Elektroorganische Synthese mit anschließender Hochskalierung

Dissertation for attaining the academic degree
of „Doctor rerum naturalium“ (Dr. rer. Nat.)
in Chemistry

Faculty of Chemistry, Pharmaceutical Sciences, and Geosciences
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by

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Für meine Eltern

Declaration

The experimental and written work of this thesis have been carried out from August 2022 to October 2025 at Evonik Operations GmbH in Hanau under the supervision of [redacted].

I, Laura Lennartz, hereby declare that I wrote this dissertation independently without any unauthorized assistance and with no other aids (this includes AI-based applications or tools) than those specified therein. I used only sources acknowledged in this work. All textual passages which are appropriated verbatim or paraphrased from texts as well as information, figures, and schemes obtained from written and oral sources are indicated and indexed according to bibliographical rules. I assure that I have not used any aids whose use has been explicitly excluded. In the appendix “Use of AI-Tools” I have documented the AI tools that I used.

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Mainz,

Laura Lennartz, M.Sc.

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Abstract

The focus of this doctoral thesis was the development and optimization of electrochemical processes with a focus on process engineering and the goal of technical implementation. One part was the electrochemical hydrogenation of carbonyl compounds. Water was utilized as the ideal hydrogen source, and commercially available materials, particularly electrodes, were employed. Economic considerations were addressed through the use of high current densities and chemicals that are available on a large scale. Furthermore, the electrochemical wastewater treatment was advanced through the implementation of a so-called quasi-division using a newly developed spacer. This innovative reactor design enabled the otherwise challenging oxidative degradation of tetrabutylammonium to levels as low as a few ppm. Moreover, the biological degradability of three different industrial wastewaters containing hard-to-oxidize contaminants were improved through the reduction of the total organic content. These developments contribute to the enhancement and simplification of electrochemical processes and bridging the gap between academic research and technical implementation.

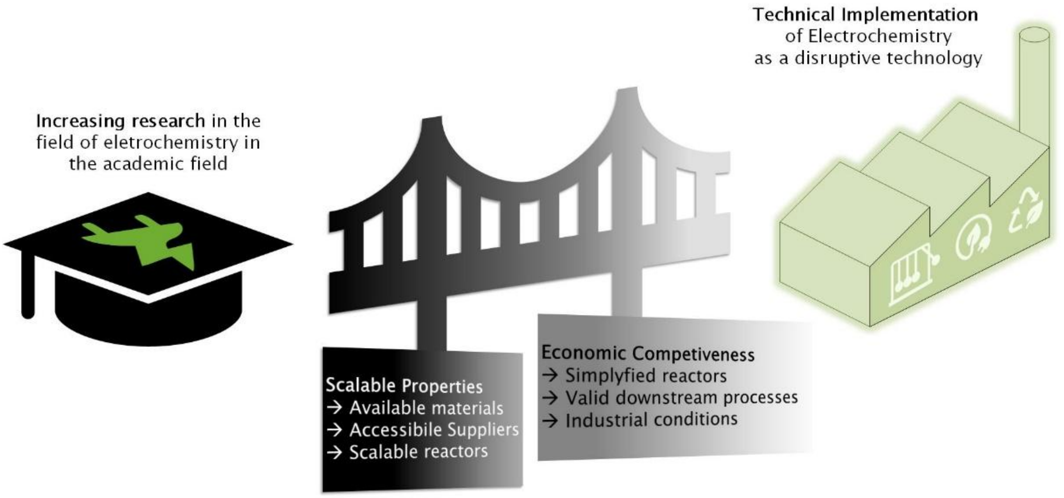


Figure 1: Bridge between the academic research and technical implementation of electrochemical processes.

Kurzzusammenfassung

Im Rahmen dieser Doktorarbeit wurde die Entwicklung und Optimierung elektrochemischer Prozesse mit einem verfahrenstechnischen Schwerpunkt und dem Ziel der technischen Implementierung angestrebt. Ein Teil beinhaltet die elektroorganische Hydrierung von Carbonylverbindungen. Dabei wurde Wasser als ideale Wasserstoffquelle eingesetzt und kommerziell erhältliche Materialien insbesondere Elektroden verwendet. Die Berücksichtigung wirtschaftlicher Aspekte erfolgte durch den Einsatz hoher Stromdichten und großmaßstäblich verfügbarer Chemikalien. Im zweiten Teil wurde die elektrochemische Abwasserbehandlung durch den Einsatz der sogenannten quasi-Teilung durch einen neu konstruierten Abstandshalter weiterentwickelt. Das innovative Reaktordesign ermöglichte den sonst anspruchsvollen oxidativen Abbau von Tetrabutylammonium auf wenige ppm. Darüber hinaus wurde die biologische Abbaubarkeit drei verschiedener industrieller Abwässer mit schwer oxidierbaren Kontaminationen durch den Abbau der Gesamtorganik verbessert. Diese Entwicklungen tragen zur Effizienzsteigerung und Vereinfachung elektrochemischer Prozesse und schlagen somit die Brücke von akademischer Forschung zur technischen Implementierung.

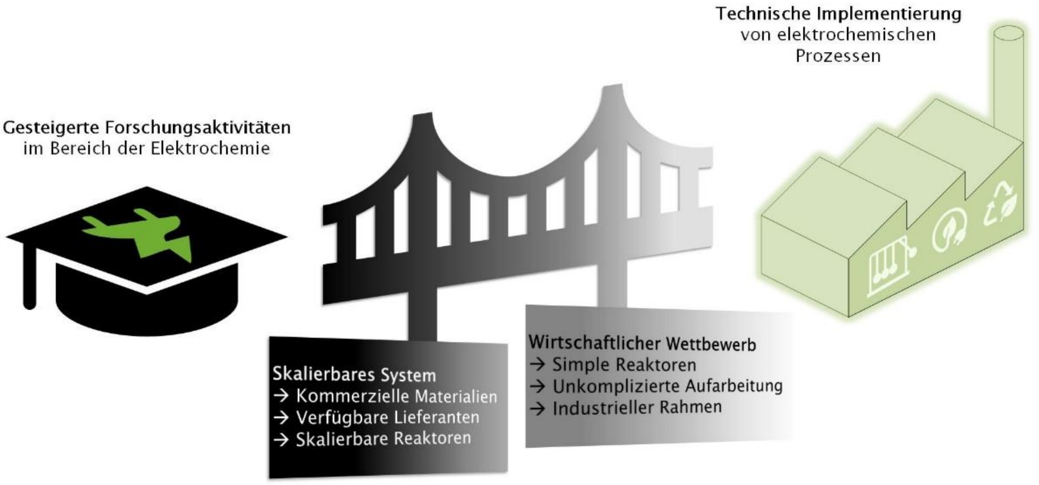


Figure 2: Brücke zwischen der ansteigenden akademischen Forschung und der Implementierung elektrochemischer Prozesse.

Contents

1. Motivation

One of the most frequently discussed challenges in modern chemical industry is the transformation of traditional processes to long-term sustainability while retaining economic competitiveness.[1-6] This target can only be achieved by employing disruptive technologies that provide a new approach to chemical processes while simultaneously enhancing resource efficiency.[7-8] Electrification of processes is one of the most promising technologies for managing the ambitious goal of a disruptive change in chemical industry.[7, 9-13] Electrochemistry can be applied throughout the entire value chain, from manufacturing to waste management.[14-17] Simplified, electrochemistry allows the replacement of chemical reagents by electrons.[18] The sustainability of electrochemical methodology is promoted by a tremendous transformation of the energy sector towards renewable energies.[4, 14, 19]

By employing electrosynthesis, the use of highly reactive chemicals can be avoided, and more moderate reaction conditions can commonly be established.[4, 20] These two key factors result in a decrease of the material consumption and the product-associated carbon footprint, thereby providing access to greener products.[4, 11, 21-23]

The establishment of a genuine sustainable process in the chemical industry not only centers on the chemical synthesis itself.[24] The purification, processing and waste generating streams of a production process contribute to the overall carbon footprint. The last step in a conventional chemical process chain is usually the waste water management. Even this environmentally important topic can be addressed by means of electrification as a resource friendly option.[11, 25-27] Considering the broad spectrum of possible applications for electrochemical process alternatives, this technology is expected to play an essential role in the disruptive transformation of the chemical industry.

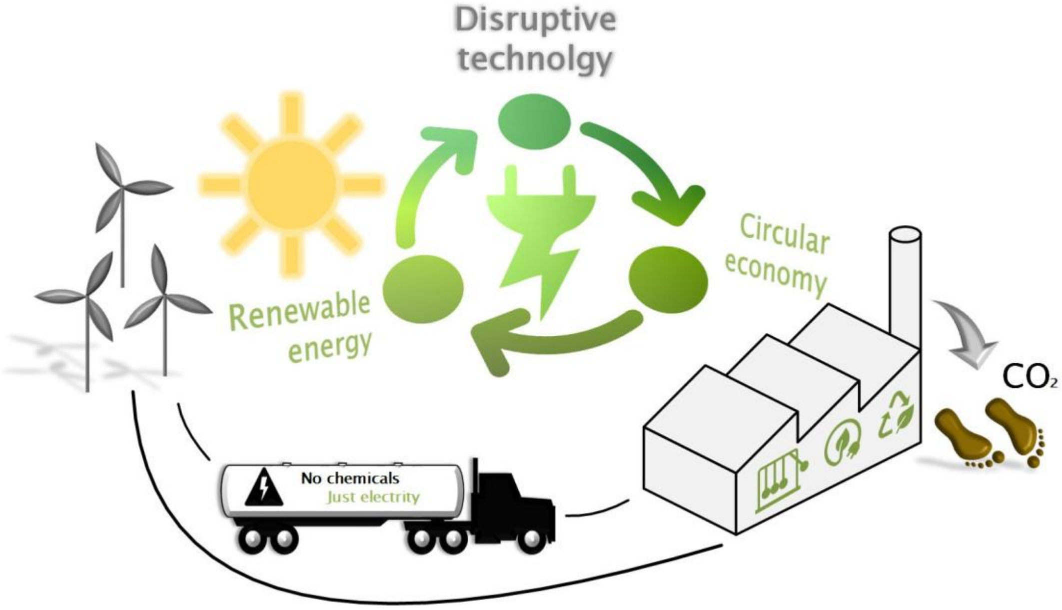


Figure 3: How to transform chemical industry towards sustainability with the combination of renewable energy, circular economy, and disruptive technology.

2. Introduction

2.1. Basic electrochemistry

In recent decades, there has been a significant push towards a more sustainable chemical industry. One of the most promising strategies to accomplish this goal is the utilization of renewable energy sources, which has led to a surge of interest in electrochemical methods.[28–31] Electrochemical processes offer the advantage of using electrons to induce redox reactions instead of traditional chemicals, resulting in a less resource-intensive approach.[32–33] Additionally, these processes enable the in-situ production of highly reactive species, thereby eliminating the need for the handling of hazardous reagents. Additionally, reaction pathways can be achieved, which would otherwise be impossible.[28, 33] The integration of electrochemistry into organic synthesis and chemical processes in general presents a promising avenue for fostering a greener chemical industry.[28, 32]

A typical galvanostatic electrochemical setup consists of two electrodes, an anode and a cathode, which are connected to a power supply. Under galvanostatic conditions, a constant current is applied by a power supply.[34] If a constant potential is required, a third electrode, known as a reference electrode, must be employed. The electrode where the desired reaction takes place is referred to as the working electrode, while the other electrode is called the counter electrode.[34] These electrodes are immersed in a conductive electrolyte that contains either inorganic or organic conductivity enhancers, precisely charged molecules. These ions facilitate the flow of negative charges from the cathode to the anode.

The most common electrochemical setups are divided and undivided cells. An undivided cell is the simplest configuration, as both electrodes are placed within a single compartment. In contrast, a divided setup is physically separated into an anode and cathode compartment by a membrane or similar component.[34] This arrangement allows for the physical separation of reduction and oxidation processes and can enhance the selectivity of the reaction.

