021**, 127, 107052.
- [41] T. Ma, Z. Pan, L. Miao, C. Chen, M. Han, Z. Shang, J. Chen, *Angew. Chemie - Int. Ed.* **2018**, 57, 3158–3162.

- [42] L. Tong, Y. Jing, R. G. Gordon, M. J. Aziz, *ACS Appl. Energy Mater.* **2019**, 2, 4016–4021.
- [43] G. Mohandass, W. Chen, S. Krishnan, T. Kim, *Environ. Sci. Technol.* **2022**, 56, 4477–4488.
- [44] L. Tang, P. Leung, Q. Xu, M. R. Mohamed, S. Dai, X. Zhu, C. Flox, A. A. Shah, *Curr. Opin. Chem. Eng.* **2022**, 37, 100833.
- [45] Y. Cho, H. Kye, B. G. Kim, J. E. Kwon, *J. Ind. Eng. Chem.* **2024**, 136, 73–88.
- [46] K. Gong, Q. Fang, S. Gu, S. F. Y. Li, Y. Yan, *Energy Environ. Sci.* **2015**, 8, 3515–3530.
- [47] P. Singh, *J. Power Sources* **1984**, 11, 135–142.
- [48] Y. Matsuda, K. Tanaka, M. Okada, Y. Takasu, M. Morita, T. Matsumura-Inoue, *J. Appl. Electrochem.* **1988**, 18, 909–914.
- [49] Y. Huang, S. Gu, Y. Yan, S. F. Y. Li, *Curr. Opin. Chem. Eng.* **2015**, 8, 105–113.
- [50] N. Mizuno, S. Hikichi, K. Yamaguchi, S. Uchida, Y. Nakagawa, K. Uehara, K. Kamata, *Catal. Today* **2006**, 117, 32–36.
- [51] Q. Li, L. Zhang, J. Dai, H. Tang, Q. Li, H. Xue, H. Pang, *Chem. Eng. J.* **2018**, 351, 441–461.
- [52] R. Xue, Y. S. Liu, M. Y. Wang, H. Guo, W. Yang, G. Y. Yang, *Mater. Horizons* **2023**, 10, 4710–4723.
- [53] M. R. Horn, A. Singh, S. Alomari, S. Goberna-Ferrón, R. Benages-Vilau, N. Chodankar, N. Motta, K. Ostrikov, J. Macleod, P. Sonar, P. Gomez-Romero, D. Dubal, *Energy Environ. Sci.* **2021**, 14, 1652–1700.
- [54] Y. Liu, J. Zhang, S. Lu, Y. Xiang, *Mater. Reports Energy* **2022**, 2, 100094.
- [55] M. Han, W. Sun, W. Hu, Y. Liu, J. Chen, C. Zhang, J. Li, *Energy Storage Mater.* **2024**, 71, 103576.
- [56] P. Sun, Y. Gu, W. You, Z. Tan, *J. Electrochem.* **1997**, 3, 67–70.
- [57] Y. Liu, S. Lu, H. Wang, C. Yang, X. Su, Y. Xiang, *Adv. Energy Mater.* **2017**, 7, 1601224.
- [58] F. Ai, Z. Wang, N.-C. Lai, Q. Zou, Z. Liang, Y.-C. Lu, *Nat. Energy* **2022**, 7, 417–426.
- [59] L. E. Vangelder, H. D. Pratt, T. M. Anderson, E. M. Matson, *Chem. Commun.* **2019**, 55, 12247–12250.
- [60] L. Yang, S. Zhang, K. Li, H. Wu, T. Wu, D. Wu, J. Chen, *Energy Storage Mater.* **2024**, 65, 103149.
- [61] L. Li, Z. wen Chang, X. B. Zhang, *Adv. Sustain. Syst.* **2017**, 1, 1700036.
- [62] Y. Li, J. Lu, *ACS Energy Lett.* **2017**, 2, 1370–1377.

-
- [63] Q. Liu, Z. Pan, E. Wang, L. An, G. Sun, *Energy Storage Mater.* **2020**, 27, 478–505.
- [64] C. Wang, Y. Yu, J. Niu, Y. Liu, D. Bridges, X. Liu, J. Pooran, Y. Zhang, A. Hu, **2019**, 9, 2787.
- [65] Z. L. Wang, D. Xu, J. J. Xu, X. B. Zhang, *Chem. Soc. Rev.* **2014**, 43, 7746–7786.
- [66] T. Zhang, Z. Tao, J. Chen, *Mater. Horizons* **2014**, 1, 196–206.
- [67] A. G. Olabi, E. T. Sayed, T. Wilberforce, A. Jamal, A. H. Alami, K. Elsaid, S. Mohammod, A. Rahman, S. K. Shah, **2021**, 14, 7373.
- [68] L. Yaqoob, T. Noor, N. Iqbal, *J. Energy Storage* **2022**, 56, 106075.
- [69] K. Chen, G. Huang, X. B. Zhang, *Chinese J. Chem.* **2021**, 39, 32–42.
- [70] X. Liu, B. Cui, S. Liu, Y. Chen, *J. Mater. Sci. Chem. Eng.* **2015**, 03, 35001.
- [71] X. W. Lv, Z. Wang, Z. Lai, Y. Liu, T. Ma, J. Geng, Z. Y. Yuan, *Small* **2024**, 20, 2306396.
- [72] Q. Wang, S. Kaushik, X. Xiao, Q. Xu, *Chem. Soc. Rev.* **2023**, 52, 6139–6190.
- [73] J. F. Parker, C. N. Chervin, E. S. Nelson, D. R. Rolison, J. W. Long, *Energy Environ. Sci.* **2014**, 7, 1117–1124.
- [74] J. Chang, G. Wang, Y. Yang, *Small Sci.* **2021**, 1, 2100044.
- [75] R. Y. Wang, D. W. Kirk, G. X. Zhang, *J. Electrochem. Soc.* **2006**, 153, C357–C364.
- [76] P. Pei, K. Wang, Z. Ma, *Appl. Energy* **2014**, 128, 315–324.
- [77] J. Lee, B. Hwang, M. S. Park, K. Kim, *Electrochim. Acta* **2016**, 199, 164–171.
- [78] J. F. Parker, C. N. Chervin, I. R. Pala, M. Machler, M. F. Burz, J. W. Long, D. R. Rolison, **2017**, 418, 415–418.
- [79] J. Fu, R. Liang, G. Liu, A. Yu, Z. Bai, L. Yang, Z. Chen, *Adv. Mater.* **2019**, 31, 1805230.
- [80] S. Anwar, Y. Zhang, F. Khan, *RSC Adv.* **2018**, 8, 28861–28873.
- [81] S. M. Lee, Y. J. Kim, S. W. Eom, N. S. Choi, K. W. Kim, S. B. Cho, *J. Power Sources* **2013**, 227, 177–184.
- [82] X. Liu, X. Fan, B. Liu, J. Ding, Y. Deng, X. Han, C. Zhong, W. Hu, *Adv. Mater.* **2021**, 33, 2006461.
- [83] S. Clark, A. R. Mainar, E. Iruin, L. C. Colmenares, J. A. Blázquez, J. R. Tolchard, Z. Jusys, B. Horstmann, *Adv. Energy Mater.* **2020**, 10, 1903470.
- [84] Y. Li, H. Dai, *Chem. Soc. Rev.* **2014**, 43, 5257–5275.
- [85] M. Xu, D. G. Ivey, W. Qu, Z. Xie, E. Dy, X. Z. Yuan, *J. Electrochem. Soc.* **2014**, 161, A128–A136.
- [86] A. A. Mohamad, *J. Power Sources* **2006**, 159, 752–757.
- [87] F. Ye, J. Zhao, P. Xu, X. Liu, J. Yu, W. Shangguan, J. Liu, X. Luo, C. Li, T. Ying, J.

- Wang, B. Yu, P. Wang, *Angew. Chemie - Int. Ed.* **2021**, *60*, 12904–12910.
- [88] P. Arora, Z. Zhang, *Chem. Rev.* **2004**, *104*, 4419–4462.
- [89] M. T. Tsehay, F. Alloin, C. Iojoiu, R. A. Tufa, D. Aili, P. Fischer, S. Velizarov, *J. Power Sources* **2020**, *475*, 228689.
- [90] H. J. Hwang, W. S. Chi, O. Kwon, J. G. Lee, J. H. Kim, Y. G. Shul, *ACS Appl. Mater. Interfaces* **2016**, *8*, 26298–26308.
- [91] M. Wang, N. Xu, J. Fu, Y. Liu, J. Qiao, *J. Mater. Chem. A* **2019**, *7*, 11257–11264.
- [92] H. Dou, X. Wu, M. Xu, R. Feng, Q. Ma, D. Luo, K. Zong, X. Wang, Z. Chen, *Angew. Chemie - Int. Ed.* **2024**, *63*, e202401974.
- [93] V. Neburchilov, H. Wang, J. J. Martin, W. Qu, *J. Power Sources* **2010**, *195*, 1271–1291.
- [94] F. Bidault, D. J. L. Brett, P. H. Middleton, N. P. Brandon, *J. Power Sources* **2009**, *187*, 39–48.
- [95] L. Li, X. Tang, B. Wu, B. Huang, K. Yuan, Y. Chen, *Adv. Mater.* **2024**, *36*, 2308326.
- [96] M. I. Jamesh, P. Moni, A. S. Prakash, M. Harb, *Mater. Sci. Energy Technol.* **2021**, *4*, 1–22.
- [97] Q. Liu, L. Wang, H. Fu, *J. Mater. Chem. A* **2023**, *11*, 4400–4427.
- [98] D. B. Kumar, W. Nie, Z. Jiang, J. Lee, T. Maiyalagan, *J. Alloys Compd.* **2023**, *960*, 170828.
- [99] L. Lu, Y. Zheng, R. Yang, A. Kakimov, X. Li, *Mater. Today Chem.* **2021**, *21*, 100488.
- [100] J. Pan, X. L. Tian, S. Zaman, Z. Dong, H. Liu, H. S. Park, B. Y. Xia, *Batter. Supercaps* **2019**, *2*, 336–347.
- [101] J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard, H. Jónsson, *J. Phys. Chem. B* **2004**, *108*, 17886–17892.
- [102] F. Cheng, J. Chen, *Chem. Soc. Rev.* **2012**, *41*, 2172–2192.
- [103] L. E. Betancourt, A. Rojas-Pérez, I. Orozco, A. I. Frenkel, Y. Li, K. Sasaki, S. D. Senanayake, C. R. Cabrera, *ACS Appl. Energy Mater.* **2020**, *3*, 2342–2349.
- [104] T. Reier, M. Oezaslan, P. Strasser, *ACS Catal.* **2012**, *2*, 1765–1772.
- [105] M. Gara, R. G. Compton, *New J. Chem.* **2011**, *35*, 2647–2652.
- [106] L. Lai, J. R. Potts, D. Zhan, L. Wang, C. K. Poh, C. Tang, H. Gong, Z. Shen, J. Lin, R. S. Ruoff, *Energy Environ. Sci.* **2012**, *5*, 7936–7942.
- [107] P. Cui, L. Zhao, Y. Long, L. Dai, C. Hu, *Angew. Chemie - Int. Ed.* **2023**, *62*, e202218269.
- [108] J. Kossmann, M. L. Ortiz Sánchez-Manjavacas, H. Zschiesche, N. V. Tarakina, M. Antonietti, J. Albero, N. López-Salas, *J. Mater. Chem. A* **2021**, *10*, 6107–6114.

-
- [109] Y. Ran, C. Xu, D. Ji, H. Zhao, L. Li, Y. Lei, *Nano Res. Energy* **2024**, *3*, e9120092.
- [110] H. Osgood, S. V. Devaguptapu, H. Xu, J. Cho, G. Wu, *Nano Today* **2016**, *11*, 601–625.
- [111] C. Shao, F. Liao, W. Zhu, Y. Zhang, M. Ma, J. Yang, K. Yin, M. Shao, B. Jiang, *Appl. Surf. Sci.* **2022**, *596*, 153642.
- [112] L. Wan, P. Wang, *Int. J. Hydrogen Energy* **2021**, *46*, 8356–8376.
- [113] J. Zhang, C. Si, T. Kou, J. Wang, Z. Zhang, *Sustain. Energy Fuels* **2020**, *4*, 2625–2637.
- [114] K. B. Ibrahim, M. C. Tsai, S. A. Chala, M. K. Berihun, A. W. Kahsay, T. A. Berhe, W. N. Su, B. J. Hwang, *J. Chinese Chem. Soc.* **2019**, *66*, 829–865.
- [115] H. Wan, F. Chen, W. Ma, X. Liu, R. Ma, *Nanoscale* **2020**, *12*, 21479–21496.
- [116] K. Fan, Z. Li, Y. Song, W. Xie, M. Shao, M. Wei, *Adv. Funct. Mater.* **2021**, *31*, 2008064.
- [117] G. Fu, J. M. Lee, *J. Mater. Chem. A* **2019**, *7*, 9386–9405.
- [118] S. Zhang, Y. Cheng, P. Wang, X. Lei, J. You, R. Guo, H. Zhang, *Int. J. Hydrogen Energy* **2024**, *51*, 545–560.
- [119] B. Wang, G. Li, *Chem. - A Eur. J.* **2022**, *28*, e202202062.
- [120] Y. Wang, Q. Wu, B. Zhang, L. Tian, K. Li, X. Zhang, *Catalysts* **2020**, *10*, 1164.
- [121] Y. J. Tang, C. H. Liu, W. Huang, X. L. Wang, L. Z. Dong, S. L. Li, Y. Q. Lan, *ACS Appl. Mater. Interfaces* **2017**, *9*, 16977–16985.
- [122] M. Feng, J. Huang, Y. Peng, C. Huang, X. Yue, S. Huang, *Chem. Eng. J.* **2021**, *428*, 131206.
- [123] Z. G. Yang, H. M. Xu, T. Y. Shuai, Q. N. Zhan, Z. J. Zhang, K. Huang, C. Dai, G. R. Li, *Nanoscale* **2023**, *15*, 11777–11800.
- [124] Z. W. Chen, L. X. Chen, C. C. Yang, Q. Jiang, *J. Mater. Chem. A* **2019**, *7*, 3492–3515.
- [125] Q. Zhang, J. Guan, *Adv. Funct. Mater.* **2020**, *30*, 2000768.
- [126] B. Qiao, A. Wang, X. Yang, L. F. Allard, Z. Jiang, Y. Cui, J. Liu, J. Li, T. Zhang, *Nat. Chem.* **2011**, *3*, 634–641.
- [127] W. Zhang, Y. Liu, L. Zhang, J. Chen, *Nanomaterials* **2019**, *9*, 1402.
- [128] J. Liu, *ACS Catal.* **2017**, *7*, 34–59.
- [129] M. Xu, M. Peng, H. Tang, W. Zhou, B. Qiao, D. Ma, *J. Am. Chem. Soc.* **2024**, *146*, 2290–2307.
- [130] C. Wan, X. Duan, Y. Huang, *Adv. Energy Mater.* **2020**, *10*, 1903815.
- [131] T. Cui, Y. Wang, T. Ye, J. Wu, Z. Chen, J. Li, Y. Lei, D. Wang, Y. Li, *Angew. Chemie* **2022**, *134*, e202115219.
- [132] X. Lin, G. Chen, Y. Zhu, H. Huang, *Energy Rev.* **2024**, *3*, 100076.

- [133] H. Tu, H. Zhang, Y. Song, P. Liu, Y. Hou, B. Xu, T. Liao, J. Guo, Z. Sun, *Adv. Sci.* **2023**, *10*, 2305194.
- [134] X. Xie, Z. Zhai, L. Peng, J. Zhang, L. Shang, T. Zhang, *Sci. Bull.* **2023**, *68*, 2862–2875.
- [135] S. Chen, M. Cui, Z. Yin, J. Xiong, L. Mi, Y. Li, *ChemSusChem* **2021**, *14*, 73–93.
- [136] H. Yan, Y. Lin, H. Wu, W. Zhang, Z. Sun, H. Cheng, W. Liu, C. Wang, J. Li, X. Huang, T. Yao, J. Yang, S. Wei, J. Lu, *Nat. Commun.* **2017**, *8*, 1070 |.
- [137] H. Chen, Y. Zhang, Q. He, H. Zhang, S. Xu, X. He, H. Ji, *J. Mater. Chem. A* **2020**, *8*, 2364–2368.
- [138] J. Wang, Z. Huang, W. Liu, C. Chang, H. Tang, Z. Li, W. Chen, C. Jia, T. Yao, S. Wei, Y. Wu, Y. Li, *J. Am. Chem. Soc.* **2017**, *139*, 17281–17284.
- [139] M. Tong, L. Wang, H. Fu, *Small Methods* **2021**, *5*, 2100865.
- [140] X. Zhang, B. B. Ward, D. M. Sigman, *Chem. Rev.* **2020**, *120*, 5308–5351.
- [141] H. Xu, Y. Ma, J. Chen, W. X. Zhang, J. Yang, *Chem. Soc. Rev.* **2022**, *51*, 2710–2758.
- [142] N. Lehnert, H. T. Dong, J. B. Harland, A. P. Hunt, C. J. White, *Nat. Rev. Chem.* **2018**, *2*, 278–289.
- [143] J. K. Ladha, M. B. Peoples, P. M. Reddy, J. C. Biswas, A. Bennett, M. L. Jat, T. J. Krupnik, *F. Crop. Res.* **2022**, *283*, 108541.
- [144] H. Liu, *Cuihua Xuebao/Chinese J. Catal.* **2014**, *35*, 1619–1640.
- [145] J. G. Chen, R. M. Crooks, L. C. Seefeldt, K. L. Bren, R. Morris Bullock, M. Y. Darensbourg, P. L. Holland, B. Hoffman, M. J. Janik, A. K. Jones, M. G. Kanatzidis, P. King, K. M. Lancaster, S. V. Lymar, P. Pfromm, W. F. Schneider, R. R. Schrock, *Science (80-.)*. **2018**, *360*, eaar6611.
- [146] K. H. R. Rouwenhorst, A. S. Travis, L. Lefferts, *Sustain. Chem.* **2022**, *3*, 149–171.
- [147] J. Humphreys, R. Lan, S. Tao, *Adv. Energy Sustain. Res.* **2021**, *2*, 2000043.
- [148] J. M. H. Knops, K. L. Bradley, D. A. Wedin, *Ecol. Lett.* **2002**, *5*, 454–466.
- [149] R. A. Pandey, B. Chandrashekhar, *Crit. Rev. Environ. Sci. Technol.* **2014**, *44*, 34–96.
- [150] A. J. Thomson, G. Giannopoulos, J. Pretty, E. M. Baggs, D. J. Richardson, *Philos. Trans. R. Soc. B Biol. Sci.* **2012**, *367*, 1157–1168.
- [151] Bijay-Singh, E. Craswell, *SN Appl. Sci.* **2021**, *3*, 518.
- [152] X. Zhang, Y. Zhang, P. Shi, Z. Bi, Z. Shan, L. Ren, *Sci. Total Environ.* **2021**, *770*, 144674.
- [153] P. Banerjee, P. Garai, N. C. Saha, S. Saha, P. Sharma, A. K. Maiti, *Water. Air. Soil Pollut.* **2023**, *234*, 333.
- [154] M. Parvizishad, A. Dalvand, A. H. Mahvi, F. Goodarzi, *Heal. Scope* **2017**, *In Press*,

- e14164.
- [155] D. E. Canfield, A. N. Glazer, P. G. Falkowski, *Science* (80-.). **2010**, *330*, 192–196.
- [156] M. Klimczyk, A. Siczek, L. Schimmelpfennig, *Sci. Total Environ.* **2021**, *771*, 145483.
- [157] N. Morlanés, S. P. Katikaneni, S. N. Paglieri, A. Harale, B. Solami, S. M. Sarathy, J. Gascon, *Chem. Eng. J.* **2021**, *408*, 127310.
- [158] J. Li, Q. Xiong, X. Mu, L. Li, *ChemSusChem* **2024**, *202301775*, e202301775.
- [159] T. Wu, W. Fan, Y. Zhang, F. Zhang, *Mater. Today Phys.* **2021**, *16*, 100310.
- [160] F. Jiao, B. Xu, *Adv. Mater.* **2019**, *31*, 1805173.
- [161] D. Chanda, R. Xing, T. Xu, Q. Liu, Y. Luo, S. Liu, R. A. Tufa, T. H. Dolla, T. Montini, X. Sun, *Chem. Commun.* **2021**, *57*, 7335–7349.
- [162] X. Cui, C. Tang, Q. Zhang, *Adv. Energy Mater.* **2018**, *8*, 1800369.
- [163] Z. W. Chen, J. M. Yan, Q. Jiang, *Small Methods* **2019**, *3*, 1800291.
- [164] B. Yang, W. Ding, H. Zhang, S. Zhang, *Energy Environ. Sci.* **2021**, *14*, 672–687.
- [165] B. H. R. Suryanto, H.-L. Du, D. Wang, J. Chen, A. N. Simonov, D. R. MacFarlane, *Nat. Catal.* **2019**, *2*, 290–296.
- [166] M. M. Shi, D. Bao, B. R. Wulan, Y. H. Li, Y. F. Zhang, J. M. Yan, Q. Jiang, *Adv. Mater.* **2017**, *29*, 1606550.
- [167] Z. Geng, Y. Liu, X. Kong, P. Li, K. Li, Z. Liu, J. Du, M. Shu, R. Si, J. Zeng, *Adv. Mater.* **2018**, *30*, 1803498.
- [168] C. Yao, N. Guo, S. Xi, C. Q. Xu, W. Liu, X. Zhao, J. Li, H. Fang, J. Su, Z. Chen, H. Yan, Z. Qiu, P. Lyu, C. Chen, H. Xu, X. Peng, X. Li, B. Liu, C. Su, S. J. Pennycook, C. J. Sun, J. Li, C. Zhang, Y. Du, J. Lu, *Nat. Commun.* **2020**, *11*, 4389.
- [169] J. Wang, L. Yu, L. Hu, G. Chen, H. Xin, X. Feng, *Nat. Commun.* **2018**, *9*, 1795.
- [170] C. Lee, Q. Yan, *Curr. Opin. Electrochem.* **2021**, *29*, 100808.
- [171] D. Liu, H. Ai, W. T. Lou, F. Li, K. H. Lo, S. Wang, H. Pan, *Sustain. Energy Fuels* **2020**, *4*, 3773–3779.
- [172] N. Hoang Truong, J.-S. Kim, J. Lim, H. Shin, *Chem. Eng. J.* **2024**, *495*, 153108.
- [173] M. W. Beutel, R. Duvil, F. J. Cubas, D. A. Matthews, F. M. Wilhelm, T. J. Grizzard, D. Austin, A. J. Horne, S. Gebremariam, *Crit. Rev. Environ. Sci. Technol.* **2016**, *46*, 673–700.
- [174] Q. Chen, M. Wang, J. Zhang, W. Shi, A. E. Mynett, H. Yan, L. Hu, *Water Res.* **2019**, *163*, 114890.
- [175] O. Strebel, W. H. M. Duynisveld, J. Böttcher, *Agric. Ecosyst. Environ.* **1989**, *26*, 189–

- 214.
- [176] E. Abascal, L. Gómez-Coma, I. Ortiz, A. Ortiz, *Sci. Total Environ.* **2022**, *810*, 152233.
- [177] Y. Pang, J. Wang, *Sci. Total Environ.* **2021**, *794*, 148699.
- [178] S. Zhao, X. Lu, L. Wang, J. Gale, R. Amal, *Adv. Mater.* **2019**, *31*, 1805367.
- [179] Y. Xiong, Y. Wang, J. Zhou, F. Liu, F. Hao, Z. Fan, *Adv. Mater.* **2024**, *36*, 2304021.
- [180] Z. Wang, D. Richards, N. Singh, *Catal. Sci. Technol.* **2021**, *11*, 705–725.
- [181] X. Zheng, Y. Yan, X. Li, Y. Liu, Y. Yao, *J. Hazard. Mater.* **2023**, *446*, 130679.
- [182] V. Rosca, M. Duca, M. T. DeGroot, M. T. M. Koper, *Chem. Rev.* **2009**, *109*, 2209–2244.
- [183] Y. Li, Y. K. Go, H. Ooka, D. He, F. Jin, S. H. Kim, R. Nakamura, *Angew. Chemie - Int. Ed.* **2020**, *59*, 9744–9750.
- [184] W. Jung, J. Jeong, Y. Chae, W. H. Lee, Y. J. Ko, K. H. Chae, H. S. Oh, U. Lee, D. K. Lee, B. K. Min, H. Shin, Y. J. Hwang, D. H. Won, *J. Mater. Chem. A* **2022**, *15*, 23760–23769.
- [185] L. Yue, W. Song, L. Zhang, Y. Luo, Y. Wang, T. Li, B. Ying, S. Sun, D. Zheng, Q. Liu, A. Farouk, M. S. Hamdy, S. Alfaifi, X. Sun, *Small Struct.* **2023**, *4*, 2300168.
- [186] D. Liu, L. Qiao, S. Peng, H. Bai, C. Liu, W. F. Ip, K. H. Lo, H. Liu, K. W. Ng, S. Wang, X. Yang, H. Pan, *Adv. Funct. Mater.* **2023**, *33*, 2303480.
- [187] H. Zhang, H. Wang, X. Cao, M. Chen, Y. Liu, Y. Zhou, M. Huang, L. Xia, Y. Wang, T. Li, D. Zheng, Y. Luo, S. Sun, X. Zhao, X. Sun, *Adv. Mater.* **2024**, *36*, 2312746.
- [188] Z. Liang, J. Cao, F. Zhao, J. Song, S. Xue, Q. Hua, X. Ren, L. Gao, T. Ma, A. Liu, *ChemCatChem* **2023**, *15*, e202300970.
- [189] M. Wu, G. Zhang, H. Yang, X. Liu, M. Dubois, M. A. Gauthier, S. Sun, *InfoMat* **2022**, *4*, e12265.
- [190] N. Borchers, S. Clark, B. Horstmann, K. Jayasayee, M. Juel, P. Stevens, *J. Power Sources* **2021**, *484*, 229309.
- [191] L. Tang, H. Peng, J. Kang, H. Chen, M. Zhang, Y. Liu, D. H. Kim, Y. Liu, Z. Lin, *Chem. Soc. Rev.* **2024**, *53*, 4877–4925.
- [192] R. Zhang, S. Zhang, Y. Guo, C. Li, J. Liu, Z. Huang, Y. Zhao, Y. Li, C. Zhi, *Energy Environ. Sci.* **2022**, *15*, 3024–3032.
- [193] L. Zhou, X. Chen, S. Zhu, K. You, Z. Wang, R. Fan, J. Li, Y. Yuan, X. Wang, J. Wang, Y. Chen, H. Jin, S. Wang, J. Lv, *Angew. Chemie* **2024**, *136*, e202401924.
- [194] Y. Guo, R. Zhang, S. Zhang, Y. Zhao, Q. Yang, Z. Huang, B. Dong, C. Zhi, *Energy Environ. Sci.* **2021**, *14*, 3938–3944.

- [195] C. Lin, X. Chen, L. Wang, W. Li, Z. Wang, M. Li, J. Feng, B. Hou, W. Yan, *Adv. Funct. Mater.* **2024**, *3*, 2401287.
- [196] S. Chen, G. Qi, R. Yin, Q. Liu, L. Feng, X. Feng, G. Hu, J. Luo, X. Liu, W. Liu, *Nanoscale* **2023**, *15*, 19577–19585.
- [197] Z. Cui, P. Zhao, H. Wang, C. Li, W. Peng, X. Fan, J. Liu, *Appl. Catal. B Environ.* **2024**, *348*, 123862.
- [198] W. Song, L. Yue, X. Fan, Y. Luo, B. Ying, S. Sun, D. Zheng, Q. Liu, M. S. Hamdy, X. Sun, *Inorg. Chem. Front.* **2023**, *10*, 3489–3514.

6. Appendix

6.1 Supporting information: Redox Self-Equilibration in Molecular Vanadium Oxide Mixtures Enables Multi-Electron Storage

Supporting Information:

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1. Instrumentation:

Single-crystal X-ray diffraction (sc-XRD) was measured on a Bruker APEX-II CCD Single-crystal X-ray diffractometer equipped with a graphite monochromator using Mo K α radiation (wavelength $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$)

Thermogravimetric analysis: (TGA) was performed on METTLER TOLEDO TGA 2 STARe system under air flow with a flow rate of 60 mL min^{-1} . A polycrystalline aluminium oxide crucible (PCA) was used. Samples were analyzed in a temperature range of 303.15–1173.15 K. A heating rate of 10 K min^{-1} was applied.

Attenuated total reflectance-Fourier-transformed infrared spectroscopy (ATR-FT-IR) were performed using a Bruker Alpha II equipped with an ATR Platinum Diamond unit. The data were recorded with 24 scans at a resolution of 4 cm^{-1} . All spectra were background-corrected within the Bruker OPUS 8.1 program suite.

^1H nuclear magnetic resonance (^1H -NMR) spectroscopy was recorded on a Bruker AVANCE Neo 400 MHz spectrometer at ambient temperature. ^1H NMR spectra were measured at 400 MHz. Chemical shifts value (δ) for are given in part per million (ppm) using residual solvent protons ($\delta\text{H} = 1.94 \text{ ppm}$ for CD_3CN).

Electron paramagnetic resonance (EPR) spectroscopy was performed on a X-band Bruker Magnetech ESR5000 spectrometer at 40°C temperature on 5 mM acetonitrile solution of **1**. The sample was filled in a glass EPR-tube (diameter 3 mm), the measurement range was 250 to 450 mT with a modulation of 1 mT, a microwave power of 100 mW and a sweep time of 120s. The SpinCount software option was used to calculate the spin quantity in the sample.

Electrochemical investigations

All experiments were carried out inside an argon-filled glovebox (MBraun LABmaster130/M200B eco) in water-free, degassed acetonitrile at room temperature, using 0.1 M $n\text{Bu}_4\text{NPF}_6$ as supporting electrolyte.

a) Voltammetry

Cyclic voltammetry and square wave voltammetry were performed on a CH Instruments 760E potentiostat in three-electrode configuration: a glassy carbon with $d = 3.0 \text{ mm}$ was used as working electrode, a silver wire in acetonitrile containing 0.1 M $n\text{Bu}_4\text{NPF}_6$ and 10 mM AgNO_3 was used as reference electrode and a platinum wire was used as counter electrode. All electrodes were cleaned with acetone and acetonitrile each time before use and the working electrode was additionally polished with $0.05 \mu\text{m Al}_2\text{O}_3$ before each measurement. The recorded potentials were then referenced against the internal standard ferrocene/ferrocenium Fc^+/Fc , unless stated otherwise.

b) Bulk Electrolysis

Chronoamperometry was performed on a CH Instruments 760E potentiostat in three-electrode configuration: platinum wires were used as working and counter electrode, a silver wire in acetonitrile containing 0.1 M $n\text{Bu}_4\text{NPF}_6$ and 10 mM AgNO_3 was used as a reference electrode. All electrodes were cleaned with acetone and acetonitrile before each experiment. During the experiment the working electrode was kept at the defined potential while the solution was stirred vigorously. The electrolysis was stopped once the current dropped below 0.5 % of the initial current.

UV/Vis/NIR spectroscopy was performed on a Cary 3500 UV/Vis/NIR spectrophotometer equipped with a Xenon flash lamp (250 Hz). Measurements were performed in quartz glass cuvettes ($d = 10.0$ mm).

High resolution electrospray ionization mass spectrometry (ESI MS) was carried out on an Agilent 6545 QTOF-HRAM-MS system in negative ion mode at a drying gas temperature of $T = 180$ °C.

CHN Elemental Analysis was carried out by the central analytical service of the Department of Chemistry at Johannes Gutenberg University Mainz using an Elementar Vario EL Cube.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed on Agilent 5800 VDV ICP-OES (optical emission spectrometer) with the automatic sampler SPS 4. The bulk samples were diluted with 5% aqueous nitric acid.

Chemicals: All chemical reagents were obtained commercially and used as received unless stated otherwise. $(n\text{Bu}_4\text{N})_4[\text{V}^{\text{IV}}_2\text{V}^{\text{V}}_8\text{O}_{24}]$ ($(n\text{Bu}_4\text{N})_4\{\text{V}_{10}\}$) was prepared according to the literature.^[1]

2. Experimental data

2.1. Synthesis of $(n\text{Bu}_4\text{N})_8[\text{V}_{14}\text{O}_{34}\text{Cl}][(\text{MgOH})\text{V}_{13}\text{O}_{33}\text{Cl}]$ (Compound 1)

1.003 g $(n\text{Bu}_4\text{N})_4\{\text{V}_{10}\}$ (0.473 mmol, 1 eq.) and 0.101 g MgCl_2 (1.061 mmol, 2.2 eq.) was dissolved in 25 mL acetonitrile. The solution was stirred for 4 h at 75 °C. During this period, the mixture turned dark green, indicating formation of mixed/valent $\text{V}^{\text{IV/V}}$ species. The solution was filtered and set up for diffusion crystallization using diethyl ether as diffusion solvent. After a few days, black cubic single crystals were obtained. The crystals were recovered by filtration, washed twice with water, ethyl acetate and ether. Upon drying, a grey powder was obtained.

Yield: 530 mg (0.234 mmol, 69 % based on V)

MW: 4499.31g/mol

FT-IR (cm^{-1}): 2960.45, 2933.71, 2871.99, 1481.40, 1460.12, 1379.97, 1150.82, 985.35, 876.58, 818.80, 733.83, 672.65, 602.97, 422.83

Elemental Analysis for $\text{C}_{128}\text{H}_{289}\text{N}_8\text{V}_{27}\text{O}_{68}\text{Cl}_2\text{Mg}$ in wt. % (calcd.): C 34.16 (33.97), H 6.43 (6.37), N 2.49 (2.48)

ICP-OES analysis revealed a V : Mg atomic ratio of 27 : 1.17, confirming the expected stoichiometry.

$^1\text{H-NMR}$ (400 MHz, MeCN-d_3): δ 3.20 (8H, $n\text{Bu}_4\text{N}^+$), 1.96 (MeCN-d_3), 1.65 (8H, $n\text{Bu}_4\text{N}^+$), 1.42 (8H, $n\text{Bu}_4\text{N}^+$), 1.00 (12H, $n\text{Bu}_4\text{N}^+$)

A purified sample of **1** for electrochemistry and EPR analyses was prepared under inert atmosphere in the glove box (to prevent traces of surface-oxidation of the crystals of **1** by air). A sample of **1** was dissolved in water-free, de-aerated acetonitrile. Diffusion of diethyl ether into the solution (in the glove box) gave pure crystals of **1** (verified by single-crystal XRD unit cell checks).

2.1. ^1H -NMR Spectroscopy

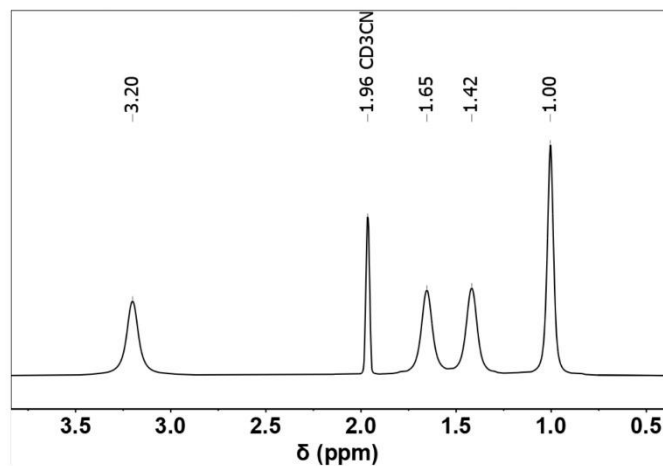


Figure S 1: ^1H NMR of compound **1** in deuterated acetonitrile.

2.2. EPR Spectroscopy

The Easyspin 6.0.2. software suite (<https://easyspin.org/>) was used to simulate isotropic and fast-motional cw EPR spectra of radicals in solution via the implemented garlic algorithm.^[2]

Experimental parameters:

Microwave frequency 9.4463 GHz; microwave power 100 mW; 100kHz modulation amplitude 1 mT.

Simulation parameters for the EPR spectrum of $\{\text{V}_{10}\}$:

Exchange interactions between two ($n = 2$) ^{51}V nuclei ($I = 7/2$; 99.2 % abundance), two hyperfine coupling constants A and two localized electrons indicated by a narrow line width, result in an $(2n)I+1$ hyperfine coupling pattern.^[3] An axial system with two g -values ($g_{\parallel}$ in the direction of the z axis and $g_{\perp}$ in the xy plane) were chosen based on the cluster symmetry.^[4] Optimum fits were obtained using Lorentzian line shapes with a line width of $34.33 \times 10^{-4} \text{ cm}^{-1}$, 103 MHz or 3.83 mT.

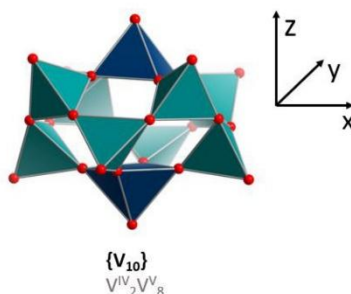


Figure S 2: Structure of the $\{\text{V}_{10}\}$ cluster indicating an axial symmetry of the system.^[1]

Table S 1: EPR simulation parameters for $\{V_{10}\}$.

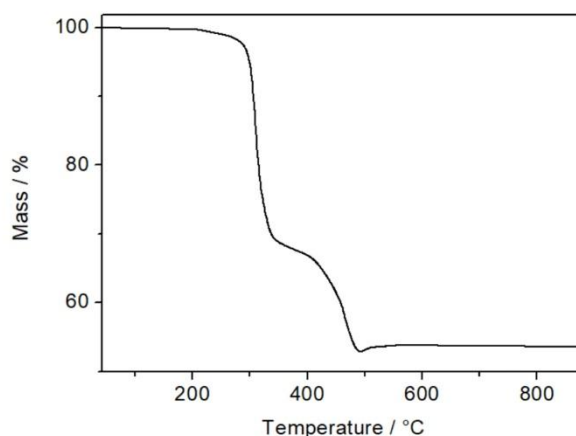
$g_{\perp}$	$g_{\parallel}$	$A_{\perp}$	$A_{\parallel}$
1.962	1.950	$47.948 \times 10^{-4} \text{ cm}^{-1}$ 144 MHz	$42.429 \times 10^{-4} \text{ cm}^{-1}$ 127 MHz

Simulation parameters for the EPR spectrum of compound 1:

For a 1:1 mixture of $\{MgV_{13}\}$ (3 V^{IV} centers) and $\{V_{14}\}$ (5 V^{IV} centers) with strong antiferromagnetic coupling and an odd number of electrons for both clusters, a total spin count of $2 \times S = \frac{1}{2}$ (caused by two unpaired electrons) is expected, which is identical to the well-known $\{V_{10}\}$ reference compound. This was simulated by the combination of two spin systems, both with a weight of 0.5 and $S = \frac{1}{2}$. Due to the interaction of the unpaired electron with the ^{51}V nucleus ($I = 7/2$; 99.2 % abundance), a hyperfine structure could be expected. However, for **1** no hyperfine structure is observed, indicative of the delocalization of the unpaired electrons over a number of structurally similar V sites. For both spin systems optimum fits were obtained with a gaussian line shape and the following line width lw , isotropic hyperfine interaction A and isotropic g-factor g , see Table S2.

Table S 2: EPR simulation parameters for compound 1.

Spin system 1			Spin system 2		
g_{iso}	lw	A_{iso}	g_{iso}	lw	A_{iso}
2.025	$174.666 \times 10^{-4} \text{ cm}^{-1}$ 524 MHz 18.485 mT	$36.44 \times 10^{-4} \text{ cm}^{-1}$ 109 MHz	1.890	$188.333 \times 10^{-4} \text{ cm}^{-1}$ 565 MHz 21.343 mT	$30.83 \times 10^{-4} \text{ cm}^{-1}$ 92 MHz

2.3. Thermogravimetric Analysis**Figure S 3:** TGA measurement of compound **1**. The observed weight loss of 45 % between 200 °C and 600 °C indicates the presence of 8 nBu_4N^+ cations in **1** (calcd.: 43 %).

2.4. Cluster Charge Calculations

Based on the EPR results an odd number of V^{IV} centers for each cluster was indicated. The overall amount of eight tetra-*n*-butylammonium cations to balance the charge results in only three different reasonable electron distributions on the two clusters $\{V_{14}\}$ and $\{MgV_{13}\}$. Based on the crystallographic analysis (four nBu_4N^+ cations are in close proximity of each cluster), a cluster charge of 4- is proposed.

Table S 3: Possible distributions of electrons on $\{V_{14}\}$.

Possible Formula for $\{V_{14}\}$	$(nBu_4N)_2[V_{14}O_{34}Cl]$	$(nBu_4N)_4[V_{14}O_{34}Cl]$	$(nBu_4N)_6[V_{14}O_{34}Cl]$
Number of V^V Centers	11	9	7
Number of V^{IV} centers	3	5	7
Total Cluster Charge	2-	4-	6-

Table S 4: Possible distributions of electrons on $\{MgV_{13}\}$.

Theoretically Calculated Formula of $\{MgV_{13}\}$	$(nBu_4N)_2[(MgOH)V_{13}O_{33}Cl]$	$(nBu_4N)_4[(MgOH)V_{13}O_{33}Cl]$	$(nBu_4N)_6[(MgOH)V_{13}O_{33}Cl]$
Number of V^V centers	12	10	8
Number of V^{IV} centers	1	3	5
Total Cluster Charge	2-	4-	6-

2.5. ESI Mass Spectrometry

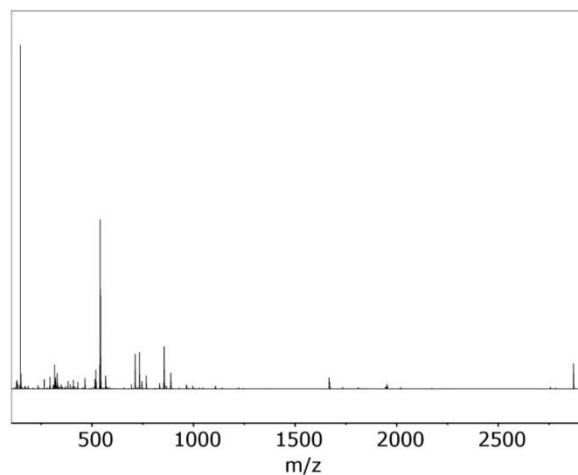


Figure S 4: High-resolution negative-ion mode ESI mass spectrum of **1** (0.05mM) in MeCN.

Table S 5: Detailed peak assignment of the high-resolution negative-ion mode ESI mass spectrum of **1**.

calculated m/z	observed m/z	peak assignment
694.702	694.717	$(^n\text{Bu}_4\text{N})_3 [\text{H}_2\text{V}_7\text{O}_{19}]^{2-}$
712.667	712.705	$(^n\text{Bu}_4\text{N})_3 [\text{V}_7\text{O}_{17}\text{Cl}_2]^{2-}$
734.203	734.181	$(^n\text{Bu}_4\text{N})[\text{HV}_{13}\text{O}_{33}\text{Cl}]^{2-}$
745.691	745.671	$(^n\text{Bu}_4\text{N})[\text{MgV}_{13}\text{O}_{33}\text{Cl}]^{2-}$
753.186	753.158	$\{(^n\text{Bu}_4\text{N})[\text{MgV}_{13}\text{O}_{34}\text{Cl}]\text{-H}\}^{2-}$
767.170	767.147	$(^n\text{Bu}_4\text{N})[\text{V}_{14}\text{O}_{34}\text{Cl}]^{2-}$
833.363	833.348	$(^n\text{Bu}_4\text{N})_2[\text{MgV}_{12}\text{O}_{32}\text{Cl}]^{2-}$
855.346	855.324	$(^n\text{Bu}_4\text{N})_2[\text{HV}_{13}\text{O}_{33}\text{Cl}]^{2-}$
874.328	874.301	$\{(^n\text{Bu}_4\text{N})_2[\text{MgV}_{13}\text{O}_{34}\text{Cl}]\text{-H}\}^{2-}$
888.289	888.313	$(^n\text{Bu}_4\text{N})_2[\text{V}_{14}\text{O}_{34}\text{Cl}]^{2-}$
1667.734	1667.691	$(^n\text{Bu}_4\text{N})_2[\text{HMgV}_{12}\text{O}_{32}\text{Cl}]^-$
1733.668	1733.623	$(^n\text{Bu}_4\text{N})_2[\text{MgV}_{13}\text{O}_{34}\text{Cl}]^-$

Note that the vanadate fragments observed are most likely artefacts formed during the ionization / gas phase transfer process and have been observed for the native **{V₁₂}** as well as other related POM species previously.