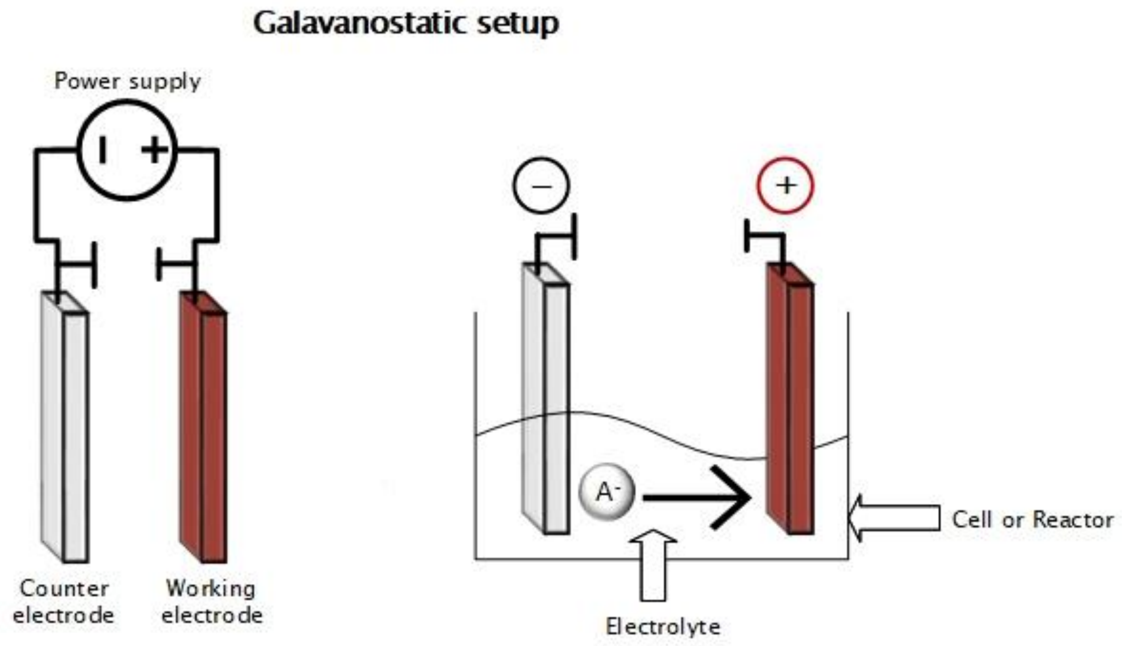
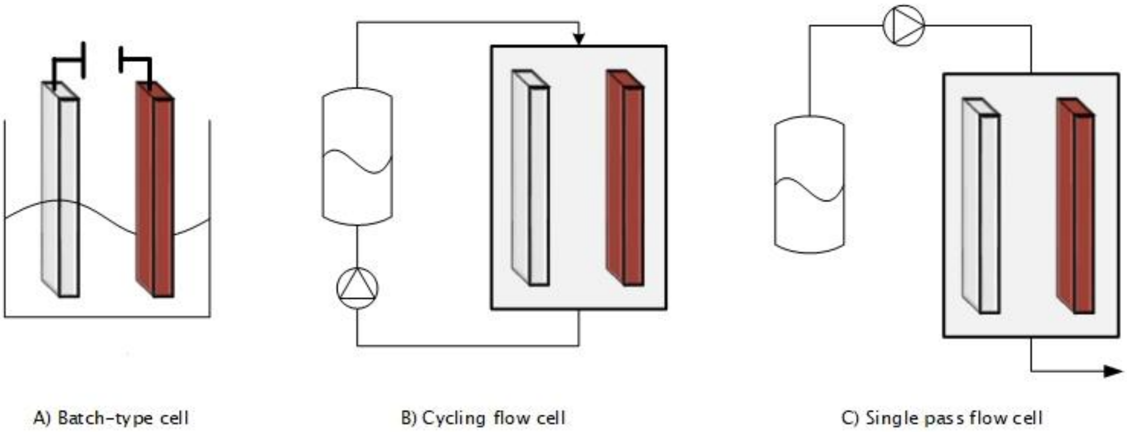


Figure 4: Galvanostatic setup of a electrochemical cell with a power supply, counter and working electrode.

In addition to the primary setup conditions, electrochemical reactions can be influenced by various other parameters. One significant factor is the electrode material itself. Beyond the electrocatalytic activity of the material and the hydrogen overpotential, the structure of the electrode also plays a crucial role.[34-35] For instance, while traditional plate electrodes can be used, alternative structures such as cylindrical, rod-shaped, foam, or mesh electrodes can significantly improve even the chemical feasibility of the desired reaction.[34-35] Another important parameter involving the electrode surface and the applied current is the current density in galvanostatic reactions, which is defined as the current divided by the surface area of the electrode.[34] Besides the electrodes and the applied current, other critical factors include the choice of solvent and the supporting electrolyte used.[34] It is essential that the solvent remains stable under the applied conditions, as do the utilized salts.[34] Moreover, the solubility of the reactant is a vital consideration when selecting a solvent.

Besides chemical and material parameters, the reactor design can influence the outcome of an electrochemical reaction. The design of the reactor is often more complex than simply having two electrodes in a cell. Various operational modes exist, such as batch and flow modes. In a batch-type cell, the electrodes are typically housed in a beaker cell or, if divided, in a classical H-cell configuration.[34] In this setup, the distance between the electrodes is a crucial factor, as it influences the resistance and, consequently, the resulting terminal voltage. Conversely, flow systems present a more sophisticated design. In these systems, the electrodes are situated within a reactor that can operate continuously or in a batch-type mode.[31] The electrolyte is pumped through the reactor, either cycling through in a semi-batch process or passing through the reactor just once. In this context, not only the reactor design is important, but also the flow rate and flow dynamics.[31]


A) Batch-type cell

B) Cycling flow cell

C) Single pass flow cell

Figure 5: Three different operation modes from electrochemical reactors.

2.1.1. Quasi-division

The selectivity of an electro organic synthesis can be enhanced by utilizing a divided cell setup.[36] A physical separator is employed to separate the compartments and therefore eliminate undesirable side or back reactions at the counter electrode.[37-39] Thus, the oxidation and reduction are spatially separated, leading to a decrease of interfering side reactions.[38-39] Various materials are known, working simultaneously as a physical separator and guaranteeing the current flow by the exchange of charged species between anode and cathode compartment.[38] Two major types are anion and cation exchange membranes, which selectively allow for the passage of anions or cations in the direction of the cathode and anode, respectively.

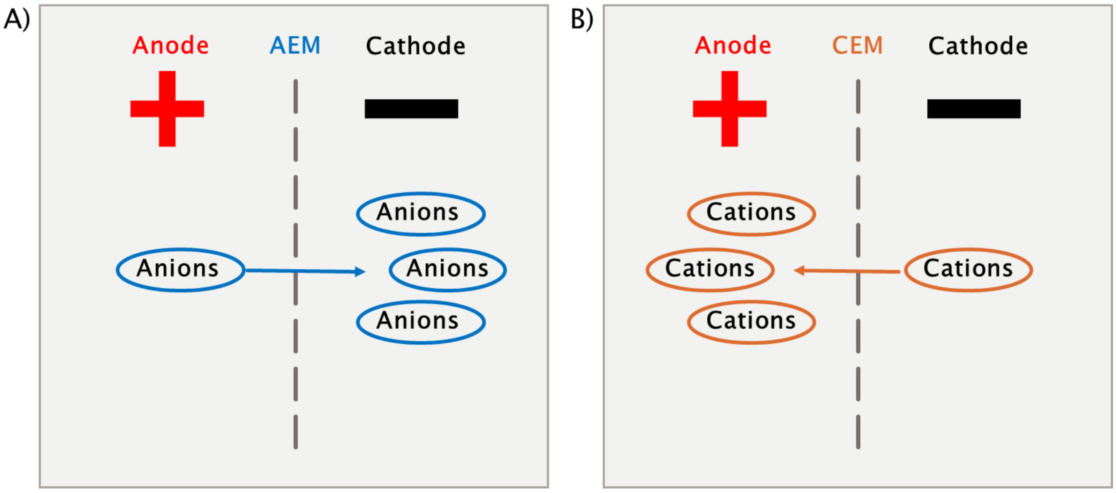


Figure 6: Possible movements of anions and cations in a divided setup through an Anion exchange membrane (A) and cation exchange membrane (B).

Regardless of the often significant benefits of a divided system, the required membranes are associated with several disadvantages.[36] Besides being cost intensive and sensitive to a broad range of chemicals, the employment of membranes is resulting in a more complicated reactor and plant design.[36] Compared to an undivided cell, a divided setup consequently needs two circulation loops with the corresponding peripheral equipment. Furthermore, a higher resistance due to the diffusion through the separator is expected, thus yielding a higher voltage. Since the voltage has a linear impact on the energy costs of a reaction, a divided setup results in overall higher energy expenses.

A compromise between both systems, is provided by a design called “quasi-division”.[37, 40] This technique immensely lowers the surface area of the counter electrode compared to the surface of the working electrode.[37, 40–42] The smaller electrode surface kinetically inhibits reactions occurring at the counter electrode.[40–41, 43] Likewise this design inhibits the undesired side reactions without the described disadvantages of a physical separation.[37, 41, 43]

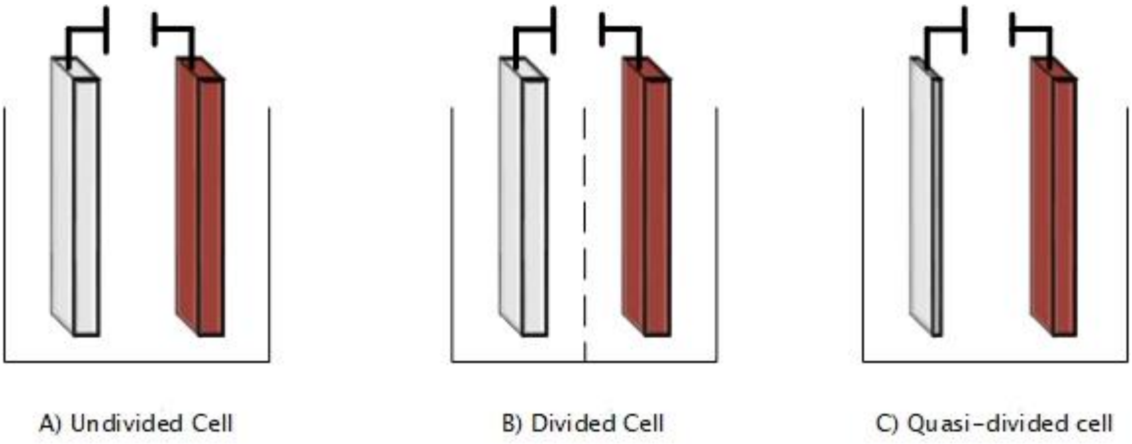


Figure 7: Schematic illustration of an undivided (A), divided (B), and quasi-divided cell (C).

2.1.2. BDD Electrodes

In addition to traditional metallic electrodes, another significant category of electrodes frequently employed in electrochemistry are carbon-based electrodes.[44] Examples of carbon-based electrodes include various types of graphite, glassy carbon, and boron-doped diamond electrodes.[44] BDD electrodes are often referred to as next-generation electrodes due to the associated versatility in various applications, including electro organic synthesis, analytical methods, and wastewater treatment.[44-48]

A BDD electrode is a type of coated electrode, meaning it consists of a support material, such as niobium, tungsten, titanium, or silicon, onto which the BDD coating is applied using chemical vapor deposition (CVD).[44, 49] For manufacturing two main methods are known, the microwave plasma-assisted CVD and the hot filament CVD.[44] For larger electrodes, hot filament CVD is required due to the size limitations of microwave plasma-assisted CVD systems.[44] As a carbon source methane is utilized and as a boron source diborane.[44]

One of the remarkable parameters of BDDs is the wide potential window in aqueous media.[48, 50] Due to this characteristic, BDD is well-known for the effectiveness in carbon dioxide reduction in cathodic applications.[44] The overpotential in aqueous media is -1.1 V for HER and 2.3 V for OER.[44] This results in a suppressed oxygen evolution at the anode, and suppressed hydrogen evolution at the cathode. Due to the high overpotential for oxygen evolution, hydroxyl radicals are generated at BDD electrodes when set as the anode. The production of hydroxyl radicals is an advantage in anodic applications for BDD electrodes, particularly in the treatment of wastewaters through the mineralization of organic contaminants.[44] Additionally, BDD electrodes have several anodic applications in electrosynthesis, such as the production of peroxo compounds like peroxodisulfate.[44] Another notable parameter is the inertness to surface absorption and chemical corrosion, which enhances the resistance of BDD electrodes to fouling, making them a durable and long-lasting material.[48-50]

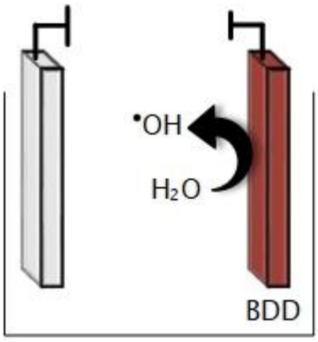


Figure 8: Hydroxyl radical generation at BDD anodes in aqueous media.