2.6. UV/Vis/NIR Spectroscopy

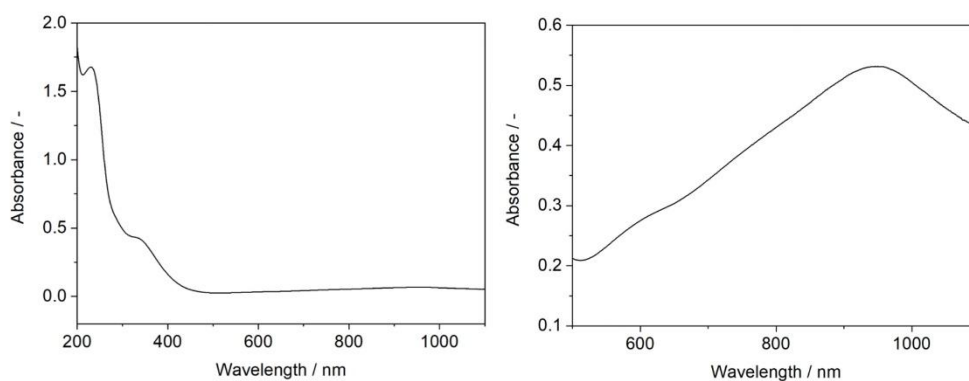


Figure S 5: UV/Vis/NIR spectra of **1** in MeCN. left: $[1] = 15.625 \mu\text{mol/L}$; right: $[1] = 125 \mu\text{mol/L}$.

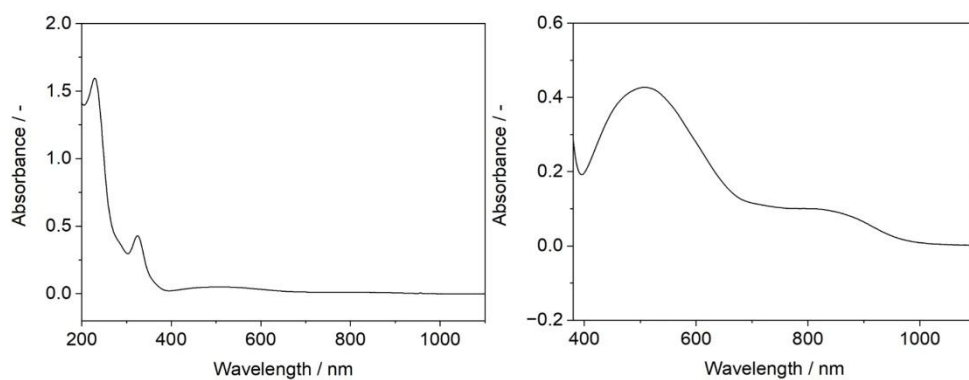


Figure S 6: UV/Vis/NIR spectra of $\{V_{10}\}$ in MeCN. left: $[V_{10}] = 31.25 \mu\text{mol/L}$; right: $[V_{10}] = 250 \mu\text{mol/L}$.

2.7. Temperature dependent UV/Vis/NIR Spectroscopy

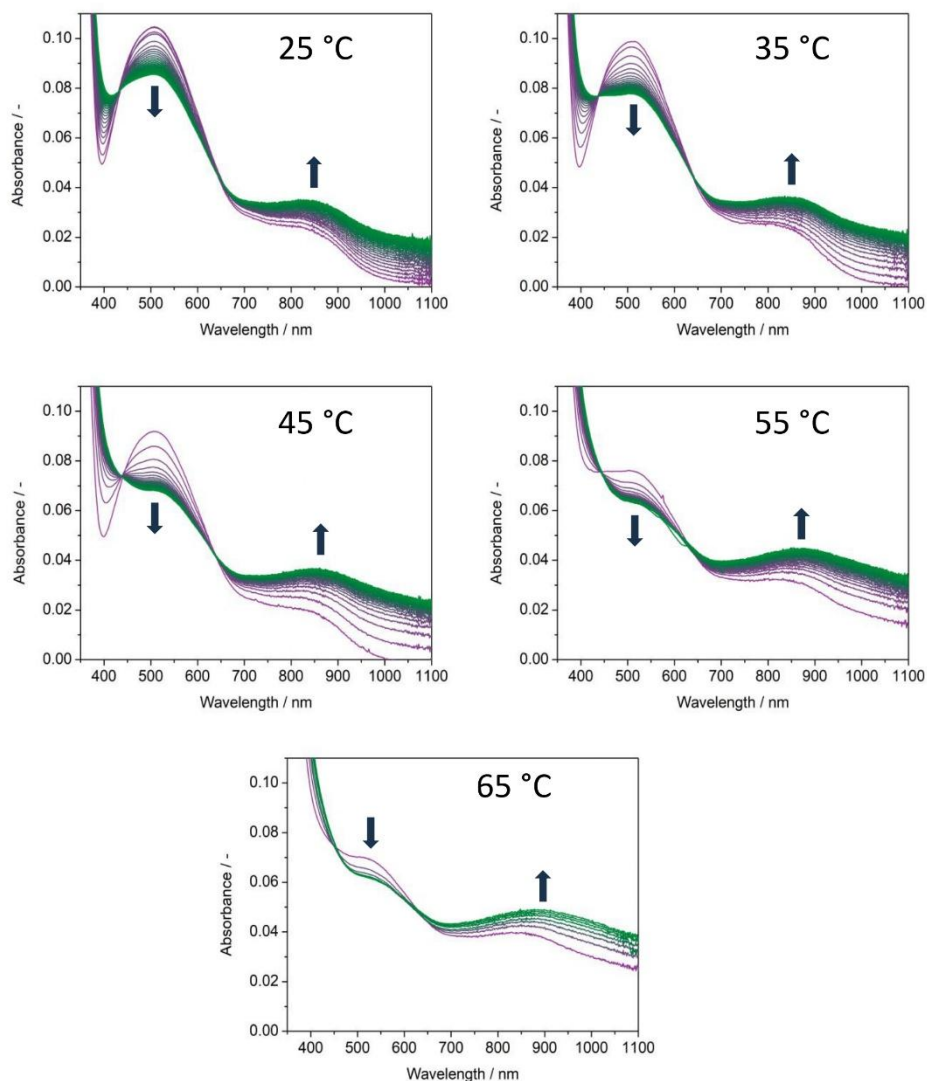


Figure S 7: Temperature dependent UV/Vis-NIR Spectra were measured with a time increment of 60 s, cuvette path length of 2.0 mm, $[\{V_{10}\}] : [MgCl_2 \text{ (anhydrous)}] = 1 : 2.2$ and $[\{V_{10}\}] = 500 \mu M$.

2.8. Determination of the Molar Activation Energy

Temperature dependent UV/Vis/NIR experiments were evaluated using the Arrhenius Equation.^[5]

Arrhenius equation:

Rate constant = k
 Absolute Temperature = T
 Pre-exponential factor = k_0
 Molar activation energy = E_a
 Universal gas constant = R

$$k = k_0 e^{-\frac{E_a}{RT}}$$

Exponential decay fit function for a reaction of first order assuming the decomposition of $\{V_{10}\}$ in presence of Mg^{2+} as the rate determining step:

$$y = y_0 + k_0 e^{-kt}$$

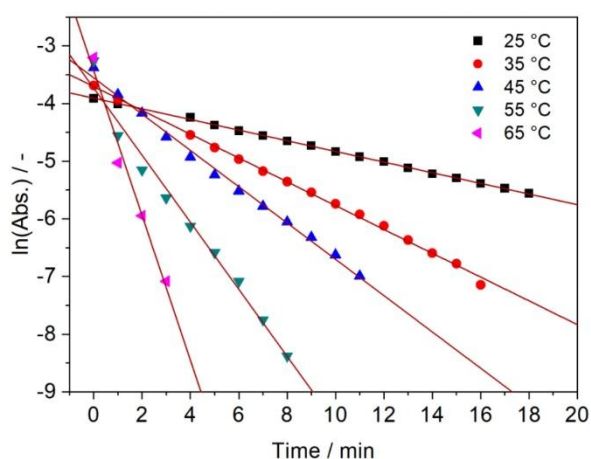


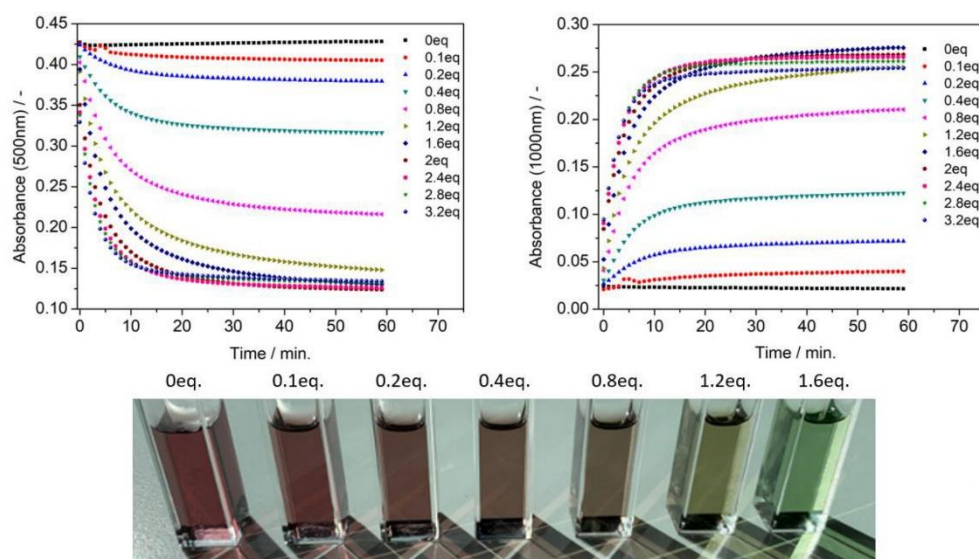
Figure S 8: Linear change of $\ln(\text{Abs } (\lambda = 500 \text{ nm}))$ vs time confirms the first order kinetics.

Table S 6: The fit parameters of the mono-exponential fit **Figure 4d** were used for the Arrhenius Plot **Figure 4c**.

Temperature dependent Exponential Decay Fit Parameters						
Temperature / °C	y_0	Δy_0	k_0	Δk_0	k	Δk
25	0.08419	3.10467E-4	0.02007	2.75406E-4	0.09191	0.00304
35	0.07918	1.31221E-4	0.02458	2.08578E-4	0.20856	0.00438
45	0.07022	2.12505E-4	0.03309	5.84747E-4	0.37575	0.01379
55	0.06567	2.83053E-4	0.0381	0.00115	1.10502	0.08029
65	0.06353	2.94462E-4	0.04062	7.84384E-4	1.74749	0.10992

Table S 7: The fit parameters of the Arrhenius Plot were used to calculate the activation energy.

Linear Fit Parameters of the Arrhenius Plot and Calculated Molar Activation Energy					
$-\frac{E_a}{R} / 1/K$	$\Delta -\frac{E_a}{R} / 1/K$	$\ln(A) / -$	$\Delta \ln(A) / -$	$E_a / \text{kJ/mol}$	$\Delta E_a / \text{kJ/mol}$
-7620.4453	-467.37833	23.1448	1.47342	63.356	3.886

2.9. Mg²⁺ Concentration-dependent UV/Vis/NIR**Figure S 9:** UV/Vis/NIR of $\{V_{10}\}$ was measured during the equilibration time of 1h with a time interval of 1 min at $[V_{10}] = 230 \mu\text{M}$, a temperature of 35 °C and a cuvette pathlength of 10 mm pathlength.

2.10. ATR-FT-IR spectroscopy

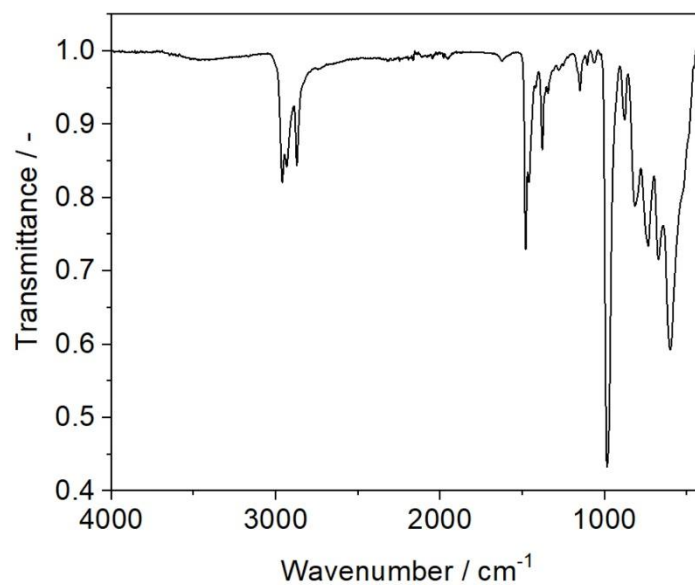
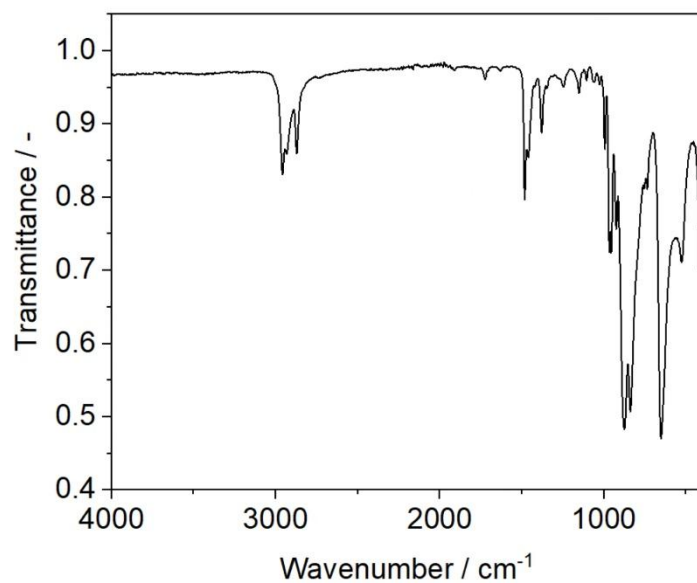


Figure S 10: ATR-FT-IR spectrum of compound 1.

Figure S 11: ATR-FT-IR spectrum of {V₁₀}.

2.11. Electrochemistry

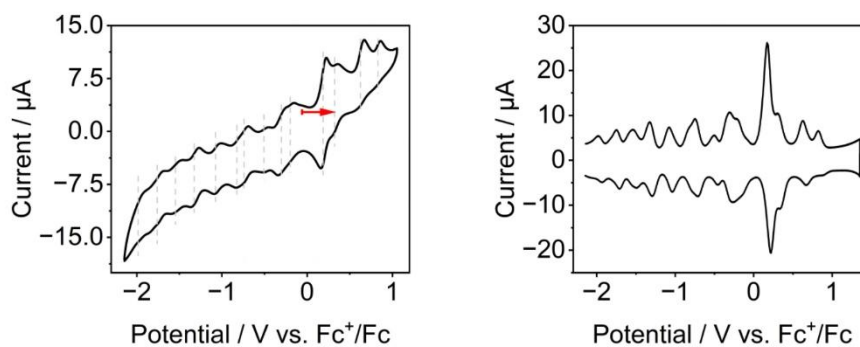
Electrochemical intervals in one-component POMs

Table S 8: Summary of electrochemical intervals between individual redox events in selected classical single-cluster polyoxometalates.

Entry	Abbreviation of POM	Average $\Delta E_{1/2}$ [V]	Reference
1	α -[PW ₁₂ O ₄₀] ³⁻	0.55	T. Ueda et.al. ^[6]
2	H ₃ [PMo ₁₂ O ₄₀]	0.30	M. A. Barteau et.al. ^[7]
3	α -[W ₁₈ O ₅₄ (SO ₃) ₂] ⁵⁻	0.45	L. Cronin et.al. ^[8]
4	[Ca ₂ V ₁₂ O ₃₂ Cl(DMF) ₃] ²⁻	0.41	C. Streb et.al. ^[9]
5	[V ₆ O ₇ (OEt) ₁₂]	0.56	E. Matson et.al. ^[10]
6	(NEt ₄) ₅ [V ₁₈ O ₄₂ (I)]	0.37	K.Y. Monakhov et.al. ^[11]
7	(nBu ₄ N) ₈ [(MgOH)V ₁₃ O ₃₃ Cl][V ₁₄ O ₃₄ Cl] (compound 1)	0.22	This work

Voltammetry

CV and SWV of **1** show fourteen quasi-reversible redox transitions in the potential range from -2.15 V to + 1.35 V (0.1 M nBu₄PF₆ in MeCN): $E_{1/2}$ (vs. Fc/Fc⁺) = - 1.98 V; - 1.76 V; - 1.55 V; - 1.33 V; - 1.08 V; - 0.83 V; - 0.74 V; - 0.51 V; - 0.30 V; - 0.20 V; + 0.18 V; + 0.32 V; + 0.62 V; + 0.82 V.

**Figure S 11:** Cyclic voltammogram (left) and square wave voltammogram (right) of **1**. Conditions: anhydrous, deoxygenated acetonitrile containing nBu₄NPF₆ (0.1 M) as supporting electrolyte (scan rate 0.05 V s⁻¹), [**1**]: 0.5 mM.

2.12. Bulk Electrolysis

Bulk Reduction (BR) of **1**

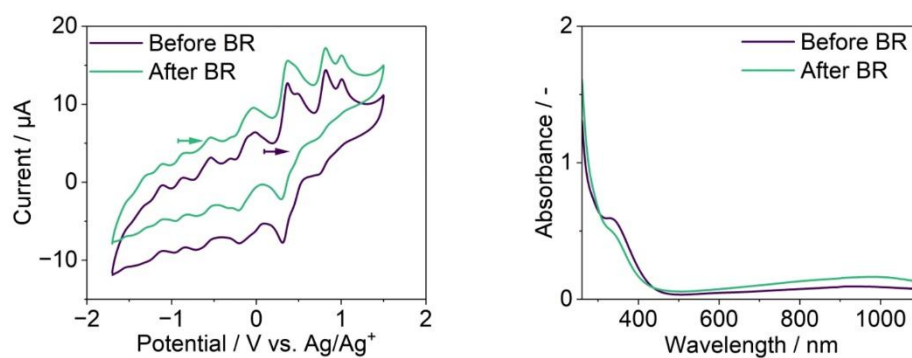


Figure S 12: Left: Comparison of CVs of **1** before (dark blue) and after (turquoise) bulk reduction (BR) ($E = -1.45$ V). Open circuit potentials and scan directions are indicated by arrows. Right: UV/Vis/NIR absorption spectra of **1** before (dark blue) and after (turquoise) bulk reduction.

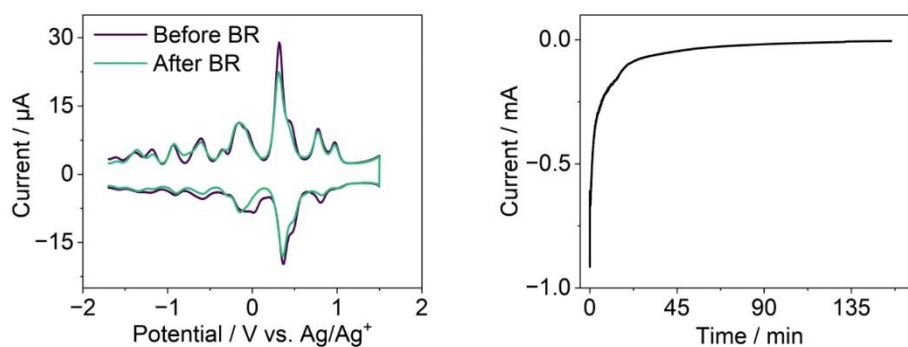


Figure S 13: Left: Square wave voltammogram of **1** before (dark blue) and after (turquoise) bulk reduction ($E = -1.45$ V). Right: Chronoamperogram of bulk electrolysis ($E = -1.45$ V).

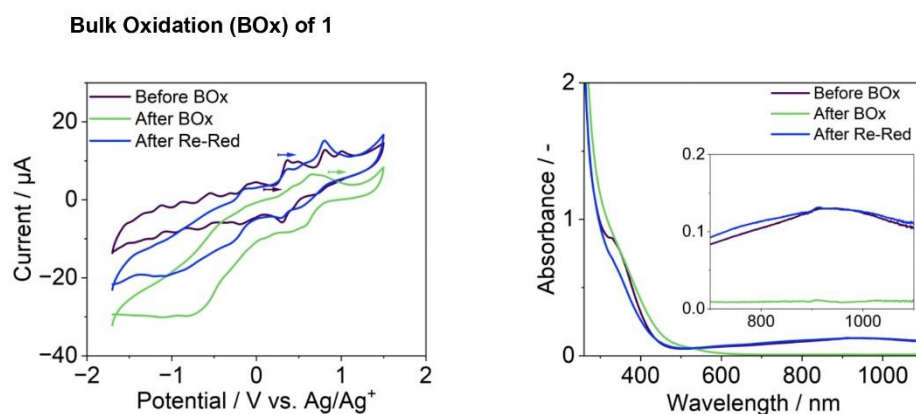


Figure S 14: Left: Comparison of CVs of **1** before (dark blue) and after (green) bulk oxidation (BOx) ($E = +1.22$ V) and after re-reduction (Re-Red) (blue) ($E = +0.09$ V). Open circuit potentials and scan directions are indicated by arrows. Right: UV/Vis/NIR absorption spectra of **1** before (dark blue) and after (green) bulk oxidation.

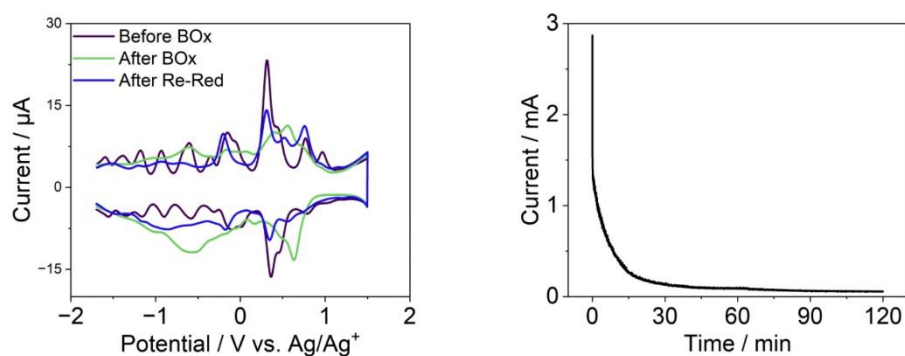


Figure S 15: Left: Square wave voltammogram of **1** before (dark blue) and after (green) bulk electrolysis ($E = +1.22$ V) and after re-reduction (Re-Red) (blue) ($E = +0.09$ V). Right: Chronoamperogram of bulk electrolysis ($E = +1.22$ V).

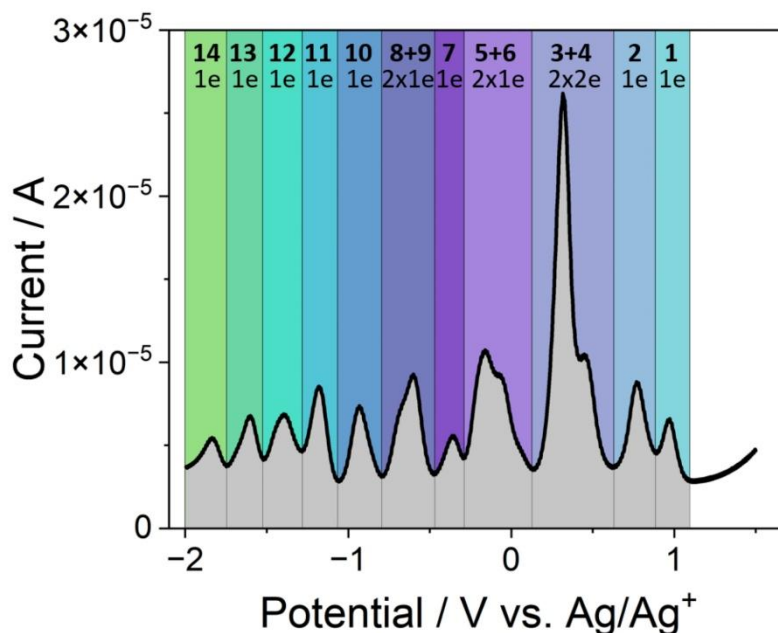
Table S 9: Summary of bulk electrolyses with calculated average number of transferred electrons per cluster.

Entry	Type of Electrolysis	Average # of transferred e^- / cluster	Average # of transferred e^- / formula unit of 1 (containing one $\{\text{MgV}_{13}\}$ and one $\{\text{V}_{14}\}$ cluster)
1	Bulk Reduction ($E = -1.45$ V)	3.93 ± 0.42	7.86 ± 0.84
2	Bulk Oxidation ($E = +1.22$ V)	$4.33 \pm 0.43^{[a]}$	$8.66 \pm 0.86^{[a]}$

^[a] the slightly increased number of electrons transferred during bulk oxidation is currently assigned to undesired oxidative side reactions.

Integration of square wave voltammetry data

To gain initial insights into the number of electrons transferred during the redox transitions in compound **1**, the oxidative branch of the square wave voltammogram (Figure S11) was integrated. In Figure S16, colored potential ranges indicate each integration region. The integrals cover all 14 observed redox transitions.

**Figure S 16:** Upper segment of square-wave voltammogram of **1** showing the integration limits indicated by differently colored regions. The integrals were used to estimate the numbers of electrons transferred for each process, see below.

To estimate the number of electrons transferred in each observed redox transition, we first determined an average integral area assigned for an expected 1-electron transfer. This mean integral area A_{mean} was obtained as average of well-separated signals 1,2,7, 10, 11, 12, 13.

This analysis gave $A_{\text{mean}} [\text{A}\cdot\text{V}] = 1.20 \times 10^{-6} \pm 0.23 \times 10^{-6}$

This value was used to normalize each integral area observed for the individual redox transitions as shown in Table S 10. Note that processes 3 and 4, 5 and 6, 8 and 9 could not be separated as they partially overlap, as shown in Figure S16. Electron transfer numbers were then rounded to the nearest integer number to give the nominal number of electrons transferred. Note that integration of the SWV data is challenging due to the complex nature of the voltammogram, the close spacing and partial overlap of the signals observed.

Table S 10: Summary of the integration of the square wave voltammogram of **1**, and the resulting electron transfer numbers for **1**.

Redox Event	Integral range		Integral Area [A·V]	Estimated number of electrons transferred ^[a]	Nominal number of electrons transferred ^[b]
	E_1 [V]	E_2 [V]			
1	0.885	1.090	9.85E-07	0.82	1
2	0.630	0.885	1.54E-06	1.28	1
3+4	0.128	0.630	5.17E-06	2 x 2.15	2 x 2
5+6	-0.289	0.128	3.03E-06	2 x 1.26	2 x 1
7	-0.469	-0.289	8.24E-07	0.69	1
8+9	-0.794	-0.469	1.95E-06	2 x 0.82	2 x 1
10	-1.065	-0.794	1.32E-06	1.10	1
11	-1.281	-1.065	1.29E-06	1.08	1
12	-1.524	-1.281	1.36E-06	1.13	1
13	-1.747	-1.524	1.16E-06	0.97	1
14	-2.000	-1.747	1.11E-06	0.93	1
			Sum	16.47	16

^[a] calculated as Integral Area divided by A_{mean}

^[b] Obtained by rounding the estimated number of electrons transferred to the nearest integer number.

2.13. Crystallographic Information

Suitable single crystals were mounted onto a microloop using Fomblin oil. X-ray diffraction intensity data were measured at 150 K on a Bruker D8 QUEST diffractometer $\lambda(\text{MoK}\alpha = 0.71073 \text{ \AA})$ equipped with a graphite monochromator. Structure solution was carried out using SHELX-2013^[12] package through OLEX2.^[13,14] Corrections for incident and diffracted beam absorption effects were applied using empirical methods.^[15] Structures were solved by a combination of direct methods and difference Fourier syntheses and refined against F^2 by the full matrix least-squares technique. Most non-hydrogen atoms were refined anisotropically. A two-component twin model was used for the refinement. The metal oxo framework was refined fully anisotropically. Restraints (SIMU and DELU) on the counter cations were applied. The CIF files can be obtained free of charge from the CCDC, reference number CCDC 2369209.

Table S10: Crystallographic parameters for the samples

Empirical formula	$\text{C}_{126}\text{Cl}_2\text{Mg}_{0.84}\text{N}_8\text{O}_{68}\text{V}_{27.2}$
CCDC reference no	2369209
Formula weight	4188.27
Temperature/K	150.00
Crystal system	monoclinic
Space group	C2
$a/\text{\AA}$	23.189(4)
$b/\text{\AA}$	23.197(4)
$c/\text{\AA}$	17.660(3)
$\alpha/^\circ$	90
$\beta/^\circ$	90.089(6)
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	9500(3)
Z	4
T / K	150(1)
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.464
μ/mm^{-1}	1.370
F(000)	4668.0
Radiation	MoK α ($\lambda = 0.71073$)
2θ range for data collection/ $^\circ$	4.6 to 52.8
Index ranges	$-28 \leq h \leq 28$, $-29 \leq k \leq 29$, $-22 \leq l \leq 22$
Reflections collected	94631
Independent reflections	19413 [$R_{\text{int}} = 0.0980$, $R_{\text{sigma}} = 0.0704$]
Data/restraints/parameters	15471/905/1069
Goodness-of-fit on F^2	1.093
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0822$, $wR_2 = 0.2142$
Final R indexes [all data]	$R_1 = 0.1084$, $wR_2 = 0.2492$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	1.24/-0.85

2.14. Electrochemical reference studies

To assess the effects of simple physical mixing of two structurally or chemically related polyoxovanadate clusters, the following studies were performed. 1:1 molar mixtures of the related species $[\text{H}_3\text{V}_{10}\text{O}_{28}]^{3-}$ ^[16] and $\{\text{V}_{10}\}$, as well as $\{\text{V}_{12}\}_{\text{half-sphere}}$ ^[17] and $\{\text{Ca}_2\text{V}_{12}\}$ ^[18] were prepared and analyzed by SWV, see Figure S17. The data show that part of the electrochemical signals is retained, while ^{51}V NMR analysis of the reaction solutions indicates that partial degradation and/or conversion of the original clusters is observed, thus the solutions are not fully redox-stable.

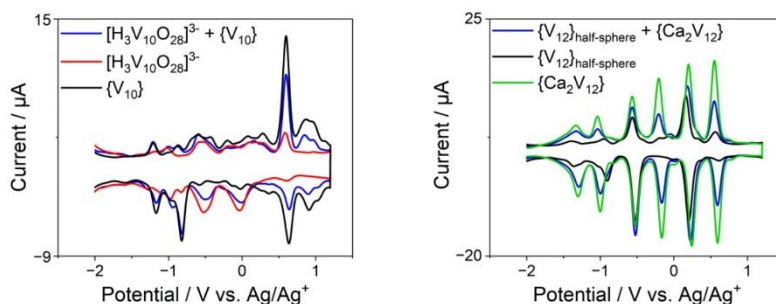
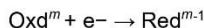


Figure S 17: Left: Square wave voltammograms of $[\text{H}_3\text{V}_{10}\text{O}_{28}]^{3-}$, $\{\text{V}_{10}\}$ and their 1:1 molar mixture. Right: Square wave voltammograms of $\{\text{V}_{12}\}_{\text{half-sphere}}$, $\{\text{Ca}_2\text{V}_{12}\}$ and their 1:1 molar mixture. Solvent: De-aerated, degassed and dry MeCN containing $(n\text{Bu}_4\text{N})\text{PF}_6$ (0.1 M).

2.15. Computational Section

Geometry optimizations of the clusters in the gas-phase and solution phase were carried out using density functional theory calculations with the B3LYP^[19] functional combined with the def2-SVP basis set.^[20] Solvation effects were considered using the SMD implicit solvation model (acetonitrile).^[21] All calculations were performed using the Gaussian 16 package.^[22]

Computational redox potentials: One-electron redox process of a redox reaction can be simply defined in terms of a half-cell reaction as follows:



Where Oxd is an oxidized species and Red is a reduced species. The absolute redox potential $E_{\text{ET}}^{\text{abs}}$ of this redox couple is calculated by eq. (1), where $\Delta G^0_{(\text{s})}$ is the free energy change in solution and F is Faraday's constant:

$$E_{\text{ET}}^{\text{abs}} = -\frac{\Delta G^0_{(\text{s})}}{F} \quad (1)$$

The thermodynamic cycle shown below is used to calculate reduction potentials. This is a schematic illustration of gas-phase and solution-phase reactions, as well as the relation between the phases.

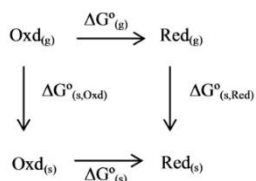


Figure S18: Thermodynamic cycle for the calculation of Gibbs free energies of a one-electron reduction process.

Based on the thermodynamic cycle, $\Delta G^0_{(s)}$ can be expressed as

$$\Delta G^0_{(s)} = \Delta G^0_{(g)} + \Delta G^0_{(s,\text{Red})} - \Delta G^0_{(s,\text{Oxd})} \quad (2)$$

Where $\Delta G^0_{(s)}$ is the free energy change in the gas phase, while $\Delta G^0_{(s,\text{Oxd})}$ and $\Delta G^0_{(s,\text{Red})}$ are the solvation free energies of the oxidized and reduced species in acetonitrile, respectively.

Experimentally, the redox potentials are quoted relative to the Fc^+/Fc external standard with a reference potential of $E_{\text{exp,RE}}^{\text{abs}} = 0.40 \text{ V}$ relative to the standard hydrogen electrode.^[23] The theoretical redox potentials with respect to the experimental reference are calculated using equation (3):

$$E_{\text{ET}}^{\text{calc}} (\text{V vs. Fc}/\text{Fc}^+) = E_{\text{ET}}^{\text{abs}} - E_{\text{SHE}}^{\text{abs}} - E_{\text{exp,RE}}^{\text{abs}} \quad (3)$$

Where $E_{\text{SHE}}^{\text{abs}}$ denotes the absolute electrode potential of the standard hydrogen electrode.

The experimental and calculated reduction potential of $\{\text{V}_{14}\}$ and $\{\text{MgV}_{13}\}$ are summarized in table S11.

Table S11. Experimental and calculated reduction potentials for $\{\text{V}_{14}\}$ and $\{\text{MgV}_{13}\}$.

No	Assignment	$E_{\text{exp.}} / \text{V}^{[a]}$	$E_{\text{calcd.}} / \text{V}^{[a]}$
8	$\{\text{MgV}_{13}\}^{4-} + e^- \rightarrow \{\text{MgV}_{13}\}^{5-}$	-0.73	-0.68
9	$\{\text{V}_{14}\}^{4-} + e^- \rightarrow \{\text{V}_{14}\}^{5-}$	-0.83	-0.81

^[a] E_{red} vs. Fc^+/Fc .

3. References

- [1] K. Okaya, T. Kobayashi, Y. Koyama, Y. Hayashi, K. Isobe, *Eur J Inorg Chem* **2009**, 2009, 5156–5163.
- [2] S. Stoll, A. Schweiger, *Journal of Magnetic Resonance* **2006**, 178, 42–55.
- [3] R. L. Belford, N. D. Chasteen, H. So, R. E. Tapscott, *J Am Chem Soc* **1969**, 91, 4675–4680.
- [4] Q. Chen, D. P. Goshorn, C. P. Scholes, X. L. Tan, J. Zubieta, *J Am Chem Soc* **1992**, 114, 4667–4681.
- [5] K. J. Laidler, *J Chem Educ* **1984**, 61, 494.
- [6] T. Ueda, K. Kodani, H. Ota, M. Shiro, S.-X. Guo, J. F. Boas, A. M. Bond, *Inorg Chem* **2017**, 56, 3990–4001.
- [7] Y. Cao, J.-J. J. Chen, M. A. Barteau, *Journal of Energy Chemistry* **2020**, 50, 115–124.

- [8] N. Fay, A. M. Bond, C. Baffert, J. F. Boas, J. R. Pilbrow, D.-L. Long, L. Cronin, *Inorg Chem* **2007**, *46*, 3502–3510.
- [9] S. Greiner, B. Schwarz, M. Ringenberg, M. Dürr, I. Ivanovic-Burmazovic, M. Fichtner, M. Anjass, C. Streb, *Chem Sci* **2020**, *11*, 4450–4455.
- [10] L. E. VanGelder, A. M. Kosswattaarachchi, P. L. Forrestel, T. R. Cook, E. M. Matson, *Chem Sci* **2018**, *9*, 1692–1699.
- [11] O. Linnenberg, M. Moors, A. Solé-Daura, X. López, C. Bäumer, E. Kentzinger, W. Pyckhout-Hintzen, K. Yu. Monakhov, *The Journal of Physical Chemistry C* **2017**, *121*, 10419–10429.
- [12] G. M. Sheldrick, *Acta Crystallogr A* **2008**, *64*, 112–122.
- [13] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J Appl Crystallogr* **2009**, *42*, 339–341.
- [14] L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard, H. Puschmann, *Acta Crystallogr A Found Adv* **2015**, *71*, 59–75.
- [15] R. H. Blessing, *Acta Crystallogr A* **1995**, *51*, 33–38.
- [16] V. W. Day, W. G. Klemperer, D. J. Maltbie, *J Am Chem Soc* **1987**, *109*, 2991–3002.
- [17] V. W. Day, W. G. Klemperer, O. M. Yaghi, *J Am Chem Soc* **1989**, *111*, 5959–5961.
- [18] S. Greiner, B. Schwarz, M. Ringenberg, M. Dürr, I. Ivanovic-Burmazovic, M. Fichtner, M. Anjass, C. Streb, *Chem Sci* **2020**, *11*, 4450–4455.
- [19] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- [20] F. Weigend, R. Ahlrichs, *Physical Chemistry Chemical Physics* **2005**, *7*, 3297.
- [21] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *Journal of Physical Chemistry B* **2009**, *113*, 6378–6396.
- [22] M. J. Frisch, G. W. Trucks, H. B. Schlegel, V. B. M. A. Robb, J. R. Cheeseman, G. Scalmani, A. V. M. G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, H. P. H. J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, D. W.-Y. J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, A. P. F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, N. R. T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, R. F. G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, H. N. J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, J. E. P. T. Vreven, K. Throssell, J. A. Montgomery, Jr., K. N. K. F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, J. N. V. N. Staroverov, T. A. Keith, R. Kobayashi, S. S. I. K. Raghavachari, A. P. Rendell, J. C. Burant, R. C. J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, O. F. J. W. Ochterski, R. L. Martin, K. Morokuma, and D. J. F. J. B. Foresman, *Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford CT* **2016**.
- [23] R. M. Olson, A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J Chem Theory Comput* **2007**, *3*, 2046–2054.

6.2 Supporting information: Mixed-Valent Redox-Equilibrated Polyoxovanadates for Symmetric Non-Aqueous Redox-Flow Batteries

Supporting Information

Mixed-Valent Redox-equilibrated Polyoxovanadates for Symmetric Non-Aqueous Redox-Flow Batteries

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1. Instrumentation

Materials and general information for synthesis: All reagents and solvents were purchased from commercial suppliers and were used without further purification. Solvents for UV-Vis spectroscopy were at least HPLC grade or spectroscopic grade. Solvents for cyclic voltammetry were HPLC grade and water-free, all other solvents were at least high purity grade or HPLC grade.

Attenuated total reflectance-Fourier-transform infrared spectroscopy (ATR-FT-IR) was performed on a Bruker Alpha II equipped with an ATR Platinum Diamond unit. The data were recorded with 24 scans at a resolution of 4 cm^{-1} .

Raman spectra were conducted on a Laser Micro Confocal Raman Spectroscopy (Witec Alpha 300R).

Operando UV-Vis spectra were recorded on a single-channel fiber-optic spectrometer (Avantes AvaSpec-ULS2048XL) using a deuterium-halogen light source (Avantes AvaLight DH-S-BAL). Gas-tight quartz glass cuvettes ($d = 10.0\text{ mm}$) were used for all measurements.

Electrochemical Measurements: The electrochemical properties of the **{MV₁₃}** were investigated with an electrochemical workstation (CHI 760E, CH Instruments, Inc. USA) with a standard three-electrode electrochemical cell at room temperature. In this study, a platinum plate ($1 \times 1\text{ cm}$) and a silver wire in $0.01\text{ M AgNO}_3 + 0.1\text{ M } (n\text{Bu}_4\text{N})\text{PF}_6$ (electrochemical grade) in acetonitrile were used as counter electrode and reference electrode, respectively. A glassy carbon rotating disk electrode (RDE with active area of 0.1256 cm^2) was utilized as working electrode, which was polished by Al_2O_3 slurries, then washed thoroughly with water, acetone and acetonitrile successively prior to use. All electrode potentials in this study were calibrated to the ferrocenium/ferrocene (Fc^+/Fc) as internal standard. All electrochemical experiments were performed in anhydrous MeCN using $(n\text{Bu}_4\text{N})\text{PF}_6$ (0.1 M , electrochemical grade) as supporting electrolyte. The solutions were purged with N_2 for at least 30 min and kept under a slight positive N_2 pressure while performing the measurements.

Redox flow battery assembly and test: the redox flow battery setup was commercially obtained from Redox-Flow (Denmark), the structure of the battery was shown in Figure S1. The serpentine flow fields are made from graphite with an effective area of 6.25 cm^2 . The Celgard 2400 membrane and carbon felts were used without any pretreatment. The reservoirs of anolyte and catholyte were both filled with the 25 ml electrolyte of $1\text{ mM } \{\text{MV}_{13}\}$ and $0.1\text{ M } n\text{Bu}_4\text{NPF}_6$. Before the test, the assembled battery was purged with nitrogen (washed through acetonitrile) for 30 min and kept under a slight positive N_2 pressure during the measurement. During the test, the electrolytes were circulated by the peristaltic pump with a flow rate of 15 ml min^{-1} . All the galvanostatic measurements of the battery were performed with a Neware battery tester CT-4008T5V6A-S1 at room temperature.

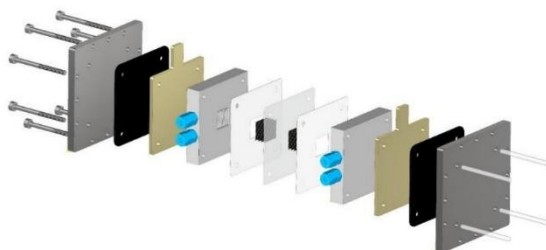


Figure S1. Structure of the RFB setup (Source from <https://redox-flow.com/shop/redox-flow-battery-test-cell/>).

2. Experimental data

2.1. The synthesis of **{MV₁₃}** is first described in reference^[1] and is given here for completeness.

Synthesis of (nBu₄N)₄[V₁₀O₂₆]: vanadium (V) oxide (3.62 g, 0.02 mol) was dispersed into 20 mL H₂O with vigorous stirring at 60 °C, then 7 mL (50.2 mmol) triethylamine was added and stirred for 20 min. Subsequently, 100 mL acetone containing (nBu₄N)Br (18.9 g, 59 mmol) and 5 mL H₂O containing VOSO₄ (2.17 g, 0.0133 mol) were added into the above solution. The mixture was stirred for 2 h at room temperature, then the precipitate was collected by filtration and washed twice with water, ethanol and diethyl ether, respectively. The product was dried at room temperature overnight. Yield: 93 % (based on V).

Synthesis of {MV₁₃} nBu₄N[MV₁₃O₃₃Cl] (M= V=O²⁺ {V₁₄} or MgOH⁺ {MgV₁₃}): the obtained precursor (nBu₄N)₄[V₁₀O₂₆] (1.00 g 0.47 mmol) and MgCl₂ (0.10 g, 1.06 mmol) were dissolved in 25 mL acetonitrile, the mixture was stirred for 4 h at 75 °C. After cooling, the precipitate was removed by filtration, and the filtrate was setup for diffusion crystallization with diethyl ether as diffusion solvent. After 3 to 4 days, black cubic crystals were collected and washed with water, ethyl acetate and diethyl ether, respectively. The final product **{MV₁₃}** was dried at room temperature. Yield: 65 % based on V.

ATR-FT-IR spectrum of **{MV₁₃}**.

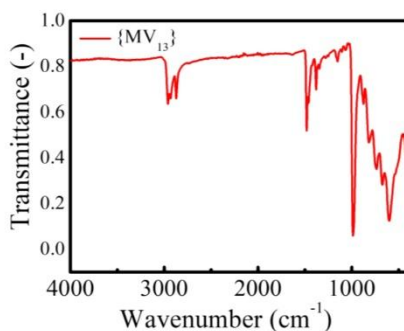


Figure S2. ATR-FT-IR of **{MV₁₃}**. Characteristic IR bands (in cm⁻¹): 2965 (C-H stretching, alkane); 2936 (C-H stretching, alkane); 2875 (C-H stretching, alkane); 1478; 1456; 1376; 1341; 1273; 1146; 1105; 1056; 985 (symmetric V=O, terminals Oxygen); 890; 874 (anti-symmetric stretching V-O); 817; 743 (V-O-V, symmetric); 667 (V3-Oμ3, asymmetric).

2.2. Analysis of diffusion coefficient and electron transfer rate

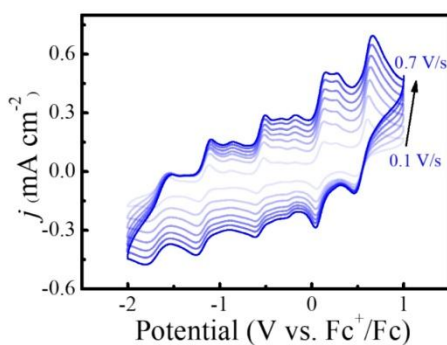


Figure S3. CV curves of {MV₁₃} at different scan rate ranging from 0.1 V s⁻¹ to 0.7 V s⁻¹ within scan range of -2 to 1 V vs. Fc^{+/0}/Fc.
Kinetic calculations: Nicholson method

For the Nicholson method, the diffusion coefficients D_0 of different redox processes for {MV₁₃} were calculated using the following formula:

$$i_p = (2.69 \times 10^5) n^{3/2} A C D_0^{1/2} \nu^{1/2} \quad (1)$$

where i_p is the peak current of the redox process, n is the number of electrons involved in the redox process, A is effective area of the working electrode, C is the concentration of the active species, ν is the scan rate, D is the diffusion coefficient which can be calculated from the gradient of i_p vs. $\nu^{1/2}$.

The electron transfer rate constant (k_0) of the {MV₁₃} redox processes were determined using the following equations:

$$\Psi = (-0.6288 + 0.0021 \Delta E_p) / (1 - 0.017 \Delta E_p) \quad (2)$$

$$\Psi = k_0 (\pi D_0 n F / RT)^{-1/2} \nu^{1/2} \quad (3)$$

where Ψ is a dimensionless parameter, ΔE_p is the peak separation of the redox process, F is the Faraday constant ($F = 96485$ C/mol), R is the universal molar gas constant ($R = 8.314$ J/mol·K), T is the temperature (here: $T = 298$ K). The electron rate constant k_0 can be obtained from the gradient of the fitted plotting of Ψ vs. $\nu^{1/2}$ line.

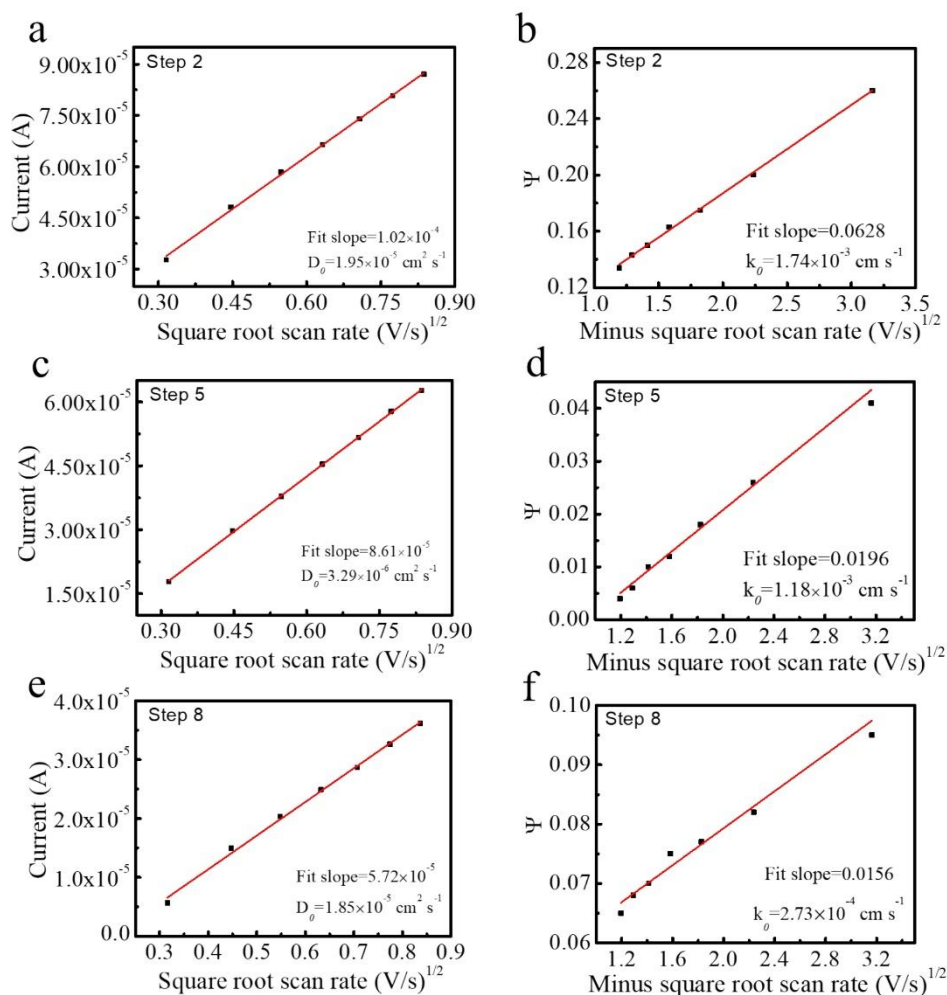


Figure S4. Data analysis for D_0 and k_0 calculation for different redox processes of $\{\text{MV}_{13}\}$ with Nicholson method. (a)-(b) for step 2, (c)-(d) for step 5, (e)-(f) for step 8. Do was obtained from the plots of peak current vs. square root of scan rate ($v^{1/2}$), k_0 was obtained from the plots of Ψ vs. minus square root of scan rate ($v^{-1/2}$).

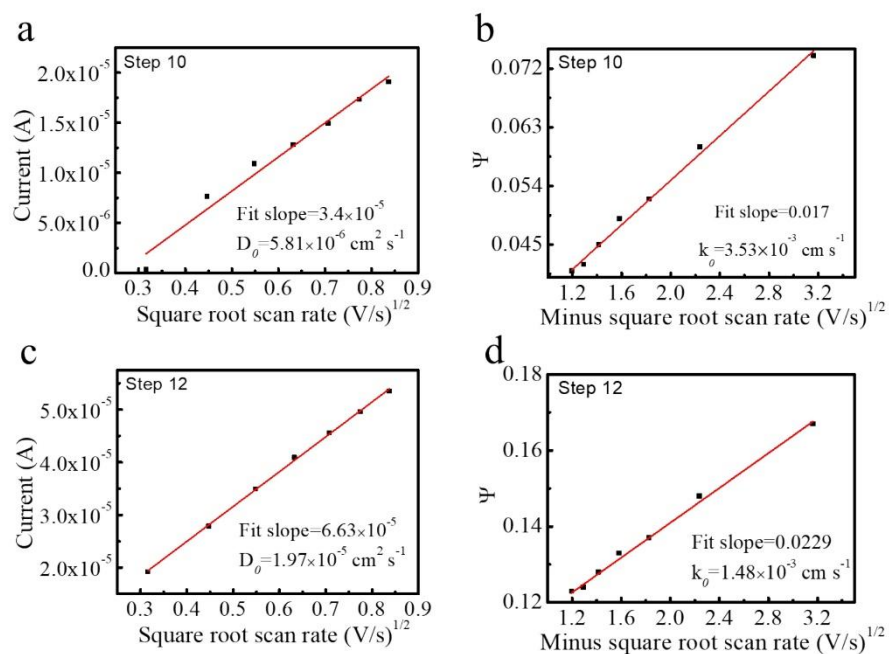


Figure S5. Data analysis for D_0 and k_0 calculation for different redox processes of $\{MV_{13}\}$ with Nicholson method. (a)-(b) for step 10, (c)-(d) for step 12. D_0 was obtained from the plots of peak current vs. square root of scan rate ($v^{1/2}$), k_0 was obtained from the plots of Ψ vs. minus square root of scan rate ($v^{-1/2}$).

Kinetic calculations: Koutecký-Levich approach

For the Koutecký-Levich approach, the diffusion coefficient D_0 of different redox processes for **{MV₁₃}** cluster were calculated according to Levich equation:

$$1/i_m = 1/i_k + 1/(B_L \omega^{1/2}) \quad (4)$$

$$B_L = 0.620nFAcD_0^{2/3}\nu^{-1/6} \quad (5)$$

In herer, $n = 1$. Faraday's constant $F = 96485$ C/mol. Electrode area $A = 0.1256$ cm². Concentration $c = 0.1$ mM for **{MV₁₃}**. ω : rotation rate (rad/s). The kinematic viscosity $\nu = 13.92$ cm²/s (experiments determination), and D_0 represents the diffusion coefficient.

By plotting i_m^{-1} vs. $\omega^{-1/2}$, the diffusion coefficient D_0 can be calculated from the gradient of the fitted line.

The kinetic currents (i_k) for different overpotentials (η) were obtained from Eq.6 by drawing the plotting i_m^{-1} vs. $\omega^{-1/2}$ and fitting the y intercept. The electron transfer rate constant was calculated according to Butler-Volmer equation:

$$\text{Log}(i_k) = \log(nFck_0) + anF\eta/2.303RT \quad (6)$$

$$i_0 = FAc k_0 \quad (7)$$

By plotting $\log(i_k)$ vs. η , i_0 can be obtained from the x intercept, and k_0 can be obtained by Eq.7.

Kinetic calculations: Koutecký-Levich method

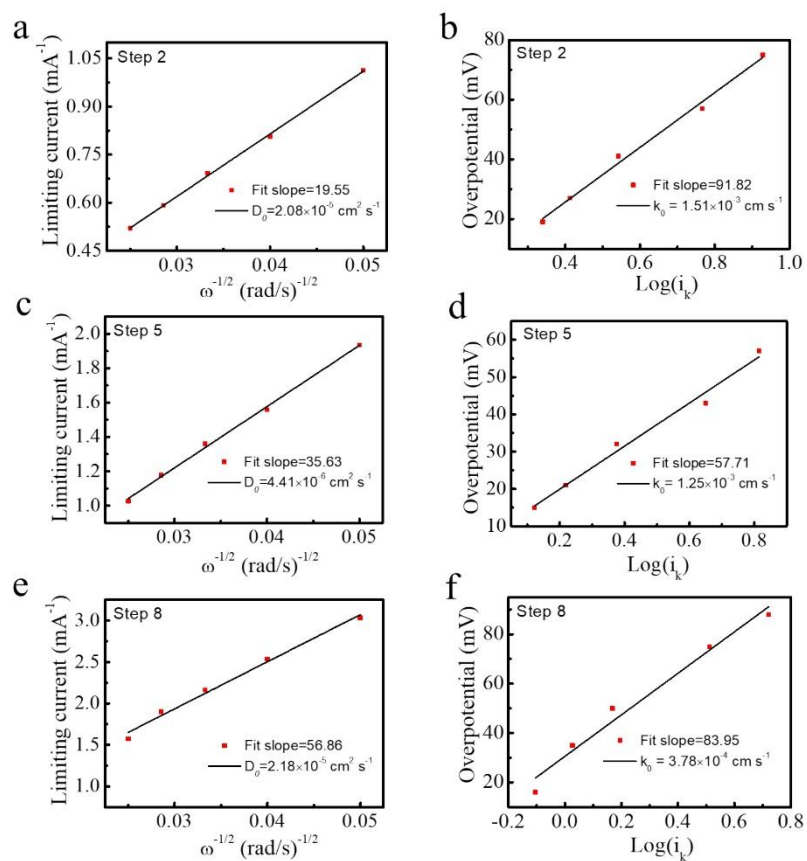


Figure S6. Data analysis for D_0 and k_0 calculation for different redox processes of {MV13} in acetonitrile with Koutecký-Levich method. (a)-(b) for step 2, (c)-(d) for step 5, (e)-(f) for step 8. D_0 and k_0 were calculated according to equation 4 - equation 7.

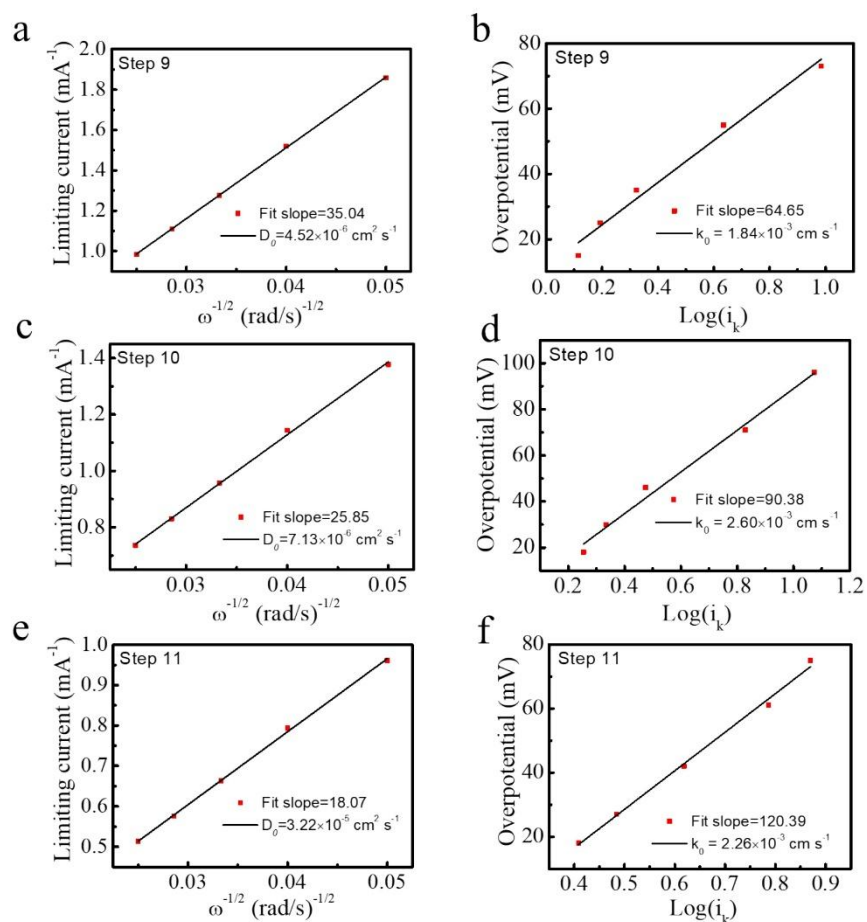


Figure S7. Data analysis for D_0 and k_0 calculation for different redox processes of {MV13} in acetonitrile with Koutecký-Levich method. (a)-(b) for step 9, (c)-(d) for step 10, (e)-(f) for step 11. D_0 and k_0 were calculated according to equation 4 - equation 7.

Table S1. Electrochemical kinetics parameters for {MV13}

Redox process ^a	D_0 (N) [cm ² s ⁻¹]	k_0 (N) [cm s ⁻¹]	D_0 (K-L) [cm ² s ⁻¹]	k_0 (K-L) [cm s ⁻¹]
2	1.95×10^{-5}	1.74×10^{-3}	2.08×10^{-5}	1.51×10^{-3}
5	3.29×10^{-6}	1.18×10^{-3}	4.41×10^{-6}	1.25×10^{-3}
8	1.85×10^{-5}	2.73×10^{-4}	2.18×10^{-5}	3.78×10^{-4}
9			4.52×10^{-6}	1.84×10^{-3}
10	5.81×10^{-6}	3.53×10^{-3}	7.13×10^{-6}	2.60×10^{-3}
11			3.22×10^{-5}	2.26×10^{-3}
12	1.97×10^{-5}	1.48×10^{-3}		

^aOnly well-separated redox processes were used in these analyses

2.3. Permeability studies

The permeability of the $\{\text{MV}_{13}\}$ cluster across the separator was measured by an H-type device with two counterpart reservoirs, which was separated by a commercial Celgard 2400 membrane. One reservoir was filled with a solution of 1 mM for $\{\text{MV}_{13}\}$ in acetonitrile, and the second reservoir was filled with acetonitrile containing 1 mM $(n\text{Bu}_4\text{N})\text{PF}_6$ to prevent significant osmotic pressure. The reservoir volume was 5 ml. The solutions were sampled at regular time intervals, and the concentration of $\{\text{MV}_{13}\}$ was determined by UV-vis spectroscopy (Cary Workstation 3500). The permeability of the membrane was calculated with the following equation:

$$P = \frac{\Delta \ln(1 - \frac{2C_t}{C})(\frac{Vd}{2A})}{\Delta t} \quad (8)$$

where V is the initial volume of the solution in the reservoir, t is the time when measure the samples, C_t is the measured concentration of the $\{\text{MV}_{13}\}$ at time t , A is effective area of the membrane exposed to solution (1.76 cm^2), d is the thickness of the membrane ($25 \text{ }\mu\text{m}$), C is the initial concentration of $\{\text{MV}_{13}\}$, P is the permeability (cm^2/s) which can be obtained from the gradient of plotting $-\ln(1 - \frac{2C_t}{C})(\frac{Vd}{2A})$ vs. Δt .

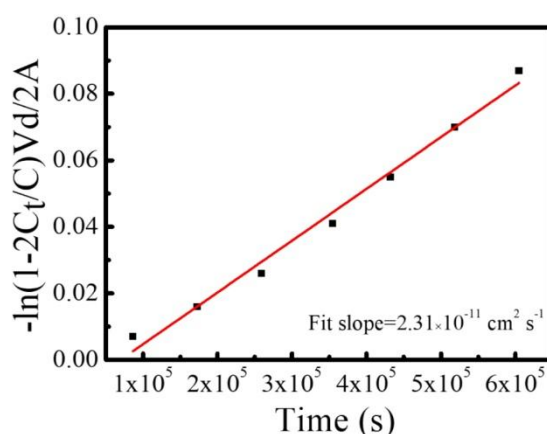


Figure S8. Permeability test to analyze the migration of $\{\text{MV}_{13}\}$ across a Celgard 2400 membrane.

Table S2. Permeability comparison of previously reported active species in electrolyte for RFBs.

Active species	Solvent	Membrane	Permeability ($\text{cm}^2 \text{ s}^{-1}$)	Ref
$\{\text{MV}_{13}\}$	Acetonitrile	Celgard 2400	2.35×10^{-11}	This work
$[\text{S}_2\text{W}_{18}\text{O}_{62}]^{4-}$	Acetonitrile	AMI-7001	1.31×10^{-7}	[2]
MV	H ₂ O	Selemon DSV AEM	3.4×10^{-9}	[3]
BTMAP-Vi	H ₂ O	Selemon DSV AEM	6.7×10^{-10}	[3]
(PPBPY)Br ₂	H ₂ O	E620K	1.17×10^{-12}	[4]
PSS-TEMPO	H ₂ O	E620K	5.36×10^{-12}	[4]
(SPR) ₂ V	H ₂ O	N212CEM	8.0×10^{-9}	[5]

BPP-Vi

H₂O

N212 CEM

 7.0×10^{-11}

[5]

2.4. Electrochemical studies

2.4.1 The charge/discharge curve and efficiencies at different current densities.

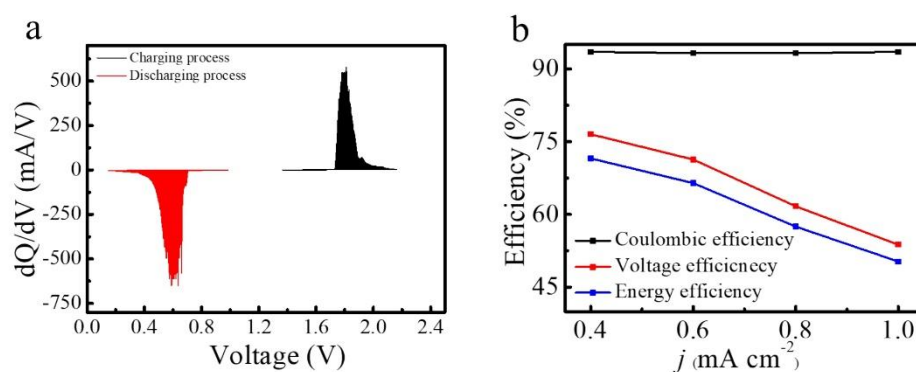


Figure S9. The dQ/dV curve of charging-discharging process of {MV₁₃} NRFBs at current density of 0.6 mA cm⁻². The coulombic efficiency, voltage efficiency and energy efficiency of this {MV₁₃} NRFB at different current densities of 0.4, 0.6, 0.8 and 1.0 mA cm⁻².

2.4.2 Electrochemical impedance spectroscopy

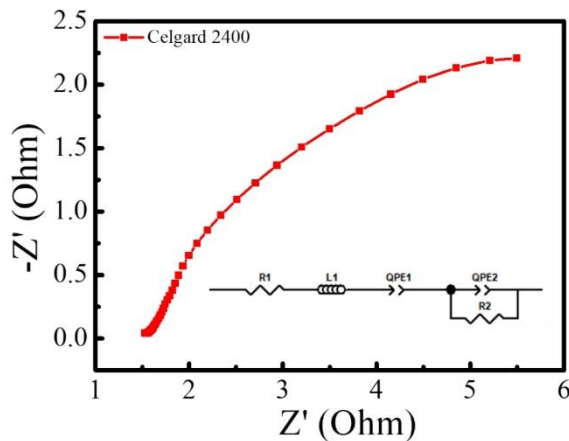


Figure S10. EIS measurement showing the ohmic resistance of {MV₁₃} based NRFB with Celgard 2400 membrane.

2.4.3 Electrochemical stability test before and after the RFBs cycling tests

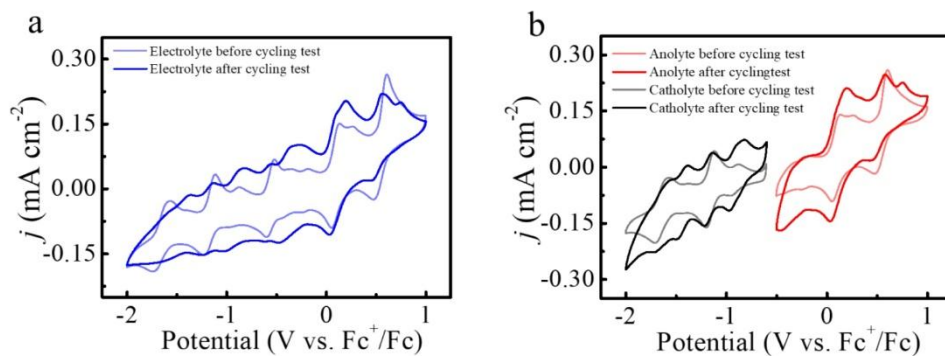


Figure S11. The electrochemical stability of {MV₁₃} after the cycling test. (a) CVs comparison of cycled electrolytes and fresh {MV₁₃} solution at scan rate of 0.1 V s⁻¹ in scan range of -2 V to 1 V vs. Fc^{+/0}/Fc. (b) CVs comparison of cycled electrolytes and fresh {MV₁₃} solution, dividing by open circuit potential.

2.4.4 Experimental NRFBs setup

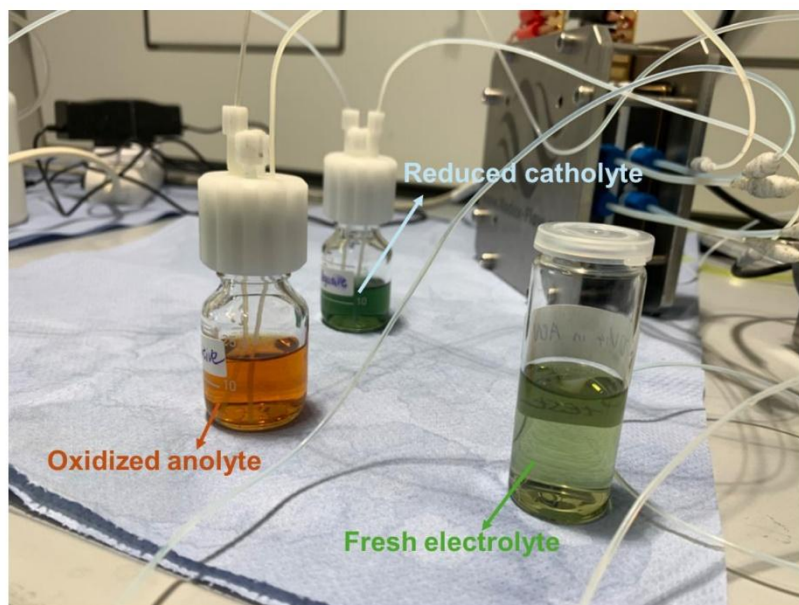


Figure S12. The color changes of the {MV₁₃} anolyte and catholyte during the charge/discharge process.

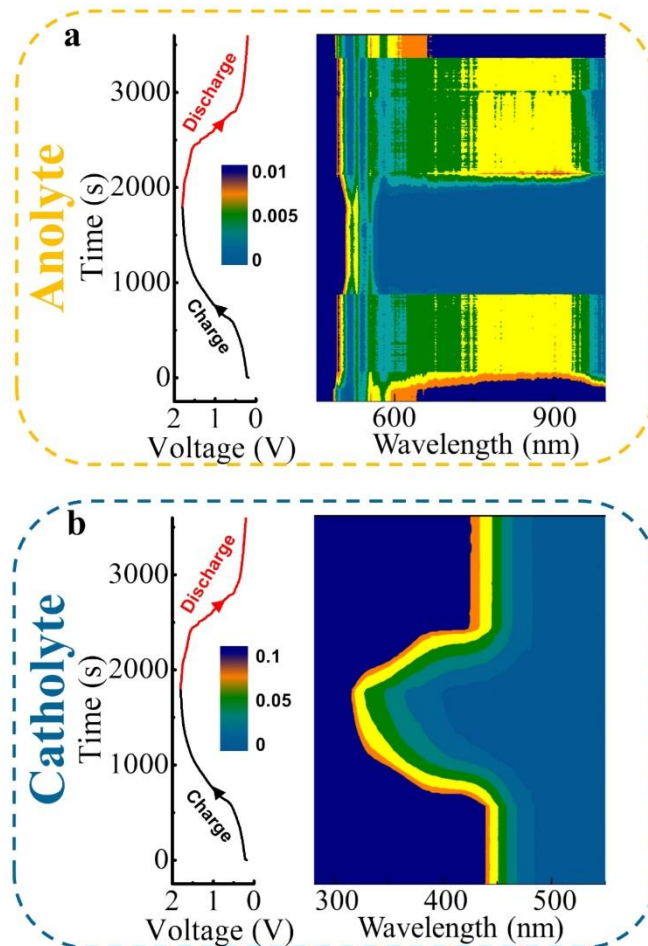
2.5. Operando spectrophotometric UV-Vis characterization of the of {MV₁₃} based electrolytes.

Figure S13. (a) Contour map of in-operando UV-Vis spectroscopy for anolyte. (b) Contour map of in-operando UV-Vis spectroscopy for catholyte.

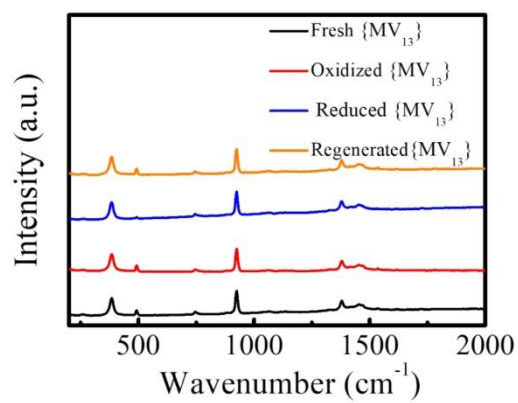
2.6. Raman spectroscopy comparison of $\{\text{MV}_{13}\}$ before/after NRFBs cycling

Figure S14. Raman spectra of $\{\text{MV}_{13}\}$ electrolytes at different oxidation states over the charge and discharge process.

Table S2. Comparison of previously reported RFBs using polyoxometalates as active species.

Redox pairs	Solvent	Number of electrons	Battery voltage (V)	Coulombic Efficiency (%)	Cycles	Ref
Non-aqueous systems						
{MV ₁₃ }	Acetonitrile	4/4	1.8	93	50	This work
[SiV ₃ W ₉ O ₄₀] ⁷⁻	propylene carbonate	3/3	1.7	87	10	[6]
[PMo ₁₂ O ₄₀] ³⁻	Acetonitrile	1/1	0.36	68	30	[7]
[PMo ₁₂ O ₄₀] ³⁻	Dimethylformamide	2/2	0.61	93	30	[7]
[S ₂ W ₁₈ O ₆₂] ⁴⁻ /benzophenone	Acetonitrile	4/1	1.54	97	80	[8]
[V ₆ O ₇ (OC ₂ H ₅) ₃]	Acetonitrile	2/2	0.56-1.67	97	4	[9]
[TiV ₅ O ₆ (OCH ₃) ₁₃]	Acetonitrile	1/1	2.3	91	20	[10]
[PW ₁₁ O ₃₉ (SiC ₆ H ₅) ₂ O] ³⁻	Acetonitrile	2/2	1.1	98	75	[11]
Aqueous systems						
[PMo ₁₂ O ₄₀] ³⁻ / Fe ²⁺	H ₂ O	4/1	-	93	24	[12]
[SiV ₃ W ₉ O ₄₀] ⁷⁻	H ₂ O	3/3	0.8	95	100	[6]
[BW ₁₂ O ₄₀] ⁵⁻ vs. I ⁻	H ₂ O	2/1	-	99.5	100	[13]
[BW ₁₂ O ₄₀] ⁵⁻ vs. [Fe(CN) ₆] ⁴⁻	H ₂ O	2/2	-	99.7	300	[13]
[PV ₁₄ O ₄₂] ⁹⁻ vs. [SiW ₁₂ O ₄₀] ⁴⁻	H ₂ O	2/4	0.7	94	155	[14]
[P ₂ W ₁₈ O ₆₂] ⁶⁻ vs. Br ⁻	H ₂ O	18/2	1.25	98	20	[15]
[PV ₃ W ₉ O ₄₀] ⁶⁻	H ₂ O	3/3	1	80	10	[16]
[CoW ₁₂ O ₄₀] ⁶⁻	H ₂ O	4/1	1.2	99.4	100	[17]

3. Author contributions

C. Streb conceived the idea, designed the experiments, planned synthesis, supervised the project, and revised the manuscript. Z. Chen carried out the experiments, performed electrochemical measurements and batteries performance test, analyzed the results and wrote the manuscript. M. Remmers, S. Repp and B. Mashtakov performed additional electrochemical characterization. K. Sowa supported operando UV-Vis data acquisition and analysis. R. Liu, K. Wang and M. Anjass contributed to the analysis and manuscript revision. All authors discussed the results, drew conclusions, and co-wrote the manuscript.

4. References

- [1] A. M. Remmers, B. Mashtakov, S. Repp, S. J. Rein, K. Wang, M. Anjass, L. M. Carrella, E. Rentschler, C. Streb, *Angew. Chem. Int. Ed* **2024**, e202418864.
- [2] Z. F. Chen, Y. L. Yang, C. Zhang, S. Q. Liu, J. Yan, *J. Energy Storage* **2021**, *35*, 102281.
- [3] E. S. Beh, D. De Porcellinis, R. L. Gracia, K. T. Xia, R. G. Gordon, M. J. Aziz, *ACS Energy Lett.* **2017**, *2*, 639–644.
- [4] M. Gao, M. Salla, Y. Song, Q. Wang, *Angew. Chemie - Int. Ed.* **2022**, *61*, e202208223.
- [5] S. Jin, E. M. Fell, L. Vina-Lopez, Y. Jing, P. W. Michalak, R. G. Gordon, M. J. Aziz, *Adv. Energy Mater.* **2020**, *10*, 2000100.
- [6] H. D. Pratt, N. S. Hudak, X. Fang, T. M. Anderson, *J. Power Sources* **2013**, *236*, 259–264.
- [7] Y. Cao, J. J. Chen, M. A. Barteau, *J. Energy Chem.* **2020**, *50*, 115–124.
- [8] Z. Chen, Y. Yang, C. Zhang, S. Liu, J. Yan, *J. Energy Storage* **2021**, *35*, 102281.
- [9] L. E. Vangelder, A. M. Kosswattaarachchi, P. L. Forrestel, T. R. Cook, E. M. Matson, *Chem. Sci.* **2018**, *9*, 1692–1699.
- [10] L. E. VanGelder, E. M. Matson, *J. Mater. Chem. A* **2018**, *6*, 13874–13882.
- [11] C. L. Peake, A. J. Kibler, G. N. Newton, D. A. Walsh, *ACS Appl. Energy Mater.* **2021**, *4*, 8765–8773.
- [12] P. Sun, Y. Gu, W. You, Z. Tan, *J. Electrochem.* **1997**, *3*, 67–70.
- [13] L. Yang, Y. Hao, J. Lin, K. Li, S. Luo, J. Lei, Y. Han, R. Yuan, G. Liu, B. Ren, J. Chen, *Adv. Mater.* **2022**, *34*, 2107425.
- [14] J. Friedl, M. V. Holland-Cunz, F. Cording, F. L. Pfanschilling, C. Wills, W. McFarlane, B. Schrickler, R. Fleck, H. Wolfschmidt, U. Stimming, *Energy Environ. Sci.* **2018**, *11*, 3010–3018.
- [15] J. J. Chen, M. D. Symes, L. Cronin, *Nat. Chem.* **2018**, *10*, 1042–1047.
- [16] H. D. Pratt, T. M. Anderson, *Dalt. Trans.* **2013**, *42*, 15650–15655.
- [17] Y. Liu, S. Lu, H. Wang, C. Yang, X. Su, Y. Xiang, *Adv. Energy Mater.* **2017**, *7*, 1601224.

6.3 Supporting information: A Bifunctional Iron-Nickel Oxygen Reduction/Oxygen Evolution Catalyst for High-Performance Rechargeable Zinc–Air Batteries



Supporting Information

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A Bifunctional Iron-Nickel Oxygen Reduction/Oxygen Evolution Catalyst for
High-Performance Rechargeable Zinc–Air Batteries

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Supporting Information

A Bifunctional Iron-Nickel Oxygen Reduction / Oxygen Evolution Catalyst for High-Performance Rechargeable Zinc-Air Batteries

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I. Experimental procedures

Materials and general information for synthesis: All reagents and solvents were purchased from commercial suppliers and were used without further purification.

Synthesis of FeNi-NC@MWCNTs: 2-methylimidazole (1.68 g, 20 mmol) and 60 mg multi-walled carbon nanotubes (MWCNTs) were dispersed in 40 ml methanol with stirring, then a solution containing methanol (30 ml), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.19 g, 4 mmol), $\text{Fe}(\text{acac})_3$ (70.63 mg, 0.2 mmol) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (58.2 mg, 0.2 mmol) was added dropwise into the above solution and stirred vigorously for 6 h at room temperature. The resulting precipitate was collected by centrifugation and washed with methanol, then dried in a vacuum oven at 50 °C overnight. The resulting powder was transferred into ceramic boat and was pyrolyzed in a tube furnace under an Ar flow by elevating the temperature from room temperature to 950 °C at a rate of 5 °C min⁻¹, maintaining at 950 °C for 3 h and then cooling down naturally. The pyrolysis products were etched with 1.5 M aqueous HCl (ca. 15 ml) to remove

Zn and ZnO (formed during the carbonation process), then final products were obtained after rinsing with DI water and drying.

Synthesis of Fe-NC@MWCNTs: Fe-NC@MWCNTs was obtained with the same procedure as above, without adding $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in the procedure.

Synthesis of Ni-NC@MWCNTs: Ni-NC@MWCNTs was obtained with the same procedure as above, without adding $\text{Fe}(\text{acac})_3$ in the procedure.

Synthesis of FeNi-NC: FeNi-NC was obtained with the same procedure as above, without adding MWCNTs in the procedure.

Powder X-ray diffraction was measured on Bruker D2 Phaser equipment with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at a scan rate of $15^\circ/\text{min}$ in the 2θ range from 5° to 90° .

Raman spectroscopy was recorded with a WITec confocal Raman spectrometer (Alpha 300 R, $\times 50$ objective) with 600 grooves/mm grating, and 532 nm excitation laser at 0.25 mW power.

X-ray photoelectron spectroscopy (XPS) was performed using a PHI Quantera SXM system with monochromatized Al K α radiation.

Scanning electron microscopy (SEM) images were obtained with Nova NanoSEM at 15 kV acceleration voltage.

Aberration-corrected high-angle annular dark-field scanning TEM (AC-HAADF-STEM) images and the elemental mapping images were acquired on a JEM-ARM300F.

Inductively coupled plasma optical emission spectroscopy (ICP OES) was performed using an Agilent 5800 VDV optical emission spectrometer with an automatic sampler SPS 4.

X-ray absorption spectroscopy (XAS) was obtained on the hard X-ray spectroscopy beamline in the Taiwan Synchrotron Radiation Facility.

Electrochemical measurements: electrochemical analyses of the as-synthesized catalysts were investigated with an electrochemical workstation (CHI 760E) with a standard three-electrode electrochemical cell. A saturated calomel electrode (SCE) and graphite rod were used as reference electrode and counter electrode, respectively. A glassy carbon rotating disk electrode (RDE with a glassy carbon surface area of 0.1256 cm^2) and a rotating Pt ring-glassy carbon disk electrode (RRDE with a glassy carbon surface area of 0.1256 cm^2 and a Pt ring surface area of 0.1884 cm^2) were used as working electrodes to evaluate electrochemical catalytic performance. All electrode potentials in this study were converted to the reversible hydrogen electrode (RHE) with the following equation:

$$E_{\text{RHE}} = E_{\text{SCE}} + 0.241 + 0.059 \times \text{pH} \quad (1)$$

The catalyst inks were prepared by the following method, 5 mg as-synthesized catalyst, 20 μL H_2O and 20 μL Nafion solution (5 wt% in water and 1-propanol, Nafion D-520, Germany) were dispersed in 960 μL ethanol to form a homogeneous ink by ultrasonication for 1 h. Then 7.54 μL of the catalyst ink was uniformly drop-cast on the surface of the glassy carbon working electrode and air-dried at room temperature, the mass loading of the catalyst is approx. 0.3 mg cm^{-2} . Before catalyst loading, the RDE or RRDE was mechanically polished with Al_2O_3 slurry to obtain a mirror-like surface.

Before the tests, the 0.1 M aqueous KOH electrolyte was purged with oxygen or argon constantly for at least 30 min, ensuring that the electrolyte was in O₂-saturated or Ar-saturated state. Cyclic voltammetry (CV) measurements were carried out at a scan rate of 100 mV s⁻¹, and the linear sweep voltammetry (LSV) curves were performed at a scan rate of 5 mV s⁻¹ with 90% IR compensation to evaluate the catalytic activity. For the ORR/OER catalytic activity evaluation, the ORR polarization curves were recorded from 0 V to 1.25 V (vs. RHE), and from 1.01 V to 1.7 V (vs. RHE) for OER with a rotation rate range from 400 to 1600 rpm. The durability of the catalysts was measured by chronoamperometry at E₁₀ (potential at j = 10 mA cm⁻²) for OER and E_{1/2} (half-wave potential) for ORR.

The Tafel slopes were calculated by the following formula:

$$\eta = a + b \times \log j \quad (2)$$

in Where η is the corresponding overpotential at a specific current density, a is the Tafel constant, b is the Tafel slope, and j is the current density.

The electron transfer number and the hydrogen peroxide yield (H₂O₂ %) were calculated to evaluate the selectivity of the catalysts for oxygen reduction. The electrolyte was saturated with oxygen before the test. In this work, the potential of Pt ring on the RRDE was set as a constant value of 1.4 V (vs. RHE) and the LSV curves were recorded with RRDE rotating rate of 1600 rpm. The hydrogen peroxide yield H₂O₂% and the average electron transfer number n were calculated using the equations as below:

$$H_2O_2\% = 200 \times \frac{I_r/N}{I_d + I_r/N} \quad (3)$$

$$n = 4 \times \frac{I_d}{I_d + I_r/N} \quad (4)$$

I_r : ring current, I_d : disk current, $N = 0.37$ (current collection efficiency of the RRDE system)

Faradaic efficiency for OER was also calculated based on RRDE experiments. The electrolyte was saturated with Argon before the test. In this study, a constant potential (1.58 V vs. RHE) was applied at the disk electrode, while the potential of ring electrode was set as 0.4 V vs. RHE to reduce the O₂ produced from the disk. The Faradaic efficiency (FE) was obtained using the following equation:

$$FE = I_r / (I_d \times N) \quad (5)$$

where I_r and I_d are the ring current and disk current, respectively. Here, N is the current collection efficiency of the RRDE, which is determined as 15.7% in this system.

The electrochemically active surface area (ECSA) of all materials was determined via the electrochemical double-layer (C_{dl}) capacitance using the below equation,

$$C_{dl} = 4 \times \frac{I_c}{v} \quad (6)$$

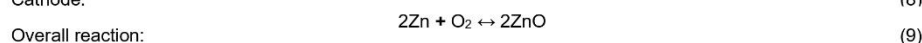
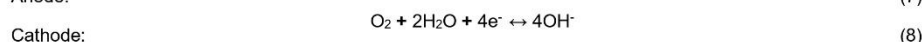
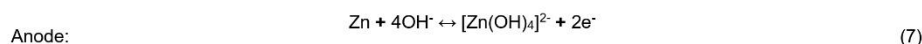
The C_{dl} was obtained from the CVs at different scan rates in a small potential range of 1.06 to 1.16 V vs. RHE, where no redox processes occur. I_c is the charging current (mA cm⁻²), v is the scan rate (mV s⁻¹). There is a linear relationship between the current and scan rate, and the slope of the plot was used to calculate C_{dl} .

Electrochemical impedance spectroscopy (EIS) of the as prepared catalysts were measured at a constant potential of 1.55 V vs. RHE with an AC amplitude of 5 mV by sweeping the frequency from 100 kHz to ~0.01 Hz.

Construction and test of zinc-air battery test: The performance of these bifunctional catalyst in zinc-air batteries (ZABs) was investigated with a custom-built cell. A zinc plate with thickness of 0.5 mm was used as anode, which was polished with commercial sandpaper to remove the surface oxide layer. The air cathode was designed as a sandwich structure which is comprised of nickel foam, gas diffusion layer and catalytic layer (commercially obtained from Changsha Spring New Energy Technology Co., Ltd). Notably, the gas diffusion layer is waterproof but breathable. The catalyst ink was prepared by adding 15 mg synthesized catalyst (for instance, FeNi-NC@MWCNTs) in a solution of 1.9 ml ethanol, 50 μ L H₂O and 50 μ L Nafion. After sonication for 1 h, the catalyst ink was loaded uniformly on the air cathode with a loading amount of 1.5 mg cm⁻². The prepared air cathode was dried at 25 °C for 24 hours to remove excess solvent. The electrolyte was a mixture solution of 6 M KOH and 0.2 M zinc acetate, the electrolyte was circulated through the battery by a peristaltic pump continuously to prevent the buildup of local concentrations of reagents. For comparison, zinc-air batteries with FeNi-NC and commercial catalyst Pt/C + IrO₂ (1:1 by mass ratio) as cathode catalyst were also assembled. The preparation of FeNi-NC and Pt/C-IrO₂ catalyst layers were performed following the above procedure.

All ZABs measurements were performed with a multi-channel battery testing system (Neware, CT-4008T5V6A-S1) at room temperature under ambient conditions. The power density of ZABs was determined by the polarization curves, the specific capacity was measured by a constant discharge current of 15 mA cm⁻² then normalized to the mass loss of the Zn anode. The rate capability of ZABs was evaluated at various current densities of 5, 10, 20, 30 and 50 mA cm⁻², respectively. The ZAB cycling durability was tested by charging and discharging at a constant current density of 15 mA cm⁻² (each cycle lasted 60 min, 30 min for charging and 30 min for discharging).