2.2. Electrochemical hydrogenation

The hydrogenation is one of the simplest ways of modifying an organic functional group in a broad variety of synthesis applications and structural motives.[51-52] Examples include the hydrogenation of alkenes to alkanes, ketones to alcohols or nitriles to amines illustrating the broad range of possible transformations.[51-53] The classic approach of a hydrogenation is the utilization of gaseous hydrogen, a precious metal catalyst and high pressures/temperatures, resulting complex setups.[51-53]

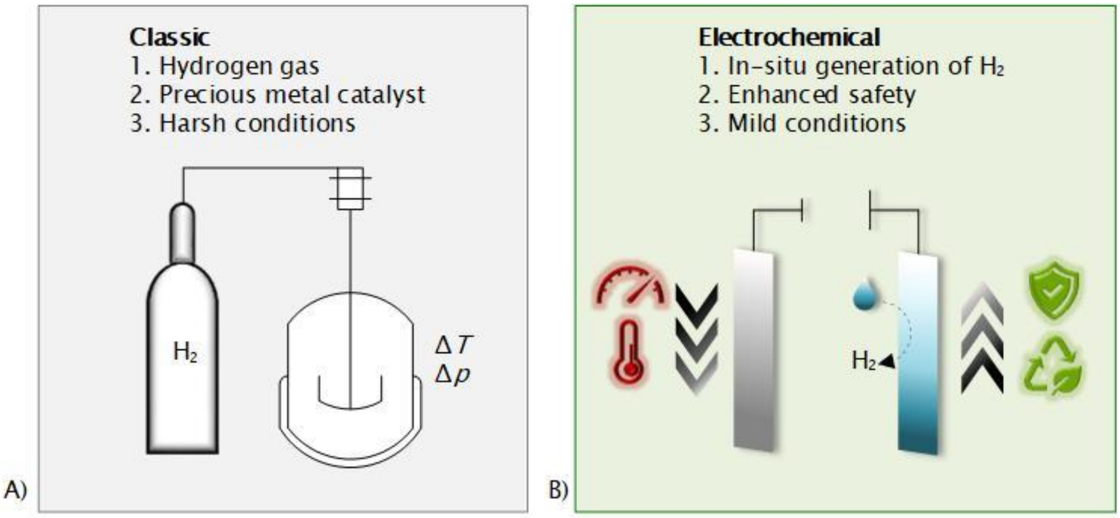
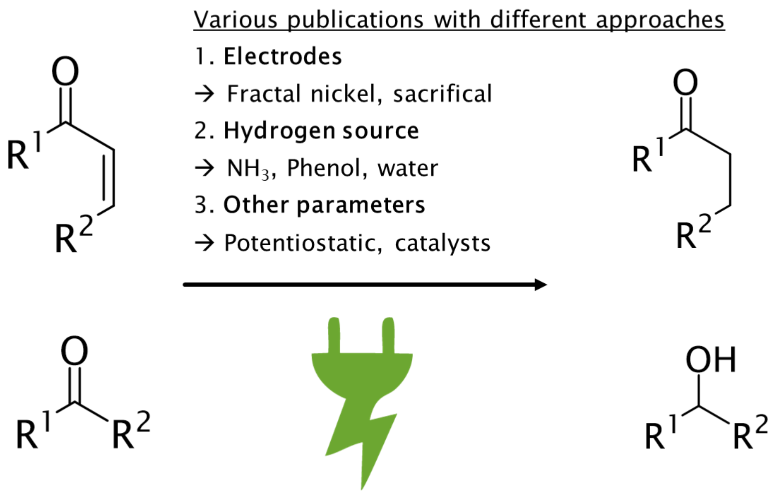


Figure 9: Classical hydrogenation vs. electrochemical hydrogenation.

As stated, traditional hydrogenation processes present numerous opportunities from reaction parameters to needed chemicals and materials for optimization in terms of sustainability. To achieve more environmentally sustainable hydrogenation processes, an alternative approach is to generate the hydrogen in-situ via electrolysis using renewable electricity. The so called electrochemical hydrogenation, follows the splitting of water or other hydrogen donors at the cathode into activated hydrogen, which in turn can be directly used to hydrogenate the organic molecule.[52, 54] This presents an opportunity for the development of more simply constructed plants, as the hydrogen source is in a non-gaseous state and does not require overcoming a high activation energy, given that the hydrogen is already activated.[55–56] Besides the construction of the reactor also the reaction parameters of an electrochemical hydrogenation have a significant contribution towards a resource-efficient and less energy-intensive methodology.[52]

Despite the pointed advantages of electrochemical hydrogenation, several challenges remain in developing a competitive process for the chemical industry. A specific class of substrates, which point out the potential and the challenges of the electrochemical hydrogenation, are carbonyl compounds. One of the ongoing challenges is the hydrogen donor as such. The subsequent step towards a truly sustainable process involves the direct utilization of water as a sustainable, simple and safe hydrogen source.[52] However, other hydrogen donors, such as phenol or ammonia, are also employed to hydrogenate carbonyl compounds into the corresponding alcohols. By employing ammonia as the hydrogen donor and using carbon based electrodes, it is possible to achieve a hydrogenation of carbonyl compounds to the secondary alcohols. For the hydrogenation of aldehydes a study with phenol as the hydrogen source and a manganese complex as a catalyst in the electrolyte achieved the electrochemical hydrogen to the corresponding alcohol.[57] This also indicates that, similar to classic hydrogenation, catalysts are frequently needed in electrochemical hydrogenation as additives in the electrolyte or as an electrode coating. Examples for electrode coatings are Pt/Ru-, Raney Nickel catalysts or other activated nickel electrodes.[58–64] As an example for the utilization of nickel as an electrocatalyst, the hydrogenation of cyclohexanone derivates was published on activated nickel electrodes.[62, 65] One study illustrated selective hydrogenation of the double bond in cyclic enones by employing self-made fractal-powder nickel or nickel boride cathodes in a divided cell setup.[62] Other groups utilized a sacrificial nickel-rod and in-situ coating of the cathode whilst using NH_4Cl as supporting electrolyte in an undivided setting.[65] Besides the use of catalysts, halogen based additives or electrochemical conditions, like the mentioned use of a sacrificial anode or the incorporation of a reference electrode, render the electrochemical method less appealing for industrial applications. Recently, a potentiostatic method was published, in which commercial nickel foams were utilized in which sulfuric acid was used as the electrolyte to convert enones to ketones.[66]



R^1 and R^2= Various structure motives

Figure 10: Overview of several publications and their published electrochemical hydrogenation methods for enones and other carbonyl substances.[57–59, 61–67]

Based on the potential of electrochemistry as a tool towards sustainable hydrogenation processes, electrochemical hydrogenation methods are heavily sought after. Nevertheless, the referred studies indicate remaining challenges in developing an all over appealing method for industrial applications.

2.3. Industrial wastewater treatment

In nearly every chemical process and synthesis the underlying process chain ends with at least one wastewater stream.[68–70] The contaminants in those waste streams are produced during chemical manufacturing and exhibit a diverse array of chemical compounds, concentrations, and varying effects on both human health and the environment.[68, 71–73] Based on the improvement of analytical methods and an increase in research towards the environmental impact of industrial wastewaters, the urgency for waste stream treatment before environmental release is gradually gaining attention.[74–75] The increasing urge to treat an expanding number and amount of waste streams prior to their release is essential for maintaining the environmental safety.[68, 76–77] However, this leads to the challenge of addressing contaminations that are difficult to manage using conventional wastewater treatment methods.[68] Most treatment processes involving an oxidative treatment step of organic residues include either energy demanding incineration or the use of hazardous oxidants. The most basic method for treating wastewater containing organic contaminants is the resource demanding incineration. In this process, aqueous solutions are typically subjected to combustion, resulting in the degradation of organic residues into carbon dioxide or carbon monoxide. This can be coupled with separation techniques such as membranes to improve the efficiency of the combustion.[78–79] A waste stream is separated to permeate and concentrate.[78] Whereas the permeate can be released, the concentrate needs further treatment, usually given by a conventional incineration.[80] This technology is often limited by the stability of the membranes in the presence of certain contaminants.[79] An additional class of treatment processes is the oxidative decomposition of organic molecules yielding partially oxidized organic species or complete mineralization to carbon dioxide and other gaseous byproducts.[81] This is accomplished through the addition of highly reactive chemical oxidation agents such as ozone in ozonolysis or hydrogen peroxide.[82–85] A method involving hydrogen peroxide is the Fenton process, which is the most common treatment option for organically contaminated wastewaters due to the broad range of applicability.[68] The process involves the addition of iron salts, sulfuric acid, and hydrogen peroxide, which generate hydroxyl radicals that subsequently oxidatively decompose the organic contaminants.[81, 86-88] Both processes ozonolysis and the Fenton process involve the use of highly reactive and resource-intensive mediators, which necessitate a complex safety infrastructure.[68]

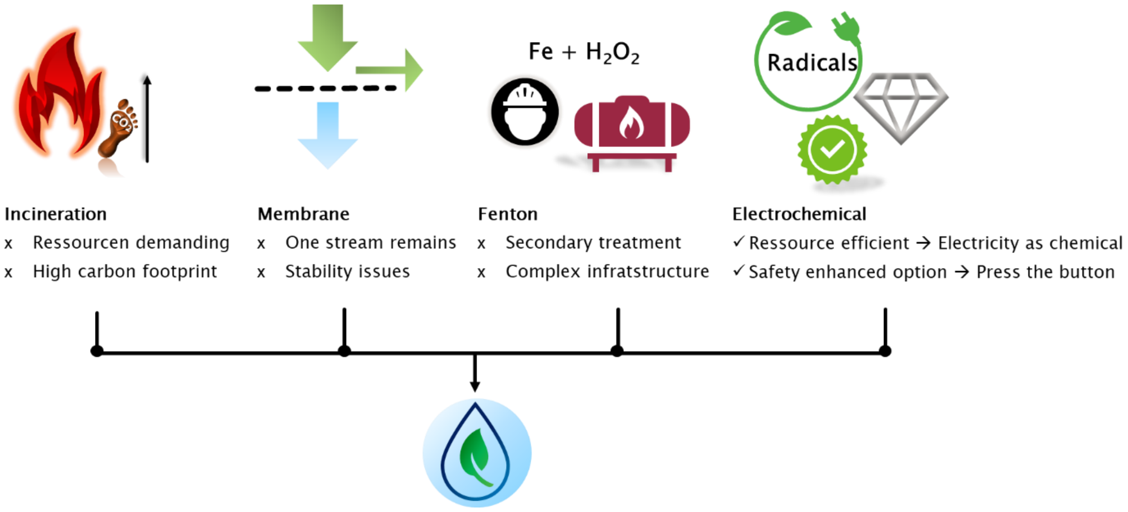


Figure 11: Four different wastewater treatment options for industrial wastewater: incineration, membrane technology, the Fenton process and the electrochemical method.

A modern approach to wastewater treatment is the electrochemical oxidation.[68, 89] Even though this technology is based on an oxidative mineralization similar to conventional processes, the oxidation mediators are generated in-situ, thereby circumventing the handling of reactive and hazardous chemical reagents.[90-92] Typically, BDD-electrodes are employed, which leads to the generation of highly reactive hydroxyl radicals from water. The highly reactive intermediates are capable of oxidizing a wide range of organic contaminants.[89-90, 93-95] Furthermore. reactive sulfur- and chlorine-based mediators like peroxo-species and radicals are generated from sulfate and chloride residues in waste streams enhancing the oxidative processes.[68, 89-90, 96] Based on the minimization of handling highly reactive chemical reagents, electrochemical wastewater treatment is considered a process alternative with enhanced safety.[97] Additionally, the method benefits from the commonly straightforward operation of an electrochemical process, which allows for a simple start-stop system.[89, 98] The reaction can be shut down directly by cutting the electricity, thus stopping any further reactions. The applicability of electrochemical wastewater treatment processes in chemical industry is primarily limited by the capability of decomposing organic contaminants, which are highly stable towards oxidation, e.g. alkylammonium salts.[98] Alkylammonium salts are often employed as electrolytes in electrosynthesis and cannot be simply discharged in the environment due to their harmful impact on the environment.[99-102] Such upcoming topics underline the importance of new approaches in wastewater management.