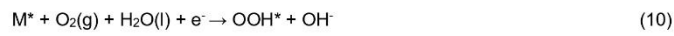
For the general working principle of the rechargeable ZABs, it is described in detail as following: the discharging process involves the coupling of the cathodic oxygen reduction reaction (ORR) and Zn anodization reaction. Typically, O₂ diffuses into the air cathode, and then is reduced to OH⁻ ions, the generated OH⁻ ions migrate to the Zn anode. Meanwhile, metal Zn is oxidized to release Zn²⁺ ions, which then combine with the migrated OH⁻ ions to form [Zn(OH)₄]²⁻. When the concentration of [Zn(OH)₄]²⁻ in the electrolyte reaches a saturated state, it will decompose into ZnO products. During the charging process, it involves the oxygen evolution reaction (OER, the reverse reaction of the ORR) and the corresponding charge process is as follows: OH⁻ ions are oxidized to O₂ at the cathode and the Zn²⁺ ions in the electrolyte are reduced to metallic Zn and deposited on the anode surface. The complete discharge/charge processes of ZABs can be illustrated as the below equations:



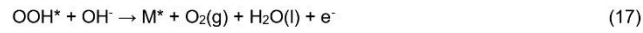
DFT Computational methods: All the density functional theory (DFT) calculations were performed by using the plane-wave method with Vienna Ab Initio Simulation Package (VASP).^[1,2] The frozen-core projector augmented wave (PAW)^[3] potential and generalized gradient approximation in the Perdew-Burke-Ernzerhof (PBE) functional were adopted to simulate the electron exchange and correlation energy.^[4] The cutoff energy for plane wave basis expansion was fixed as 400 eV to describe the interaction between core electrons and valence electrons. The force

on all atoms in each structure was controlled less than 0.01 eV/Å for convergence criterion of geometry relaxation. The Zero damping DFT-D3 method^[5] of Grimme was used to describe the long-range Van der Waals interactions between atoms. The self-consistent calculations apply a convergence energy threshold of 10^{-5} eV. And a Γ -centered Monkhorst-Pack k-point scheme of $3 \times 3 \times 1$ mesh grid was utilized for all structural optimizations. All structure models were constructed by a $6 \times 6 \times 1$ hexagonal graphene, the dimension of the supercell is $14.76 \times 12.78 \times 15.00$ Å³ along x-, y-, and z- directions, respectively. And the vacuum space was chosen as 15 Å to avoid artificial interactions between periodic structures in z direction.

The free energy of each elementary step in the proton coupled electron transfer reactions was computed using the computational hydrogen electrode (CHE) model for both ORR and OER. For ORR calculation in this work, the general four electrons pathway occur in alkaline media as the following steps:



For OER, the pathway goes through the steps as below:



Where * represents the active site on the exposed catalyst surface and OH*, O*, and OOH* denote adsorbed intermediates.

For each single step, the Gibbs free energy ΔG_i ($i = 1, 2, 3, 4$) can be calculated according to the equation:

$$\Delta G_i = \Delta E + \Delta ZPE - T\Delta S \quad (18)$$

Where ΔE is the total energy difference between the reactants and products in these reactions, ΔZPE means the zero-point energy (ZPE) correction.

The thermodynamic overpotential η ORR/OER for a certain material can be determined by:

$$\Delta G_{ORR/OER} = \max\{\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\} \quad (19)$$

$$\eta_{ORR/OER} = \Delta G_{ORR/OER}/e - 1.23 \text{ V} \quad (20)$$

where ΔG_1 , ΔG_2 , ΔG_3 and ΔG_4 are the Gibbs free energy for each elementary step of ORR/OER pathway.

II. Supplementary figures and tables

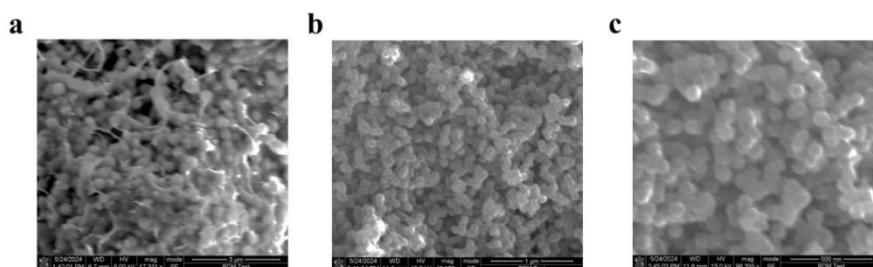


Figure S1. The SEM images of (a) FeNi-NC@MWCNTs, (b) and (c) for FeNi-NC.

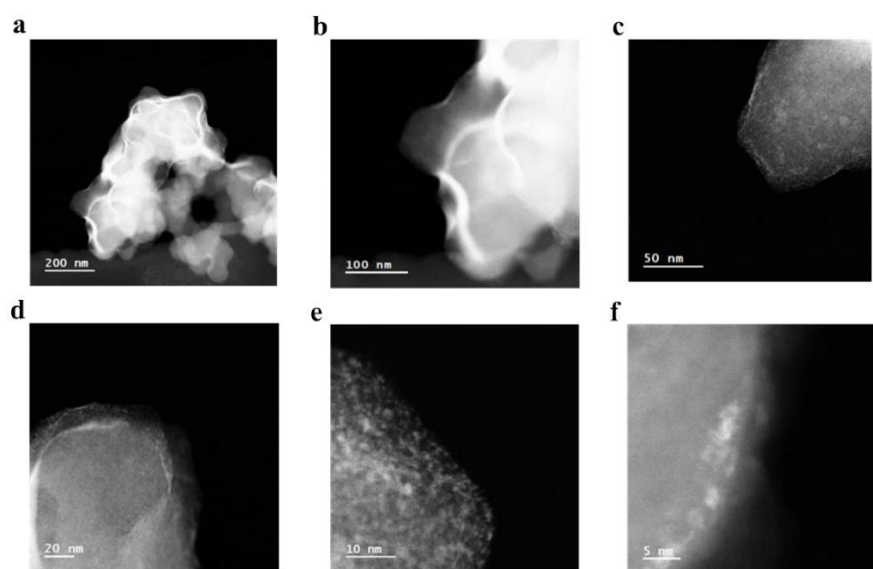


Figure S2. The aberration-corrected HAADF-STEM images of FeNi-NC@MWCNTs.

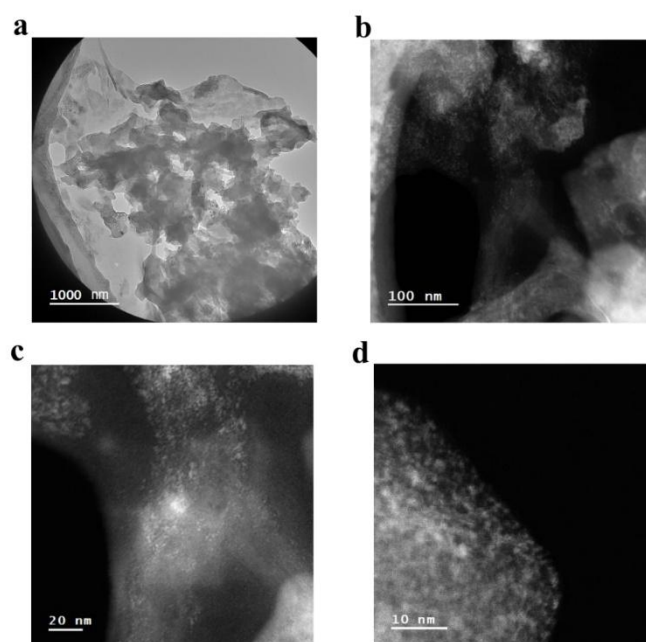


Figure S3. The aberration-corrected HAADF-STEM images of FeNi-NC.

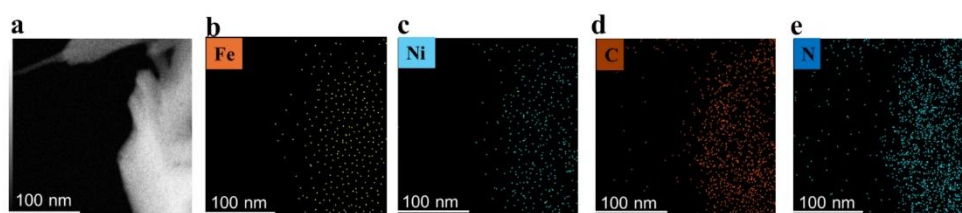


Figure S4. EDS mapping patterns for C, N, Fe and Ni of the FeNi-NC@MWCNT catalyst.

Table S1. Metal element contents of FeNi-NC@MWCNTs and FeNi-NC determined by ICP-OES

Catalyst materials	ICP-OES	
	Fe (wt. %)	Ni (wt. %)
FeNi-NC@MWCNT	0.57	0.62
FeNi-NC	0.45	0.38

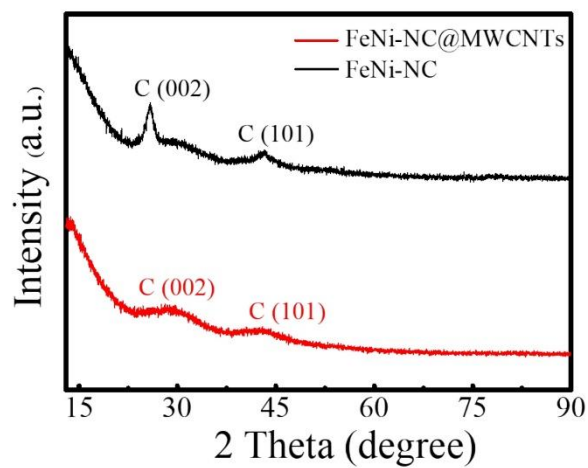


Figure S5. The XRD pattern of FeNi-NC@MWCNTs and FeNi-NC.

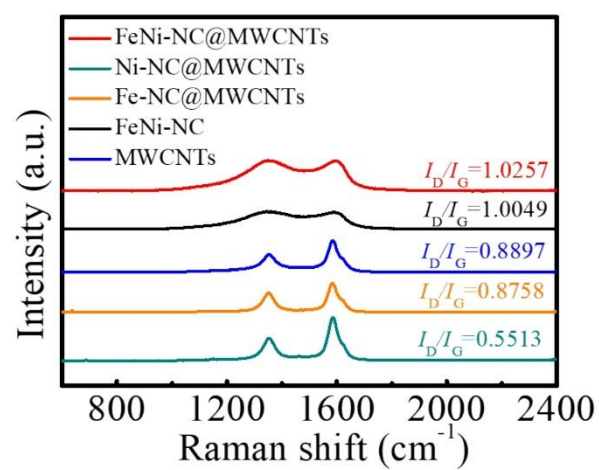


Figure S6. The Raman spectra of FeNi-NC@MWCNTs, Fe-NC@MWCNTs, Ni-NC@MWCNTs, FeNi-NC and MWCNTs.

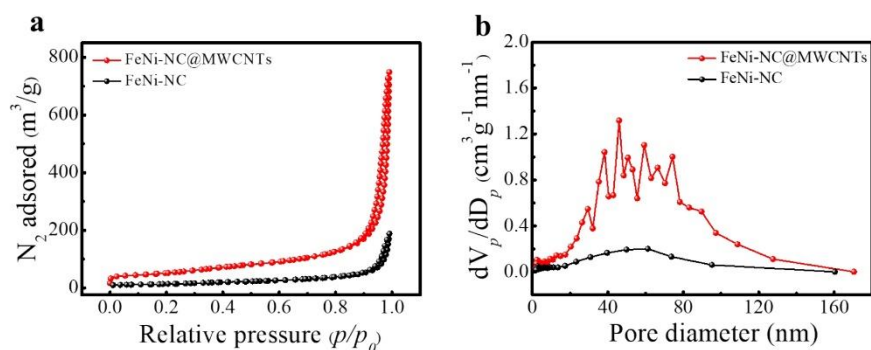


Figure S7. (a) Nitrogen adsorption-desorption isotherms of FeNi-NC@MWCNTs and FeNi-NC. (b) Pore-size distributions.

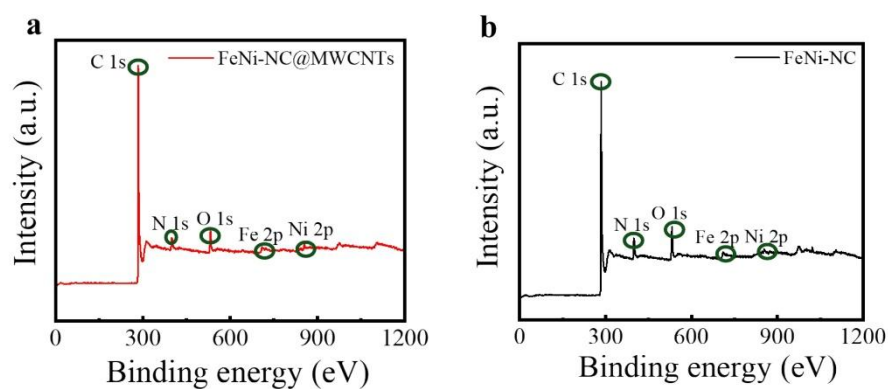


Figure S8. Survey XPS of FeNi-NC@MWCNTs (a) and FeNi-NC (b), revealing the presence of C, N, Fe and Ni.

Table S2. The Fe K-edge EXAFS curve fitting parameters and the Ni K-edge EXAFS curve fitting parameters.

FeNi-NC@MWCNTs	Shell	C.N.	R($\text{\AA}$)	σ^2 ($\text{\AA}^2$)	R factor
Fe K-edge	Fe-N	2.62 ± 0.524	2.12 ± 0.021	0.0005 ± 0.0001	1.0×10^{-2}
	Fe-Ni	1.31 ± 0.262	2.51 ± 0.025	0.0030 ± 0.0006	
Ni K-edge	Ni-N	3.58 ± 0.71	2.09 ± 0.021	0.01243 ± 0.00248	1.9×10^{-3}
	Ni-Fe	1.79 ± 0.35	2.51 ± 0.025	0.00515 ± 0.00103	

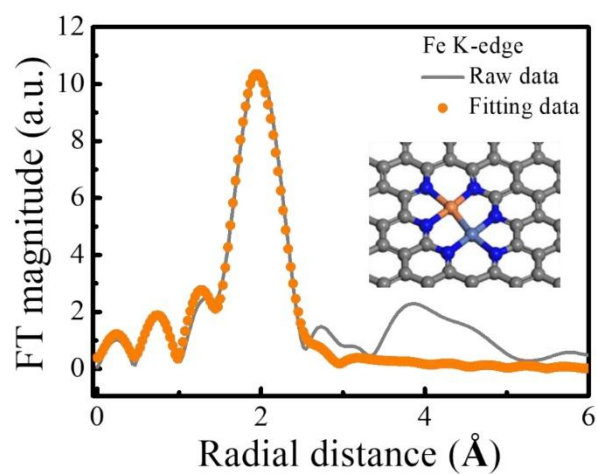


Figure S9. (a) Experimental and fitted FT-EXAFS curves at Fe K-edge of FeNi-NC@MWCNTs in R space and the fitting curves based on the monomeric FeNi-N₆ model (inset).

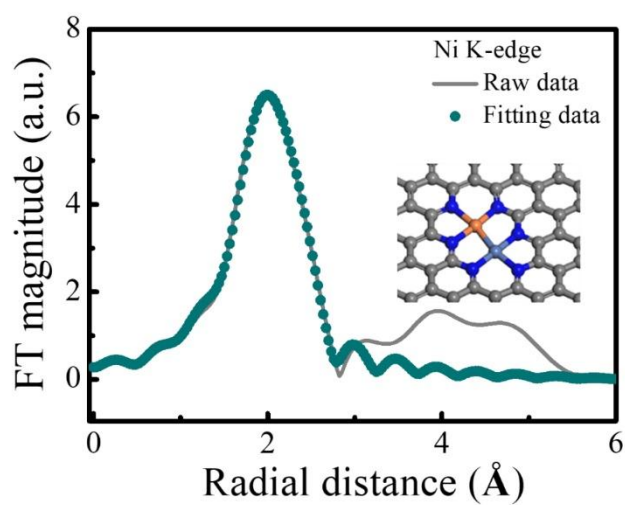


Figure S10. (a) Experimental and fitted FT-EXAFS curves at Ni K-edge of FeNi-NC@MWCNTs in R space and the fitting curves based on the monomeric FeNi-N₆ model (inset).

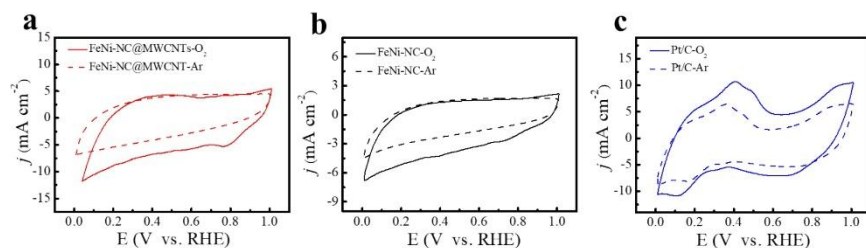


Figure S11. CV curves of FeNi-NC/MWCNTs, FeNi-NC, and Pt/C at scan rate of 0.1 V s⁻¹. The solid and dashed lines correspond to the measurement in O₂- and Ar-saturated 0.1M KOH solution, respectively.

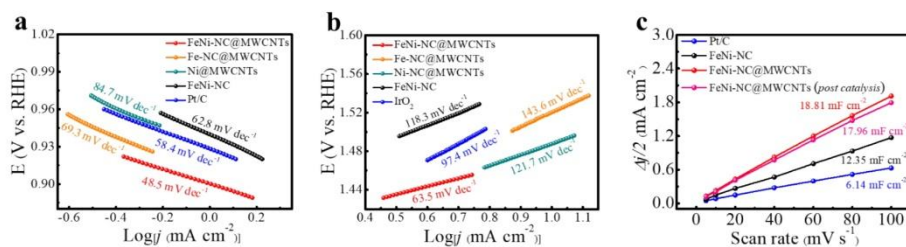


Figure S12. (a) ORR Tafel plots of FeNi-NC/MWCNT, Fe-NC/MWCNTs, Ni-NC/MWCNTs, FeNi-NC and commercial Pt/C. (b) OER Tafel plots of FeNi-NC/MWCNT, Fe-NC/MWCNTs, Ni-NC/MWCNTs, FeNi-NC and commercial Pt/C. (c) Half of the capacitive current density ($\Delta j/2$) at 1.1 V (vs. RHE) as a function of the scan rates of FeNi-NC/MWCNT, FeNi-NC, Pt/C and FeNi-NC/MWCNT post OER catalysis.

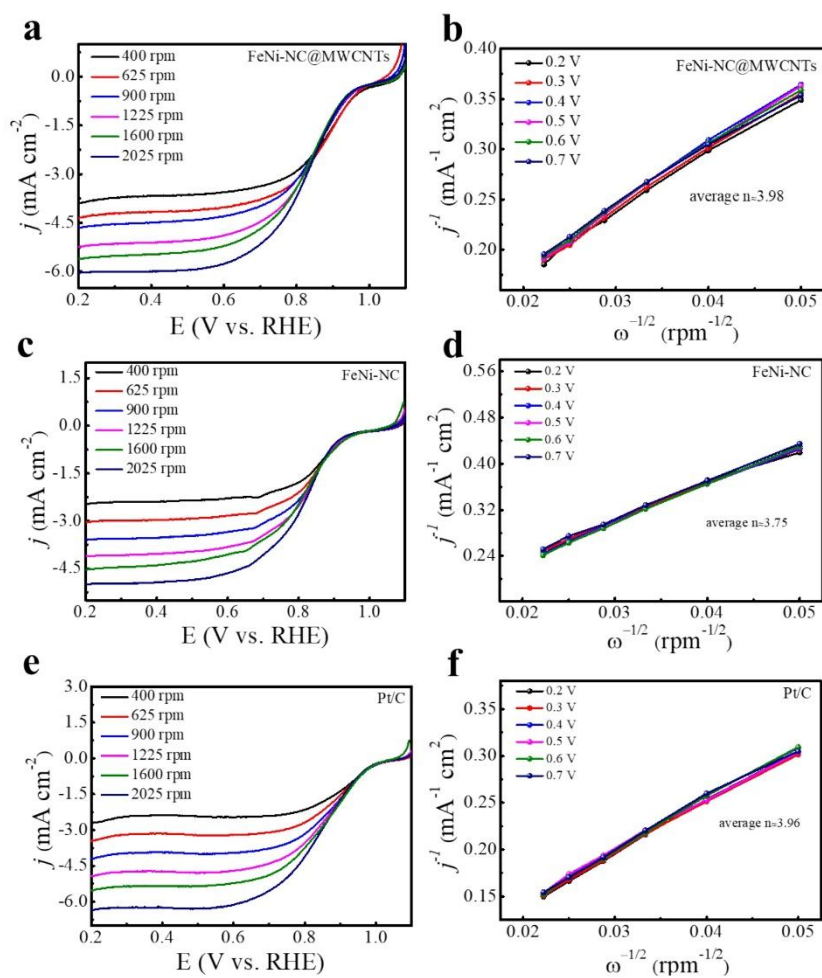


Figure S13. ORR LSV curves of FeNi-NC@MWCNTs, FeNi-NC, and Pt/C at different rotating rates (a, c, e) corresponding K-L plot and electron transfer numbers (b, d and f).

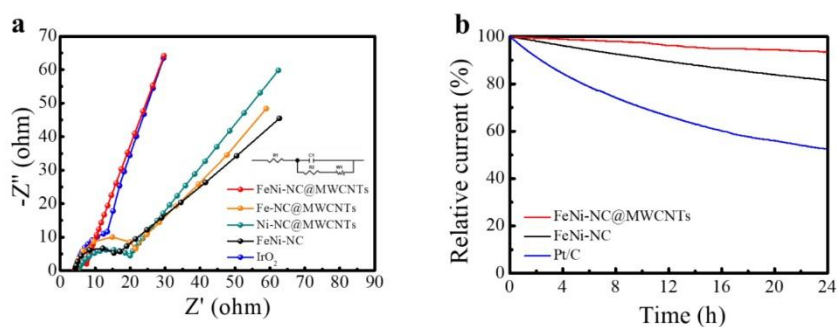


Figure S14. (a) The Nyquist plot for FeNi-NC@MWCNTs, Fe-NC@MWCNTs, Ni-NC@MWCNTs, FeNi-NC and IrO₂ in 0.1 M KOH solution. In this study, the electrochemical impedance spectroscopy (EIS) measurements were conducted at the potential of 1.56V. (insert: equivalent circuit). (b) The Chronoamperometry curves of FeNi-NC@MWCNTs, FeNi-NC and Pt/C at 0.8 V vs. RHE in O₂ saturated electrolyte for ORR stability test.

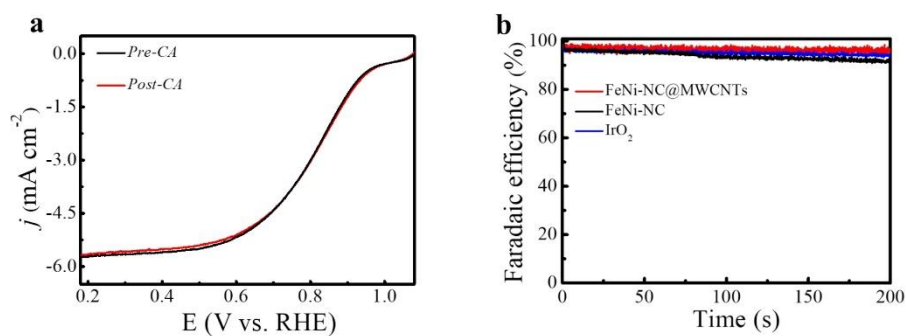


Figure S15. (a) The ORR polarization curves of FeNi-NC@MWCNTs before and after chronoamperometry test. (b) The OER faradaic efficiency of FeNi-NC@MWCNTs, FeNi-NC and IrO₂ for OER were determined by RRDE analysis.

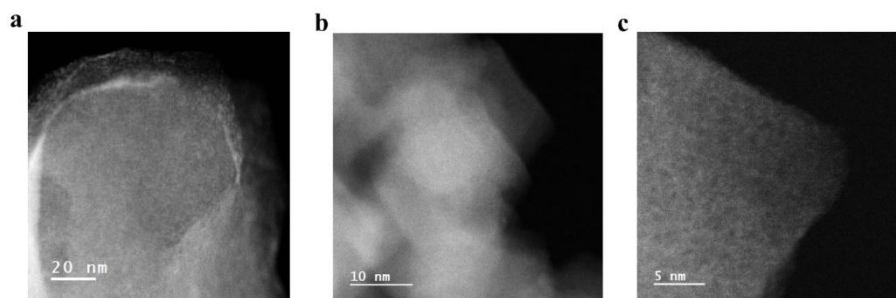


Figure S16. The aberration-corrected HAADF-STEM images of FeNi-NC@MWCNTs after ORR chronoamperometric test.

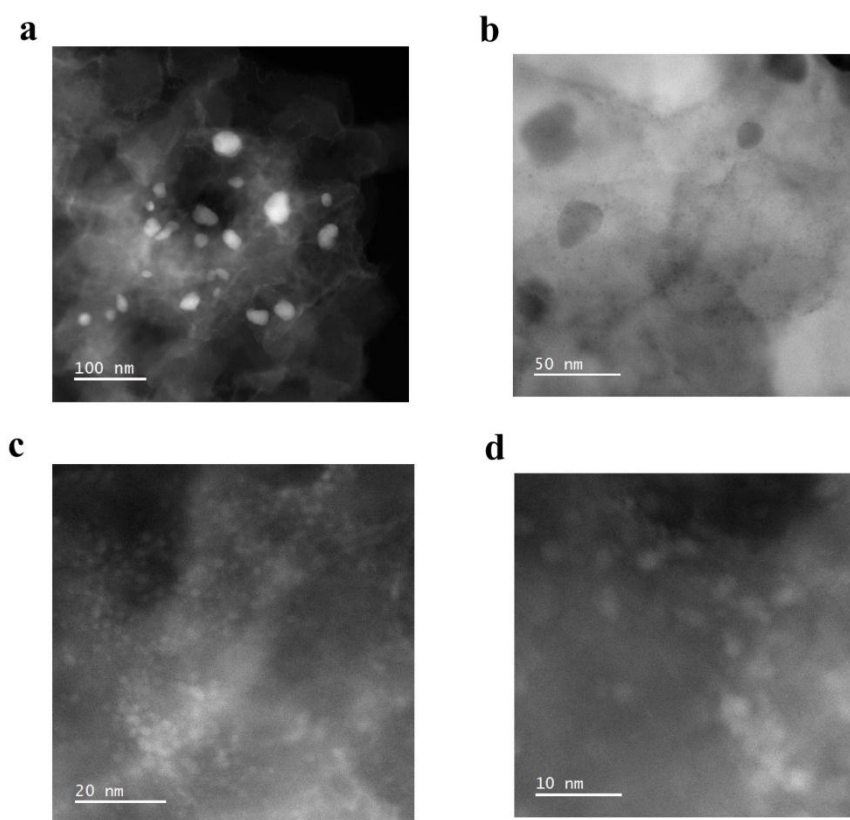


Figure S17. The aberration-corrected HAADF-STEM images of FeNi-NC@MWCNTs after OER chronoamperometric test.

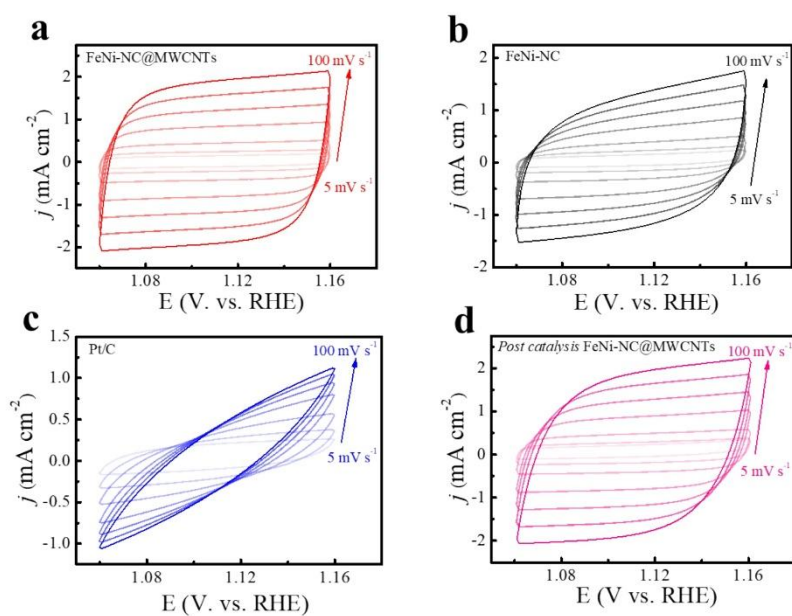


Figure S18. Double-layer capacitance measurements for determining electrochemically active surface area of the catalysts. CV curves of (a) FeNi-NC@MWCNTs, (b) FeNi-NC (c) Pt/C, and (d) FeNi-NC@MWCNTs post OER catalysis respectively. The CVs were scanned from 1.06 to 1.16 V vs. RHE with the scan rates from 5 to 100 mV s⁻¹.

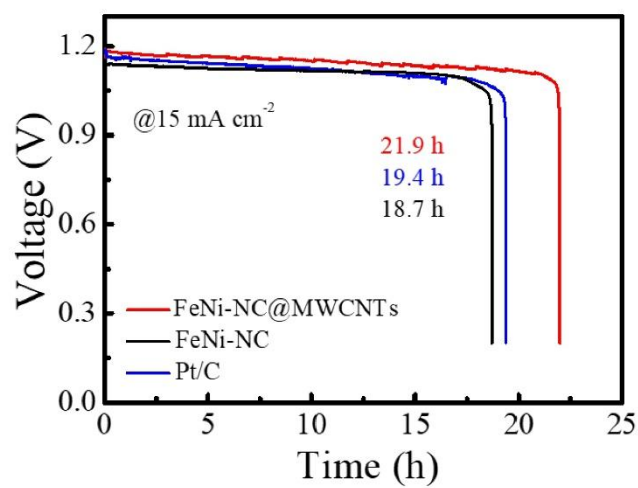


Figure S19. Galvanostatic discharge curves of ZABs with different catalysts at a constant current density of 15 mA cm⁻².

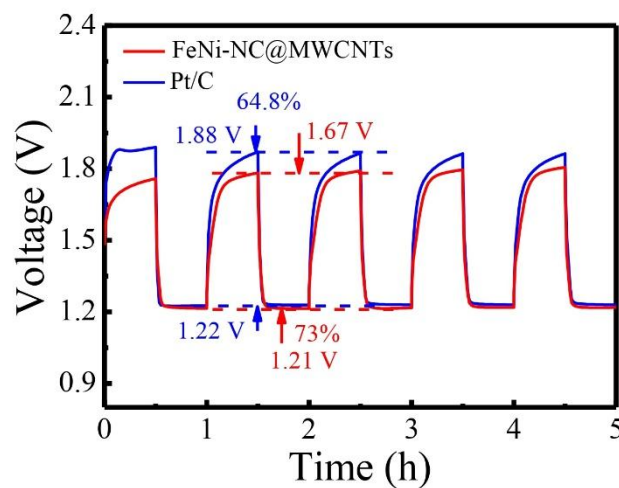


Figure S20. The charge-discharge profiles of ZABs driven by FeNi-NC@MWCNTs and Pt/C catalysts with a duration of 1 h per cycle. The round-trip efficiency was calculated according to the cut-off voltage of the second cycle.

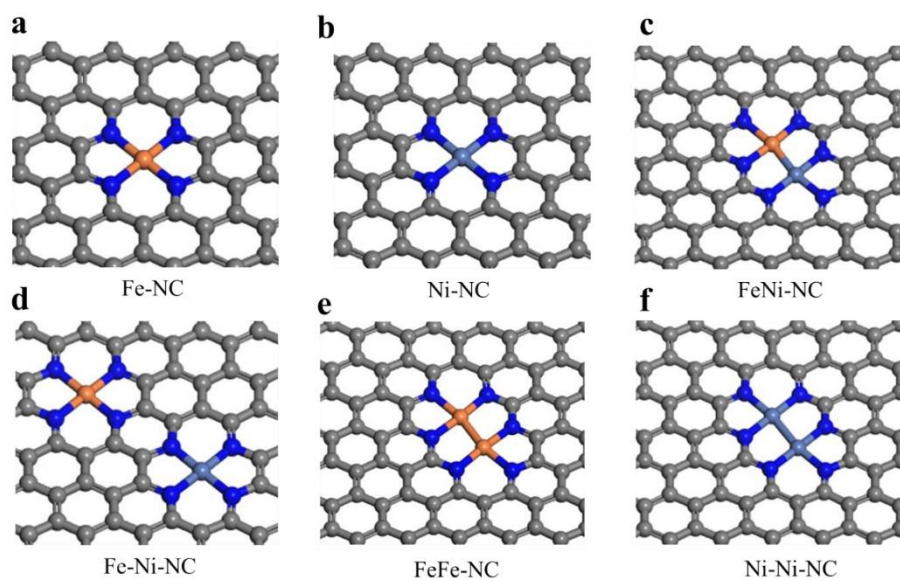
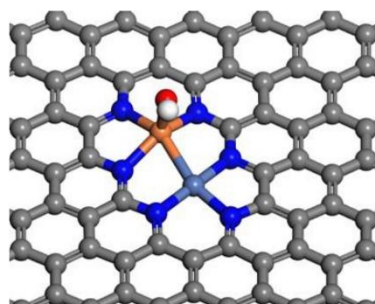


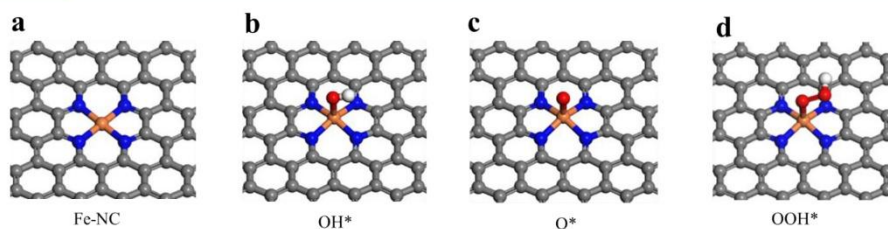
Figure S21. Initial unit cell of Fe-NC (a), Ni-NC (b), FeNi-NC (c), Fe-Ni-NC (d), FeFe-NC (e) and NiNi-NC (f). The grey, blue, orange, and cyan balls represent carbon, nitrogen, iron, and nickel atoms, respectively.

Table S3. Adsorption energy of OH* (ΔG_{OH^*}) on active sites in different models Fe-NC, Ni-NC, FeNi-NC, Fe-Ni-NC, FeFe-NC and NiNi-NC, respectively.

	Fe-NC	Ni-NC	FeNi-NC	Fe-Ni-NC
ΔG_{OH^*}	0.20	1.67	-0.24	0.19

**Figure S22.** Unit cell after adsorption of *OH on FeNi-NC model (FeNi-OH-NC). The grey, blue, orange, and cyan balls represent carbon, nitrogen, iron, and nickel atoms, respectively.**Table S4.** Formation energy of oxygen intermediates adsorbed on active sites in different models Fe-NC, Ni-NC, FeNi-NC, Fe-Ni-NC, FeFe-NC, NiNi-NC and FeNi-OH-NC, respectively.

	Fe-NC	Ni-NC	Fe@Fe-Ni-NC	Ni@Fe-Ni-NC	FeFe-NC	NiNi-NC	FeNi-NC	FeFe-OH-NC	FeNi-OH-NC
ΔG_{OH^*}	0.20	1.67	0.19	1.65	-0.62	1.97	-0.24	0.50	0.82
ΔG_{O^*}	1.04	2.47	1.07	2.46	0.52	1.11	0.64	0.99	1.82
ΔG_{OOH^*}	1.86	0.34	1.83	0.35	2.85	2.23	2.51	2.10	1.38
$\Delta G_{\text{O}_2^*}$	1.82	0.44	1.83	0.46	2.17	-0.39	2.01	1.33	0.90

**Figure S23.** Unit cell before (a) and after adsorption of *OH (b), *O (c) and OOH* (d) on Fe-NC model. The grey, blue, and orange balls represent carbon, nitrogen and iron atoms, respectively.

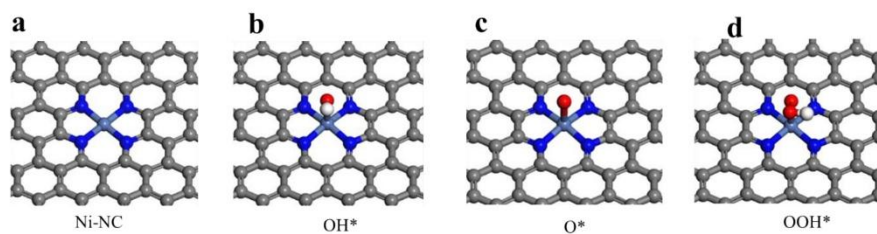


Figure S24. Unit cell before (a) and after adsorption of OH^* (b), O^* (c) and OOH^* (d) on Ni-NC model. The grey, blue, and cyan balls represent carbon, nitrogen, and nickel atoms, respectively.

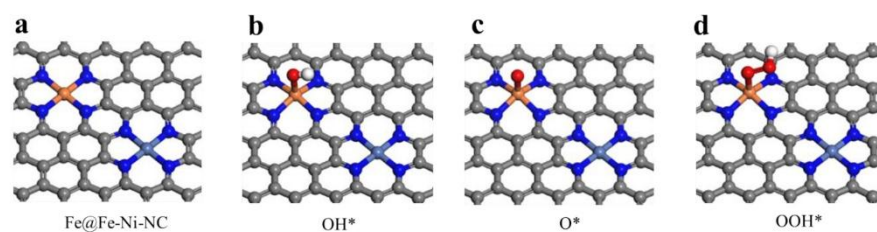


Figure S25. Unit cell before (a) and after adsorption of OH^* (b), O^* (c) and OOH^* (d) on Fe@Fe-Ni-NC model. The grey, blue, orange, and cyan balls represent carbon, nitrogen, iron, and nickel atoms, respectively.

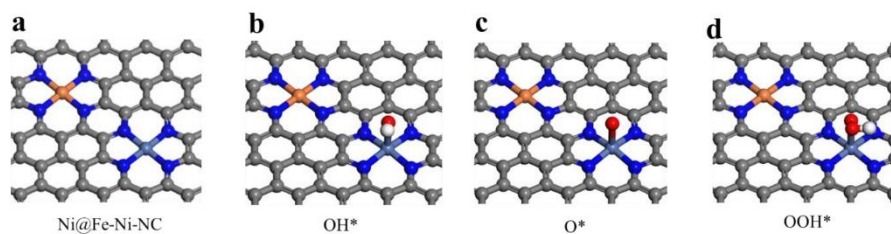


Figure S26. Unit cell before (a) and after adsorption of OH^* (b), O^* (c) and OOH^* (d) on Ni@Fe-Ni-NC model. The grey, blue, orange, and cyan balls represent carbon, nitrogen, iron, and nickel atoms, respectively.

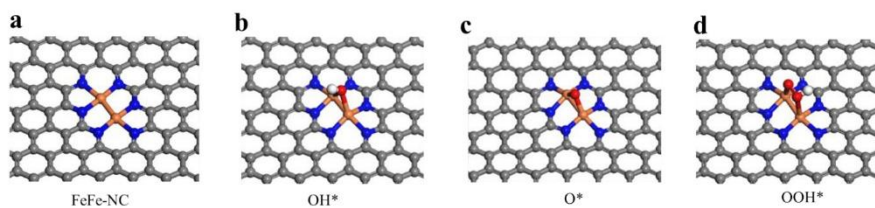


Figure S27. Unit cell before (a) and after adsorption of $^*\text{OH}$ (b), $^*\text{O}$ (c) and $^*\text{OOH}$ (d) on FeFe-NC model. The grey, blue, and orange balls represent carbon, nitrogen, and iron atoms, respectively.

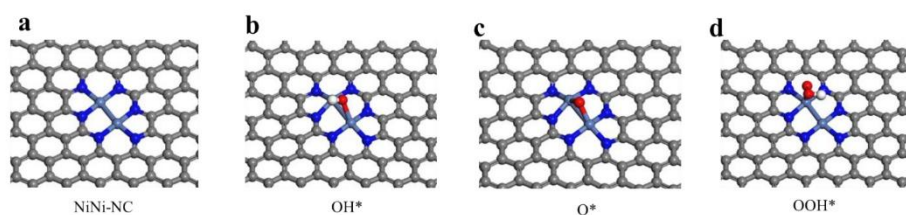


Figure S28. Unit cell before (a) and after adsorption of $^*\text{OH}$ (b), $^*\text{O}$ (c) and $^*\text{OOH}$ (d) on NiNi-NC model. The grey, blue, and cyan balls represent carbon, nitrogen, and nickel atoms, respectively.

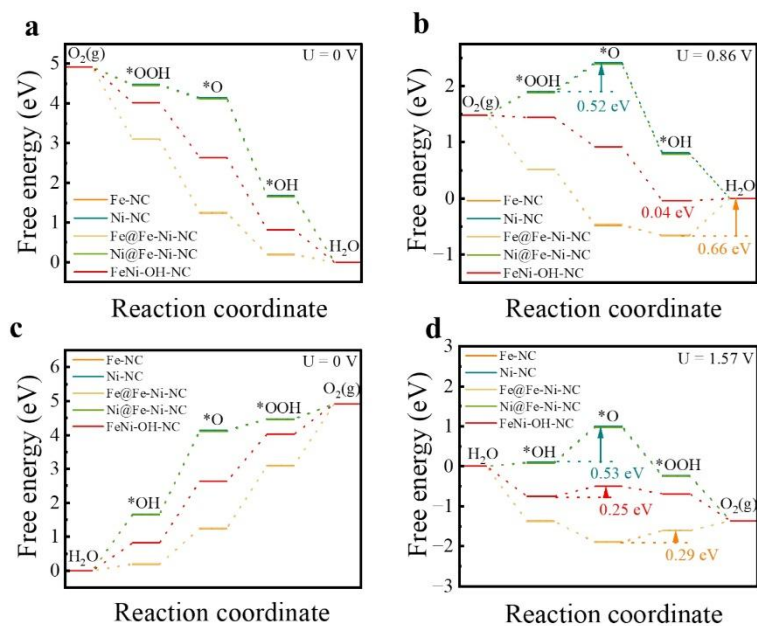


Figure S29. Free energy diagrams of ORR intermediates on Fe-NC, Ni-NC, FeNi-OH-NC and Fe-Ni-NC models at potential of 0 V (a) and 0.86 V (b). Free energy diagrams of OER intermediates on Fe-NC, Ni-NC, FeNi-OH-NC and Fe-Ni-NC modes at potential 0 V (c) and 1.57 V (d).

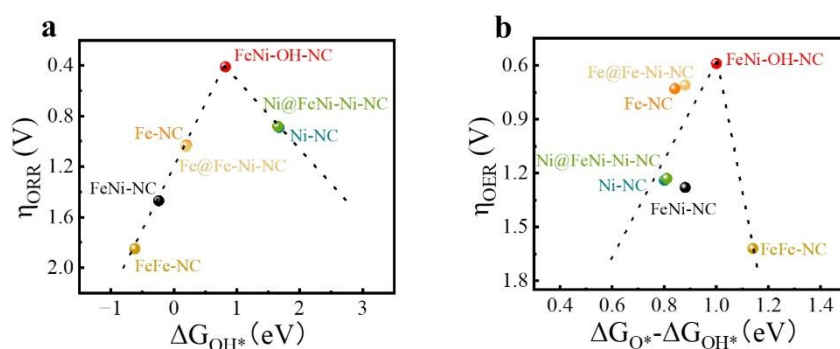


Figure S30. (a) Volcano plot of overpotential η of ORR versus ΔG_{OH^*} for Fe-NC, Ni-NC, FeNi-OH-NC and Fe-Ni-NC models. (b) Volcano plot of overpotential η of OER versus $\Delta G_{\text{O}^*} - \Delta G_{\text{OH}^*}$ for Fe-NC, Ni-NC, FeNi-OH-NC and Fe-Ni-NC models.

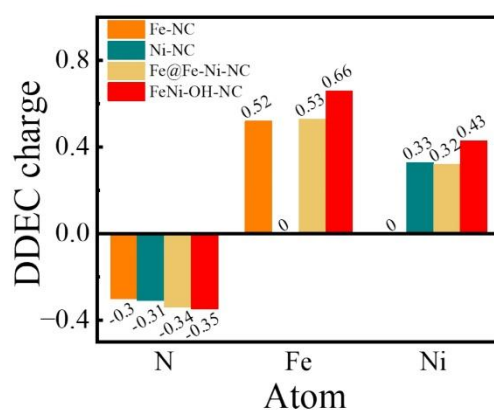


Figure S31. Density derived electrostatic and chemical (DDEC) charge distributions of the constructed models Fe-NC, Ni-NC, Fe@Fe-Ni-NC and FeNi-OH-NC on Fe, Ni and N, respectively. The Bader effective charge of N is given as the average value.

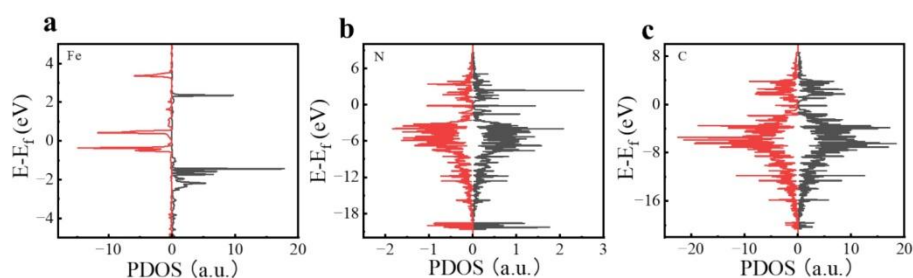


Figure S32. Projected density of states of metal Fe d orbitals and non-metal (N and C) p orbitals for the Fe-NC model.

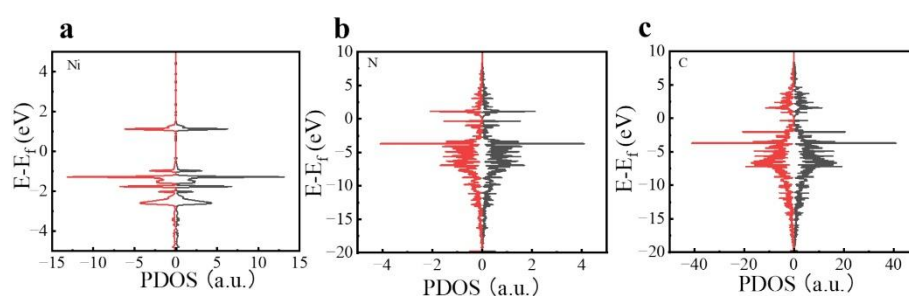


Figure S33. Projected density of states of metal Ni d orbitals and non-metal (N and C) p orbitals in the Ni-NC model.

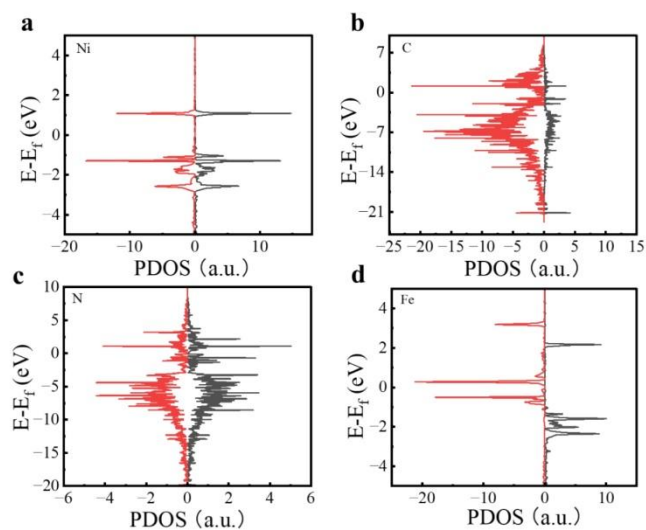


Figure S34. Projected density of states of metal (Fe and Ni) d orbitals and non-metal (N and C) p orbitals in the Fe-Ni-NC model.

Table S5. Comparison of the ORR and OER performance between FeNi-NC@MWCNTs and other recently reported single/dual atom catalysts.

Catalysts	$E_{1/2}$ (V vs. RHE)	$E_{j=10}$ (V vs. RHE)	ΔE ($E_{j=10}-E_{1/2}$) (V vs. RHE)	Electrolyte	Reference
FeNi-NC@MWCNTs	0.9	1.61	0.71	0.1 KOH	This work
FeNi ₄ B-NiN ₄ B	0.9	1.618	0.718	0.1 KOH	[6]
P doped Fe-NC	0.85	1.64	0.79	0.1 KOH	[7]
Pd/WO _{2.72}	0.86	1.59	0.73	0.1 KOH	[8]
NiFe LDH-A Fe/NC-CNT	0.84	1.59	0.78	0.1 KOH	[9]
SAC(Fe, Ni, Zn)	0.88	1.63	0.75	0.1 KOH	[10]
FeNi-HPNC	0.868	1.59	0.72	0.1 KOH	[11]
PA@Z8-Fe-N-C	0.88	1.77	0.89	0.1 KOH	[12]
FeCo-DACs/NC	0.877	1.6	0.723	0.1 KOH	[13]
CoNC SAC	0.86	1.65	0.79	0.1 KOH	[14]
Fe,Co,N-C	0.9	1.64	0.74	0.1 KOH	[15]
Fe ₁ Co ₁ -CNF	0.86	1.73	0.87	0.1 KOH	[16]
MS-CoSA-N-C	0.86	1.60	0.76	0.1 KOH	[17]
Ni-N4/GHSs/ Fe-N4	0.83	1.62	0.79	0.1 KOH	[18]
FeCo-NPC-1100	0.79	1.60	0.81	0.1 KOH	[19]
FeNi/N-LCN	0.85	1.57	0.72	0.1 KOH	[20]

Table S6. Comparison between the performance of rechargeable ZABs with FeNi-NC@MWCNTs and other recently reported ZABs with single/dual atom catalysts.

Cathode Catalysts	Peak power density (mW cm^{-2})	Specific capacity (mAh g^{-1})	Stability test	Reference
FeNi-NC@MWCNTs	218.3	781.7 @15 mA cm^{-2}	300 h @15 mA cm^{-2}	This work
FeMn _{ad} /Mn-N ₄ C	207	720.2 @5 mA cm^{-2}	100 h @5 mA cm^{-2}	[21]
FeCo-DACs/NC	175	-	240 h @15 mA cm^{-2}	[22]
Cu-Se DAs	206.5	809.3 @10 mA cm^{-2}	70 h @10 mA cm^{-2}	[23]
Pd/WO _{2.72}	168	633 @25 mA cm^{-2}	-	[8]
Fe SAs@NC	107.9	734.5 @10 mA cm^{-2}	183 h @10 mA cm^{-2}	[24]
Fe-Zn-SA/NC	167.2	756.6 @10 mA cm^{-2}	120 h @10 mA cm^{-2}	[25]
Ru-SAS/SNC	229	728 @10 mA cm^{-2}	270 h @5 mA cm^{-2}	[26]
CoMn/NC	176	-	22 h @5 mA cm^{-2}	[27]
Fe ₂ Co ₂ N-C	198.4	726 @2 mA cm^{-2}	51 h @5 mA cm^{-2}	[15]
Fe ₁ Co ₁ -CNF	201.7	814 @10 mA cm^{-2}	200 h @20 mA cm^{-2}	[16]
SA&NP-FeCo-NTS	102.2	770 @20 mA cm^{-2}	250 h @5 mA cm^{-2}	[28]
FeMn-DSAC	184	-	80 h @2 mA cm^{-2}	[29]
Fe-N/P-C-700	133.2	723.6 @100 mA cm^{-2}	40 h @10 mA cm^{-2}	[30]
FeSA/N-PSCS	164.5	725.3 @10 mA cm^{-2}	150 h @10 mA cm^{-2}	[31]
FeCo SAs@Co/N-GC	162	741 @5 mA cm^{-2}	300 h @5 mA cm^{-2}	[32]

III. Author contributions:

C. Streb, R. Liu, Z. Chen conceived the idea, designed the experiments, planned synthesis, supervised the project, and revised the manuscript. Z. Chen designed the experiments, performed catalyst synthesis, and electrochemical measurements, analyzed the characterization results and wrote the manuscript. K. Cao and M. Jin carried out the TEM measurements. S. Rahali performed the ICP-OES tests. E. Ebrahimi performed the SEM measurements. W. Cheng and N. Ma conducted the DFT calculations and performed data analysis. B.J. Huang, K. Lakshmanan and S. A. Chala performed XAS analyses. C.-Y. Chang and C.C. Cheung performed XAS fitting. H. Luo, Y. Wang performed Raman analysis. All authors discussed the results, drew conclusions, and commented on the manuscript.

IV. References:

- [1] G. Kresse, J. Hafner, *Phys. Rev. B* **1994**, 49, 14251–14269.
- [2] G. Kresse, J. Furthmüller, *Comput. Mater. Sci.* **1996**, 6, 15–50.
- [3] D. Joubert, *Phys. Rev. B - Condens. Matter Mater. Phys.* **1999**, 59, 1758–1775.
- [4] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1998**, 80, 891.
- [5] K. Lee, É. D. Murray, L. Kong, B. I. Lundqvist, D. C. Langreth, *Phys. Rev. B - Condens. Matter Mater. Phys.* **2010**, 82, 3–6.
- [6] Z. Wang, R. Xu, Q. Ye, X. Jin, Z. Lu, Z. Yang, Y. Wang, T. Yan, Y. Liu, Z. Pan, S. J. Hwang, H. J. Fan, *Adv. Funct. Mater.* **2024**, 2315376.
- [7] W. Huang, B. Hai, G. Su, H. Mao, J. Li, *Mater. Lett.* **2024**, 360, 135976.
- [8] Z. Yang, N. Jiang, S. Bei, K. Bao, M. Xiang, C. Yu, S. Dong, H. Qin, *Electrochim. Acta* **2024**, 476, 143768.
- [9] W. H. Wang, C. H. Han, W. X. Hong, Y. C. Chiu, I. H. Tseng, Y. H. Chang, H. Pourzolfaghar, Y. Y. Li, *J. Energy Storage* **2024**, 85, 111058.
- [10] J. E. Tsai, W. X. Hong, H. Pourzolfaghar, W. H. Wang, Y. Y. Li, *Chem. Eng. J.* **2023**, 460, 141868.
- [11] J. Yan, M. Tian, R. Shi, T. Gu, K. Zeng, J. Zhou, Q. Zhang, M. H. Rummeli, R. Yang, *Mater. Today Energy* **2022**, 30, 101171.
- [12] L. Gao, X. Gao, P. Jiang, C. Zhang, H. Guo, Y. Cheng, *Small* **2022**, 18, 2105892.
- [13] M. Liu, N. Li, S. Cao, X. Wang, X. Lu, L. Kong, Y. Xu, X. H. Bu, *Adv. Mater.* **2022**, 34, 2107421.
- [14] C. X. Zhao, J. N. Liu, J. Wang, C. Wang, X. Guo, X. Y. Li, X. Chen, L. Song, B. Q. Li, Q. Zhang, *Sci. Adv.* **2022**, 8, eabn5091.
- [15] S. Sarkar, A. Biswas, E. E. Siddharthan, R. Thapa, R. S. Dey, *ACS Nano* **2022**, 16, 7890–7903.
- [16] Y. Wang, Z. Li, P. Zhang, Y. Pan, Y. Zhang, Q. Cai, S. R. P. Silva, J. Liu, G. Zhang, X. Sun, Z. Yan, *Nano Energy* **2021**, 87, 106147.
- [17] K. Wang, Z. Lu, J. Lei, Z. Liu, Y. Li, Y. Cao, *ACS Nano* **2022**, 16, 11944–11956.
- [18] J. Chen, H. Li, C. Fan, Q. Meng, Y. Tang, X. Qiu, G. Fu, T. Ma, *Adv. Mater.* **2020**, 32, 2003134.
- [19] B. Guo, Q. Ju, R. Ma, Z. Li, Q. Liu, F. Ai, M. Yang, S. Kaskel, J. Luo, T. Zhang, J. Wang, *J. Mater. Chem. A* **2019**, 7, 19355–19363.
- [20] X. Li, Y. Liu, H. Chen, M. Yang, D. Yang, H. Li, Z. Lin, *Nano Lett.* **2021**, 21, 3098–3105.
- [21] H. Liu, L. Jiang, J. Khan, X. Wang, J. Xiao, H. Zhang, H. Xie, L. Li, S. Wang, L. Han, *Angew. Chemie* **2023**, 135, 22–27.
- [22] M. Liu, N. Li, S. Cao, X. Wang, X. Lu, L. Kong, Y. Xu, X. H. Bu, *Adv. Mater.* **2022**, 34, 2107421.
- [23] Z. Sun, H. Zhang, L. Cao, X. Liu, D. Wu, X. Shen, X. Zhang, Z. Chen, S. Ru, X. Zhu, Z. Xia, Q. Luo, F. Xu, T. Yao, *Angew. Chemie* **2023**, 135, e202217719.
- [24] W. J. Niu, Y. Y. Yan, R. J. Li, W. W. Zhao, J. L. Chen, M. J. Liu, B. Gu, W. W. Liu, Y. L. Chueh, *Chem. Eng. J.* **2023**, 456, 140858.
- [25] J. Xu, S. Lai, D. Qi, M. Hu, X. Peng, Y. Liu, W. Liu, G. Hu, H. Xu, F. Li, C. Li, J. He, L. Zhuo, J. Sun, Y. Qiu, S. Zhang, J. Luo, X. Liu, *Nano Res.* **2021**, 14, 1374–1381.
- [26] J. Qin, H. Liu, P. Zou, R. Zhang, C. Wang, H. L. Xin, *J. Am. Chem. Soc.* **2022**, 144, 2197–2207.
- [27] G. Dey, R. Jana, S. Saifi, R. Kumar, D. Bhattacharyya, A. Datta, A. S. K. Sinha, A. Aijaz, *ACS Nano* **2023**, 17, 19155–19167.
- [28] Q. Zhang, P. Liu, X. Fu, Y. Yuan, L. Wang, R. Gao, L. Zheng, L. Yang, Z. Bai, *Adv. Funct. Mater.* **2022**, 32, 2112805.
- [29] T. Cui, Y. P. Wang, T. Ye, J. Wu, Z. Chen, J. Li, Y. Lei, D. Wang, Y. Li, *Angew. Chemie - Int. Ed.* **2022**,

61, e202115219.

- [30] K. Yuan, D. Lützenkirchen-Hecht, L. Li, L. Shuai, Y. Li, R. Cao, M. Qiu, X. Zhuang, M. K. H. Leung, Y. Chen, U. Scherf, *J. Am. Chem. Soc.* **2020**, *142*, 2404–2412.
- [31] M. Shen, J. Liu, J. Li, C. Duan, C. Xiong, W. Zhao, L. Dai, Q. Wang, H. Yang, Y. Ni, *Energy Storage Mater.* **2023**, *59*, 102790.
- [32] N. K. Wagh, D. H. Kim, S. H. Kim, S. S. Shinde, J. H. Lee, *ACS Nano* **2021**, *15*, 14683–14696.

6.4 Supporting information: Atomically Engineered Defect-Rich Palladium Metallene for High-Performance Alkaline Oxygen Reduction Electrocatalysis



Supporting Information

for *Adv. Sci.*, DOI 10.1002/advs.202405187

Atomically Engineered Defect-Rich Palladium Metallene for High-Performance Alkaline Oxygen Reduction Electrocatalysis

Yupeng Zhao, Zhengfan Chen, Nana Ma, Weiyi Cheng, Dong Zhang, Kecheng Cao, Fan Feng, Dandan Gao, Rongji Liu*, Shujun Li* and Carsten Streb*

Supporting Information

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S1 Experimental procedures

Chemicals and Materials: Palladium (II) acetylacetonate ($\text{Pd}(\text{acac})_2$, 99%), 12-Molybdophosphoric acid hydrate ($\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$, analysis), and cyclohexane ($\geq 99.9\%$) were purchased from Merck. Tungsten hexacarbonyl ($\text{W}(\text{CO})_6$, 97%) and Nafion solution (D-520 dispersion 5% w/w aq. and 1-propanol) were purchased from Alfa Aesar. Potassium hydroxide (KOH , $\geq 85\%$), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, absolute), commercial Pt/C (20 wt%), and commercial Pd/C (10 wt%), and N, N-Dimethylformamide (DMF, 99.5%) were purchased from Fisher Scientific. Acetic acid (CH_3COOH , 99.5%) was purchased from VWR. Cetyltrimethylammonium bromide (CTAB, $\text{C}_{19}\text{H}_{42}\text{BrN}$), citric acid (CA, $\text{C}_6\text{H}_8\text{O}_7$, $\geq 99.5\%$), polyvinyl pyrrolidone (PVP, $M_w = 55\,000$) were purchased from Sigma-Aldrich. Vulcan XC-72 carbon was purchased from BC Berlin Catalysts GmbH. All chemicals were used in this experiment without further purification.

Synthesis of D-Pd M and Pd M:

The defect-rich Pd metallene (**D-Pd M**) was synthesized by a simple wet-chemical method. Typically, 42 mg of $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ was dissolved in 10 mL of DMF solution followed by deaeration with Ar for 15 min. Then the solution was irradiated under UV light (Wavelength = 254 nm) for 30 min to get solution A. In addition, 10.0 mg of $\text{Pd}(\text{acac})_2$ and 20 mg of $\text{W}(\text{CO})_6$ were added into a 25 mL bottle containing 8 mL of DMF and then sonicated for half an hour to yield a homogeneous solution (B). Afterward, solution A was added to solution B and was placed in an oil bath at 50 °C for 6 h. After cooling to room temperature, the black colloidal product was collected by centrifugation and washed six times with a mixture of ethanol and cyclohexane ($V_{\text{ethanol}}/V_{\text{cyclohexane}} = 1:1$). The final product was dispersed in cyclohexane for further use.

The hexagonal Pd metallene (Pd M) for comparison were prepared according to a previous approach with slight modifications.^[1,2] 16 mg of $\text{Pd}(\text{acac})_2$, 90 mg of CA, 60 mg of CTAB, and 30 mg of PVP were added into 10 mL of DMF and stirred for 1 h to get a homogeneous orange-red solution. The obtained solution was then transferred into a 25 mL vial and 100 mg of $\text{W}(\text{CO})_6$ was added to the vial under N_2 atmosphere. The vial was capped and heated at 80 °C for 1 h. After the reaction, Pd nanosheets were collected by centrifugation using enough acetone and then redispersed in acetone for further use.

S2 Characterizations

Powder X-ray diffraction (XRD): Bruker D2 Phaser equipment, with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$).

Transmission electron microscopy (TEM): Tecnai G2 Spirit operated at 120 kV (Imaging).

High-resolution transmission electron microscopy (HRTEM) and energy-dispersive X-ray spectroscopy (EDX): Jeol F200 equipped with a SuperX EDX detector, operated at 200 kV (Imaging and diffraction pattern).

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES): Agilent 5800 VDV ICP-OES (optical emission spectrometer) with the automatic sampler SPS 4.

X-ray photoelectron spectroscopy (XPS): Monochromatized Al K α exciting X-radiation using a PHI Quantera SXM system. The binding energies were calibrated based on C1s (284.8 eV).

Ultraviolet - visible spectroscopy (UV-vis): Cary 3500 UV-Vis Spectrophotometer equipped with a Xenon flash lamp (250 Hz). Measurements were performed in standard 1 cm cuvettes.

Atomic force microscopy (AFM): Bruker Dimension Icon.

X-ray absorption spectroscopy (XAS) experiment and data processing: Pd K-edge, W L₃-edge, and Mo L₃-edge X-ray absorption fine structure (XAFS) analyses were performed with Si (111) crystal monochromators at the BL14W Beam line at the Shanghai Synchrotron Radiation Facility (SSRF) (Shanghai, China). Before the analysis at the beamline, samples were placed into aluminum sample holders and sealed using Kapton tape film. The XAFS spectra were recorded at room temperature using a 4-channel Silicon Drift Detector (SDD) Bruker 5040. Pd K-edge and W L₃-edge extended X-ray absorption fine structure (EXAFS) spectra were recorded in transmission mode. Mo L₃-edge extended X-ray absorption fine structure (EXAFS) spectra were recorded in fluorescence mode. Negligible changes in the line shape and peak position of Pd K-edge, W L₃-edge, and Mo L₃-edge XANES spectra were observed between two scans taken for a specific sample. The spectra were processed and analyzed by the software code Athena.

S3 Electrochemical measurements:

The as-prepared **D-Pd M** and Pd M catalysts were loaded on carbon black (Vulcan XC-72) before electrochemical tests. Typically, the **D-Pd M** (2 mg) was mixed with carbon black (8 mg) in cyclohexane (10 mL) under ambient sonication for 1 h. After stirring for another 12 h, the product was collected by centrifugation and washed three times with ethanol. Afterward, the product was treated in pure acetic acid (10 mL) at 70 °C for 2 h to remove excess impurities and excess surfactants for further use. At the end, **D-Pd M/C** was collected by centrifugation, washed three times with ethanol, and dried at 60°C for 3 hours. Pd M/C was prepared by the same method.

To prepare the catalyst inks, the as-prepared **D-Pd M/C** (1 mg) was re-dispersed in a solution containing 15 µL DI water, 980 µL ethanol, and 5 µL Nafion solution by at least 30 min sonication in an ice-water bath to form a catalyst ink. Then the **D-Pd M/C** catalyst ink was dipped on the electrode with a controllable amount of **D-Pd M** catalyst being 10 µg·cm⁻². Likewise, the Pd M/C was processed in the same way. The controllable amount of commercial Pd/C, and commercial Pt/C were 15 µg·cm⁻² to reach the well-defined limited current density. The loading amount on the electrode of prepared catalysts was determined by ICP-OES.

Electrochemical tests were conducted using a three-electrode system on an Ametek electrochemical workstation (channel PMC 1000) equipped with an RRDE setup (Pine, USA). A glassy carbon rotating disk electrode (GC RDE, diameter: 5 mm, area: 0.196 cm²), a saturated calomel electrode (SCE), and a graphite rod were used as the working electrode, reference electrode, and counter electrode, respectively. All potentials in this study were reported on a reversible hydrogen electrode (RHE) scale according to the Nernst equation ($E_{\text{RHE}} = E_{\text{SCE}} + E^0_{\text{SCE}} + 0.059 \text{ V} \times \text{pH}$). The cyclic voltammetry (CV) curves were recorded in N₂-saturated 0.1 M KOH at a scan rate of 50 mV·s⁻¹. ORR linear sweep voltammetry (LSV) was recorded in O₂-saturated 0.1 M KOH at 20 mV·s⁻¹ and a rotating rate of 1600 rpm. It is worth noting that the ORR LSV curves have been corrected in the N₂-saturated 0.1 M KOH to eliminate the interference of double-layer capacity. The current densities (*j*) were normalized regarding the geometric area of the GC RDE. Notably, all ORR LSV curves were iR-corrected (95%) before applying the K-L equation: $I_k = (I_d \times I)/(I_d - I)$, where *I_k*, *I_d*, and *I* represent the kinetic, diffusion limiting, and measured current, respectively.

The electrochemical active surface areas (ECSAs) of all the catalysts were calculated using the underpotentially deposited H (*H_{upd}*) and Cu stripping. The underpotentially deposited H (*H_{upd}*)

data was obtained in the N₂-saturated 0.1 M HClO₄. The peaks of H_{upd} were recorded by cyclic voltammetry (CV) with a scan rate of 50 mV·s⁻¹ to calculate the ECSAs. In the calculation, we used a charge density of 210 μC·cm⁻² for one monolayer of hydrogen coverage on commercial Pt/C and Pd/C, and a charge density of 240 μC·cm⁻² (a value for the (111) surface) for one monolayer of hydrogen coverage on D-Pd M/C and Pd M/C. For the Cu stripping experiments, an Ar-saturated solution containing 2 mM CuSO₄ and 0.05 M H₂SO₄ was used as the electrolyte. The potential was first held at 0.3 V versus RHE for 100 s to form a Cu_{upd} monolayer, and then CVs were obtained from 0.3 V to 1.0 V at 20 mV·s⁻¹. The ECSAs were calculated by subtracting the background CVs that were collected in Ar-saturated 0.05 M H₂SO₄ at 20 mV·s⁻¹, assuming a charge density of 470 μC·cm⁻².

The electron transfer number (*n*) and the hydrogen peroxide yield (**H₂O₂%**) were tested by a rotating Pt ring - GC disk electrode (RRDE) device (Pine, USA), where the surface area of the GC disk and Pt ring are 0.2475 cm² and 0.1866 cm², respectively. The disk electrode was conducted LSV scan, and the ring electrode potential was set to 1.4 V vs. RHE. The **H₂O₂%** and *n* were calculated by the following equations:

$$\mathbf{H_2O_2\%} = 200 \times \frac{\frac{I_r}{N}}{\frac{I_r}{N} + I_d}$$

$$n = 4 \times \frac{I_d}{\frac{I_r}{N} + I_d}$$

where *I_d* is the disk current, *I_r* is the ring current, and *N* is the ring collection efficiency (*N*=0.37). In addition, the electron transfer number during the ORR process of **D-Pd M** was also determined by applying different rotating rates to the Koutecky-Levich equation:

$$\frac{1}{j} = \frac{1}{j_K} + \frac{1}{j_L} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_L}$$

$$B = 0.2nFC_0D_0^{2/3}\nu^{-1/6}$$

where *j*, *j_k*, and *j_L* represent measured current density, the kinetic and limiting current densities the kinetic, respectively. *F* is the Faraday constant (96485 C mol⁻¹), *C₀* is the bulk concentration of O₂ (1.26×10⁻⁶ mol·cm⁻³), *D₀* is the diffusion coefficient of O₂ in 0.1 M KOH (1.93×10⁻⁵ cm²·s⁻¹), and *ν* is the kinetic viscosity (0.01 cm²·s⁻¹). The rotation speed is expressed in rpm.

Accelerated durability tests (ADTs) were conducted by cycling between 0.6 V and 1.0 V vs. RHE at 200 mV/s for 5,000 cycles and 10,000 cycles in 0.1 M O₂-saturated KOH solution at 1600 rpm.

S4 Computational details

All DFT calculations in the present work were performed using the Vienna Ab initio Simulation Package (VASP)^[3,4] with the Perdew-Burke-Ernzerhof (PBE)^[3] functional. The ion-electron interactions were modeled using the projector-augmented wave (PAW) method^[5]. The plane wave cutoff energy was set to 400 eV in all calculations. The convergence criteria were set to be 10⁻⁵ eV and 0.01 eV/Å for wavefunction and geometry optimization, respectively. A Γ -centred Monkhorst–Pack k-point mesh with a size of 3×3×1 was applied for all supercells. The vacuum region was set to 15 Å. The DFT-D3 scheme of dispersion correction was employed to describe van der Waals interactions^[6]. The electronic density of the structure was processed using VASPKIT^[7].

S5 Zn-air battery measurement

The zinc-air battery was measured in a labmade battery mode, consisting of an anode and a cathode. The anode is a polished Zn foil (with a thickness of 0.5 mm), the air cathode is the catalyst-loaded carbon paper (ThermoFisher Scientific), and the electrolyte is a 6 M KOH solution containing 0.2 M Zn(CH₃COO)₂. The catalyst inks were prepared with the same method we mentioned above but at a concentration of 10 mg·mL⁻¹. The catalyst-loaded carbon paper was prepared by spreading as-prepared catalyst ink onto carbon paper and drying at room temperature. The mass loading of 20% **D-Pd M/C** and 20% Pt/C catalysts is 130 µg·cm⁻², and the mass loading of Pd/Pt is 26 µg·cm⁻². The polarization curves were performed at the CHI 760E electrochemistry station. Galvanostatic cycling tests were collected at the **LAND CT2003A** multi-channel battery testing system. When testing the specific capacity of zinc-air potential, the discharge current was set at 15 mA and the cut-off voltage was 0.5 V. The charge and discharge current density was set at 15 mA, the discharge cut-off voltage was set to 0.2 V, and the charge cut-off voltage was set to 1.85 V.

S6 Supplementary figures

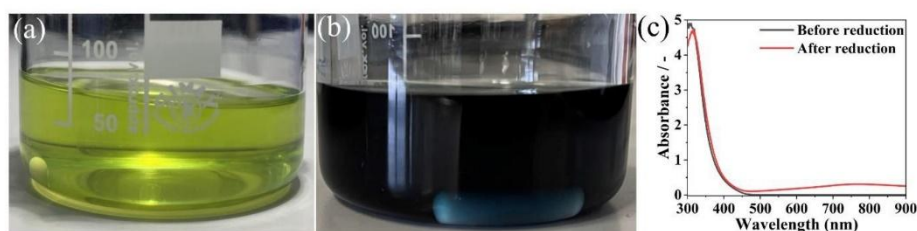


Figure S1. The optical photographs of PMo₁₂ in DMF solution before (a) and after (b) reduction, and corresponding UV-visible spectra after being diluted to 1/10 of original concentration.

The color changes from bright yellow to dark blue and newly appeared broad in reduced solution indicate the reduction of PMo₁₂ clusters to heteropoly blue. Approximately 5.2% of PMo₁₂ underwent reduction to form heteropoly blue,^[8,9] according to the Beer-Lambert law: $A = \epsilon bc$; A is absorbance, ϵ is molar absorptivity (here: $2600 \text{ M}^{-1} \cdot \text{cm}^{-1}$), b is length of light path (here: 1 cm), and c is concentration, respectively.

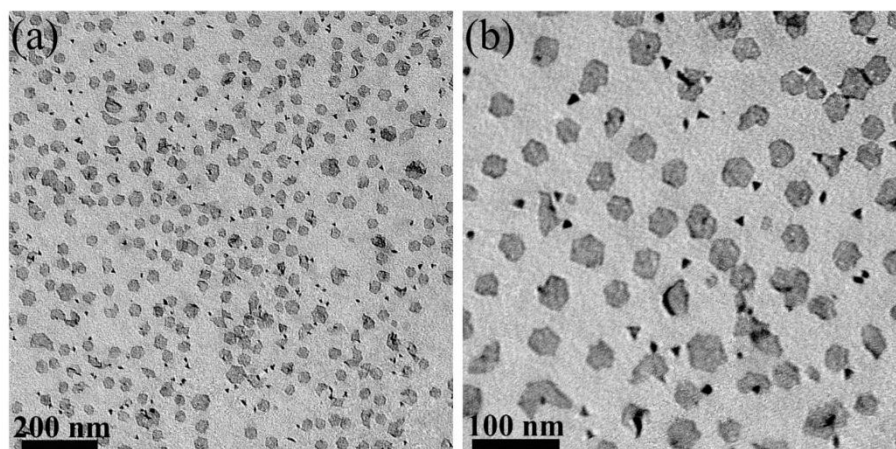


Figure S2. TEM images of Pd M at low (a) and (high) magnification.

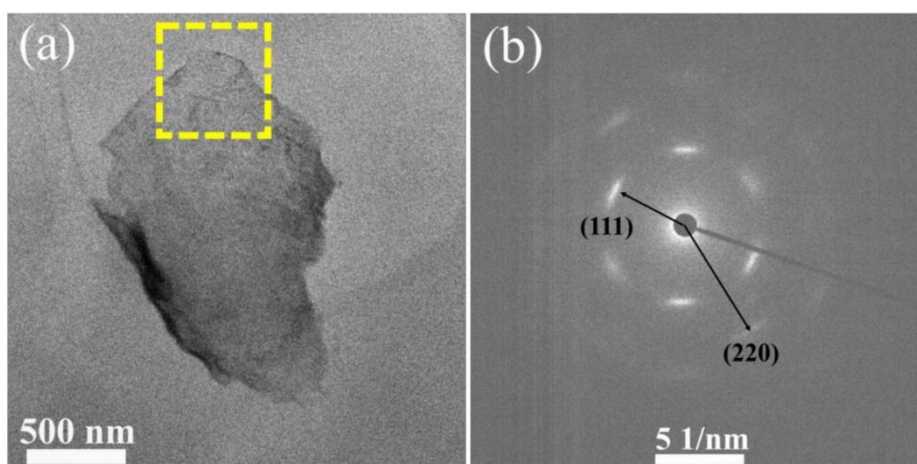


Figure S3. (a) TEM image and (b) the corresponding selected area electron diffraction (SAED) pattern in selected area in (a) of **D-Pd M**.

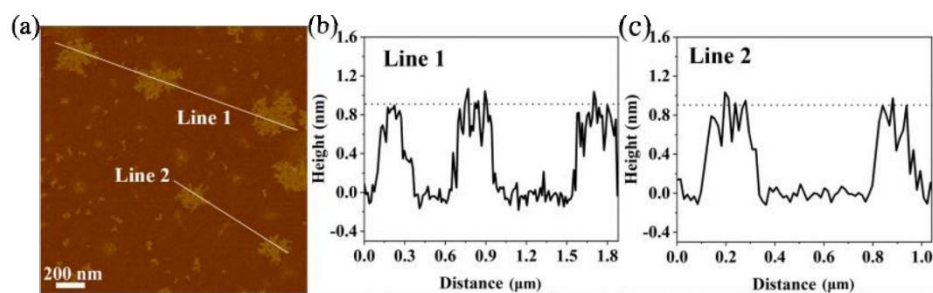


Figure S4. Atomic force microscopy (AFM) image (a) and corresponding height profiles (b and c) of **D-Pd M**.

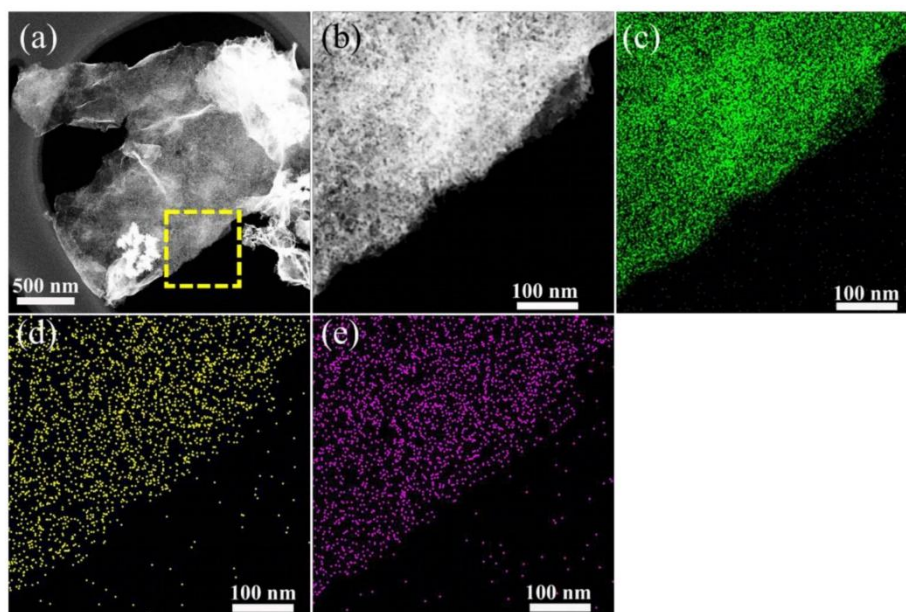


Figure S5. (a) HAADF-STEM image, (b) the magnification of selected area (in a, yellow square), (c-d) and the corresponding elemental mapping of Pd, Mo, and W elements of the **D-Pd M**.

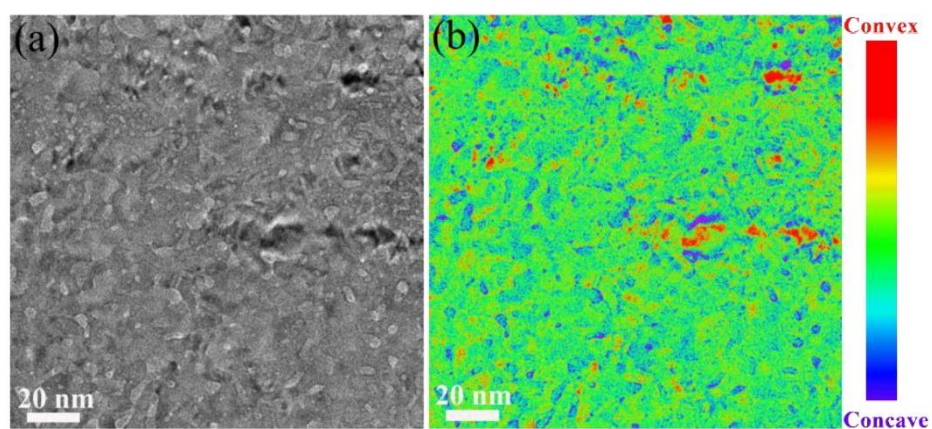


Figure S6. (a) TEM images and (b) corresponding false color mode of **D-Pd M**.

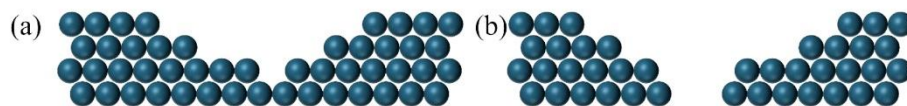


Figure S7. Schematic of pores (a) and concave (b) defects from side view.

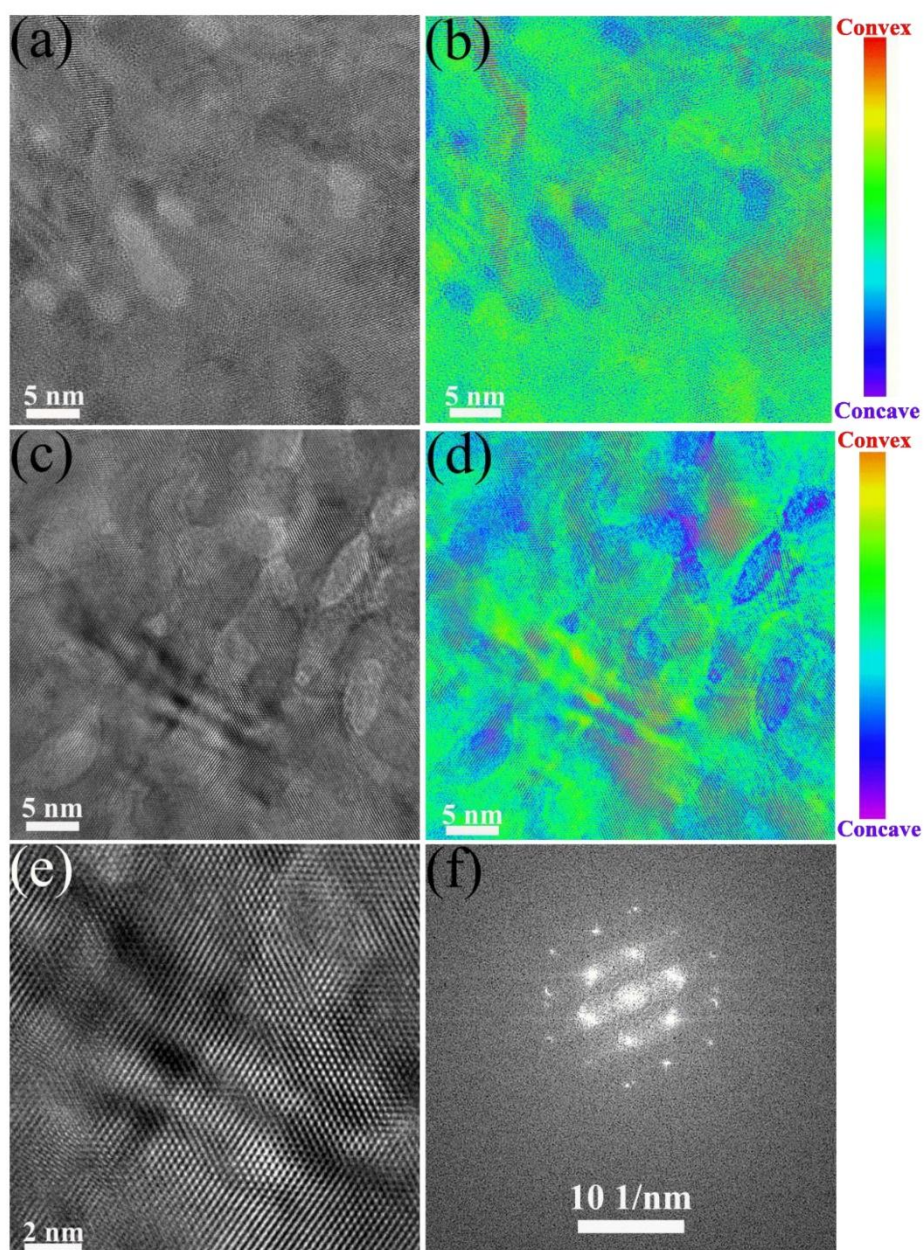


Figure S8. HRTEM images of **D-Pd M**. (a, c, and e) crude images, (b and d) temperature mode of corresponding images, in which dark blue represents concave sites and bright orange represents convex sites. (f) fast Fourier transform pattern of (e).

Table S1. EXAFS fitting parameters at the Mo&Pd *K*-edge and W *L₃*-edge for **D-Pd M**.

Sample	Shell	CN ^a	R(Å) ^b	σ ² (Å ²) ^c	ΔE ₀ (eV) ^d	R factor	
Pd							
Pd foil	Pd-Pd	12*	2.737±0.002	0.0055±0.0002	3.4±0.2	0.0020	
PdO	Pd-O	4.0±0.2	2.017±0.001	0.0023±0.0006	7.9±0.3	0.0042	
	Pd-Pd	3.7±0.8	3.018±0.001	0.0089±0.0017	1.5±0.9		
	Pd-Pd	7.7±0.8	3.388±0.001	0.0124±0.0001	2.3±0.7		
D-Pd M	Pd-Pd/Mo/W	10.7±1.0	2.738±0.005	0.0060±0.0006	6.0±0.7	0.0062	
W							
W-foil	W-W	8*	2.734±0.006	0.0037±0.0007	5.3±1.0	0.0049	
	W-W	6*	3.160±0.012	0.0043±0.0010	8.4±1.7		
WO ₂	W-O	4.0±0.7	2.013±0.001	0.0015±0.0021	11.4±1.0	0.0081	
D-Pd M	W-O	1.4±0.3	1.779±0.001	0.0070±0.0014	-7.9±1.0	0.0062	
	W-O	2.8±0.4	2.111±0.001				
	W-Pd	6.3±0.8	2.605±0.001	0.0189±0.0011	2.0±0.6		
	W-O	15.9±1.8	3.499±0.001				
Mo							
Mo foil	Mo-Mo	8*	2.724±0.003	0.0041±0.0003	4.9±0.5	0.0040	
	Mo-Mo	6*	3.150±0.005	0.0040±0.0004	7.5±1.0		
MoO ₂	Mo-O	6.0±0.3	1.999±0.001	0.0033±0.0006	2.8±0.3	0.0035	
	Mo-Mo	3.1±0.6	2.569±0.001	0.0105±0.0017	8.8±0.8		
	Mo-Mo	1.9±0.2	3.087±0.001	0.0040±0.0001	-11.1±0.5		
	Mo-Mo	6.2±0.3	3.642±0.001				
	Mo-Mo	7.4±1.6	4.058±0.001				
MoO ₃	Mo-O	2.0±0.2	1.685±0.001	0.0037±0.0006	4.5±0.9	0.0080	
	Mo-O	2.7±0.3	1.975±0.001		14.0±0.1		
	Mo-O	3.1±0.4	2.286±0.001	0.0095±0.0001	-		
	Mo-Mo	6.3±1.1	3.430±0.001	0.0086±0.0006			12.0±0.4
	Mo-Mo	15.4±1.9	3.625±0.001				
	Mo-Mo	2.5±0.4	4.062±0.001	0.0051±0.0001			13.3±1.3
D-Pd M	Mo-O	1.4±0.2	1.745±0.001	0.0023±0.0009	8.5±0.8	0.0070	
	Mo-O	0.4±0.2	2.044±0.001				
	Mo-O	0.5±0.2	2.429±0.001	0.0046±0.0014	-3.0±1.2		
	Mo-Pd	0.9±0.2	2.681±0.001				

^aCN, coordination number; ^b*R*, the distance to the neighboring atom; ^c σ^2 , Debye-Waller factor, the Mean Square Relative Displacement (MSRD); ^d ΔE_0 , inner potential correction; *R* factor indicates the goodness of the fit. S_0^2 was fixed to 0.992, 0.812, and 0.958, according to the experimental EXAFS fit of Mo foil, Pd foil, and W foil by fixing CN as the known crystallographic value. * This value was fixed during EXAFS fitting, based on the known structure of Mo, Pd, and W. Fitting range: $3.0 \leq k$ (Å) ≤ 14.0 and $1.0 \leq R$ (Å) ≤ 3.3 (Mo foil); $3.0 \leq k$ (Å) ≤ 12.0 and $1.1 \leq R$ (Å) ≤ 3.9 (MoO₂); $3.0 \leq k$ (Å) ≤ 13.0 and $1.0 \leq R$ (Å) ≤ 4.1 (MoO₃); $3.0 \leq k$ (Å) ≤ 13.0 and $1.0 \leq R$ (Å) ≤ 3.0 (D-Pd M_Mo); $3.0 \leq k$ (Å) ≤ 13.0 and $1.0 \leq R$ (Å) ≤ 2.9 (Pd foil); $3.0 \leq k$ (Å) ≤ 12.0 and $1.0 \leq R$ (Å) ≤ 3.6 (PdO); $3.0 \leq k$ (Å) ≤ 13.0 and $1.9 \leq R$ (Å) ≤ 3.0 (D-Pd M_Pd); $3.0 \leq k$ (Å) ≤ 12.0 and $1.0 \leq R$ (Å) ≤ 3.5 (W foil); $3.0 \leq k$ (Å) ≤ 11.0 and $1.2 \leq R$ (Å) ≤ 2.0 (WO₂); $3.0 \leq k$ (Å) ≤ 10.0 and $1.0 \leq R$ (Å) ≤ 3.8 (D-Pd M_W). A reasonable range of EXAFS fitting parameters: $0.700 < S_0^2 < 1.000$; $CN > 0$; $\sigma^2 > 0$ Å²; $|\Delta E_0| < 15$ eV; *R* factor < 0.02 .