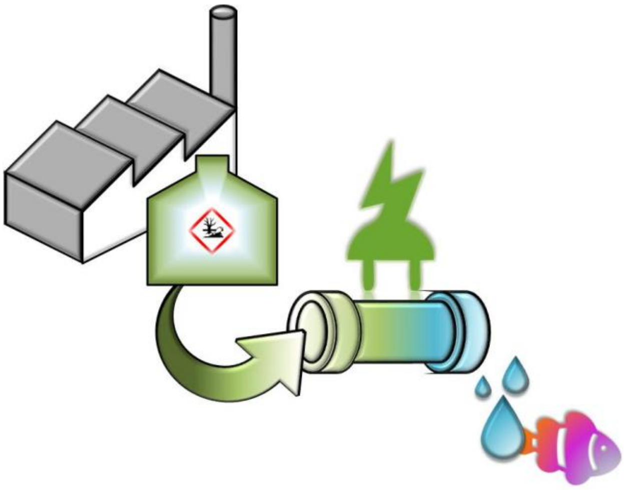


Figure 12: Electrochemical wastewater treatment for the purification of industrial wastewater.

2.4. Electrochemical process technology

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Explanation of my contribution

The literature research was done mainly by me and was supported by S. Beil. The concept of the manuscript was done by me and supported by S. Beil under the supervision of P. Stenner and S. R. Waldvogel. The manuscript was written by me with the support of S. Beil and S.R. Waldovgel.

A direct comparison of electrochemical processes to conventional chemical processes shows a broad range of advantages.[103-105] The most important aspect of a chemical process in the context of chemical industry is safety. [106-107] In this critical topic electrochemical process engineering has a decisive benefit compared to the majority of classical processes. Since electricity induces the desired chemical reaction, the processes can be shut down by removing the power source, known as on-off functionality.[106] If a reaction was to diverge from the planned course, an emergency shutdown can be induced directly by switching off the applied current. Additionally, the often milder conditions are contributing to an enhanced safety.[28] Generally, highly reactive species like radicals are generated in an electrochemical cell in-situ, leading to a simpler infrastructure compared to the employment of highly reactive chemicals themselves. Moreover, this direct generation of active species circumvents the otherwise required harsh process conditions, leading to a simpler reactor design and improved safety. [106, 108-109]

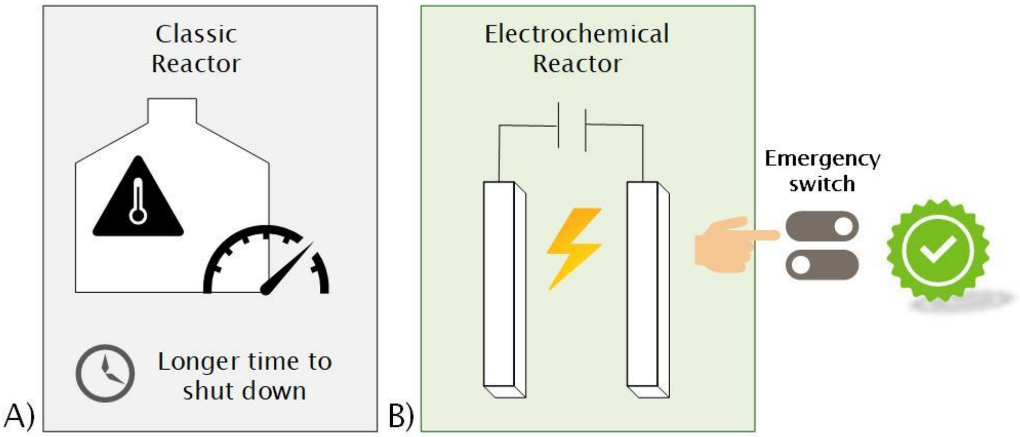

Figure 13: (A) a classic chemical reaction; (B) a electrochemical process.

For the purpose of utilizing conventional electrochemical methods in an industrial context, the gap from academic research to technical implementation must be bridged.[106-107, 110] Since electrochemical methods are becoming more prominent due to the search of environmentally benign industrial processes, a substantial amount of fundamental research is currently being conducted. As the focus is usually related to laboratory associated problems, technical issues regarding pilot plant construction, safe handling, practical technical implementation and engineering is scarcely reported. [107, 110] Therefore, a major challenge in electrochemical process development is the initial phase of the transition of electrochemical methods from lab to an industrially relevant scale.[107-108, 110] In the event that an electrochemical reaction is feasible on laboratory scale, a one-to-one transfer to industrial scales is not straightforward to accomplish.[110] A crucial development step is the reactor design, specifically the operation mode, electrode stability and availability of materials and suppliers as well as fluid mechanics in the cell.[15, 108, 110-112]

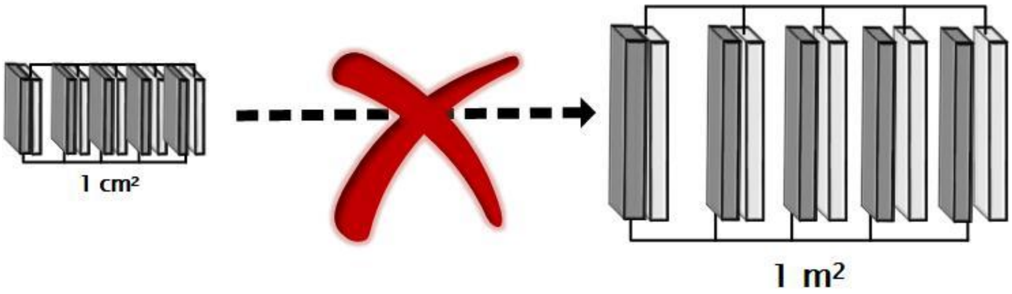

Figure 14: Difficulties in transferring electrochemical processes from a 1 cm² to 1 m² scale.

One advantage of electrochemical processes is the modular nature allowing scale-up via numbering up. This characteristic ensures a more convenient expansion of production capacities without the need for a complete redesign and reconstruction of the entire plant. Besides easy adaption to production expansions, the modular system allows for a simple maintenance without the necessity of regular production shutdowns. However, fluid dynamics and mechanical issues in technical flow-cells need to be included in the optimization of an electrochemical process.[110, 113]

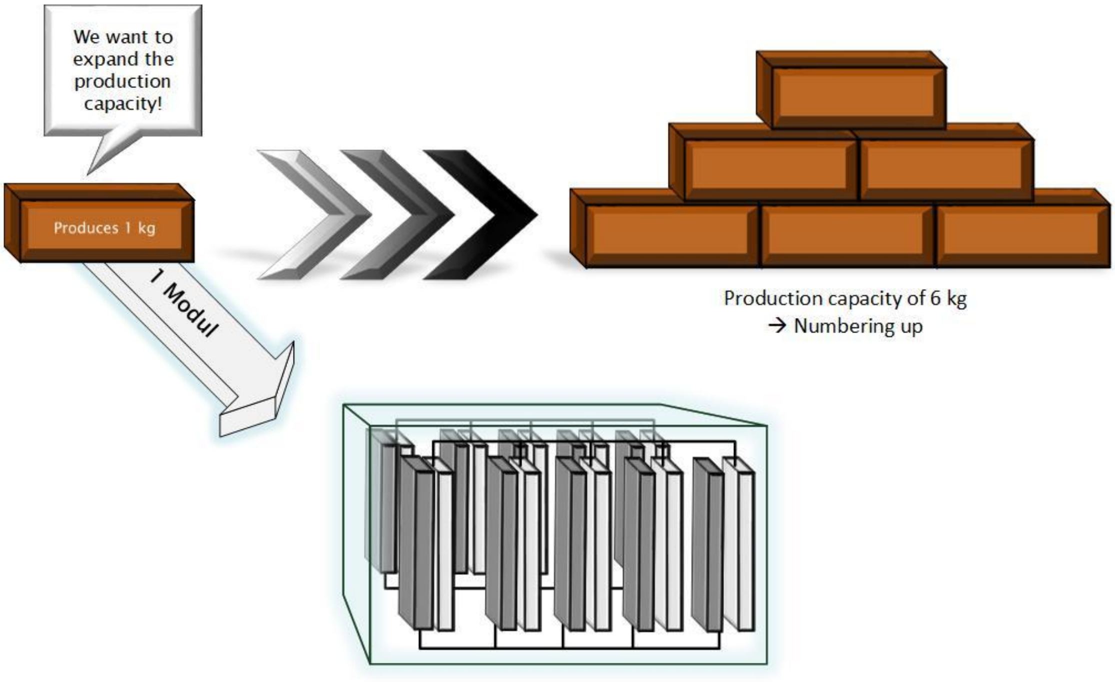

Figure 15: The modular characteristics of an electrochemical plant.

However, the optimization of an electrochemical process does not end within a laboratory. Usually the implementation of a feasible lab scale electrochemical reaction is initiated with a pilot plant in a technical center, to prove the scalability of the process. When the pilot phase is initiated a determining factor for the feasibility is the availability of materials and their suppliers.[114] On small scales, manufactured or even self-made electrodes are available or can be produced in house. Since custom made electrodes are often not reproducible in quality or available in larger amounts, the electrodes are not suitable for industrial applications. Thus, a scaled technical system requires the immediate availability of electrode material in bulk, preferably providing a buy off-the-shelf option.[106] In conclusion, the limited selection of electrode suppliers and the companies who construct of pilot systems slow down a straightforward implementation.[114]

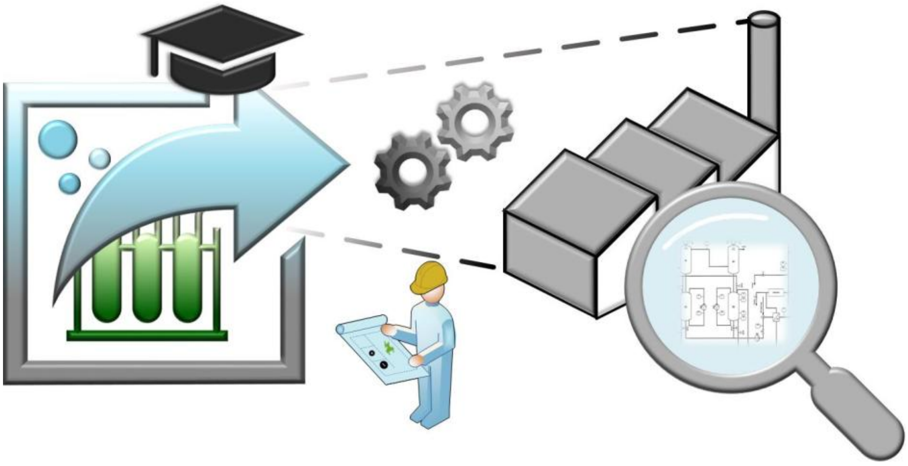

Figure 16: The transition from academic laboratory research to an industrially applicable process.

While technological considerations are crucial, they are not the sole factors influencing the scaling or implementation of new processes in chemical production. From an economic perspective, certain electrochemical parameters can significantly impact cost-effectiveness. When evaluating total expenses, it is essential to monitor not only chemical and electricity costs but also the initial capital expenditures associated with the project. Traditional operational costs are just one aspect of economic efficiency, the infrastructure of the plant itself must be established prior to operations. In this context, optimizing parameters such as current densities and substrate concentrations become critical. These parameters can lead to a minimization of the required electrode surface area, which in turn addresses the need to lower capital expenditure.[115] A smaller electrode surface results in a more compact reactor, which is often the most expensive component in the plant. This offers a huge impact on reducing investment costs, and therefore being cost competitive with classic methods. Despite all the benefits of an electrochemical cell on paper, the key point relates to the economic feasibility of a process.

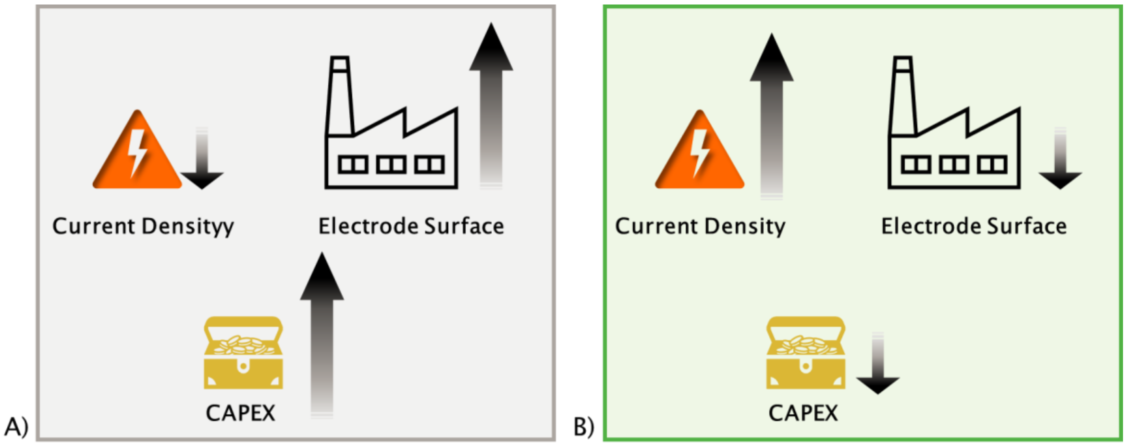

Figure 17: (A) a lower current density relates to a higher electrode surface thus increasing the capex; (B) Increase in the current density result in lower electrode surfaces thus decreasing the capex.