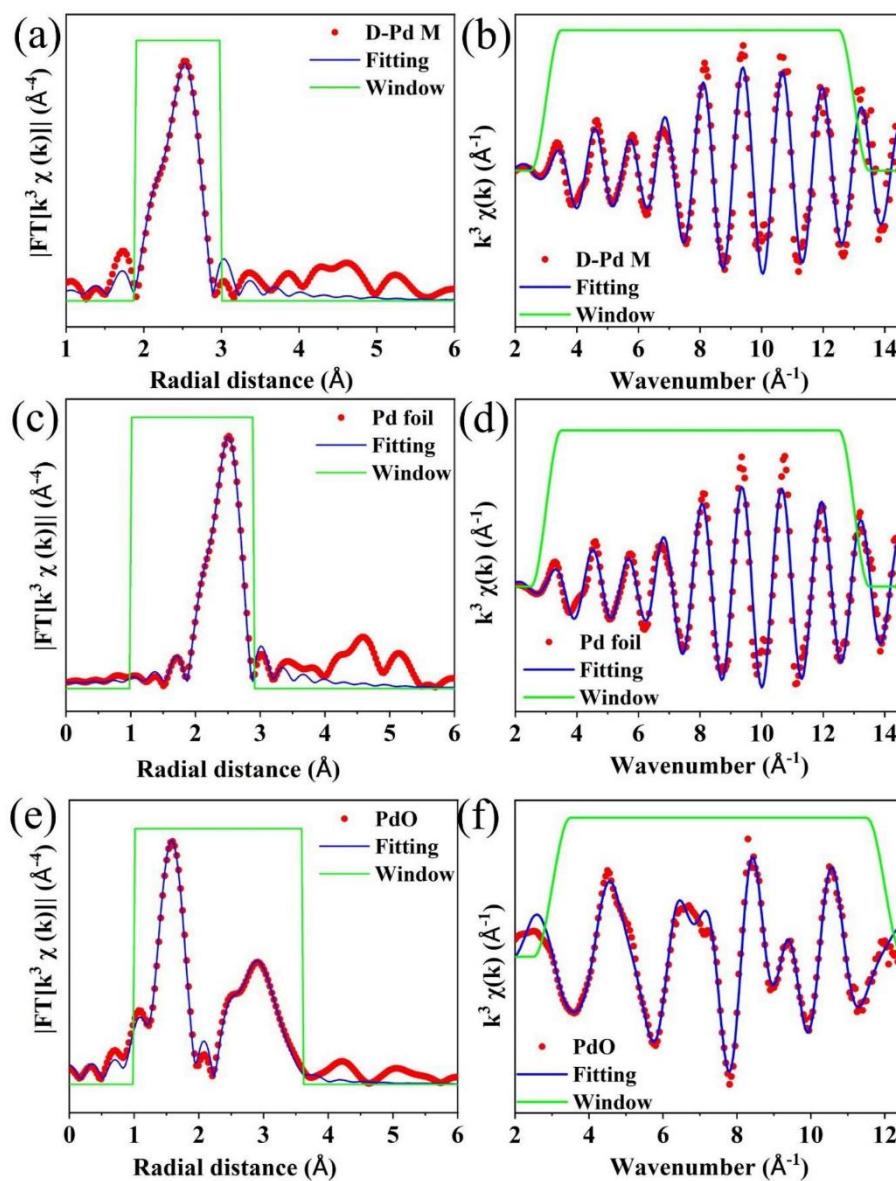


Fig. S9. R space and k space fitting results of Pd K-edge. (a and b) **D-Pd M**, (c and d) Pd foil, and (e and f) PdO. The dots or lines in red, blue, and green represent raw data, fitting results and FT fitting range windows.

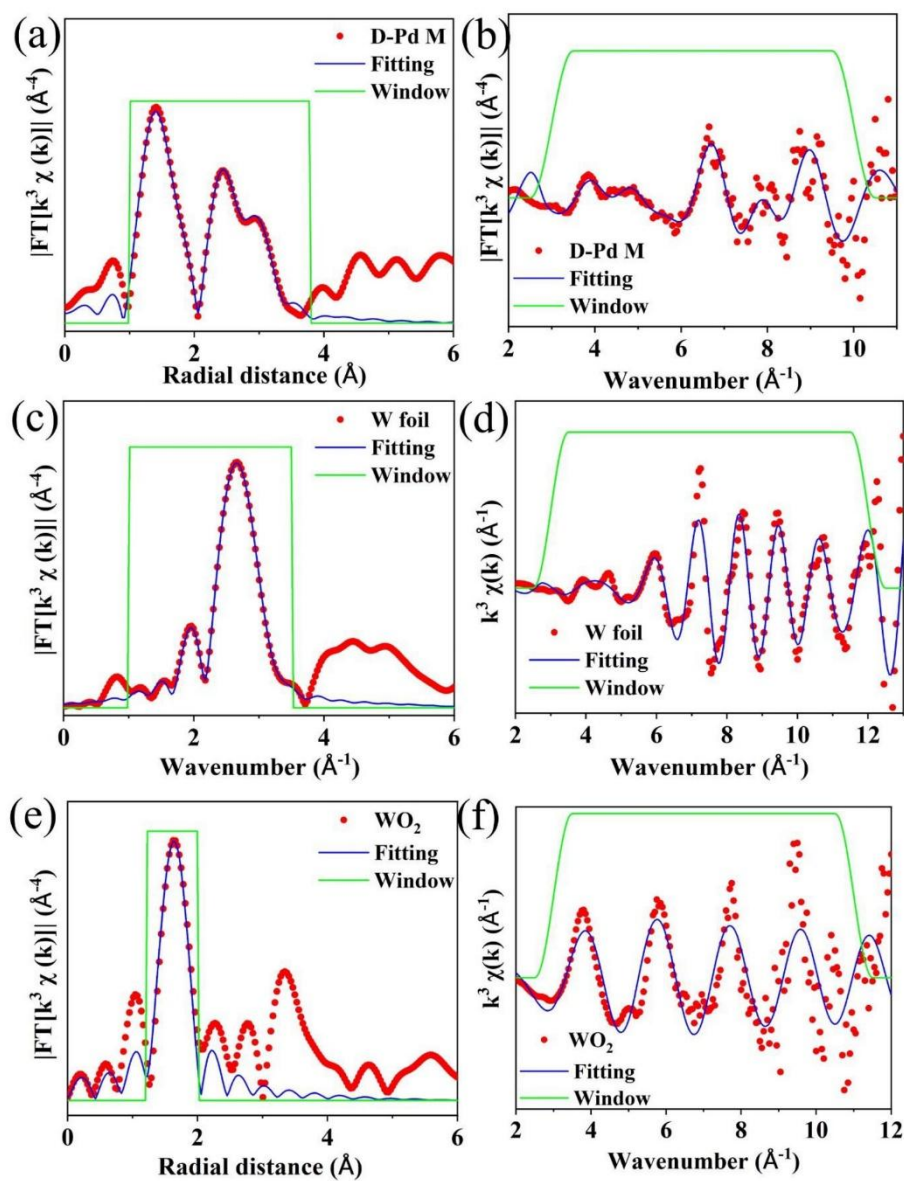


Fig. S10. R space and k space fitting results of W L-edge. (a and b) **D-Pd M**, (c and d) **W foil**, and (e and f) **WO₂**. The dots or lines in red, blue, and green represent raw data, fitting results and FT fitting range windows.

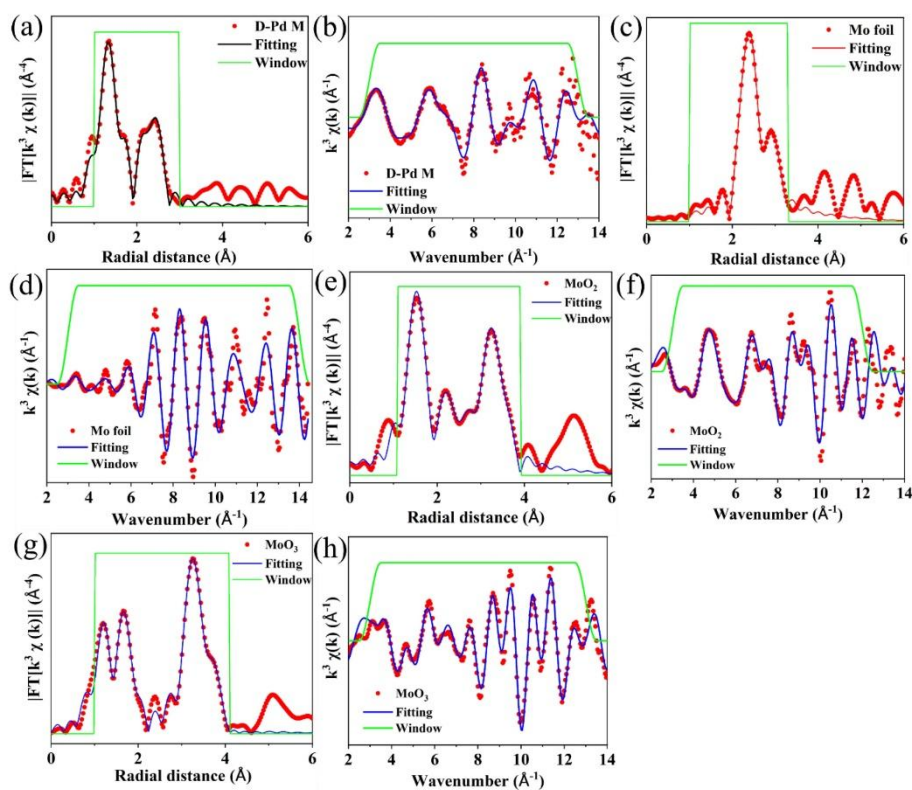


Fig. S11. R space and k space fitting results of Mo K-edge. (a and b) **D-Pd M**, (c and d) Mo foil, (e and f) MoO₂, and (g and h) MoO₃. The dots or lines in red, blue, and green represent raw data, fitting results and FT fitting range windows.

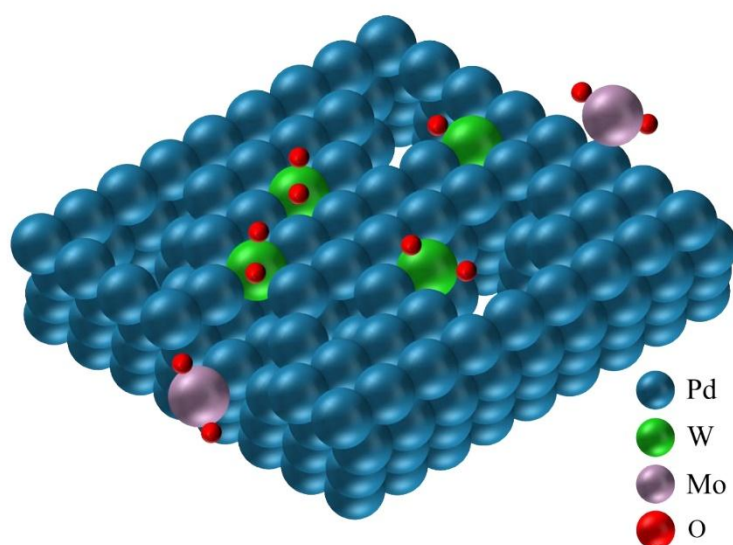


Figure S12. Schematic of MoO_x and WO_x doping. W atoms substitute the position of Pd, but Mo just dispersed on the edge of Pd.

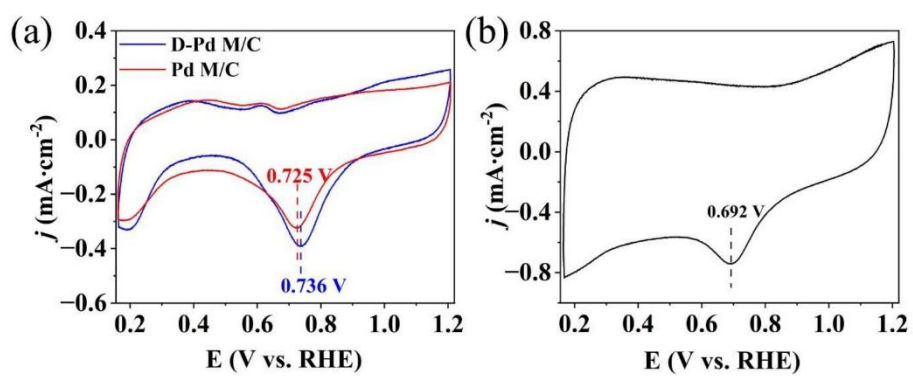


Figure S13. CV curves of (a) **D-Pd M/C**, Pd M/C, and (b) Pd/C in N_2 -saturated 0.1 M KOH solution at a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$.

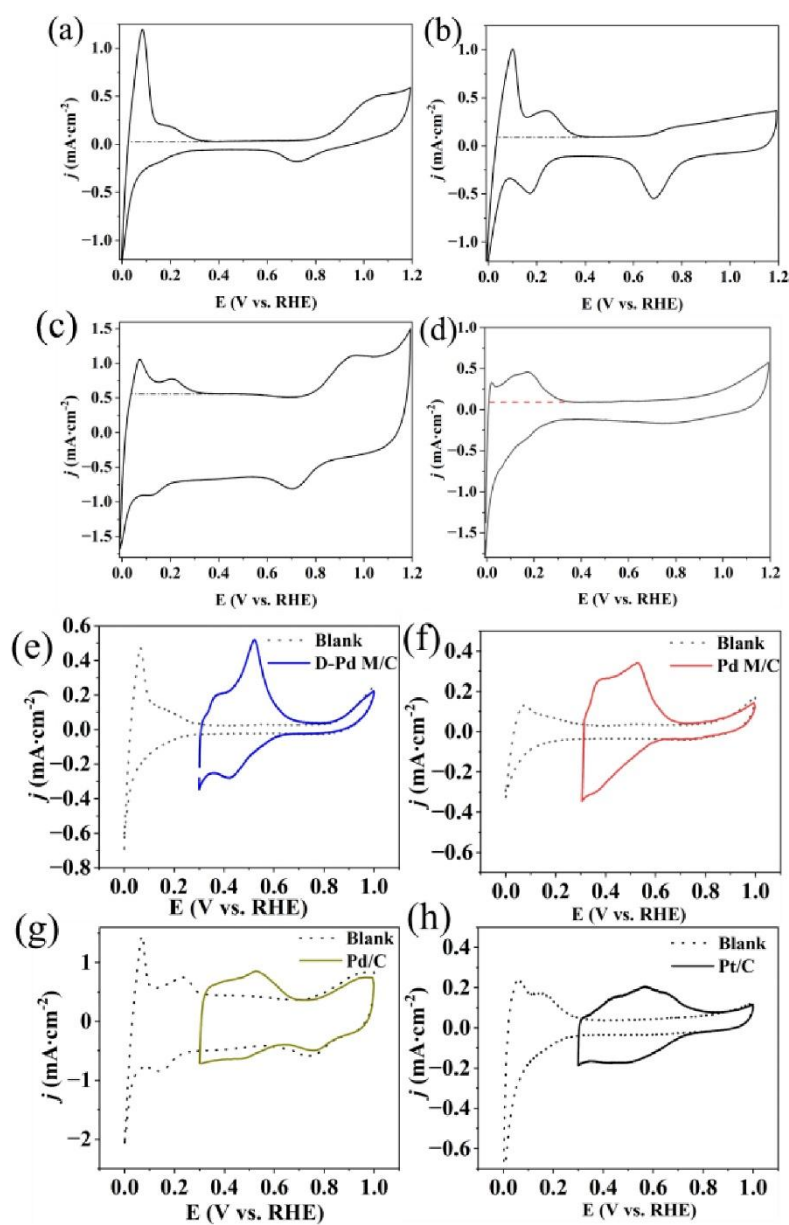


Figure S14. CVs of (a) **D-Pd M/C**, (b) **Pd M/C**, (c) **Pd/C**, and (d) **Pt/C** in N_2 -saturated 0.1 M HClO_4 at a scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$ (e-h) CVs and Cu stripping voltammograms of **D-Pd M/C**, **Pd M/C**, **Pd/C**, and **Pt/C**.

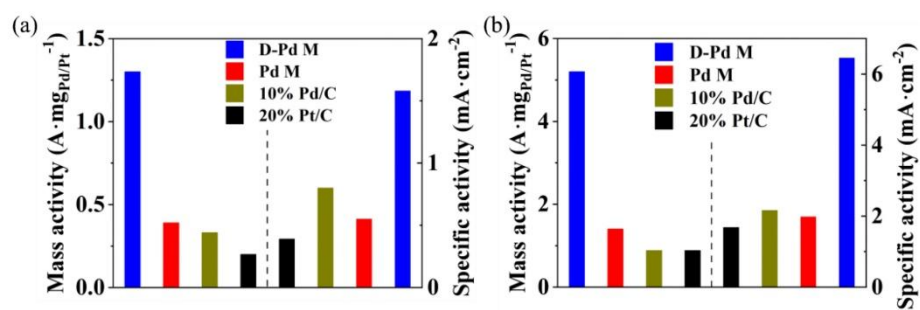
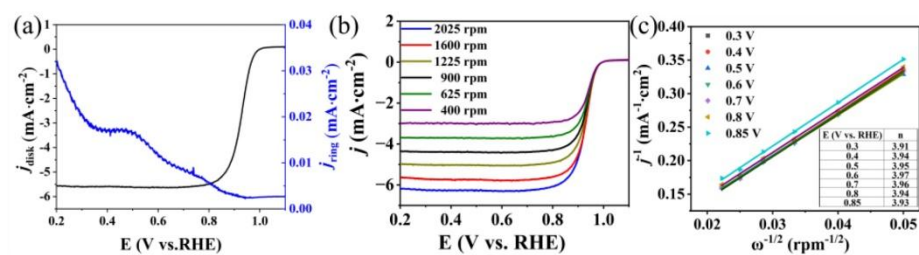


Figure S15. MAs and SAs of D-Pd M/C, Pd M/C, Pd/C, and Pt/C at (a) 0.9 V vs. RHE and (b) 0.85 V vs. RHE.



S18

Figure S16. (a) Ring and disk current density of **D-Pd M** in O_2 -saturated 0.1 M KOH solution, potential applied on ring was set 1.4 V vs. RHE, (b) LSV curves of **D-Pd M/C** at different scan rates and (c) corresponding K–L plot and electron transfer numbers (insert).

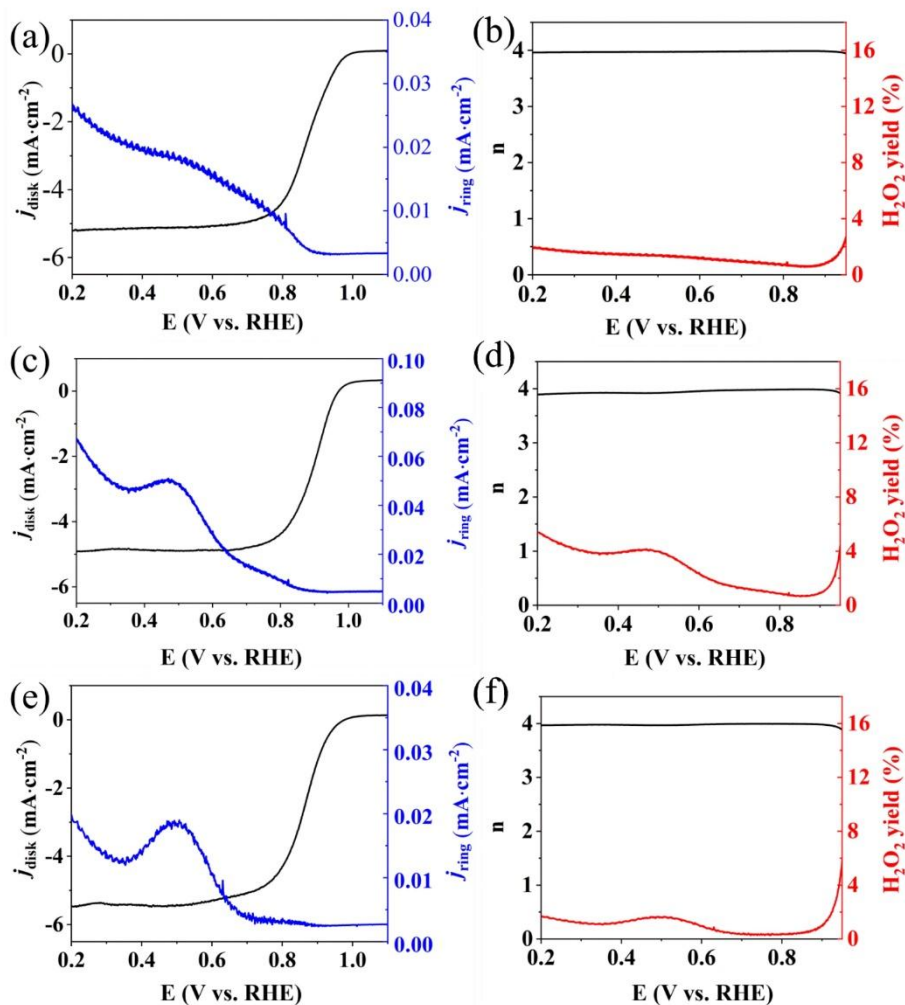


Figure S17. Ring and disk current density of (a) Pd M/C, (c) Pd/C, and (e) Pt/C in O_2 -saturated 0.1 M KOH solution, potential applied on ring was set 1.4 V vs. RHE. The electron transfer number and H_2O_2 yield of (b) Pd M/C, (d) Pd/C, and (f) Pt/C.

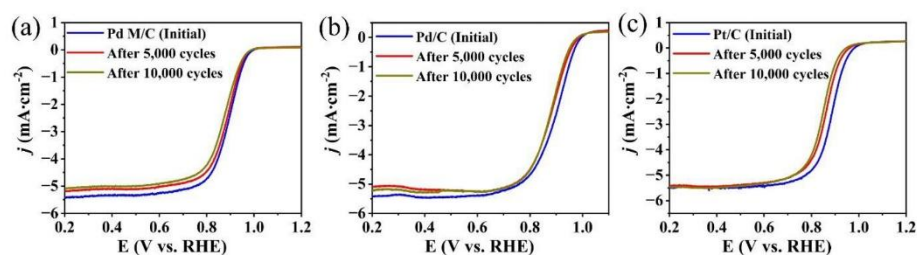


Figure S18. LSVs of (a) Pd M/C, (c) Pd/C, and (e) Pt/C in O_2 -saturated 0.1 M KOH solution before and after 5,000 and 10,000 CV scans.

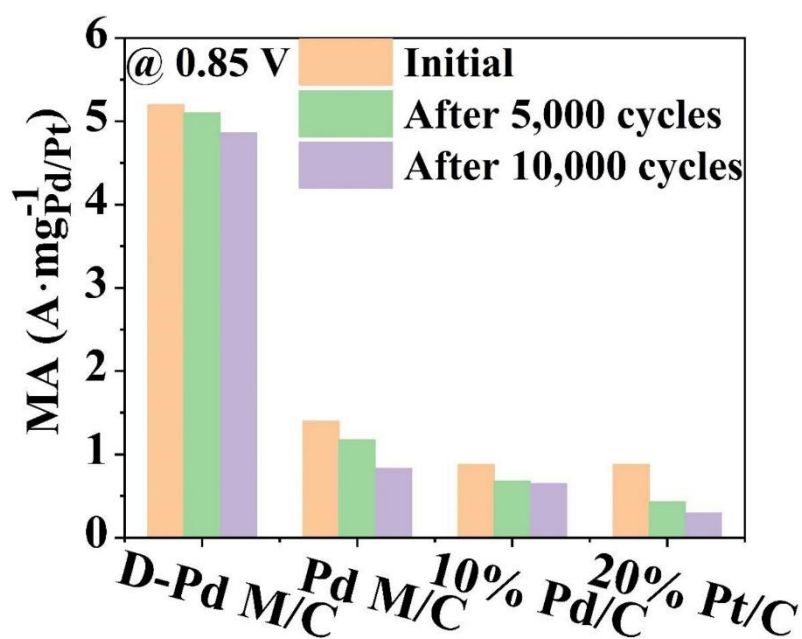


Figure S19. MAs of D-Pd M/C, Pd M/C, Pd/C, and Pt/C at 0.85 V vs. RHE before and after 5,000 and 10,000 cycles

Table S2. Comparison of electroactivity of recent reported representative Pd-based catalysts for alkaline ORR

Samples	Half-wave potential (V vs. RHE)	Specific activity ($\text{mA} \cdot \text{cm}^{-2}$ at 0.9 V)	Mass activity ($\text{A} \cdot \text{mg}_{\text{Pd}}^{-1}$ at 0.9 V)	Reference
D-Pd M	0.93	6.13	1.3	This work
Pd M	0.87	1.86	0.39	This work
PdCu Metallene	0.943	1.67	0.905	[10]
Defect-Rich Pd Metallene	0.90	1.336	0.892	[11]
$\text{Pd}_9\text{Pt}_1\text{Ni}_1$	0.928	1.22	0.29	[12]
Fe-Pd UPM	0.914	0.89	0.736	[13]
PdMo bimetallene	0.95	11.64	16.37	[14]
$\text{Pd}_3\text{Pb}/\text{Pd}$ Tetragonal Nanosheets	0.9	1.31	0.57	[15]
Pd_3Pb Nanosheet	0.91	0.989	0.697	[16]
$\text{Pd}@ \text{PEI-EDA}$ metallene	0.968	1.3	0.93	[17]
N-Pd MNRs	0.95	1.29	0.68	[18]

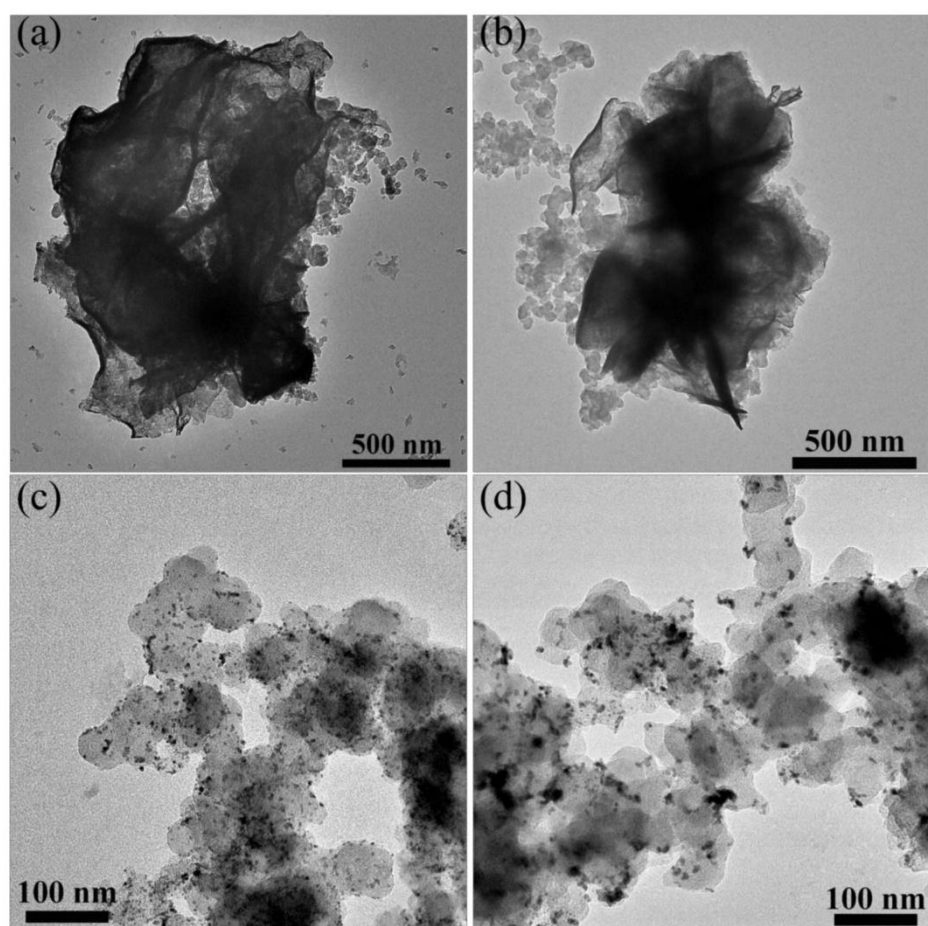


Figure S20. The morphologies of **D-Pd M** (a, b) and **Pt/C** (c, d) before and after ADT test.

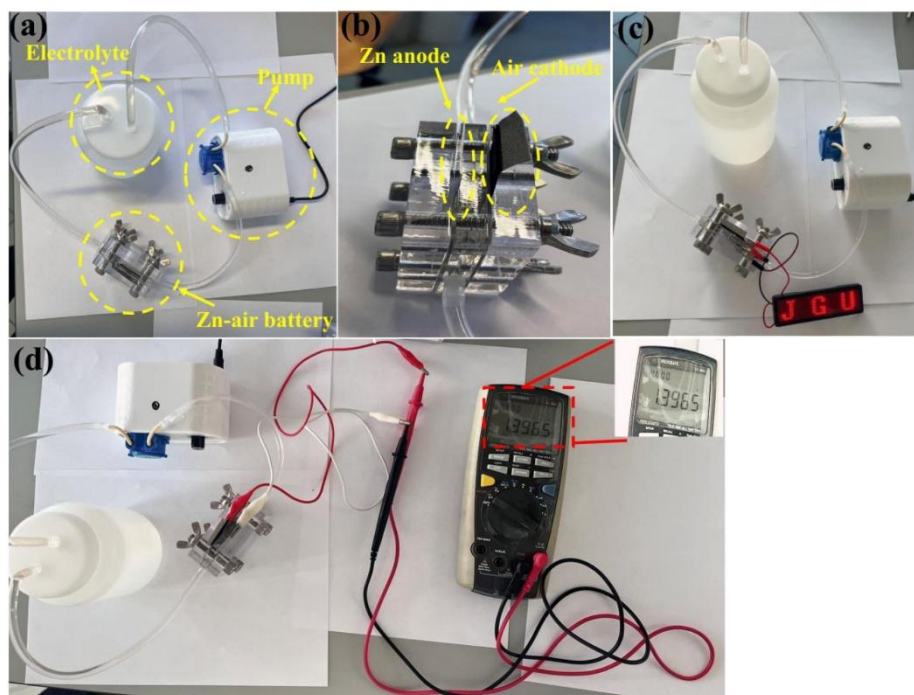


Figure S21. Photographs of the whole Zn-air battery system (a) and Zn-air battery (b), (c) red LED (the operating voltage only > 1 V) powered by **D-Pd M** based Zn-air battery, and (c) an open-circuit voltage of 1.397 V obtained with **D-Pd M** based Zn-air battery.

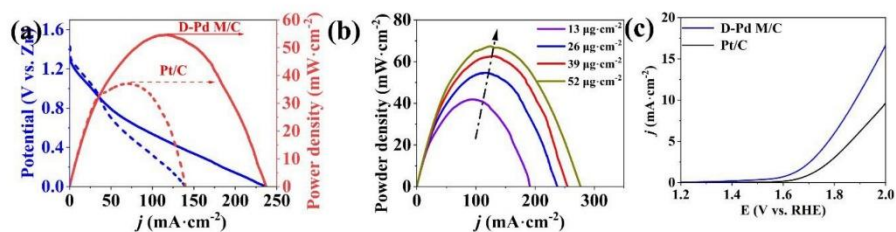


Figure S22. (a) Polarization and corresponding power density curves of **D-Pd M/C** (line) and **Pt/C** (dashes), (b) power density curves of **D-Pd M/C** at different loading, (c) OER polarization curves of **D-Pd M/C** and **Pt/C** in O_2 -saturated 0.1 M KOH at a scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$.

Table S3. Comparison of the performance of the Zn-air battery prepared in this work and representative literature.

Air cathode	Catalyst loading (mg·cm ⁻²)	Open circuit Voltage (V)	Specific capacity (mAh·g _{Zn} ⁻¹)	Voltage (V)	Reference
D-Pd M	0.026	1.4	809	1.25 V @ 15 mA·cm⁻²	This work
PdMo bimetalene	0.2	1.48	798	1.35 V @ 10 mA·cm ⁻²	[14]
Pd-Gd ₂ O ₃ /C+RuO ₂	NA	1.46	724	1.3 V @ 5 mA·cm ⁻²	[19]
Pd/B ₄ C	0.6	1.43	NA	1.2 V @ 5 mA·cm ⁻²	[20]
Commercial Pt/C + IrO ₂	1	1.36	499	1.21 @ 10 mA·cm ⁻²	[14]
Pd/CoO _x /d-NC	1	1.476	760	1.2 @ 10 mA·cm ⁻²	[21]
Ni SAs-Pd@NC	10	1.44	719.2	1.3 @ 5 mA·cm ⁻²	[22]
Pd ₅₅ Au ₄₅	2	1.44	821.4	1.3 V @ 10 mA·cm ⁻²	[23]
PdMoCrW Tetrametalene	1	1.48	895	1.21 @ 10 mA·cm ⁻²	[24]

S7 Reference

- [1] W. Zhu, L. Zhang, P. Yang, C. Hu, Z. Luo, X. Chang, Z.-J. Zhao, J. Gong, J. W. Zhu, J. L. Zhang, P. Yang, C. Hu, Z. Luo, X. Chang, Z. Zhao, J. Gong, *Angewandte Chemie International Edition* **2018**, *57*, 11544–11548.
- [2] Y. Li, Y. Yan, Y. Li, H. Zhang, D. Li, D. Yang, *CrystEngComm* **2015**, *17*, 1833–1838.
- [3] G. Kresse, J. Furthmüller, *Comput Mater Sci* **1996**, *6*, 15–50.
- [4] G. Kresse, J. Hafner, *Phys Rev B* **1994**, *49*, 14251.
- [5] G. Kresse, D. Joubert, *Phys Rev B* **1999**, *59*, 1758.
- [6] K. Lee, É. D. Murray, L. Kong, B. I. Lundqvist, D. C. Langreth, *Phys Rev B Condens Matter Mater Phys* **2010**, *82*, 081101.
- [7] V. Wang, N. Xu, J. C. Liu, G. Tang, W. T. Geng, *Comput Phys Commun* **2021**, *267*, 108033.
- [8] E. A. Nagul, I. D. McKelvie, P. Worsfold, S. D. Kolev, *Anal Chim Acta* **2015**, *890*, 60–82.
- [9] H. Zhou, Z. Ma, G. Yang, X. Jiang, S. Duan, Y. Wu, M. Wang, L. Ni, L. Feng, G. Diao, *Batter Supercaps* **2024**, e202300563.
- [10] L. Zhang, Z. Zhao, X. Fu, S. Zhu, Y. Min, Q. Xu, Q. Li, *ACS Appl Mater Interfaces* **2023**, *15*, 5198–5208.
- [11] H. Yu, T. Zhou, Z. Wang, Y. Xu, X. Li, L. Wang, H. Wang, *Angewandte Chemie International Edition* **2021**, *60*, 12027–12031.
- [12] Q. Yang, L. Shi, B. Yu, J. Xu, C. Wei, Y. Wang, H. Chen, *J Mater Chem A Mater* **2019**, *7*, 18846–18851.
- [13] S. Huang, S. Lu, S. Gong, Q. Zhang, F. Duan, H. Zhu, H. Gu, W. Dong, M. Du, *ACS Nano* **2022**, *16*, 522–532.
- [14] M. Luo, Z. Zhao, Y. Zhang, Y. Sun, Y. Xing, F. Lv, Y. Yang, X. Zhang, S. Hwang, Y. Qin, J. Y. Ma, F. Lin, D. Su, G. Lu, S. Guo, *Nature* **2019**, *574*, 7776–7776, 81–85.
- [15] C. Tang, N. Zhang, Y. Ji, Q. Shao, Y. Li, X. Xiao, X. Huang, *Nano Lett* **2019**, *19*, 1336–1342.
- [16] L. Bu, C. Tang, Q. Shao, X. Zhu, X. Huang, *ACS Catal* **2018**, *8*, 4569–4575.
- [17] Z. Wang, S. Xu, Q. Mao, K. Deng, Y. Xu, H. Wang, H. Yu, L. Wang, *Inorg Chem* **2023**, *62*, 13537–13543.
- [18] H. Wang, Y. Li, S. Liu, H. Yu, K. Deng, Z. Wang, Y. Xu, L. Wang, *Chemical Communications* **2023**, *59*, 11101–11104.
- [19] S. Ning, M. Li, X. Wang, D. Zhang, B. Zhang, C. Wang, D. Sun, Y. Tang, H. Li, K. Sun, G. Fu, *Angewandte Chemie International Edition* **2023**, *62*, e202314565.
- [20] Y. N. Chen, X. Zhang, H. Cui, X. Zhang, Z. Xie, X. G. Wang, M. Jiao, Z. Zhou, *Energy Storage Mater* **2018**, *15*, 226–233.
- [21] T. Kang, D. Nam, J. Kim, *Appl Surf Sci* **2022**, *582*, 152442.

- [22] S. Wang, Z. Lin, M. Li, Z. Yu, M. Zhang, M. Gong, Y. Tang, X. Qiu, *J Mater Chem A Mater* **2022**, *10*, 6086–6095.
- [23] S. Qiao, H. Shou, W. Xu, Y. Cao, Y. Zhou, Z. Wang, X. Wu, Q. He, L. Song, *Energy Environ Sci* **2023**, *16*, 5842–5851.
- [24] Z. Zheng, K. Dong, X. Yang, Q. Yuan, *Langmuir* **2024**, DOI:10.1021/ACS.LANGMUIR.4C01196.

S8 Author contributions

Y.Z., R.L., S. Li, and C.S. conceived the project. R.L., S. Li, and C.S. supervised the project. Y.Z. carried out the material fabrication. Y.Z., F. F, D. G, and R.L. designed and performed electrocatalytic studies. R.L. Y.Z., and C.S. performed data analysis. S. Li. and Y. Z. performed XAS analyses. Z.C. and Y. Z. performed battery tests. K.C. and D.Z. performed (S)TEM analyses. N. M. and W. C. performed computational calculations. All authors co-wrote the manuscript.

6.5 Supporting information: Metal Alloy-Functionalized 3D-Printed Electrodes for Nitrate-to-Ammonia Conversion in Zinc-Nitrate Batteries

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Supporting Information

Metal Alloy-Functionalized 3D-Printed Electrodes for Nitrate-to-Ammonia Conversion in Zinc-Nitrate Batteries

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Supporting Information

Metal Alloy-Functionalized 3D-Printed Electrodes for Nitrate-to-Ammonia Conversion in Zinc–Nitrate Batteries

Si Liu,^{[a],†} Yupeng Zhao,^{[a,b],†} Zhengfan Chen,^[a,b] Dandan Gao,^[a,b] Fan Feng,^[a,b] Tobias Rios-Studer,^[b] Joachim Bansmann,^[c] Johannes Biskupek,^[d] Ute Kaiser,^[d] Rongji Liu^{*[a,b]} and Carsten Streb^{*[a,b]}

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1. Instrumentation and Chemicals

3D printing: The electrodes were 3D printed on a Prusa Research i3 Mk3S 3D printer using commercial ABS filament as reported previously.^[1]

Scanning electron microscopy (SEM): SEM images were recorded on a Hitachi 5200 SEM instrument.

X-ray photoelectron spectroscopy (XPS): The XPS measurements were performed on a PHI 5800 XPS apparatus from Physical Electronics equipped with a monochromatic Al K α X-ray source. The X-ray source was operated at 250 W, survey spectra were recorded with a pass energy of 93.9 eV, detail spectra with 29.35 eV. Data evaluation was carried out using CasaXPS software (version 2.3.23PR1.0).

Powder X-ray diffraction (XRD): (pXRD) patterns were recorded on a Rigaku XRD-6000 diffractometer under the conditions of 40 kV, 40 mA, Cu K α radiation ($\lambda = 0.154$ nm).

Transmission electron microscopy (TEM): TEM analysis was carried out on a Thermofisher Talos 200X (Scanning) (S) TEM at an accelerating voltage of 200 kV equipped with a SuperX energy-dispersive X-ray (EDX) detector. The samples were

dispersed on holey carbon films prior to the TEM investigations. HRTEM and overview images were acquired on CETA2 4K camera. Measurements of the elemental composition were carried out in STEM mode using a high angle annular dark-field (HAADF) detector for imaging together with parallel acquisition of EDX spectra. EDX data were analyzed, quantified, and plotted using the Velox software package (ThermoFisher company).

Chemicals: All listed chemicals were obtained commercially and were used without further purification. Tin chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, Alfa Aesar), Palladium chloride (PdCl_2), trisodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, Merck), ammonium chloride (NH_4Cl , Sigma-Aldrich), sodium hypophosphite monohydrate ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, Acros Organics), aqueous ammonia solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$, VWR), Nickel (II) sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, Fluka), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, VWR), chloride acid (HCl , Acros Organics), sulfate acid (H_2SO_4 , Sigma-Aldrich), Phosphoric acid (H_3PO_4 , VWR), Manganese oxide (MnO_2 , MERCK), Copper (II) sulfate (CuSO_4), Sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$), sodium hydroxide (NaOH), boric acid (H_3BO_3 , Sigma-Aldrich), formaldehyde (HCHO , Sigma-Aldrich), 2,2'-Bipyridine ($\text{C}_5\text{H}_5\text{N}$, Sigma-Aldrich), Potassium hexacyanoferrate(II) trihydrate ($\text{K}_4\text{F}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, Sigma-Aldrich), sodium nitrate (NaNO_3 , Sigma-Aldrich), sulfanilic acid ($\text{C}_6\text{H}_7\text{NO}_3\text{S}$, Sigma-Aldrich), acetic acid (CH_3COOH), dimethyl sulfoxide (DMSO), sodium nitrite (NaNO_2), hydrogen peroxide (H_2O_2 , Sigma-Aldrich), sodium sulphate (Na_2SO_4 , Sigma-Aldrich), n-(1-naphthyl)-ethylenediamine dihydrochloride ($\text{C}_{12}\text{H}_{14}\text{N}_2 \cdot 2\text{HCl}$, Sigma-Aldrich), salicylic acid ($\text{C}_7\text{H}_6\text{O}_3$, Sigma-Aldrich), Sodium hypochlorite solution (NaClO , Sigma-Aldrich), sodium nitroferricyanide ($\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$, Sigma-Aldrich), maleic acid ($\text{C}_4\text{H}_4\text{O}_4$, Sigma-Aldrich), Sodium nitrate- ^{15}N ($\text{Na}_{15}\text{NO}_3$, Sigma-Aldrich).

2. Synthetic Section

Methods for the process of printing ABS meshes, chemical etching of printed mesh's surface of and preparation of **Electrode 1** (Ni plated electrode) were reported in our previous manuscript.^[1]

Preparation of Electrode 2 (Electroless plating Cu on chemically etched ABS meshes): Before the coating of Cu, the etched ABS polymer was modified with Pd seeds as the initial catalyst for Cu deposition. In detail, the pretreated ABS was immersed in sensitizing agent containing 0.24 M aqueous HCl and 0.04 M $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ for 5 min. After washing thoroughly and air-dried, the substrates were activated in aqueous HCl solution (0.24 M) containing 0.5 g/L PdCl_2 (3 mM). After 5 min, the substrates were removed from the above solution and washed with water thoroughly and air-dried. Then the meshes were immersed in Cu electroless plating solution for 40 min at room temperature. The solution contains 14g/L CuSO_4 , 12g/L EDTA- Na_2 , 12g/L NaOH, 45mL/L HCHO, 20mg/L 2,2'-Bipyridine and 10 mg/L $\text{K}_4\text{F}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$.

Preparation of Electrode 3 (Electroless plating NiCu on chemical etched meshes): The sensitization and activation procedures are same as that of **Electrode 2**. The substrates were electroless plated in NiCu plating aqueous solution at 60°C for 40 min.

The NiCu plating solution contains 15g/L $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 18g/L CuSO_4 , 45g/L $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, 30g/L H_3BO_3 , 30g/L $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, and 24g/L NaOH .

3. Electrochemical test

Electrochemical analyses were carried out in three electrode systems on a Pine Wavedriver 200 Bipotentiostat. The electrochemical test was carried out in a Pine Research H-type glass cell, using Nafion 117 as a proton exchange membrane separating the two compartments. Pretreatment of the Nafion 117 began with a half-hour soak in a 5 % H_2O_2 aqueous solution at 80°C, followed by a half-hour soak in deionized water at ambient temperature. Finally, the membrane was immersed in a 5% H_2SO_4 aqueous solution for another half an hour at 80°C. The prepared electrodes and saturated calomel electrode (SCE) were set as working electrode and reference electrode and were placed in the cathode chamber. Pt wire was applied as counter electrode in anode chamber. Both chambers were filled with 25 mL electrolyte containing 0.5 M Na_2SO_4 and specific concentration NaNO_3 . The immersed area in the working electrodes in the electrolyte is $1 \times 0.5 \text{ cm}^2$. The potentials were recorded using the formula in reference to the reversible hydrogen electrode (RHE) scale ($E_{(\text{RHE})} = E_{(\text{SCE})} + 0.0591 \times \text{pH} + 0.241$). Cyclic voltammetry (CV) curves were collected at 20 mV/s without iR compensation at the range from -0.8 to 0.75 V. Linear sweep curves were (LSV) carried out at 5 mV/s with 95% iR and the data was recorded after several cycles until the curves were stable. Electrolyte samples for product analysis were collected in 0.5 M Na_2SO_4 containing 50 mM NaNO_3 for 2 hours at the target potential.