3. Objectives

With the growing demand for greener products and safer processes in the chemical industry, electrochemical methods have emerged as one of the most promising enabling technologies. However, the challenge in realizing industrial uses of electrochemistry lies in bridging the gap between this promising technology, the industrial environment and the specific needs of an industrially suitable method. While electrifying processes offers a tool for disruptive change across various sectors of the chemical industry, the industrial implementation remains complex.

Figure 18: Implementing electrochemical research in the industrial environment.

This work focuses on designing an industrially applicable process rather than merely conducting a chemical feasibility study of an electrochemical method. A scalable hydrogenation process was conceived in the field of organic electrochemical synthesis successfully, alongside the development of a new reactor design for two different wastewater management applications. This work demonstrates the possibility of providing new methods in various fields of electrochemical processes and of developing innovative approaches in a practical manner directly from the initial idea.

4. Overview of the Results

4.1. Enhancing the biodegradability of organic contaminated wastewater via electrochemical treatment

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Explanation of my contribution

The experiments presented in this paper were executed mainly by me and supported by L. Jonescheit. The reactor design was conceptualized by T. Stadtmüller and me. The optimization of the treatment efficiency, based on pH and sulfate promotion was devised by me as well as the interpretation and visualization of the results. The analysis was executed by J. Holl and M. Woyciechowski. The concept of the manuscript and supporting information was prepared by me and finalized in collaboration with J. Metternich under the supervision of S.R. Waldvogel.

The contents of this chapter were patented by Evonik.

Based on the increasing importance of environmental research on the effluent of chemical products, especially their impact on human health and nature, wastewater treatment has become a prominent topic to ensure the sustainability of chemical processes.[68, 71, 116] The biodegradability of chemical contaminants is one of the key parameters of industrial wastewater.[116-118] A sewage treatment plant is the critical connection between the production site and the environment.[116, 119] If a molecule is not removed during the process in the sewage plant via bacterial degradation, it will be emitted and may accumulate in nature.[116-119] Therefore, improving the biodegradability of an effluent stream from a production site is essential to circumvent the accumulation of potentially harmful chemicals in the environment.

The project aimed for enhancing the biodegradability of three wastewaters accruing at an Evonik site including a proof of concept for electrochemical methods as a treatment option. The objective not only focused on the improvement of the biodegradability through TOC (total of carbon) reduction, but also in the elimination of the free cyanide concentration. Additionally, the treatment process was reviewed regarding the economic feasibility compared to conventional methods, such as the Fenton process, whilst being resource-efficient and safe.

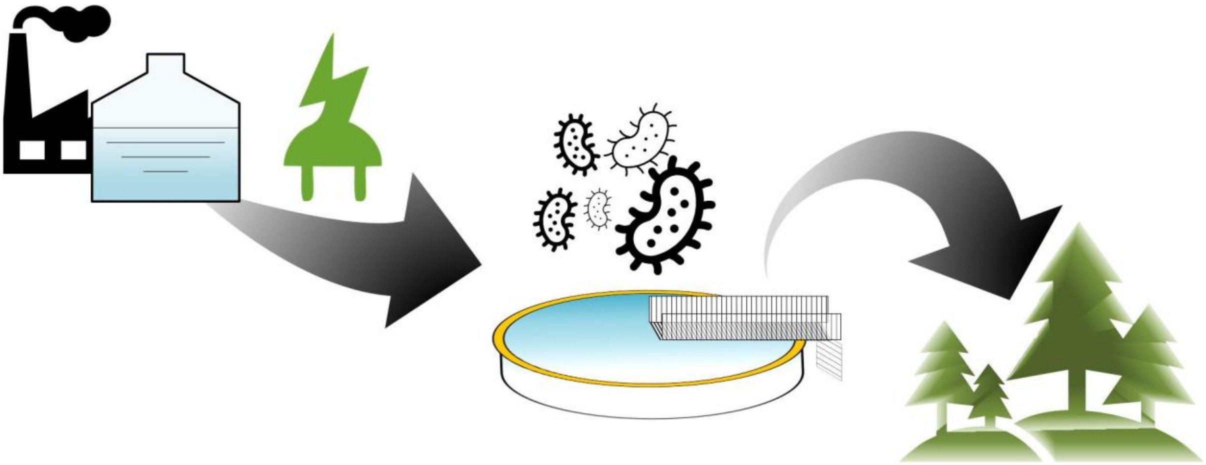

Figure 19: Lifecycle of an industrial wastewater stream, from production plant to environment.

The development of the electrochemical treatment process was initiated using a conventional flow apparatus (see Figure 20). The implementation of a membrane led to a two-chamber system, requiring a more complex infrastructure including two separate systems, such as dual pumps. Therefore, the undivided system was selected as the preferred option. The experimental setup incorporated a boron-doped diamond (BDD) anode, as supported by existing literature on electrochemical wastewater treatment methodologies.[120-121]

The chosen approach was based on the hypothesis of in-situ generation of oxidation mediators, primarily hydroxyl radicals. The utilized counter electrode was a custom-fabricated tantalum sheet with platinum strips welded on the surface. Following several experimental trials, it became apparent that the contaminants present in the wastewater were not easily oxidizable. Thus, the subsequent objective focused on the enhancement of system efficiency while maintaining its simplicity.

A quasi-divided design was evaluated to mitigate reductive back- or side-reactions within the cell, while retaining the simplicity of the undivided system. This was accomplished by significantly altering the surface area of the electrodes. The original size of the working electrode was maintained, whereas the area of the counter electrode was substantially reduced. This configuration resulted in the suppression of reactions occurring directly at the counter electrode, thereby confining undesired processes to the bulk solution. The goal was to enhance oxidation reactions, while suppressing reductive reactions within the reactor. To ensure an easy scalability in the system, a novel spacer (see Figure 20) was designed to leverage a two-plate electrode configuration.

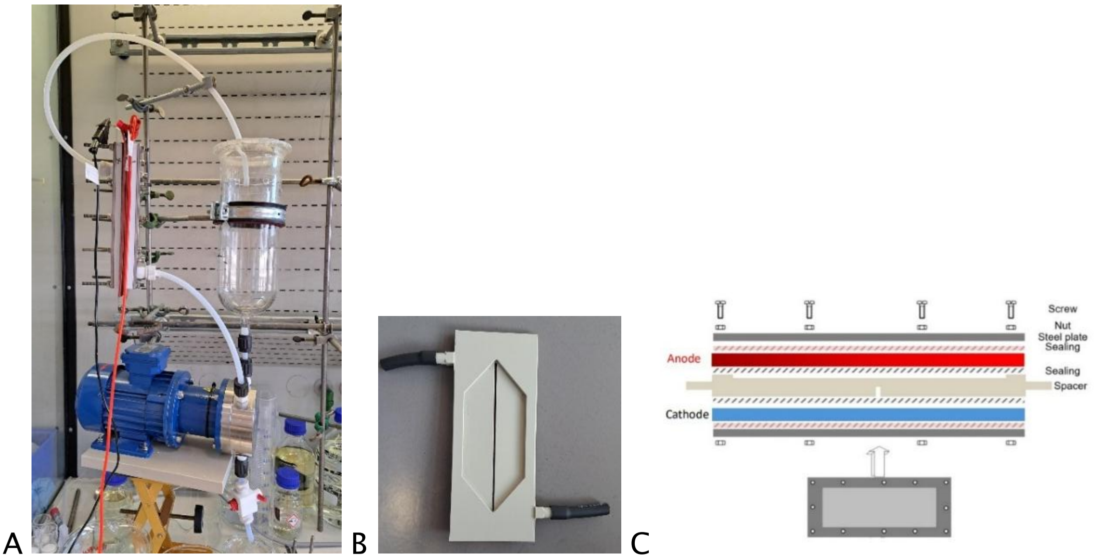

Figure 20: A The flow apparatus utilized in first experimental trails with the glass vessel, the circular pump and the reactor, B the designed slit spacer for quasi-divided electrochemical wastewater treatment, and C a schematic representation of the designed slit spacer.

This reactor design enabled a significant increase in total organic carbon (TOC) elimination. However, the required rates could still not be achieved. To enhance the oxidative degradation of organic contaminants further, the influence of lowering the pH was investigated. The results showed a substantial improvement, with high elimination rates exceeding 95% for all wastewater samples when the pH was adjusted from a caustic level to neutral via the addition of sulfuric acid. The choice of acid not only avoided the potential chlorine gas evolution, associated with the cost-effective option of hydrochloric acid, but additionally introduced an oxidation mediator into the cell.

Sulfate ions are known to be oxidized at BDD anodes to peroxosulfate radicals, which subsequently act as in-situ generated oxidation agents (see Figure 21).[68, 90] In order to delineate the influence of the pH-adjustment and the addition of oxidizable ions on the elimination rate enhancement, further experiments were conducted. A comparative analysis of sodium sulfate and sulfuric acid as additives were performed. The addition of sodium sulfate did not alter the initial basic pH. However, the elimination performance was found to be comparable to sulfuric acid as an additive. This observation confirms that sulfate additives, contribute to the enhancement of the system efficiency and a lowering of the pH is not essential.

To confirm the hypothesis that sulfur-based oxidation mediators can oxidize the investigated contaminants, the classic oxidizing agent peroxodisulfate was added to the wastewater and stirred for 8 hours without the application of electricity. The results of a TOC reduction of over 25% confirmed the underlying, providing a qualitative insight in which sulfur-based oxidative agents are effective in eliminating this specific class of organic contaminants. Nevertheless, it could be observed that the electrochemical system not only reduces the contaminants to lower levels but also generates oxidation mediators in-situ including regeneration after conversion of the organic contaminants. Consequently, the electrochemical process is more resource-efficient than conventional chemical treatment processes involving stoichiometric addition of oxidants.

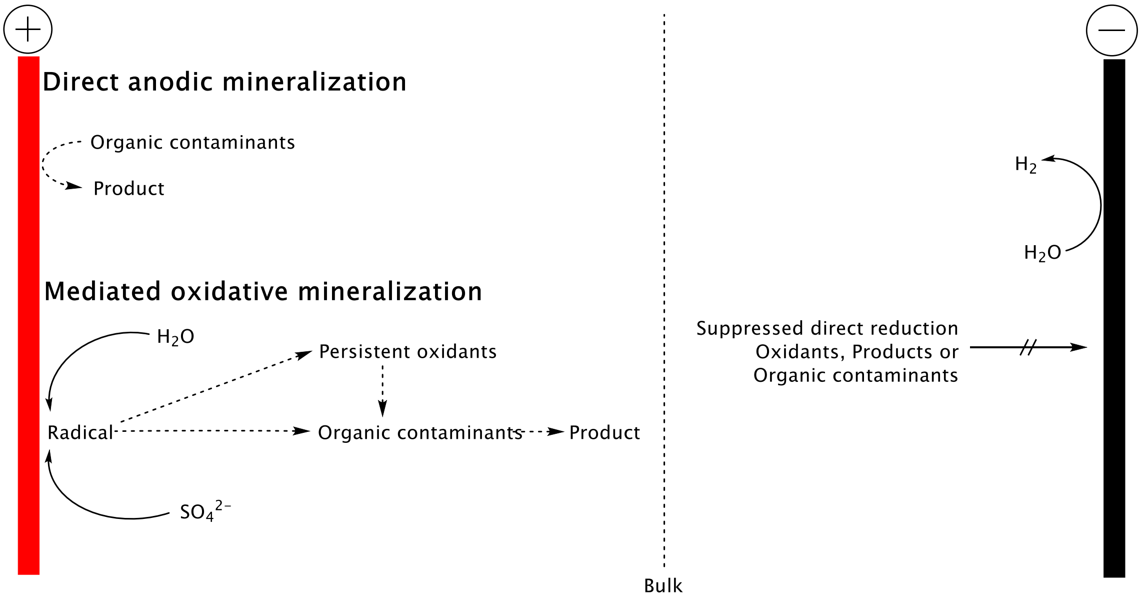

Figure 21: Proposed mechanism of the direct anodic mineralization at a BDD electrode with direct oxidation of the organic contaminant is at the electrode surface vs. mediated mineralization via generation of persistent oxidants. [68, 90]

The newly developed reactor design with the quasi-divided system not only meets the established objectives, but also retains the simplicity required for an industrial application. In addition to demonstrating chemical feasibility, the process technology's applicability at a technical scale was demonstrated. The initial pilot experiment, conducted with a scale-up factor of 10, validated the potential for scaling the system yielding promising results in contaminant elimination. Thus, a sustainable wastewater treatment option was established utilizing only sulfuric acid as an additive to generate and regenerate oxidation mediators in-situ using electricity as the primary reactant. The necessary elimination of the total organic carbon (TOC) could be achieved, along with improved biodegradability and cyanide removal.