The electrochemical performance of hybrid aqueous Zn-nitrate battery in a two-electrode system was determined in an H-type cell. A piece of ($1 \times 0.5 \text{ cm}^2$) **Electrode 3** cathode in 50 mM NaNO_3 /0.5 M Na_2SO_4 and Zn foil anode ($1 \times 1 \text{ cm}^2$) in 1 M KOH were separated by Nafion 117 membrane. The OCV and discharging polarization curves were recorded in CHI 760e electrochemical workstation. While the other data were recorded in Neware battery tester CT-4008T5V6A-S1.

4. Product analysis

Quantification of NO_2^- : NO_2^- concentration was determined by a colorimetric test.^[2] For the calibration curve, a series of electrolytes containing NaNO_2 with known concentrations were prepared first. Then, 90 mL aqueous solution containing 0.5 g sulfanilic acid and 5 mL acetic acid were prepared. To this, 5 mg of n-(1-naphthyl)-ethylenediamine dihydrochloride was added and the total solution volume was set to 100 mL using deionized water. 1 mL of the respective electrolyte was combined with 4 mL of this solution and kept in the dark at rt for 15 minutes. Finally, the UV-Vis absorption spectrum at 540 nm was recorded using a JASCO V-670 UV-VIS-NIR spectrometer.

The following equation was used to determine the NO_2^- faradaic efficiency:

$$\text{NO}_2^- \text{ Faradaic efficiency (\%)} = \frac{2 \times F \times c_{\text{NO}_2^-} \times V}{46 \times Q} \times 100\%$$

where $c_{\text{NO}_2^-}$ ($\mu\text{g mL}^{-1}$) is the measured NO_2^- concentration, V (mL) is the volume of the electrolyte, F (96498 C mol^{-1}) is the Faraday constant, Q (C) is the charge passed.

Quantification of NH_3 : The amount of NH_3 produced by electrocatalysis was determined by the indophenol blue method.^[3] Calibration of NH_3 was accomplished using the reference electrolytes with varying concentrations of NH_4Cl . Solution **A** contains 1 M NaOH, 5 wt.% salicylic acid, and 5 wt.% sodium citrate. Aqueous solution **B** consists of 0.05 M NaClO and aqueous solution **C** contains 1 wt.% sodium nitroferricyanide. The electrolytes were diluted 50–100 fold depending on the amount of charge generated during electrocatalysis. The coloring agent is composed of 2 mL diluted electrolyte, 2 mL **A**, 1 mL **B** and 0.2 mL **C**. The above mixed solution was allowed to stand for 2h for reaction. Finally, the absorbance at 655 nm was recorded on a UV-vis spectrophotometer.

The following equations was used to determine the yield rate and faradaic efficiency of ammonia:

$$\text{NH}_3 \text{ yield } \left(\frac{\mu\text{g}}{\text{h} \cdot \text{cm}^2} \right) = \frac{c_{\text{NH}_3} \times V}{t \times A}$$

$$\text{NH}_3 - \text{Faradaic efficiency (\%)} = \frac{8 \times F \times c_{\text{NH}_3} \times V}{17 \times Q} \times 100\%$$

where c_{NH_3} ($\mu\text{g mL}^{-1}$) is the measured NH_3 concentration, V (mL) is the volume of the electrolyte, t (h) is the electrolysis time and A (cm^2) is the surface area of the working electrode (1 cm^2). F (96498 C mol^{-1}) is the Faraday constant, Q (C) is the charge passed.

NMR studies: NMR spectroscopy was used to confirm the amount of ammonia generated. Known amounts of maleic acid were used as internal standard for quantification of NH_4^+ . In detail, 20 mg maleic acid and 5 mL of 4 M aqueous H_2SO_4 were added into 20 mL of the collected electrolyte. After thorough mixing, 0.54 mL of the above solution and 0.06 mL DMSO were mixed in a quartz NMR tube. Then the samples were tested using nitrogen-NMR (400 MHz) spectroscopy. For ^{15}N labelling experiment, the NaNO_3 was replaced by $\text{Na}^{15}\text{NO}_3$, all the steps were same as described above.

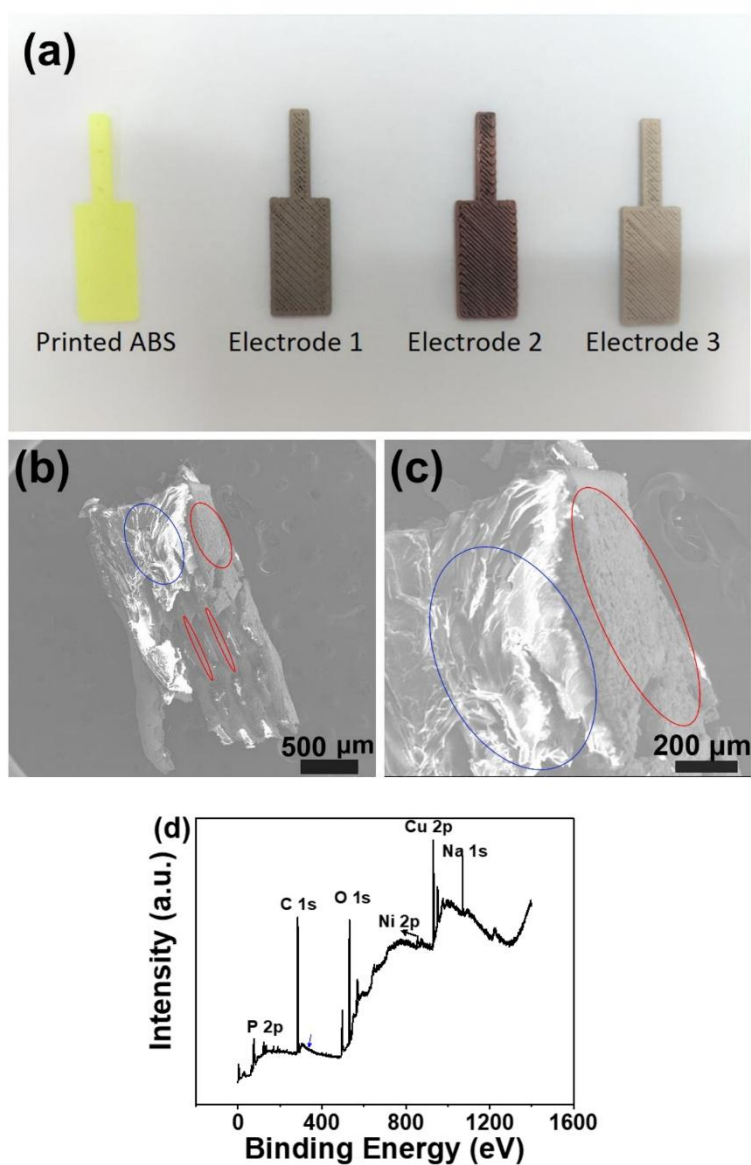


Figure S1. (a) photograph of 3D printed ABS, and the metal-coated **Electrode1**, **Electrode2** and **Electrode 3**. (b, c) Cross-sectional SEM images of the **Electrode 3**. The dark coating layer (shown with the red elliptical) can be observed both in the surface of the electrode and the internal pores of the printed ABS microstructured lattice pattern, and the bright part in images (shown with the blue elliptical) is ABS substrate. Because of its poor conductivity, charging occurred during measurement. (d) Survey XPS spectrum of **Electrode 3**, showing no signal of Pd as indicated by the blue arrow.

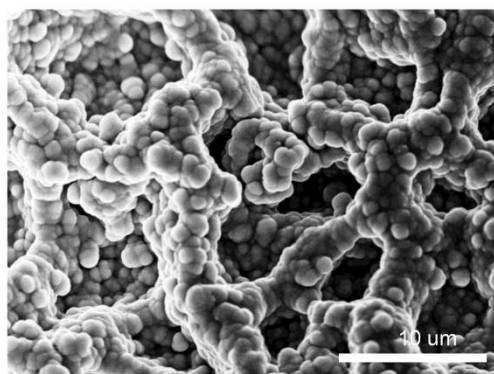


Figure S2. SEM image of **Electrode 1**

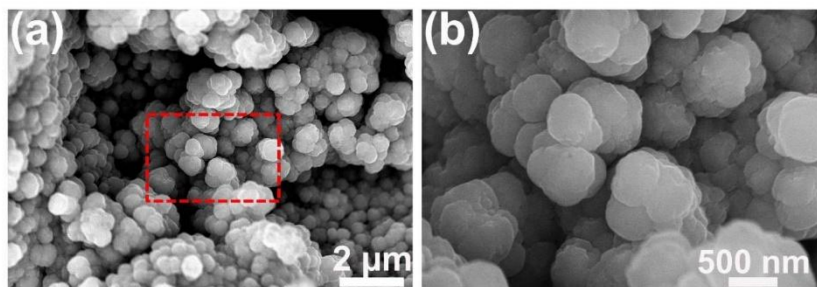


Figure S3. (a) SEM images of **Electrode 2**. (b) magnification of the rectangular area in (a)

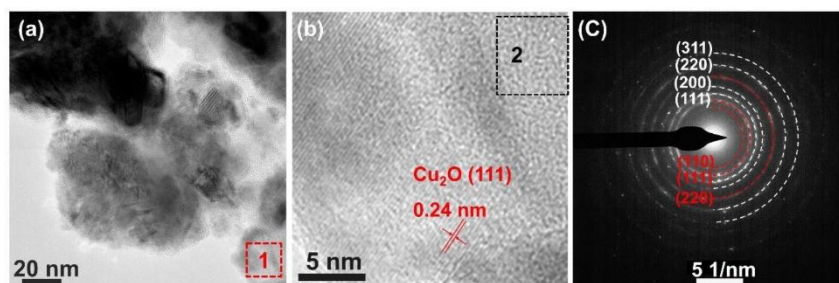


Figure S4. (a)TEM image of Cu particles from **Electrode 2**, and corresponding high magnification (b) and SAED (c) of area 1. Amorphous feature can be found in area 2.

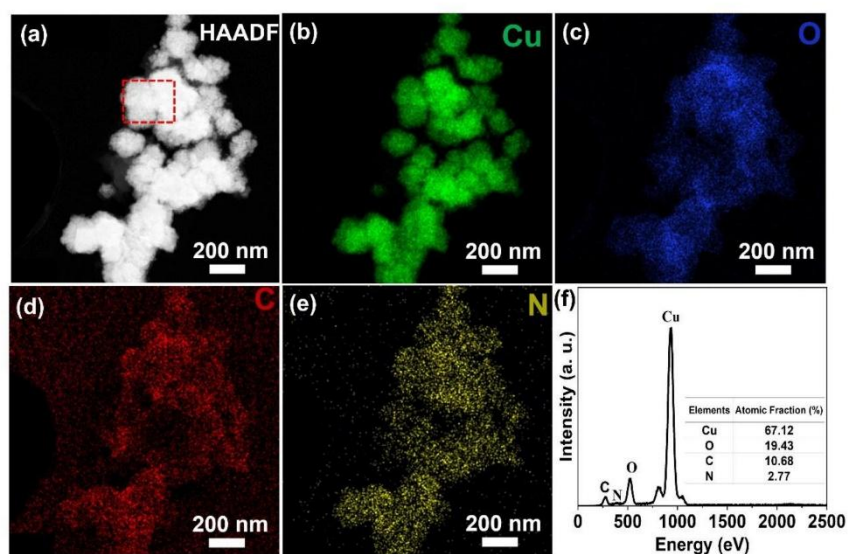


Figure S5. HAADF-STEM pattern and corresponding EDX mapping analysis of the coating layers scratched from **Electrode 2**

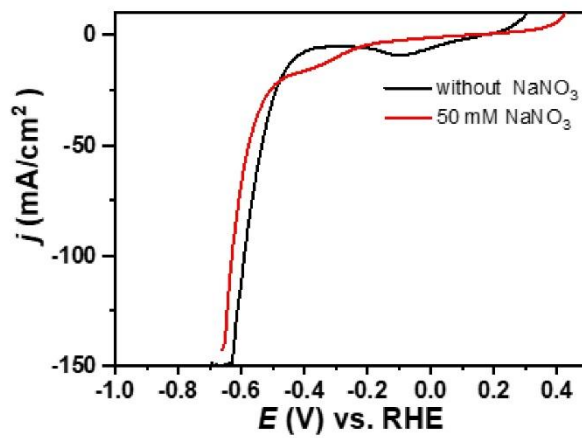


Figure S6. LSV curves of **Electrode 1** in 0.5 M Na_2SO_4 and 0.5 M Na_2SO_4 + 50 mM NaNO_3

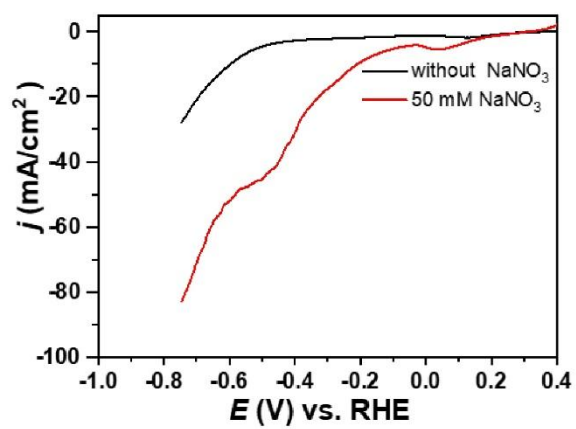


Figure S7. LSV curves of **Electrode 2** in 0.5 M Na₂SO₄ and 0.5 M Na₂SO₄+ 50 mM NaNO₃

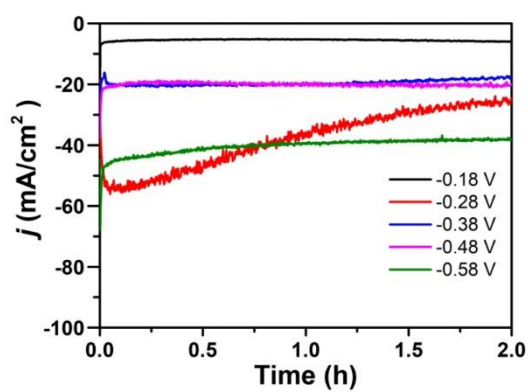


Figure S8. The corresponding i-t curves of **Electrode 1** in 0.5 M Na₂SO₄+ 50 mM NaNO₃ at different potentials

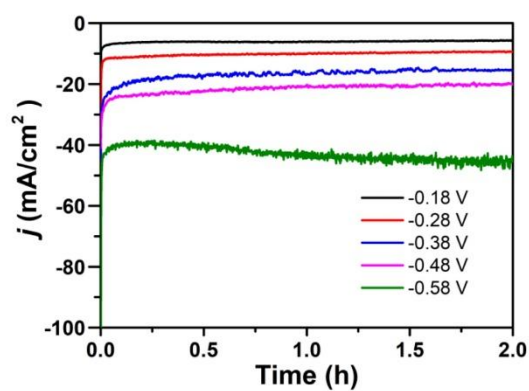


Figure S9. The corresponding i-t curves of **Electrode 2** in 0.5 M Na₂SO₄ + 50 mM NaNO₃ at different potentials

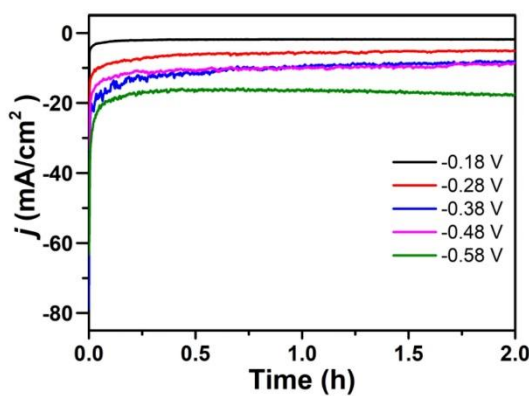


Figure S10. The corresponding i-t curves of **Electrode 3** in 0.5 M Na₂SO₄ + 50 mM NaNO₃ at different potentials

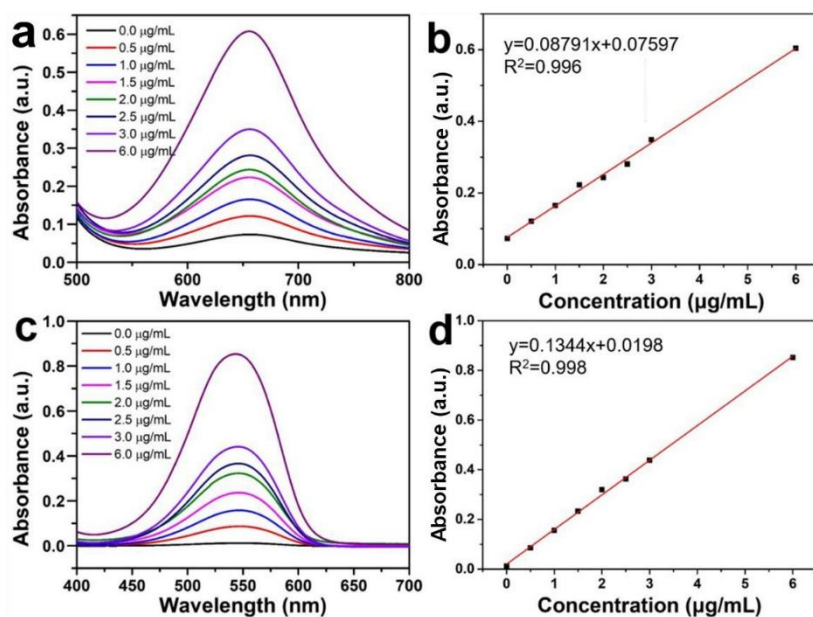


Figure S11. NH_4^+ and NO_2^- detection using colorimetric approaches. (a) The UV-VIS absorption spectra at different NH_4Cl concentrations. (b) The linear calibration curve for the calculation of NH_4^+ formation. (c) UV-Vis absorption spectra of different NaNO_2 concentrations. (d) linear calibration curve for the calculation of NO_2^- production

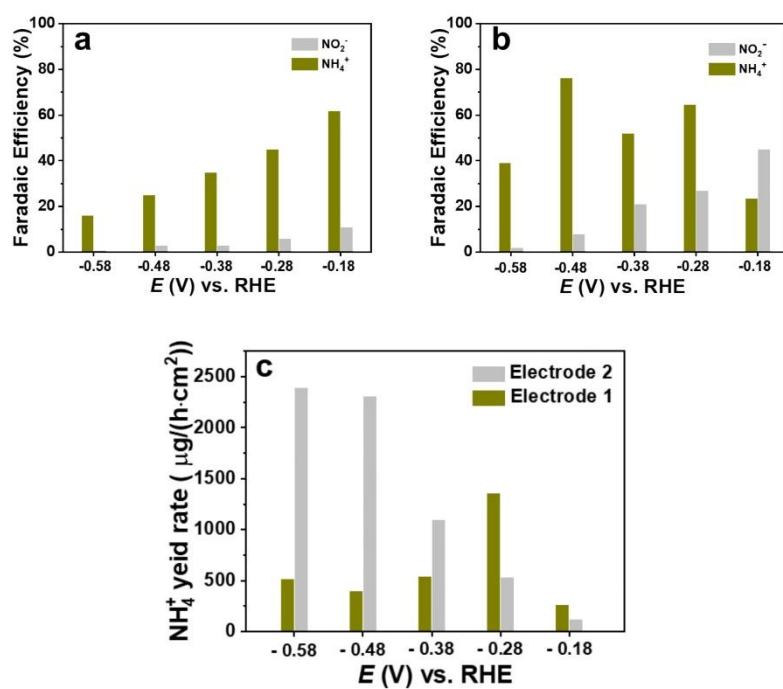


Figure S12. Faradaic efficiency of NH_4^+ and NO_2^- formation for (a) **Electrode 1** and (b) **Electrode 2** at different potentials. (c) NH_4^+ yield rate of **Electrode 1** and **Electrode 2** in 0.5 M Na_2SO_4 + 50 mM NaNO_3 at different potentials.

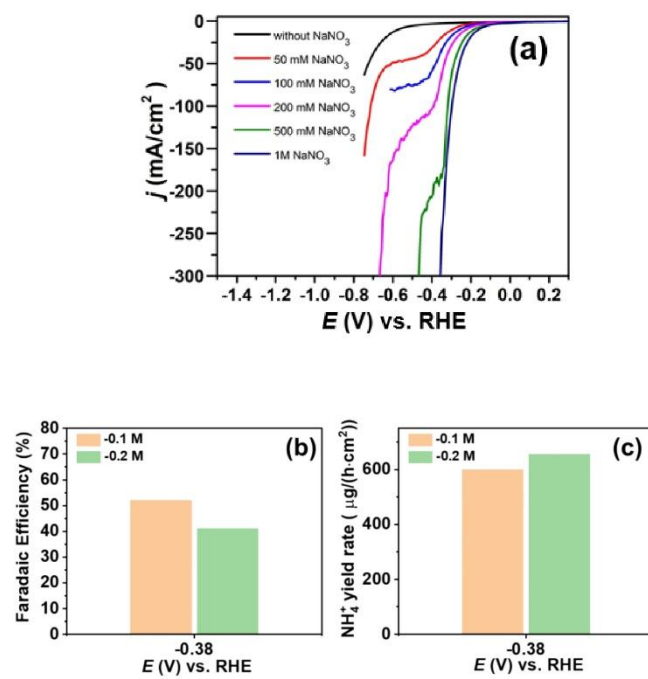


Figure S13. (a) LSV curves of **Electrode 3** in 0.5 M Na₂SO₄ containing different concentration of NaNO₃. (b) FE and (c) NH₄⁺ yield rate of the **Electrode 3** in 0.5 M Na₂SO₄ + 100 and 200 mM NaNO₃ at -0.38V.

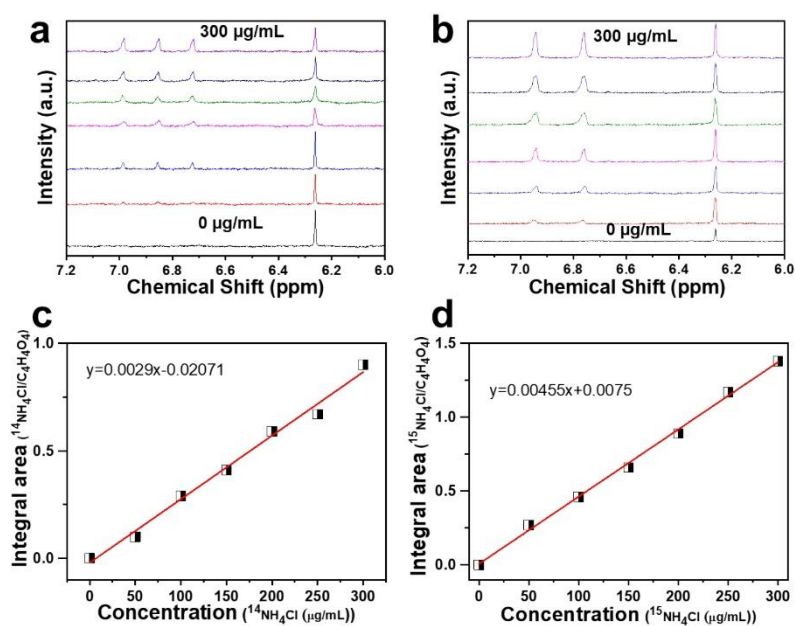


Figure S14. ^1H NMR spectra of the electrolyte containing 0, 50, 100, 150, 200, 250 and 300 $\mu\text{g/mL}$ (a) $^{14}\text{NH}_4\text{Cl}$ and (b) $^{15}\text{NH}_4\text{Cl}$. And the linear standard curve for the calculation of (c) $^{14}\text{NH}_4^+$ and (d) $^{15}\text{NH}_4^+$ production.

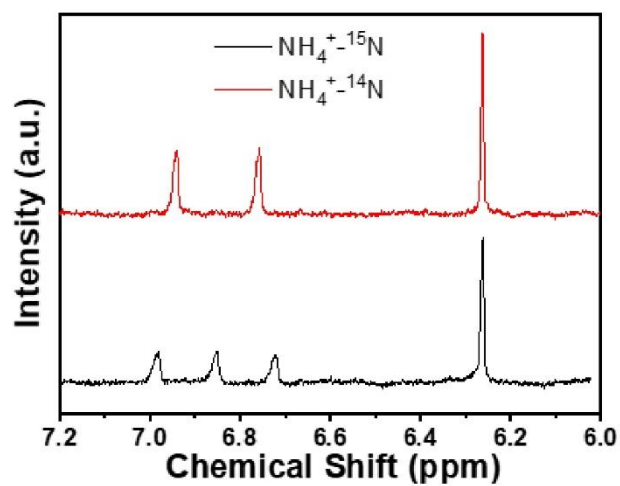


Figure S15. ^1H NMR spectra of the products obtained by electroreduction of ^{14}N and ^{15}N nitrate.

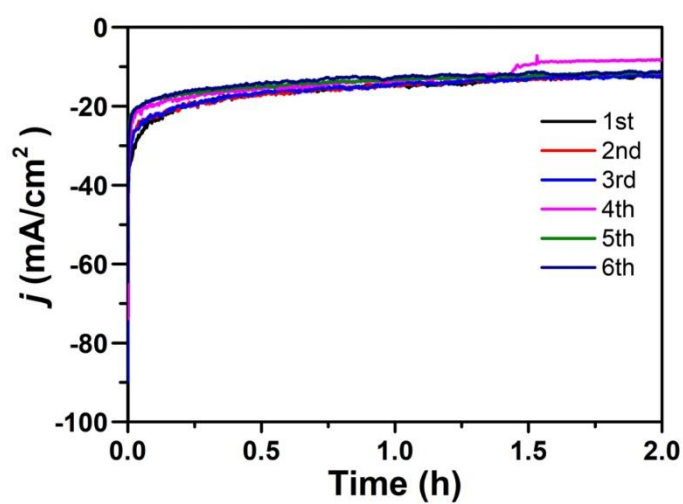


Figure S16. The corresponding i - t curves of **Electrode 3** in 0.5 M Na_2SO_4 +50 mM NaNO_3 at different cycles

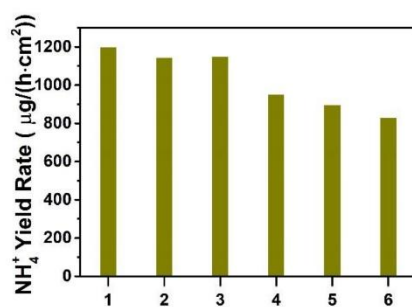


Figure S17. Cycled NH₄⁺ yield rate of **Electrode 3** at -0.38 V vs. RHE

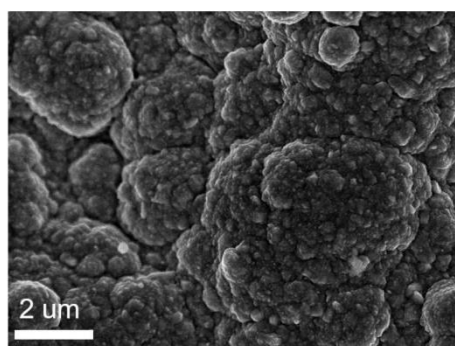


Figure S18. SEM images of 6 times cycled **Electrode 3**

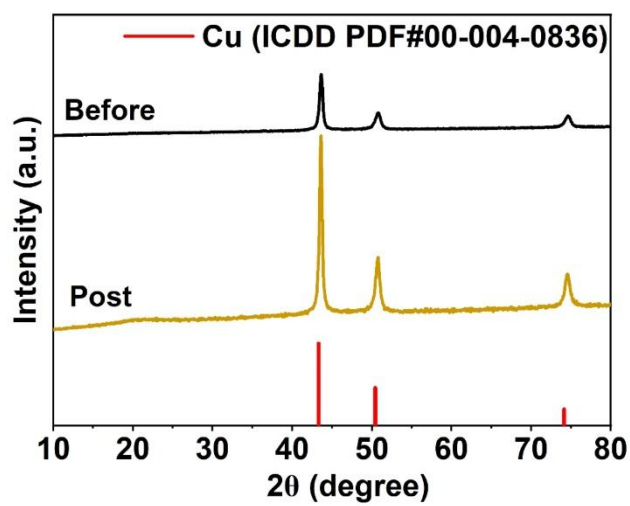


Figure S19. XRD pattern of 6 times cycled **Electrode 3**

Table S1. The comparison of catalytic performance over recently reported NiCu electrocatalysts toward NO_3^- electroreduction

Catalyst	Electrolyte	FE_{NH_3} (%)	Yield rate	Ref.
Cu/Ni	50 mg/L NO_3^- -N + 0.1 M Na_2SO_4	99.0	/	[4]
Ni ₁ Cu SAAO NW ^a	0.1 M KNO_3 + 1 M KOH	80.0	9.7 mg h ⁻¹ cm ⁻²	[5]
CuNi/TM ^b	0.1 M NO_3^- + 0.1 M KOH	93.1	5644 $\mu\text{g h}^{-1} \text{cm}^{-2}$	[6]
Cu _x Ni _y /NC ^c	50 mg/L NO_3^- -N + 0.5 M Na_2SO_4	49.5	/	[7]
CuNi/M/GF ^d	50 mg/L NO_3^- -N + 0.05 M Na_2SO_4	/	/	[8]
Cu ₅₀ Ni ₅₀	100 mM KNO_3 + 1 M KOH	99.0	/	[9]

Note:

a: SAAO NW (Single-atom-alloy oxides nanowire)

b: TM (titanium mesh)

c: (N-doped carbon film)

d: M/GF (multi-walled carbon nanotube/graphite felt)

Literature

- [1] S. Liu, R. Liu, D. Gao, I. Trentin, C. Streb, *Chem. Commun.* **2020**, 56, 8476–8479.
- [2] Y. Feng, H. Yang, Y. Zhang, X. Huang, L. Li, T. Cheng, Q. Shao, *Nano Lett.* **2020**, 20, 8282–8289.
- [3] X. Zhao, G. Hu, F. Tan, S. Zhang, X. Wang, X. Hu, A. V. Kuklin, G. V. Baryshnikov, H. Ågren, X. Zhou, H. Zhang, *J. Mater. Chem. A* **2021**, DOI 10.1039/d1ta05718a.
- [4] Y. J. Shih, Z. L. Wu, Y. H. Huang, C. P. Huang, *Chem. Eng. J.* **2020**, 383, 123157.
- [5] K. Liu, H. Li, M. Xie, P. Wang, Z. Jin, Y. Liu, M. Zhou, P. Li, G. Yu, *J. Am. Chem. Soc.* **2024**, 146, 7779–7790.
- [6] R. Li, D. Zhao, L. Zhang, K. Dong, Q. Li, G. Fan, *Sustain. Energy Fuels* **2023**, 7, 4417–4422.

- [7] L. Fang, S. Wang, C. Song, X. Yang, Y. Li, H. Liu, *J. Hazard. Mater.* **2022**, *421*, 126628.
- [8] C. Lu, X. Lu, K. Yang, H. Song, S. Zhang, A. Li, *J. Mater. Sci.* **2021**, *56*, 7357–7371.
- [9] Y. Wang, A. Xu, Z. Wang, L. Huang, J. Li, F. Li, J. Wicks, M. Luo, D. H. Nam, C. S. Tan, Y. Ding, J. Wu, Y. Lum, C. T. Dinh, D. Sinton, G. Zheng, E. H. Sargent, *J. Am. Chem. Soc.* **2020**, *142*, 5702–5708.

6.6 Supporting information: Ruthenium-doped Copper Nanowires for Nitrite/Nitrate to Ammonia Conversion and Their Integration in Zinc - Nitrite Batteries

Supporting Information

Ruthenium-doped Copper Nanowires for Nitrite/Nitrate to Ammonia Conversion and Their Integration in Zinc - Nitrite Batteries

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S1 Materials

Chemicals and Materials: Potassium hydroxide (KOH, ca 85%, for analysis pellets), and Sodium hypochlorite (NaClO, 5% active chlorine) were purchased from ThermoFisher Scientific. Ruthenium(III) chloride hydrate (RuCl₃·H₂O), and ammonium chloride (NH₄Cl, BioUltra for molecular biology, ≥99.5%) were purchased from Fluka. Sodium hydroxide (NaOH, pellets), and hydrochloric acid (HCl_{aq}, S.G. 1.18 (~37%)) were purchased from ThermoFisher Scientific. Potassium nitrate (KNO₃, ACS reagent, ≥99.0%), sodium-nitrite-¹⁵N (Na¹⁵NO₂, 98 atom % ¹⁵N, 95%), and ammonium-¹⁵N chloride (¹⁵NH₄Cl, ≥98 atom % ¹⁵N, ≥99%) were purchased from Sigma Aldrich. Dimethyl sulfoxide-d₆ (d₆-DMSO, (CD₃)₂SO 99.8 %) was purchased from Deutero. Nitric acid (HNO₃, 69%) was purchased from Supelco. Salicylic acid (C₇H₆O₃) was purchased from VWR. Sodium nitrite (NaNO₂, ≥99%) was purchased from Carl

Roth. Sodium pentacyanonitrosylferrate(III)dihydrate ($\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$, 98%+) was purchased from Alfa Aesar. Tri-sodium citrate dihydrate was purchased from Merck. All chemicals were used without further purification.

S2 Instrumentation

Scanning electron microscopy / energy dispersive X-ray spectroscopy (SEM EDX).

Samples for SEM were prepared with carbon film pads on aluminium holders. A small piece of about $0.5 \times 0.5 \text{ cm}^2$ was cut from the electrode and fixed on the sample pad. The measurements were performed using a *Hitachi SU 8000*. The acceleration voltage used was in the range from 3 kV to 8 kV.

Transmission electron microscopy / High-resolution transmission electron microscopy (TEM and HRTEM).

The surface layer of the CuRu-3h/CF was scratched off and dispersed in ethanol. For TEM characterization, the samples were drop-cast onto a lacey carbon coated TEM grid. Microstructural characterization was done using a FEI Tecnai F20 transmission electron microscope operated at an acceleration voltage of 200 kV. Micrographs were acquired using a Gatan K2 electron counting camera.

Powder X-Ray Diffractometry (pXRD).

Samples for pXRD were prepared by cutting a $1 \times 1 \text{ cm}^2$ piece from the electrode. The samples were fixed using a PMMA custom sample holder. The samples were measured with a *Bruker D2 Phaser* equipped with a LYNXEYE-2 detector using $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.54184 \text{ \AA}$). The measurements were performed in the 2θ range from 5° to 90° with a step size of 0.0202847° (continuous scan, 50 s/degree). Crystalline phases were identified using the software *Match! 3*.

Inductively coupled plasma optical emission spectrometry (ICP-OES).

The samples for ICP were prepared by cutting a small piece with a weight of about 1 mg from the electrode. This was then dissolved in 1 mL aqua regia overnight and then diluted with 10 mL distilled water. The measurement was performed using an Agilent 5800 VDV ICP-OES with an automated SPS4 sampler.

Ammonia quantification using Nuclear magnetic resonance (NMR) spectroscopy.

To quantify the ammonia a calibration line was used. The calibration line was obtained by using NH_4Cl solutions with different NH_4^+ concentrations as standard. To prepare the standard solutions, a 100 mL solution with a NH_4^+ concentration of 100 ppm in 1 M KOH was prepared. This solution was then diluted to obtain 10 mL standard solutions of NH_4^+ with concentrations of 1, 2, 4, 6, 8 and 10 ppm. Then 2.5 mL of 4 M aqueous H_2SO_4 was added and mixed thoroughly. 540 μL of the solution were taken and added in an NMR tube with 60 μL $\text{d}_6\text{-DMSO}$, containing 0.04 wt.% of maleic acid as internal standard, and a ^1H NMR was measured. The

samples were then measured using the same method.

Ammonia quantification using Ultraviolet-visible (UV-vis) spectroscopy. To quantify the ammonia concentration, a calibration line was used. The calibration line was obtained by using aqueous NH_4Cl solutions with different concentrations as standard. To prepare the standard solutions a 100 mL solution with a NH_4^+ concentration of 100 ppm in 1 M aqueous KOH was prepared. This solution was then diluted to obtain 2 mL standard solutions of NH_4Cl with concentrations of 0, 1, 2, 4, 6 and 8 ppm. Then 2 mL of a 1 M aqueous NaOH solution containing 5 wt.% salicylic acid and 5 wt.% sodium citrate was added. Next 1 mL of a 0.05 M NaClO solution was added and lastly 0.2 mL of water containing 1 wt.% sodium-nitroprusside was added as a colouring agent. The solution was then stored in the dark for 120 min. Then a UV-vis spectrum was measured in the range of 800 to 500 nm with a scan rate of 0.2 nm/s. The samples were then measured using the same method. The absorption at the maximum of 655 nm was used for the calibration line. The measurements were performed with an *Agilent Cary 3500 UV-vis spectrometer*.

X-ray photoelectron spectroscopy (XPS). XPS measurements were carried out on *Kratos Axis Ultra DLD imaging photoelectron spectrometer*. Measurements were carried out using the instrument's Hybrid mode with monochromated Al K α radiation operating at 10 mA emission current and 15 kV voltage bias in a UHV chamber with a base pressure of approx. 1×10^{-10} mbar. The source line width is approximately 1.0 eV FWHM, as calibrated with the Ag 3d $_{5/2}$ line. The analysis area was $700 \mu\text{m} \times 300 \mu\text{m}$ (i.e., X-ray spot size). The data was collected using a hemispherical analyzer at an angle of 0° to the surface normal. The takeoff angle was kept fixed along the surface normally in all experiments. Survey spectra were measured at a pass energy of 80 eV and elemental spectra at 20 eV pass energy.

S3 Synthetic section

Catalysts synthesis: Commercially available copper foam (CF) (450 μm pores; $\sim 800 \text{ g/m}^2$; 1.6 mm in thickness, Alantum Europe GmbH) was cut into $1 \times 4 \text{ cm}^2$ pieces and sonicated for 30 min with 0.5 M aqueous HCl, then acetone, then isopropanol, to remove surface impurities. Next the pretreated CF was electrochemically oxidized to copper(II) hydroxide ($\text{Cu}(\text{OH})_2/\text{CF}$) under ambient conditions with a current density of 10 mA cm^{-2} until the voltage reached a stable value at about 0.63 V vs. RHE using a H-cell three-electrode system in 3 M aqueous KOH, where Pt wire was used as the counter electrode, and Hg/HgO in 1 M KOH was used as the reference electrode. The $\text{Cu}(\text{OH})_2/\text{CF}$ was then doped with ruthenium using the galvanic replacement reaction with aqueous ruthenium(III) chloride (10 mM) as ruthenium source with different immersion time ($\text{Ru}/\text{Cu}(\text{OH})_2/\text{CF}$). Finally, the $\text{Ru}/\text{Cu}(\text{OH})_2/\text{CF}$ electrodes were thermally reduced to $\text{CuRu-xh}/\text{CF}$ (x refers to the time for the galvanic replacement reaction)

by annealing in an argon/hydrogen (90:10) atmosphere at 300 °C for 3h. The pure Cu(OH)₂/CF was also thermally reduced to nanostructured CF (NCF) with the same annealing method.

S4 Electrochemical measurements

Electrocatalytic NO₂RR performance test

The electrocatalytic NO₂RR performance tests were performed using a H-cell three-electrode system in 1 M aqueous KOH containing 0.1 M NaNO₂ (V = 80 mL), where CF-based electrodes (1 x 1 cm²) were used as the working electrode, Pt wire was used as the counter electrode, and Hg/HgO in 1 M KOH was used as the reference electrode. Before the electrocatalytic reaction, the electrolyte solution was purged with Argon for 30 min. Then, the electrocatalytic reaction was performed for 30 min using a *Parstat 2273 Potentiostat*.

Electrocatalytic NO₃RR performance test

The electrocatalytic NO₃RR performance tests were done using a seal-tight H-cell three-electrode system in 1 M aqueous KOH containing 0.1 M KNO₃ (V = 55 mL), where a Pt plate was used as the counter electrode, and saturated calomel electrode was used as the reference electrode. Before the electrocatalytic reaction, the electrolyte solution was purged with Argon for 30 min. Then, the electrocatalytic reaction was performed for 30 min using a *Parstat 2273 Potentiostat*. During the reaction, gaseous ammonia was trapped using 0.05 M aqueous H₂SO₄ (100 ml). Afterwards the total ammonia yield was quantified from both the reaction solution and the acid solution.

Calculation of NH₃ FE and yield rate

The FE was calculated using the following equation:

$$FE = (n \times F \times c) / Q$$

where n is the number of electrons transferred to form ammonia, which is 6 for NO₂RR and 8 for NO₃RR, c is the concentration of ammonia obtained from UV-vis or NMR measurements, F is the Faraday constant (96485 C mol⁻¹), and Q is the total electric charge used in the reaction obtained by integrating the current density curves of the reaction. The yield rate was calculated using the following equation:

$$\text{Yield rate} = \frac{c * V}{t * S}$$

where c is the concentration of ammonia obtained from UV-vis or NMR measurements, V is the volume of the electrolyte used in the reaction, t is the total reaction time and S is the geometric area of the electrode.

Ammonia selectivity calculation

The ammonia selectivity during the conversion study was calculated using the equation:

$$Selectivity = \frac{c(NH_3)}{c_0(NO_2^-) - c_1(NO_2^-)}$$

Where $c(NH_3)$ is the concentration of ammonia formed in the reaction, $c_0(NO_2^-)$ is the initial concentration of nitrite that was used in the reaction and $c_1(NO_2^-)$ is the final concentration of nitrite at the end of the reaction.

Quantification of NO_2^-

NO_2^- was determined using a modified N-(1-naphthyl)-ethylenediamine dihydrochloride spectrophotometric method. Specifically, 0.5 g of sulfanilic acid was dissolved in 90 mL of H_2O and 5 mL of acetic acid. Then, 5 mg of N-(1-naphthyl)-ethylenediamine dihydrochloride was added, and the solution was diluted to 100 mL to prepare the chromogenic agent. Next, 1 mL of the diluted electrolyte was mixed with 4 mL of the chromogenic agent and kept in the dark for 15 min. The UV-Vis absorption spectrum was then measured between 700 nm and 400 nm, and the calibration line was measured at 500 nm.

Electrochemically active surface area (ECSA) analysis

The ECSA was determined using the equation:

$$ECSA = C_{dl}/C_s$$

where C_{dl} is the double layer capacitance and C_s is the specific capacitance. A specific capacitance (C_s) of 0.04 mF cm^{-2} was used based on values reported in the literature.^[1] The double layer capacitance was obtained using the equation:

$$C_{dl} = (\Delta j/2)/\nu$$

where $\Delta j/2$ is the current density difference in the middle of the measured potential range and ν is the scan rate of the cyclic voltammogram (CV). A series of CV measurements was performed in a potential range without Faradaic charge transfer. Then $\Delta j/2$ was plotted against ν and a linear fit was used to obtain C_{dl} from the slope.

Electrochemical impedance spectroscopy (EIS)

EIS was performed using a single cell with a three-electrode setup in 1 M aqueous KOH, where a Pt plate was used as the counter electrode, and Hg/HgO in 1 M KOH was used as the reference electrode. Before the measurement, the electrolyte was purged with Argon for 30 min. Then, an alternating current with an amplitude of 5 mV was used as a perturbation signal and the resulting impedance was measured for an alternating current frequency range of 10 mHz to 100 kHz. The data was then fitted using the software Zview.

Zn-nitrite battery test

The electrochemical performance of a hybrid aqueous Zn-nitrite battery in a two-electrode system was determined in an H-type cell. A piece of CuRu-3h/CF cathode in 0.1 M NaNO_2 /1 M KOH and Zn foil anode ($1 \times 1 \text{ cm}^2$) in 1 M KOH were separated by the Nafion 117 membrane. The OCV and discharging polarization curves were recorded in CHI 760e electrochemical workstation. While the other data were recorded in Neware battery tester CT-4008T5V6A-S1.

S5 Supplementary Figures

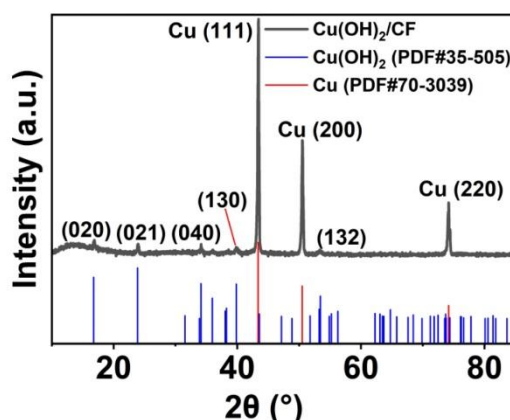


Figure S1. pXRD pattern of the $\text{Cu(OH)}_2/\text{CF}$ obtained after the electrochemical oxidation of pure CF, as well as the reference patterns of Cu (PDF#70-3039) and Cu(OH)_2 (PDF#35-505).