4.2. Electrochemical Treatment of Industrial Wastewater Degrading Tetrabutylammonium Bromide Using a Quasi-Divided Cell Design

L. Lennartz, T. Stadtmüller, S. Arndt, P. Stenner, S. R. Waldvogel

Status: accepted

Explanation of my contribution

The experiments presented in this paper were executed by me. The reactor design was conceptualized by S. Arndt, T. Stadtmüller and me. The optimization was planned by me and supervised by S. Arndt and T. Stadtmüller. The manuscript was written by me under the support of S. Arndt and S.R. Waldvogel. The project administration was done by me and P. Stenner.

The contents of this chapter were patented by Evonik.

The emerging field of organic electrochemical synthesis is increasingly associated with the use of alkylammonium salts as supporting electrolytes. These compounds play a significant role not only this sector, but also as a phase-transfer catalysts.[122] Despite their widespread application, recent studies have indicated that these substances may have detrimental effects on both human health and the environment. Consequently, it is imperative to develop effective solutions for the disposal of waste streams associated with contaminated alkylammonium salts.[123]

This investigation sought to develop a practical solution for the treatment of alkylammonium salt containing waste streams by employing an electrochemical method. A real industrial effluent contaminated with tetrabutylammonium bromide (TBABr) was utilized for the development of this study, In addition to TBABr the effluent contained sodium sulfide and sodium chloride. Given that the target substance, tetrabutylammonium is a cationic species, the initial approach involved a divided cell setup. This configuration was envisioned to prevent the attraction of cations to the cathode, thereby promoting the oxidative degradation of the organic cation in the anolyte. The use of a cation exchange membrane, specifically Nafion 424, allowed the cationic species tetrabutylammonium to pass through the membrane and accumulate in the cathode chamber, hindering the oxidative decomposition. Conversely, employing an anion exchange membrane suppressed degradation due to the accumulation of hydroxide ions in the anode chamber, which led to an increase in pH. Additionally, issues with residues on the anode arising from sulfur species further complicated the process, prompting the need to address both challenges effectively.

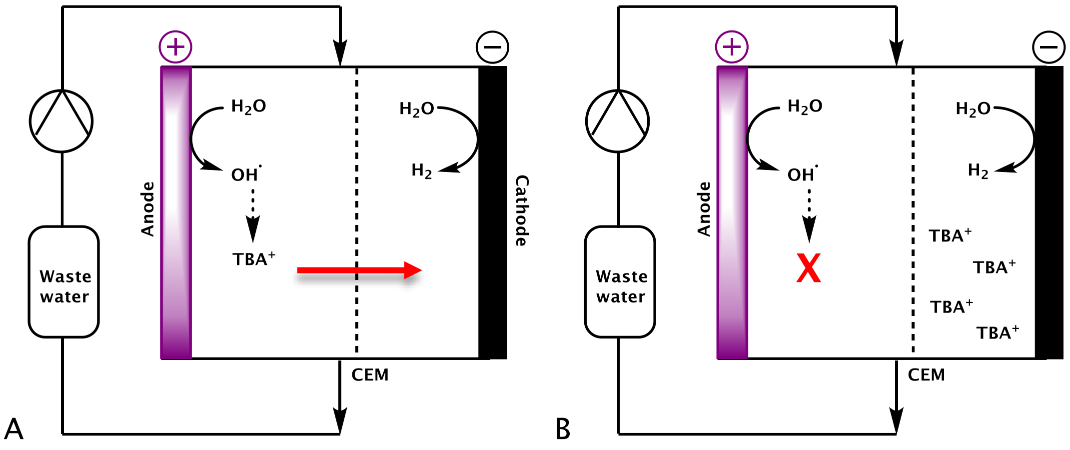

Figure 22: Observed issues with the treatment of tetraalkylammonium cation electrochemically. A) TBA^+ can pass through the CEM from the anolyte to the catholyte. B) TBA^+ accumulation in the catholyte, preventing the hydroxyl radicals produced at the anode from mineralizing the organic compound.

In our experiments, we successfully addressed the coating issues and the accumulation of tetrabutylammonium in the cathode compartment. Hydrochloric acid was added to facilitate the release of sulfide in the form of hydrogen sulfide (H_2S). This step was introduced to prevent the coating of the boron-doped diamond electrode with sulfur-based byproducts, thereby enhancing the efficiency of the overall electrochemical process. The next phase of the investigation related to a solution for the TBA movement within a divided cell setup. The quasi-divided cell configuration was envisioned to mitigate the tendency of cationic tetrabutylammonium ions to accumulate at the cathode, based on significant decrease in cathode surface compared to the surface area of the anode. Additionally, using this approach undesired reductive processes were primarily confined to the bulk solution. Nevertheless, the efficiency of the destruction of the organic load did not meet the desired expectations. It was hypothesized that further reduction of the cathode area would enhance the desired efficiency. This hypothesis proved correct with a decreased cathode surface area facilitating the reproducible elimination of the tetrabutylammonium compound.

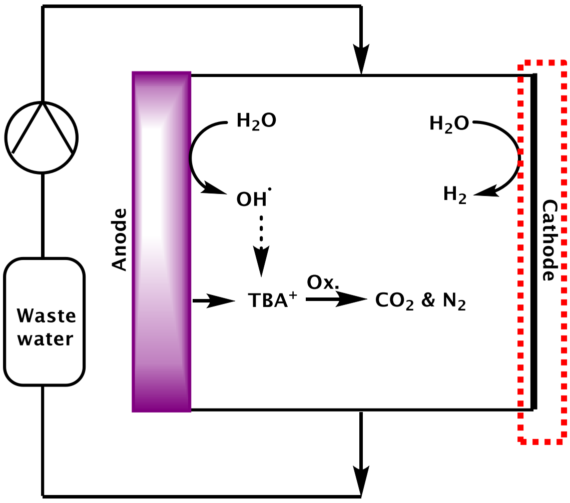

Figure 23: Treatment of tetrabutylammonium cations with a quasi-divided cell setup. The CEM is absent, allowing for the accumulation of TBA^+ in the catholyte.

To allow for an industrial implementation of the quasi-divided approach to wastewater treatment, a comprehensive process solution was developed. Based on the obtained experimental results, pre-treatment of the wastewater with hydrochloric acid was selected to allow for the removal of sulfides from the contaminated wastewater in form of H_2S, which can be absorbed in a sodium hydroxide solution for further application in chemical manufacturing. Following acidification, the wastewater electrolysis in a quasi-divided cell yields material, which can be discharged into the sewage treatment system. The gases emitted during the treatment process are in a first step treated with a sodium hydroxide scrubber to neutralize chlorine gases, while other insoluble gases are incinerated in a conventional thermal oxidizer. The resulting sodium chloride solution can be recycled via electrodialysis to regenerate sodium hydroxide and hydrochloric acid, effectively closing the material loop of the treatment process. Additionally, the gases emitted from the electrodialysis process, namely hydrogen and oxygen, are incinerated in a thermal oxidizer to recover a fraction of the energy input during the electrochemical treatment.

Ultimately, this development task not only demonstrated the suitability of electrochemistry for treating tetrabutyl-contaminated wastewaters, but additionally provided a practical process solution.

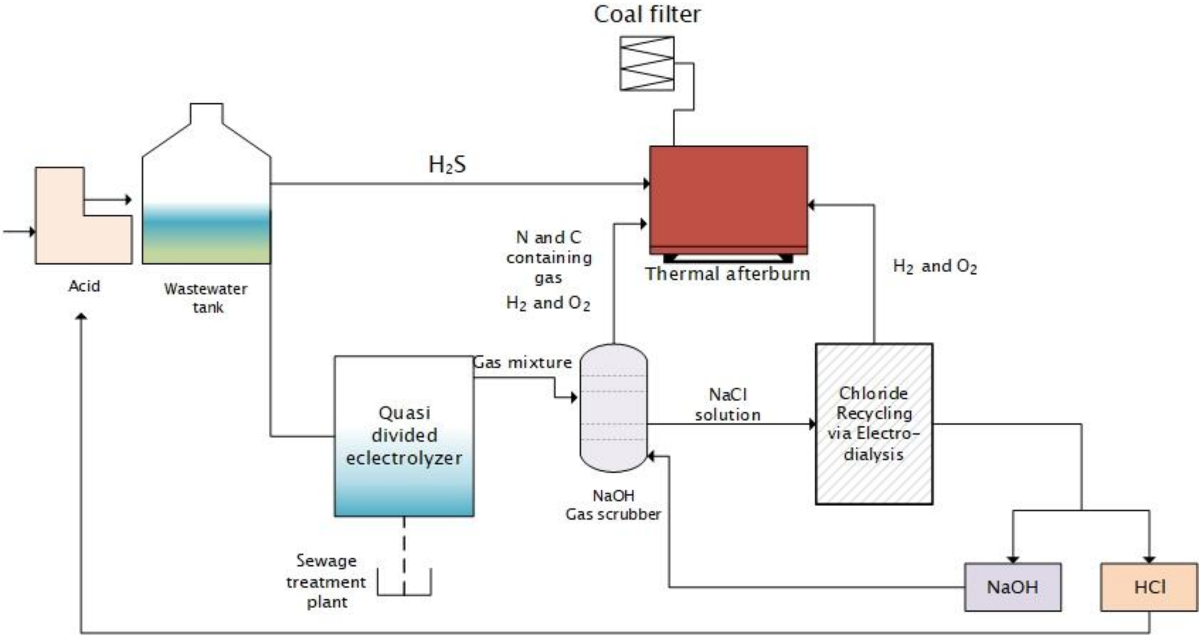

Figure 24: The combined process solution for the treatment of tetra-alkylammonium salt-containing wastewater.

4.3. Electrochemical hydrogenation of Carbonyl Compounds

L. Lennartz, V. Beier, J. B. Metternich, P. Stenner, S. R. Waldvogel

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Explanation of my contribution

The experimental execution was done by V. Beier and me. The optimization of the reaction was designed by V. Beier and me. The analysis was executed by V. Beier and me. The concept of the manuscript and supporting information was done by me and finalized in collaboration with J. Metternich with the support of V. Beier under the supervision of S.R. Waldvogel. The manuscript was written by me, finalized with J. Metternich under the supervision of S. R. Waldvogel. The supporting information was written by V. Beier and me under the supervision of S. R. Waldvogel.

The contents of this chapter were patented by Evonik.

As with many synthetic approaches, there is a significant demand for methods in the field of hydrogenation that are less resource-intensive and safer than their conventional routines.[57, 124-125] Traditional hydrogenation relies on the use of hydrogen gas, along with elevated pressures and temperatures.[57, 124-126] Additionally, complex and expensive transition metal catalysts are often employed. This combination of parameters demands complex safety infrastructures and results in high energy consumption.[124] In contrast, electrochemical hydrogenation which does not require hydrogen gas, represents a milder alternative to classical methods.[57, 125] The most efficient and safest hydrogen source is water, from which hydrogen can be generated in-situ. This can typically be achieved at room temperature, allowing for direct hydrogenation of the molecule in solution without the need for a gas infrastructure.[54, 57, 125] Additionally, this approach requires less energy due to the operation at room temperature and atmospheric pressure.[57] However, a challenge within this electrochemical process relates to many existing methods being primarily academic and not easily scalable. Additionally, most reported examples are prohibitively expensive making the technology not competitive with highly optimized conventional methods.[54, 57] Therefore, the objective of the research presented in this chapter targets the development of an electrochemical hydrogenation process that harnesses its advantages while also addressing industrial requirements.