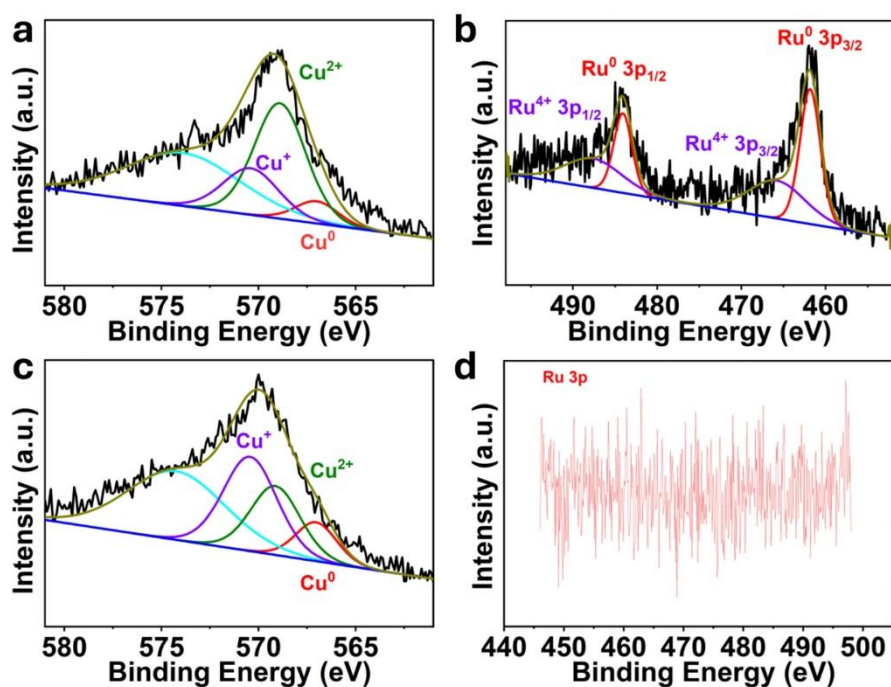


Figure S2. (a) Cu LMM Auger spectrum before the reaction, (b) Ru 3p XPS spectrum before the reaction, (c) Cu LMM Auger spectrum of Cu after the reaction, and (d) Ru 3p XPS spectrum after the reaction.

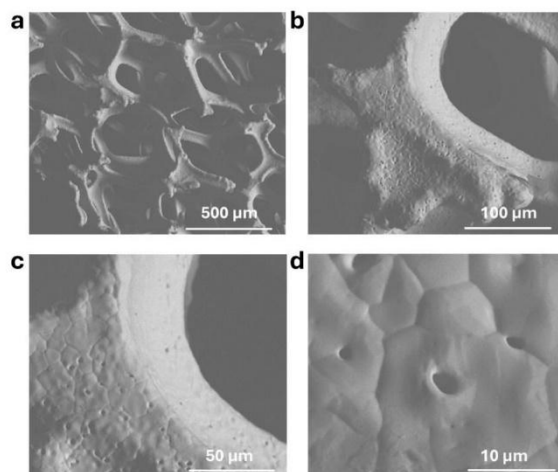


Figure S3. SEM images of pure CF at different magnifications.

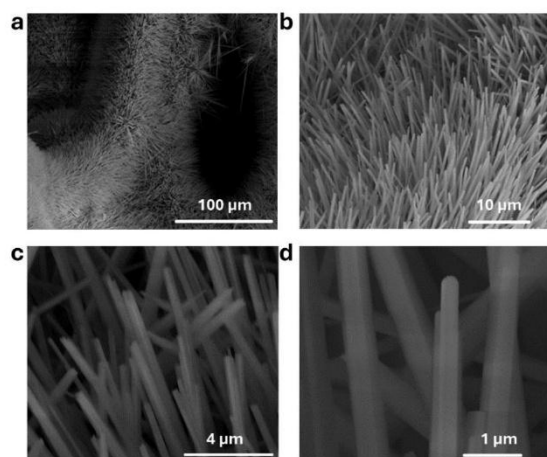


Figure S4. SEM images of Cu(OH)₂/CF at different magnifications.

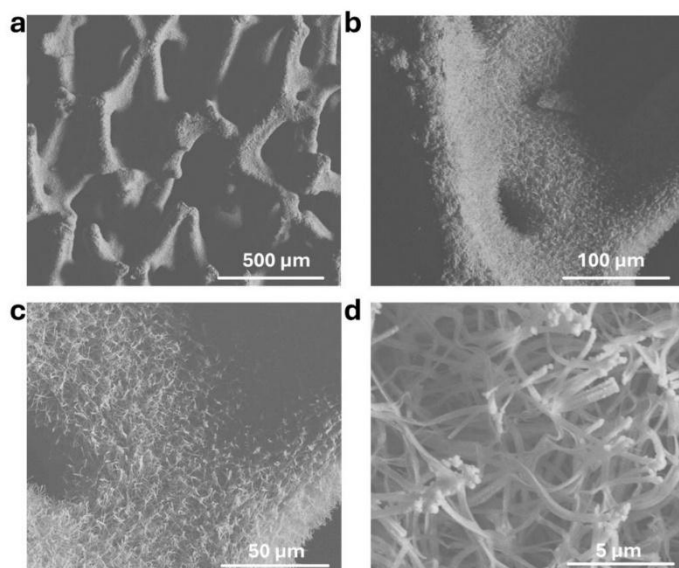


Figure S5. SEM images of CuRu-1h/CF at different magnifications.

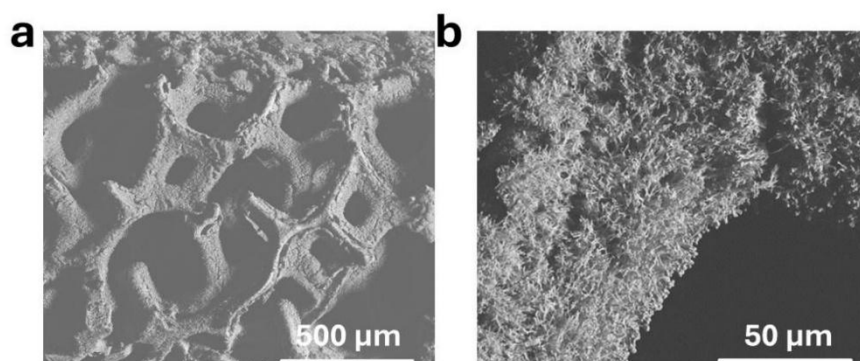


Figure S6. SEM images of CuRu-3h/CF at different magnifications.

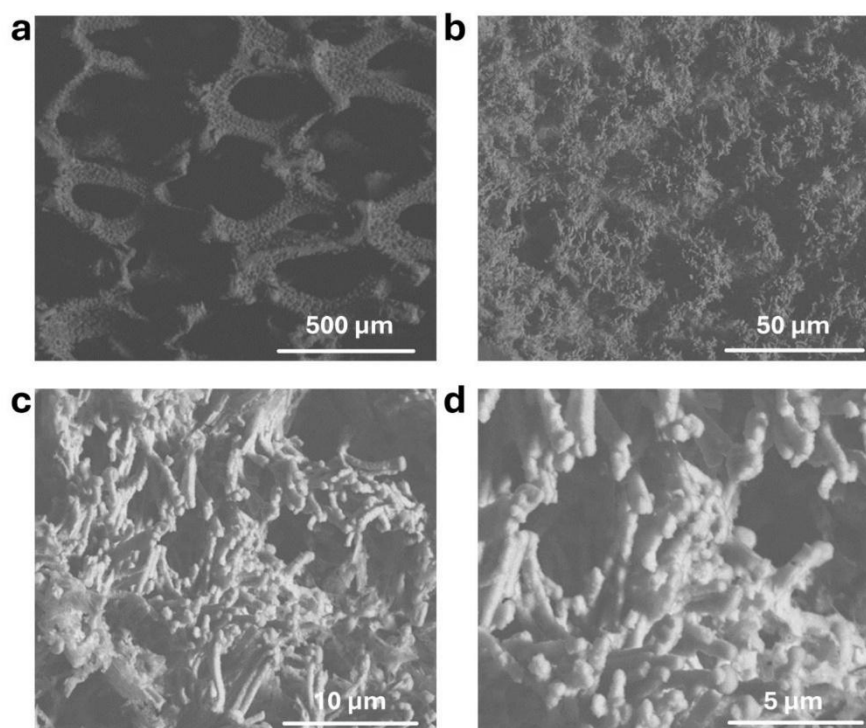


Figure S7. SEM images of CuRu-5h/CF at different magnifications.

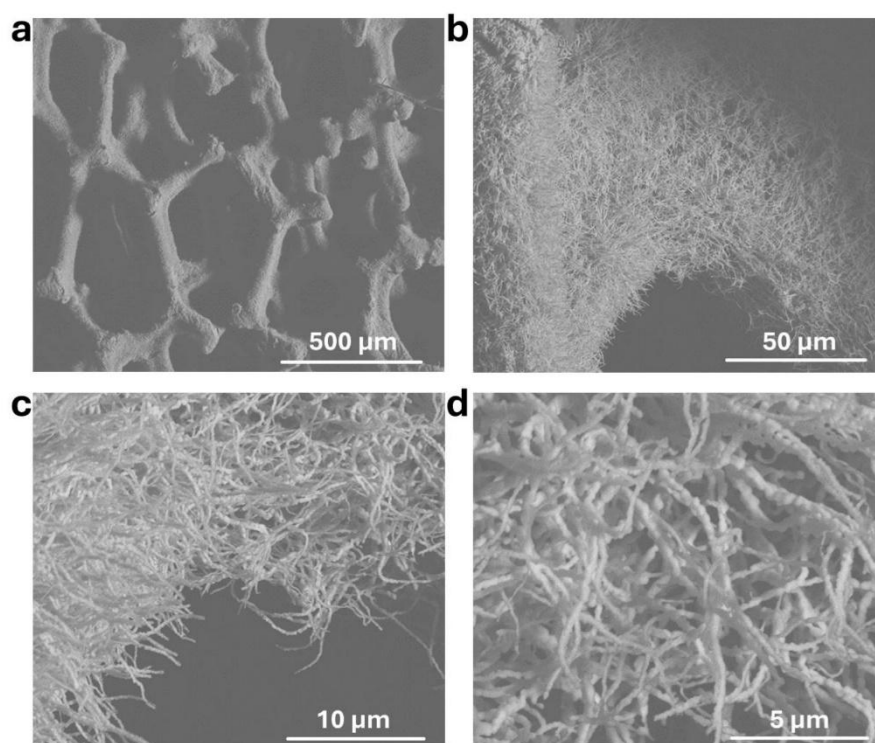


Figure S8. SEM images of NCF at different magnifications.

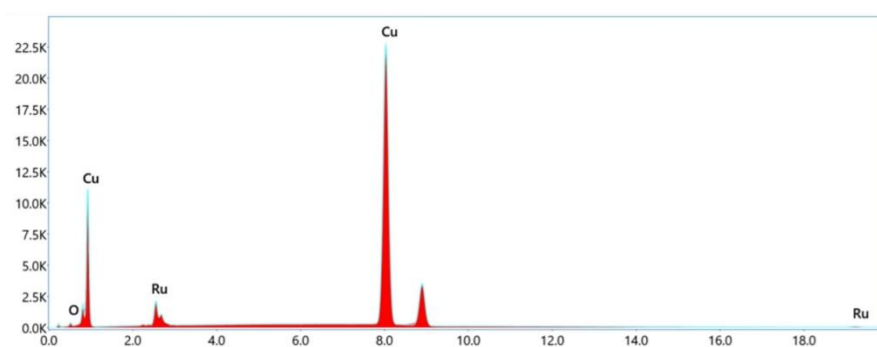


Figure S9. SEM-EDX spectrum of CuRu-3h/CF.

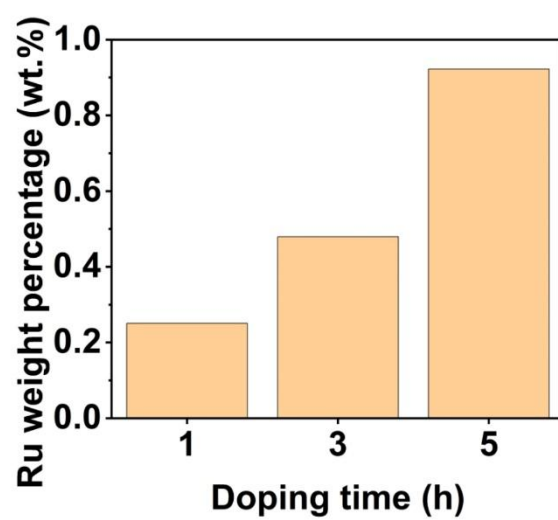


Figure S10. Ruthenium weight percentage in CuRu-xh/CF based on ICP-OES.

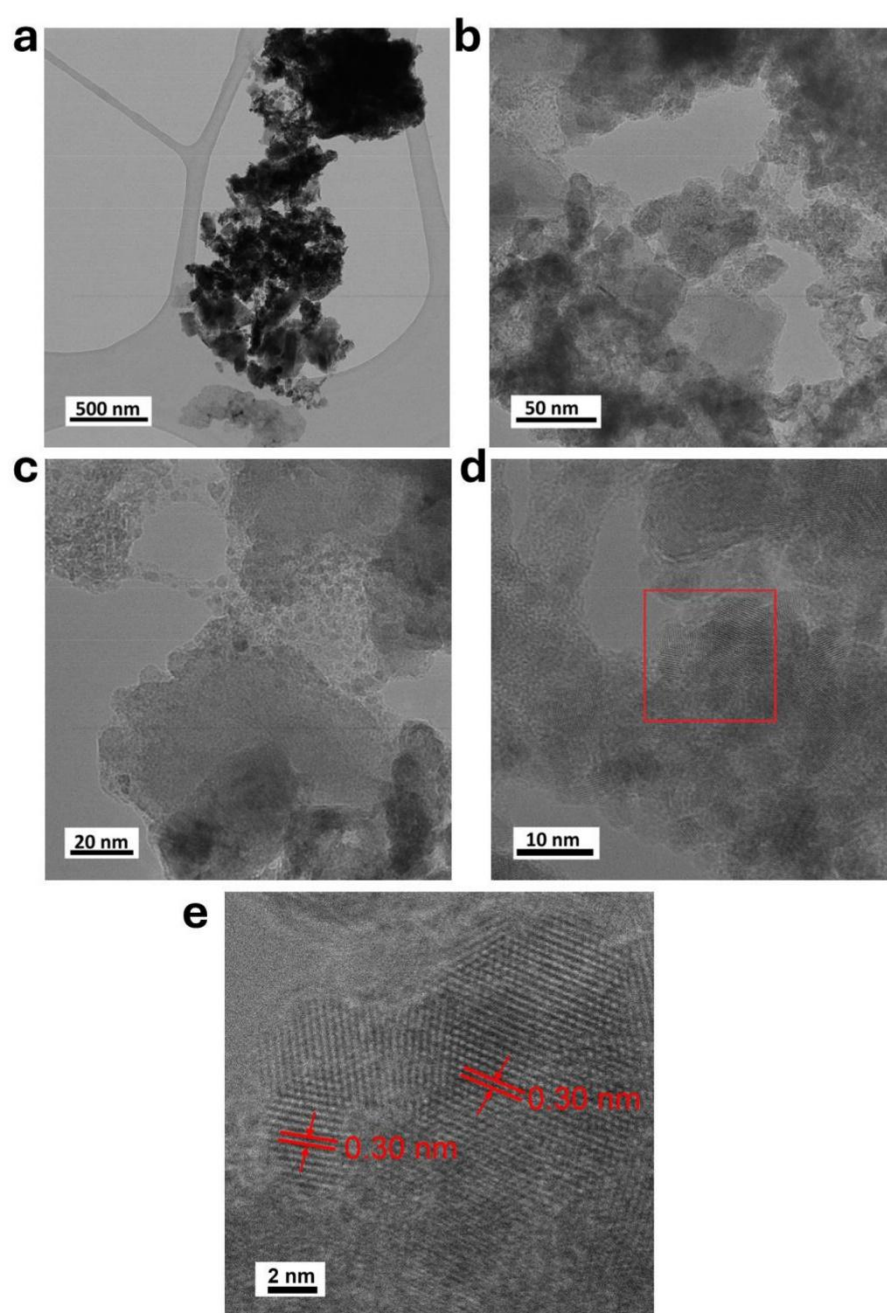


Figure S11. TEM and HRTEM images of the surface layer structure of CuRu-3h/CF. e corresponds to the magnified part of the square area in d. The d-spacing of 0.30 nm is assigned to Cu₂O (110).

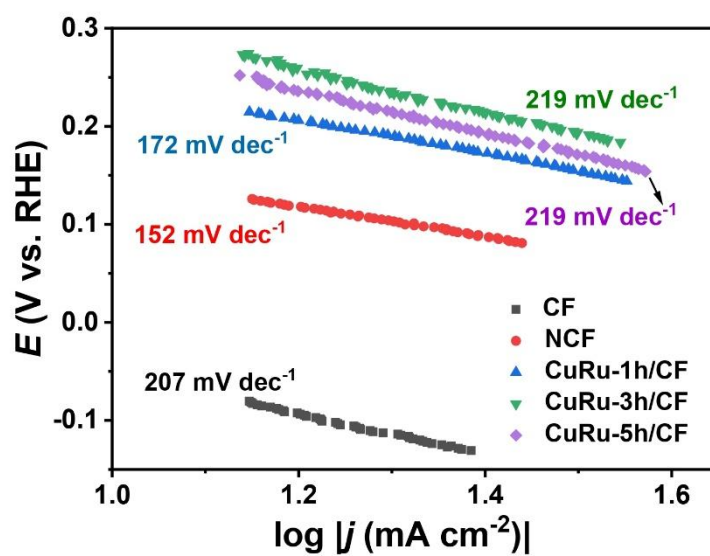


Figure S12. Tafel slope analysis of different electrodes for NO₂RR.

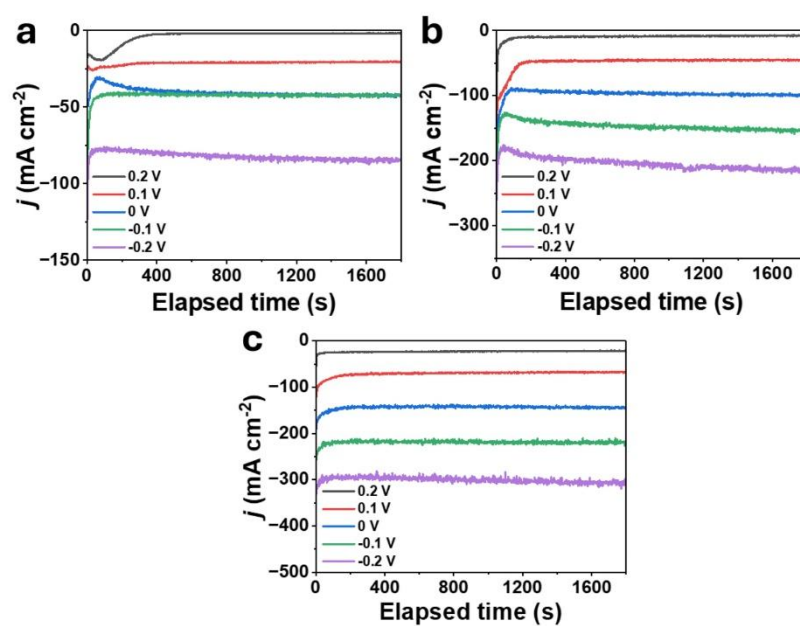


Figure S13. Current densities during the controlled electrolysis used to test the nitrite reduction performance of pure CF (a), NCF (b) and CuRu-3h/CF (c).

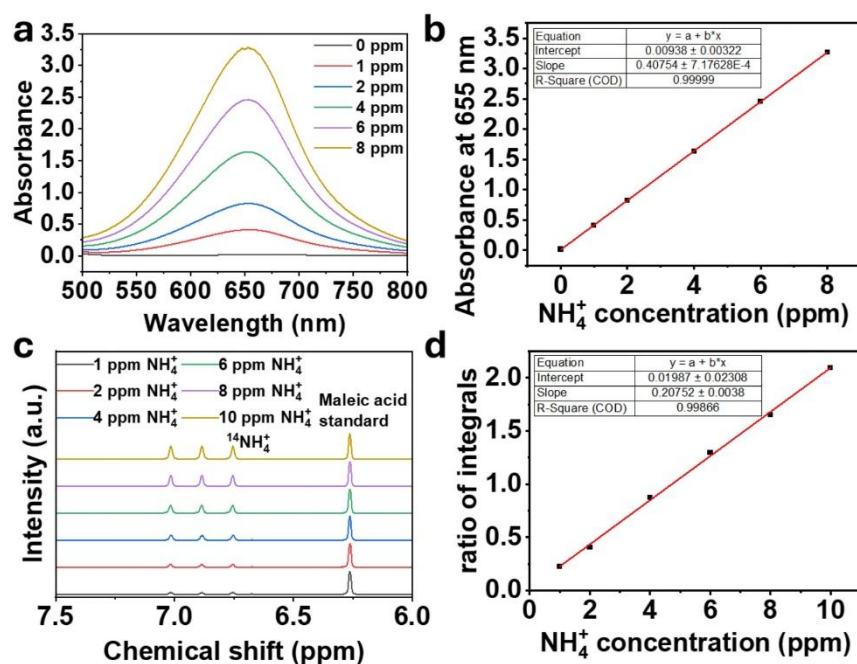


Figure S14. (a) UV-vis absorbance curves of NH_4^+ ions using IBM with different concentrations, and (b) resulting linear fit of the calibration curves. (c) ^1H NMR spectra of NH_4^+ ions with different concentrations, and (d) resulting linear fit of the calibration curves.

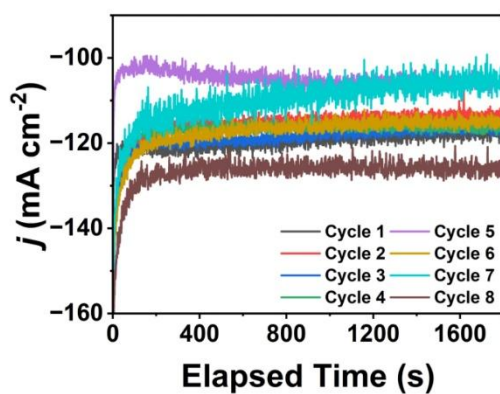


Figure S15. Current densities for the different cycles of the stability test performed to test the long-term stability of CuRu-3h/CF.

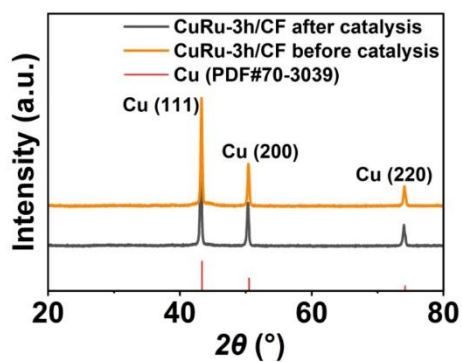


Figure S16. pXRD patterns of CuRu-3h/CF before and after catalysis.

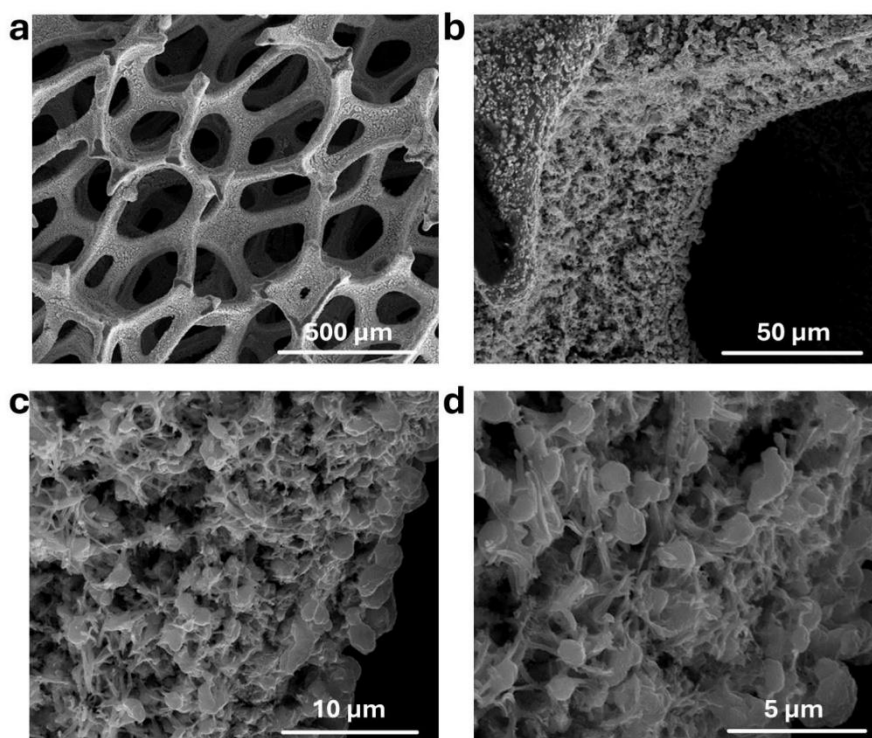


Figure S17. SEM images of CuRu-3h/CF after catalysis at different magnification.

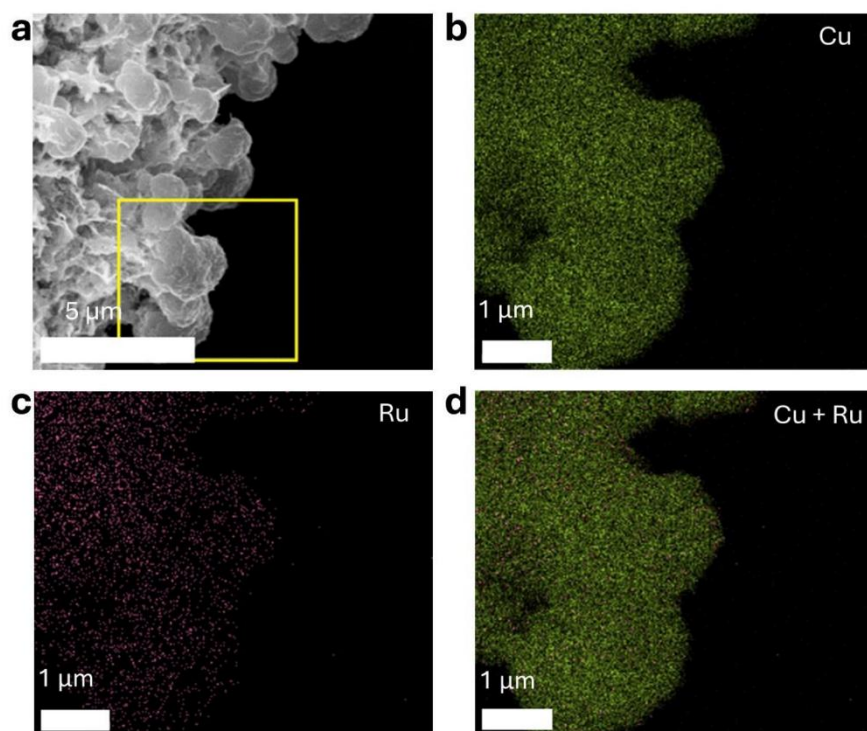


Figure S18. SEM-EDX elemental mapping of CuRu-3h/CF after catalysis.

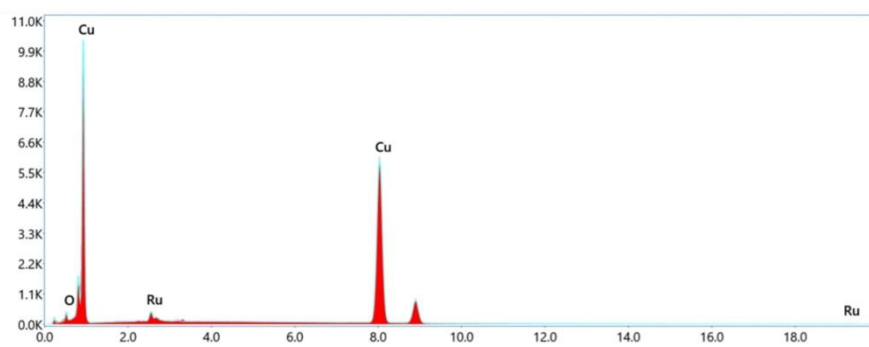


Figure S19. SEM-EDX spectrum of CuRu-3h/CF after the catalysis.

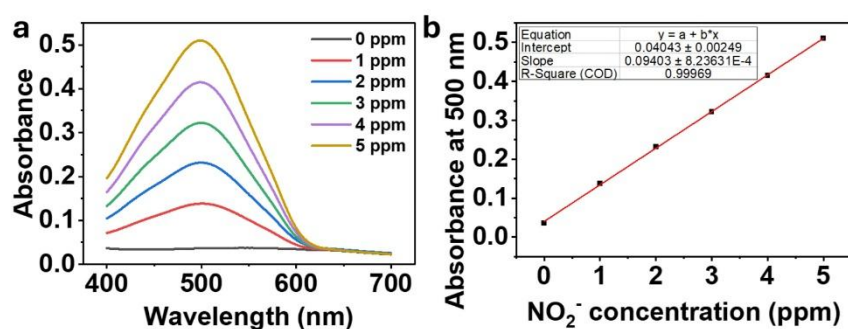


Figure S20. (a) UV-vis absorbance curves of NO_2^- with different concentrations, and (b) resulting linear fit of the calibration curves.

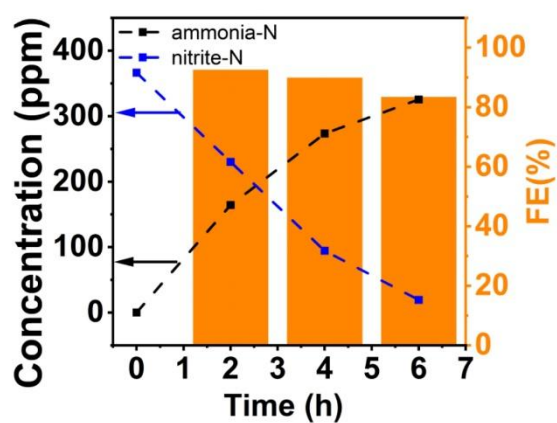


Figure S21. NO_2^- removal using CuRu-3h/CF with an initial nitrite-N concentration of 365 ppm at a potential of 0.1 V vs. RHE.

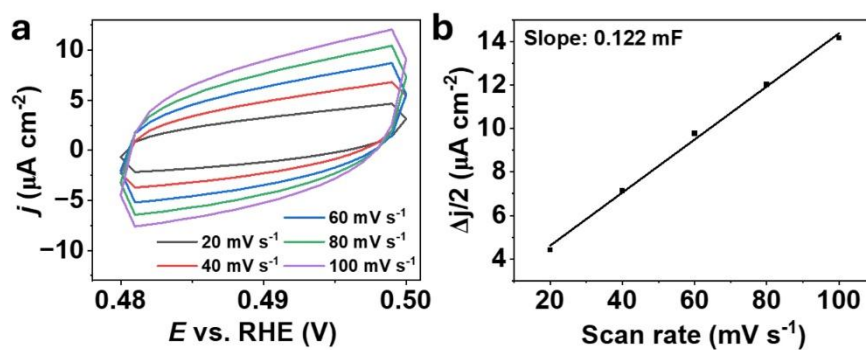


Figure S22. (a) CV curves of pure CF with different scan rates, and (b) the corresponding current density difference with the resulting linear fit to determine the double-layer capacitance.

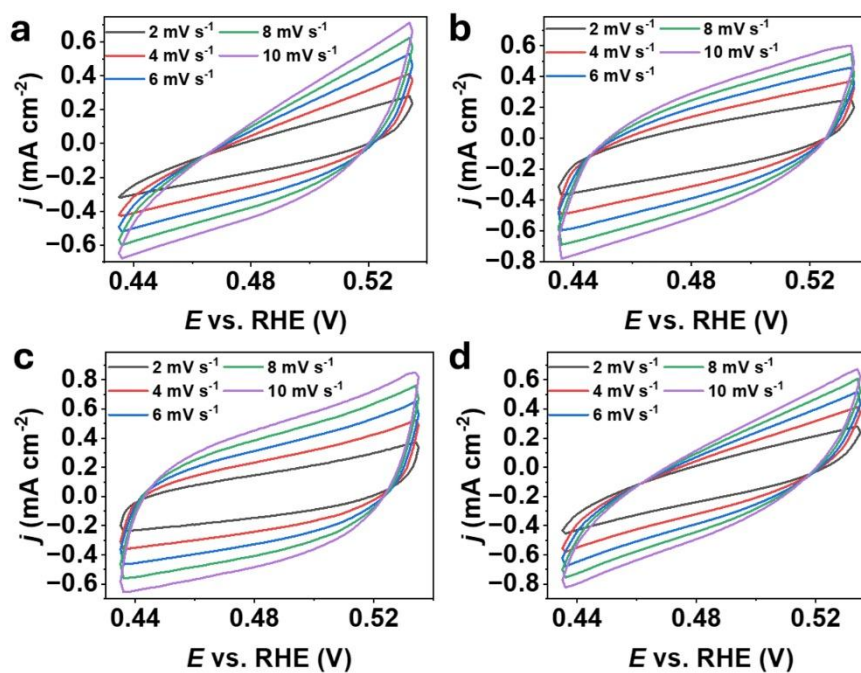


Figure S23. CV curves at different scan rates for (a) NCF, (b) CuRu-1h/CF, (c) CuRu-3h/CF, and (d) CuRu-5h/CF.

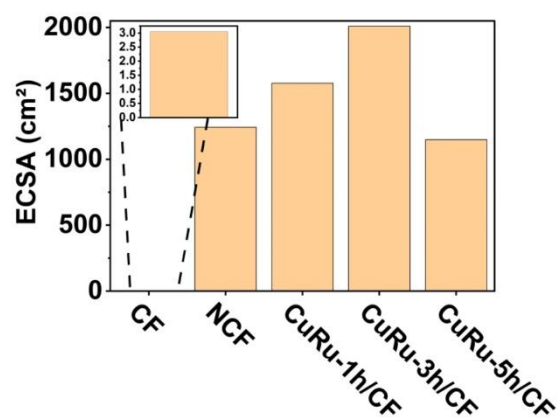


Figure S24. ECSA of the different materials determined using the double-layer capacitance.

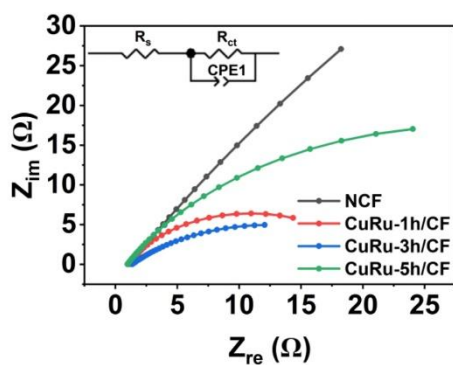


Figure S25. Fits for the EIS of the different materials with the equivalent circuit.

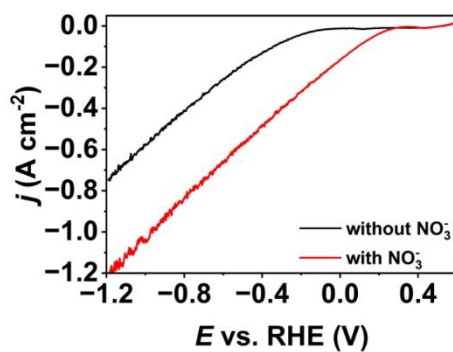


Figure S26. LSV curves of CuRu-3h/CF in the presence and absence of nitrate.

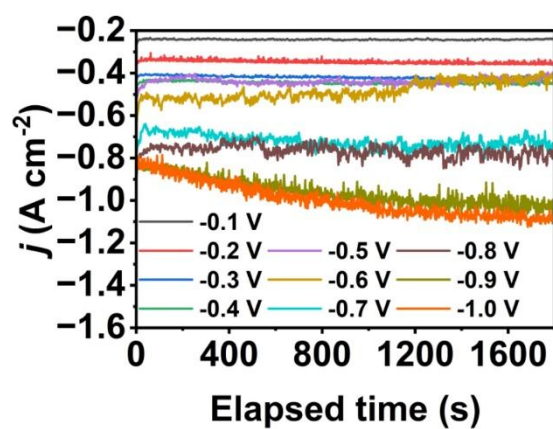


Figure S27. Current densities during the controlled electrolysis used to test the nitrate reduction performance of CuRu-3h/CF.

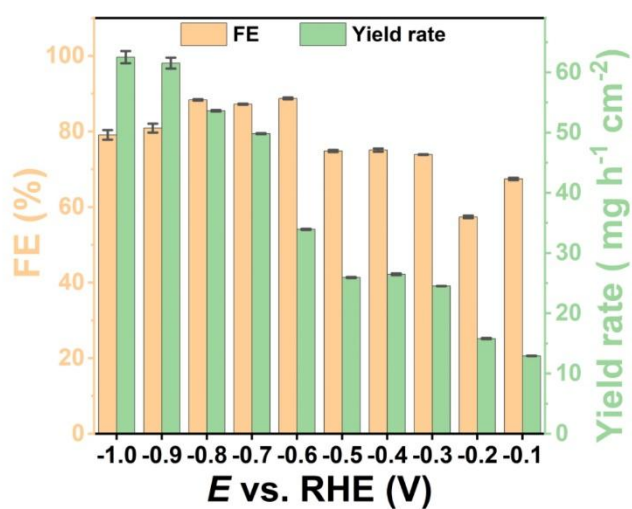


Figure S28. NH_3 FE and yield rate for the nitrate reduction using CuRu-3h/CF.

S6 Supplementary Tables

Table S1. Charge transfer resistance of the different materials determined by EIS

Electrode	R_{ct} (Ω)
NCF	358.40
CuRu-1h/CF	19.70
CuRu-3h/CF	22.24
CuRu-5h/CF	55.67

Table S2. The comparison of catalytic performance over recently reported CF-based electrocatalysts toward NO_2^- electroreduction

Catalyst	Electrolyte	FE_{NH_3} (%)	Yield rate	Ref.
CuRu-3h/CF	1 M KOH + 0.1 M NaNO_2	100	$33.2 \text{ mg h}^{-1} \text{ cm}^{-2}$	This work
CF@ Cu_2O	0.1 M PBS + 0.1 M NaNO_2	94.21	$7.51 \text{ mg h}^{-1} \text{ cm}^{-2}$	[2]
Cu_3P NA/CF ^a	0.1 M PBS + 0.1 M NaNO_2	91.2	$1.626 \text{ mg h}^{-1} \text{ cm}^{-2}$	[3]
Ru-Cu NW/CF ^b	0.1 M PBS + 500 ppm NO_2^- (NaNO_2)	94.1	$211.73 \text{ mg h}^{-1} \text{ cm}^{-2}$	[4]

Note:

a: NA/CF (nanowire array supported on copper foam)

b: NW/CF (nanowire array on three-dimensional copper foam)

Table S3. The comparison of catalytic performance over recently reported CF-based electrocatalysts toward NO_3^- electroreduction

Catalyst	Electrolyte	FE_{NH_3} (%)	Yield rate	Ref.
CuRu-3h/CF	1 M KOH + 0.1 M KNO_3	88.4	$62.5 \text{ mg h}^{-1} \text{ cm}^{-2}$	This work
Ru-Cu NW	1 M KOH + 2000 ppm NO_3^-	96	$76.5 \text{ mg h}^{-1} \text{ cm}^{-2}$	[1]
Rh@Cu-0.6%	0.1 M Na_2SO_4 + 0.1 M KNO_3	93	$1.27 \text{ mmol h}^{-1} \text{ cm}^{-2}$	[5]
CuO NWAs@ Co_3O_4 ^a	1 M KOH + 0.606 g KNO_3	96.96	$1.915 \text{ mmol h}^{-1} \text{ cm}^{-2}$ 2	[6]
Cu/CuO _x /CF ^f	0.5 M K_2SO_4 + 200 mg/L NO_3^- -N	93.58	$0.23 \text{ mmol h}^{-1} \text{ cm}^{-2}$	[7]
Au/Cu	1 M NaOH + 0.5 M NO_3^-	98.02	$73.4 \text{ mg h}^{-1} \text{ cm}^{-2}$	[8]
Cu/Cu-Mn ₃ O ₄ NSAs/CF ^b	0.5 M K_2SO_4 + 200 mg/L NO_3^- -N	92.4	$0.21 \text{ mmol h}^{-1} \text{ cm}^{-2}$	[9]
Cu-RD-KOH ^c	0.1 M KOH + 500 ppm NO_3^-	96.5	/	[10]
Cu ₅₀ Ni ₅₀ /Cu foam	1 M KOH + 100 mM KNO_3	95	/	[11]
oxide-derived Cu (OD-Cu)	1 M KOH + 100 mM NO_3^-	92	$1.1 \text{ mmol h}^{-1} \text{ cm}^{-2}$	[12]

Note:

a: NWAs (nanowire arrays)

b: NSAs/CF (nanosheet arrays on copper foam)

c: Cu-RD-KOH: The Cu nanowire array being composed of pure Cu^0 was synthesized through an electrochemical pre-reduction process at -0.4 V vs. RHE in 0.1 M KOH solution

S7 References

- [1] F. Chen, Z. Wu, S. Gupta, D. J. Rivera, S. V. Lambeets, S. Pecaut, J. Yoon, T. Kim, P. Zhu, Y. Z. Finck, D. M. Meira, G. King, G. Gao, W. Xu, D. A. Cullen, H. Zhou, Y. Han, D. E. Perea, C. L. Muhich, H. Wang, *Nat. Nanotechnol.* **2022**, *17*, 759–767.
- [2] Q. Chen, X. An, Q. Liu, X. Wu, L. Xie, J. Zhang, W. Yao, M. S. Hamdy, Q. Kong, X. Sun, *Chem. Commun.* **2022**, *58*, 517–520.

- [3] J. Liang, B. Deng, Q. Liu, G. Wen, Q. Liu, T. Li, Y. Luo, A. A. Alshehri, K. A. Alzahrani, D. Ma, X. Sun, *Green Chem.* **2021**, *23*, 5487–5493.
- [4] N. Q. Tran, L. T. Duy, D. C. Truong, B. T. Nguyen Le, B. T. Phan, Y. Cho, X. Liu, H. Lee, *Chem. Commun.* **2022**, *58*, 5257–5260.
- [5] H. Liu, X. Lang, C. Zhu, J. Timoshenko, M. Rüschler, L. Bai, N. Guijarro, H. Yin, Y. Peng, J. Li, Z. Liu, W. Wang, B. R. Cuenya, J. Luo, *Angew. Chem. Int. Ed.* **2022**, *61*, e202202556.
- [6] H. Liu, J. Li, F. Du, L. Yang, S. Huang, J. Gao, C. Li, C. Guo, *Green Energy Environ.* **2023**, *8*, 1619–1629.
- [7] H. Wang, Y. Guo, C. Li, H. Yu, K. Deng, Z. Wang, X. Li, Y. Xu, L. Wang, *ACS Appl. Mater. Interfaces* **2022**, *14*, 34761–34769.
- [8] B. Bi, A. Q. Dong, M. M. Shi, X. F. Sun, H. R. Li, X. Kang, R. Gao, Z. Meng, Z. Y. Chen, T. W. Xu, J. M. Yan, Q. Jiang, *Small Struct.* **2023**, *4*, 2200308.
- [9] H. Wang, Q. Mao, T. Ren, T. Zhou, K. Deng, Z. Wang, X. Li, Y. Xu, L. Wang, *ACS Appl. Mater. Interfaces* **2021**, *13*, 44733–44741.
- [10] H. Jiang, G. F. Chen, O. Savateev, J. Xue, L. X. Ding, Z. Liang, M. Antonietti, H. Wang, *Angew. Chemie - Int. Ed.* **2023**, *62*, e202218717.
- [11] Y. Wang, A. Xu, Z. Wang, L. Huang, J. Li, F. Li, J. Wicks, M. Luo, D. H. Nam, C. S. Tan, Y. Ding, J. Wu, Y. Lum, C. T. Dinh, D. Sinton, G. Zheng, E. H. Sargent, *J. Am. Chem. Soc.* **2020**, *142*, 5702–5708.
- [12] J. Yuan, Z. Xing, Y. Tang, C. Liu, *ACS Appl. Mater. Interfaces* **2021**, *13*, 52469–52478.

7. Acknowledgements

8. Curriculum Vitae