The general goal aimed at the investigation of a hydrogenation method for various carbonyl compounds, feasible for industrial use. As a model substance the enone isophorone was chosen due to its relevance to industrial applications. Due to the high relevance for conventional system, a literature research provided the starting point for the underlying method development. The study by Mahdavi *et al.* was adapted to create a scalable system, especially considering electrolyte and the used self-made electrodes.[62] The electrolyte composition was modified, replacing the electrolyte and additive combination of sodium chloride, boric acid, and sulfuric acid with sodium sulfate and sulfuric acid.[62] Sodium chloride was removed to mitigate the risk of chlorine gas emission, and boric acid was excluded due to the high associated toxicity. Additionally, the self-made electrode was changed to commercially available nickel foam. Nickel was chosen for its catalytic activity and the increased surface area provided by the nickel foam was expected to be advantageous.[62] Besides the changes in electrolyte and electrode materials, the current density previously reported in the literature was increased as well. This higher current density was selected, because it allows for a smaller and more efficient reactor design, thereby potentially reducing capital expenditures (capex) for a technical plant.

The study commenced with an electrolyte mixture comprising sodium sulfate (0.1 M) and sulfuric acid (0.3 M) in a 1:1 methanol-water solution, along with an isophorone concentration of 0.05 M. Current densities were evaluated from 30 mA/cm² up to 90 mA/cm². After the reaction, the catholyte solution changed to a caustic pH. Therefore in the next step in the optimization trial the sulfuric acid concentration was changed to 0.5 M. This adjustment allowed for the testing of higher current densities. Notably, the optimal current density for achieving a yield of 68% was identified as 90 mA/cm², facilitated by the elevated proton concentration and promoted conductivity. With these initial parameters established, the influence of additional variables was subsequently investigated to optimize the yield and gain a better knowledge on the influences of the reaction.

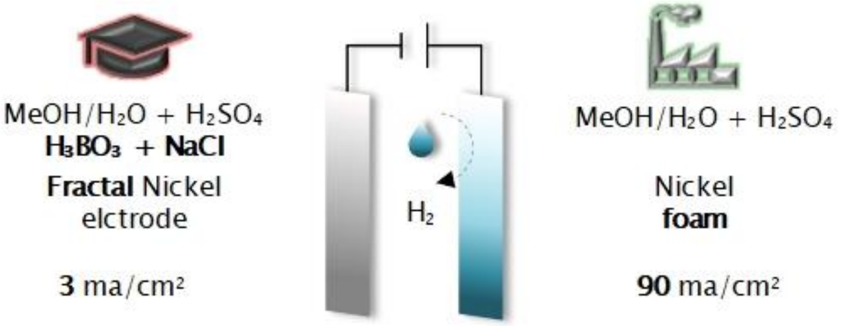

Figure 25: The Comparison of established electrochemical hydrogenation methods from the literature with a newly developed approach.

Initially, it was established that electricity is essential for the hydrogenation process, followed by a thorough investigation of the electrolyte solution. It was demonstrated that sodium sulfate was not required, with a yield of 72% in the absence of sodium sulfate. Other co-solvents, including THF, ethanol, and acetonitrile, were found to be less effective in terms of yield and in minimizing side reactions. Furthermore, the 1:1 methanol-water mixture was confirmed to be the most effective ratio. An increase in the methanol concentration resulted in an insufficient supply of water and therefore a lack in hydrogen supply, leading to a decrease in yield. Conversely, increasing the water content reduced the solubility of isophorone resulting in poor reproducibility of the obtained conversion.

The final step involved investigating the impact of the cathode material. When carbon-based materials or lead were utilized, a coating of the electrode surface was observed after the reaction, which was associated with suppressed yields and recovery of starting materials. This observation is consistent with polymerization and other side reactions. Subsequently other metals known for their catalytic activity in hydrogenation were tested. Copper foam and mesh exhibited decreased yields, in addition to differences based on the specific electrode structure. Cobalt foam was also tested due to its high redox activity, comparable to nickel. Additionally, a cobalt-nickel foam was examined. Results indicated that nickel was a superior choice compared to cobalt and an increased nickel content in cobalt-nickel electrodes correlated with improving yields. This finding suggests that nickel provides favorable catalytic properties for this type of hydrogenation. To further demonstrate the significance of the electrode structure, different types of nickel foams were tested, and scanning electron microscopy images were obtained to illustrate the surface properties of the different electrodes. It was found that within a single class of metal foam the yield was influenced by the electrode structure itself.

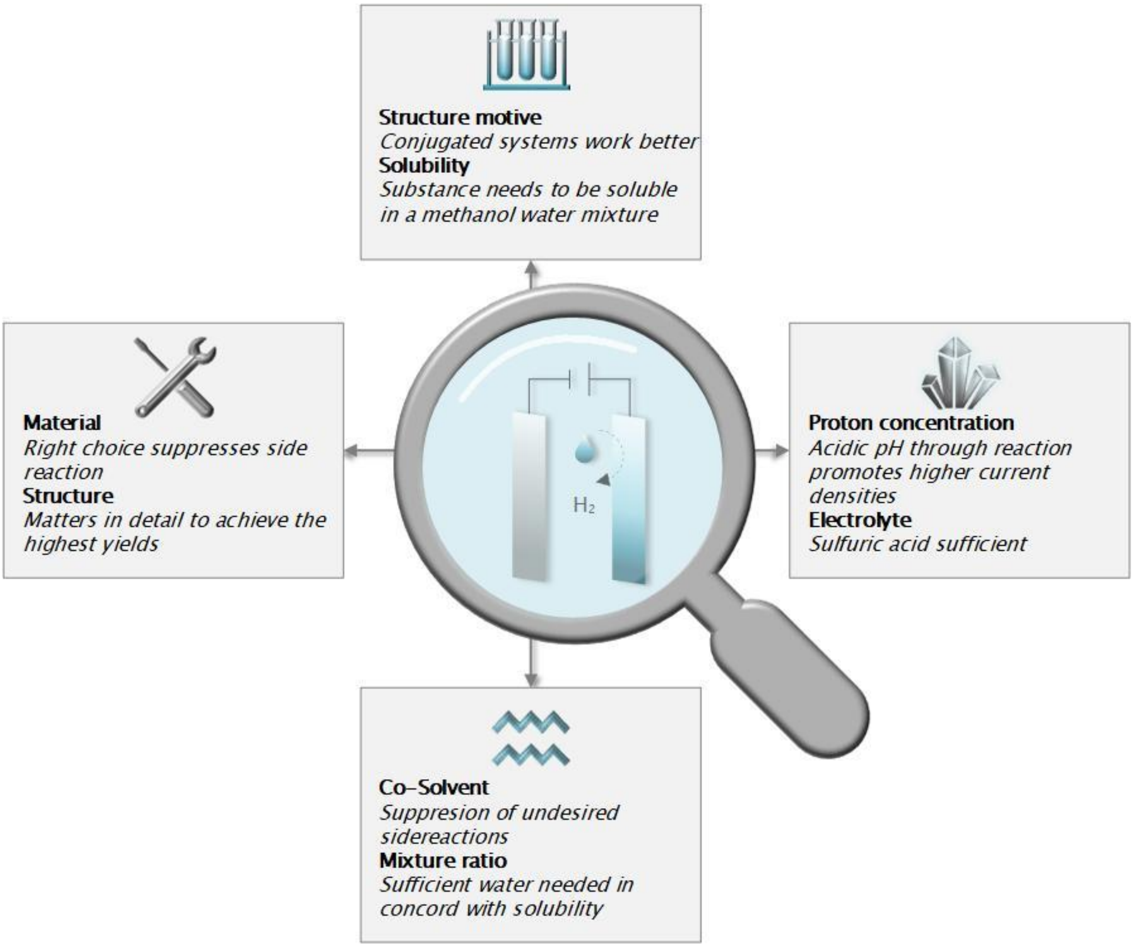

Figure 26: Process parameter impacting the electrochemical hydrogenation.

In the final phase of this investigation, additional potential structural motifs were screened. Alongside other enones, specific methacrylates, as well as aldehydes and ketones were evaluated using the developed electrochemical hydrogenation method. It was demonstrated that the limitations of the optimized conditions were primarily influenced by the solubility of the organic compound in the methanol-water mixture. The hydrogenation of the double bond in methacrylates yielded 58% conversion for butyl methacrylate, while only 9% conversion was observed for the benzyl derivative. This highlights the constraints of the method when applied to more lipophilic structures. The hydrogenation of the aromatic compound benzaldehyde resulted in better yields, achieving 50%, compared to the non-aromatic derivative cyclohexanecarboxaldehyde, which yielded only 28% of the hydrogenated product. This phenomenon is further supported by the results obtained with the evaluated ketones. The highest yield was achieved with acetophenone, reaching a 56% yield, in contrast to cyclohexanone with 21% yield and trimethylcyclohexanone, for which only 5% were achieved.

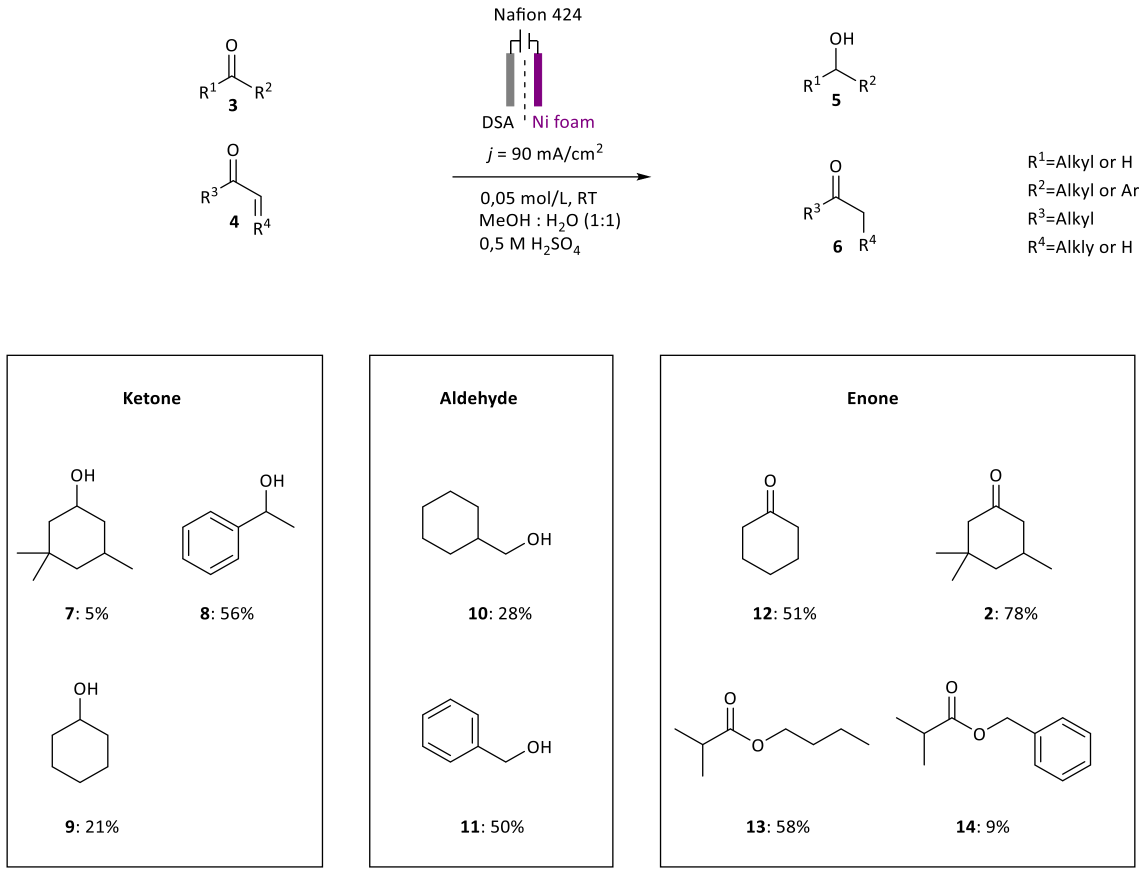

Figure 27: Evaluated structural motifs in the developed electrochemical hydrogenation.

5. Conclusions

In the demonstrated research projects, two industrially relevant topics were explored via electrochemical methods. The emphasis was not merely placed on assessing feasibility but on the comprehensive design of an industrially viable process. This work demonstrates that electrochemistry can be applied in diverse ways, ranging from organic synthesis to wastewater treatment, and can be effectively tailored for industrial applications.

A novel and simplified method for the hydrogenation of carbonyl compounds was developed. Throughout the optimization process, not only a deeper understanding of the reaction could be achieved, but the development also resulted in a scalable method for the hydrogenation of enones, ketones, aldehydes and acrylates. The approach utilized only three cost-effective and readily available chemicals in the electrolyte solution: a) methanol, which functions as an co-solvent b) water, as an inherently safe hydrogen source c) sulfuric acid, as a electrolyte and pH mediator. Moreover, the equipment employed commercially available materials, such as nickel foam electrodes and DSA. The method's appeal lies not only in the use of attractive materials and chemicals suitable for industrial applications, but also in the high current density of 90 mA/cm^2. This combination of process parameters combined with the galvanostatic operation aligns with industrial requirements for compact reactors and straightforward setups. Additionally, the method's application to relevant industrial compounds, including isophorone, methacrylates, aldehydes, and ketones, highlights the versatility and practical applicability.

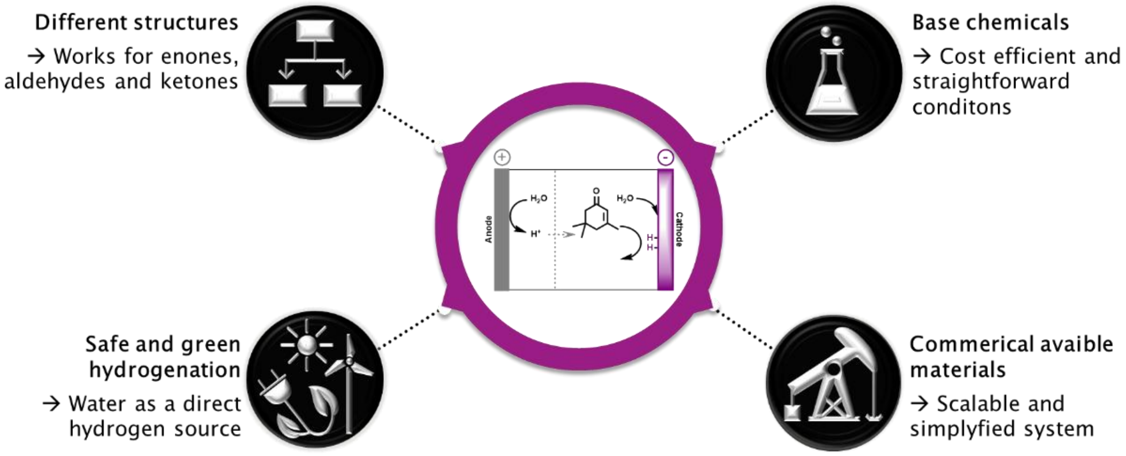

Figure 28: Summary of the newly developed electrochemical hydrogenation method.

In the second research project, two wastewater-related topics were investigated. The first focused on the increasing challenge of poorly biodegradable wastewater, while the second addressed the removal of the common electrolyte class of tetrabutyl ammonium salts. In both scenarios, a quasi-divided cell setup was utilized to facilitate the oxidation of the organic contaminants, while maintaining an industrially suitable configuration. By utilizing a newly designed reactor system the TOC elimination goals were achieved. These two studies demonstrate that electrochemical methods are advantageous and more importantly, industrially feasible in organic synthesis and in the downstream processes of the chemical industry.

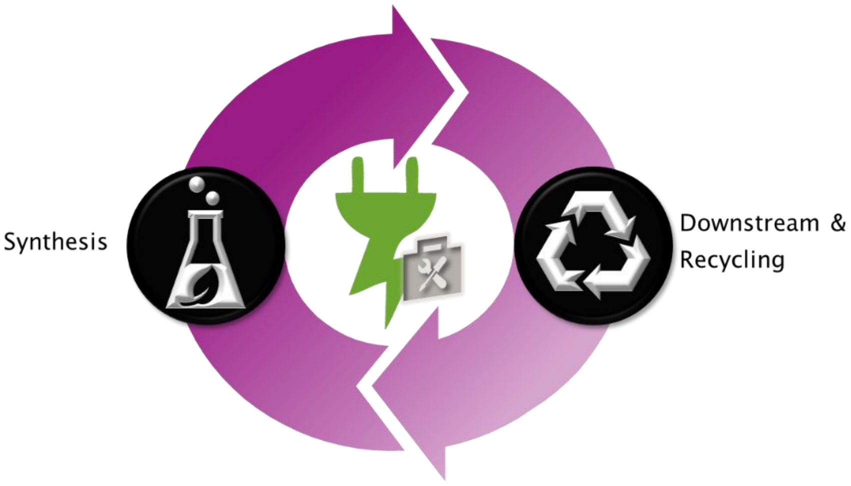

Figure 29: Electrochemistry as a versatile toolbox for organic synthesis and downstream or recycling processes.

6. Outlook

This work establishes a connection between academic laboratory studies in the fields of electrochemical synthesis and electrochemical wastewater treatment, thereby paving the way for practical process design. It represents a crucial initial step toward the technical implementation of electrochemical methods aimed at electrifying the chemical industry across all essential stages, from synthesis to downstream processing, e.g. waste management. The approach offers valuable insights that can translate into new electrochemical methods and potential technical applications, thus serving as a guide for developing electrochemical techniques for greener processes and ensuring practical applicability.

The developed electrochemical hydrogenation process is ready for transition into the scale-up phase. The next step could involve the actual scaling of this method and validating the design through practical applications, such as a flow reactor and pilot plant. In addition to hydrogenation of the model substrate isophorone, the developed process method can be applied to other interesting substrate motifs, including enones, ketones, and aldehydes. The method offers a safe and mild alternative for conventional hydrogenation processes, allowing to bypass traditional hydrogen gas infrastructure and the conventional unit operation under high pressures and temperatures. Thus, it serves as a new electrochemical tool for the hydrogenation of various carbonyl compounds, while addressing industrial needs.

The newly developed reactor for electrochemical wastewater treatment has the potential to harness the green properties of electrochemistry, while addressing the challenges posed by sometimes harmful substances. In addition to providing a solution for the emerging issue of alkylammonium salt emissions, it can also be utilized for traditional wastewater management by enhancing or completely eliminating the necessity for biological degradability. Evidence has shown that this new reactor design is not only feasible for achieving wastewater treatment goals but also offers advantages over other methods like circumventing the need of stoichiometric oxidation agents. With these results at hand, it is essential to explore the electrification of waste management processes, particularly in the terms of complex waste issues.

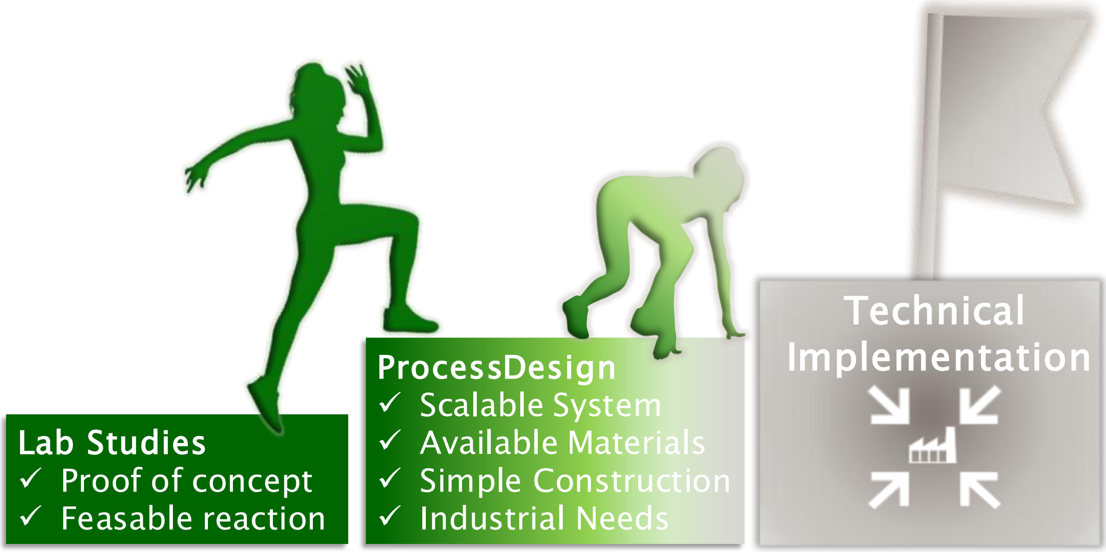

Figure 30: Next step for the implementation of new electrochemical methods, starting from laboratory studies to technical implementation.

7. Abbreviations

A	surface
AEM	Anion exchange membrane
Ar	Aryl
BDD	Boron doped diamond
c	Concentration
C	Coulomb
CAPEX	Capital expenses
CEM	Cation exchange membrane
cm	Centimeter
COD	Chemical oxygen demand
DSA	Dimensional stable anodes
eq.	Equivalents
et al.	And other (*lat. et alli*)
F	Faraday
GC	Gas chromatography
GC	Glassy carbon
GC-MS	Gas chromatography coupled to a mass detector
h	Hour
HPLC	High pressure liquid chromatography
HR-MS	High resolution mass spectrometry
I	Electric current
j	Current density
L	Liter
Lit	Literature
m	mass
m	meter
mA	Milliampere
mL	Milliliter
mm	Millimeter
MS	Mass spectrometry
n	Amount of substance
NMR	Nuclear magnetic resonance
OPEX	Operational expenses
p	pressure
Q	Amount of applied charge
R	(organic) substituent
RCS	Reactive chlorine species
$\mathbf{R_f}$	Retention factor
RSS	Reactive sulfur species

RT	Room temperature
s.a.	Surface area
t	tonne
t	time
T	Temperature
TOC	Total of carbon
V	Volt
V	Volume
z	Charge number

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9. Publications, Conferences and Supervision

9.1. Conferences

[redacted]

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9.3. Supervised Students

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9.4. Publications

2024

Lennartz, L., Beil, S. B., Waldvogel, S. R., Stenner, P. (2024). Electrochemical Processes for the Chemical Industry: The push toward decarbonization is driving an increased interest in electrochemical processes. Here, the authors share their experience in industrializing these processes. *Chemical Engineering*, *131*(12).

2025

Lennartz, L., Metternich, J. B., Stadtmüller, T., Jonescheit, L., Stenner, P., & Waldvogel, S. R. (2025). Efficiency enhanced electrochemical treatment of industrial wastewater by quasi-division. *Electrochimica Acta*, 146422.

10. Appendix

A.1 Contents – Appendix

KI-Tool	Used for	Why	When
ChatGPT (Evonik intern Version)	Ideas for rephrasing text passages	Enhance readability	Throughout the whole text

Electrochemical Processes for the Chemical Industry

The push toward decarbonization is driving an increased interest in electrochemical processes. Here, the authors share their experience in industrializing these processes

Sebastian B. Beil, Siegfried R. Waldvogel
Max Planck Institute for Chemical Energy Conversion
Laura Lennartz, Patrik Stenner
Evonik

IN BRIEF

- SYNTHETIC CONVERSIONS
- DOWNSTREAM PROCESSING
- CHALLENGES
- SPECIFIC CONSIDERATIONS
- SCALING UP: STEP-BY-STEP GUIDE

The field of electrochemistry offers a disruptive methodology to revolutionize the chemical process industries (CPI) by electrifying processes. However, scaling up and implementing a new electrochemical synthesis poses challenges that can best be overcome through a combination of academic research and industrial expertise. This article discusses the potential of electrochemistry as a tool to revolutionize and decarbonize the CPI, while also examining the obstacles and unique considerations involved when implementing it in an industrial setting. Examples are given to demonstrate the versatility and exceptional performance of electrosynthesis. Having collaborated for many years between academia and industry, the authors share experiences gained from industrializing such timely methods, and aim to eliminate any concerns readers may have about scaling new electrochemical processes.

Within the CPI, lowering the carbon footprint and increasing efficiency, in line with so-called "green" processes, is becoming progressively important. Topics such as the circular economy, recycling and upcycling of raw materials and the energy transition are in focus. Processes must be redesigned in a resource-friendly and sustainable manner to circumvent the ongoing climate crisis. Disruptive technologies will play a major role in these activities to develop and establish more efficient processes.

Synthetic conversions

The use of electricity instead of chemical reagents has applications in organic syntheses, purification processes and downstream technology. By application of electricity, electrons can participate directly as reagents. An example of how a classical organic oxidative coupling could be made not only greener but also more economically efficient, by saving several synthetic steps, is the synthesis of non-symmetrical derivatives of 2,2'-biphenol shown in Figure 1.

Thus, a ligand backbone for a catalyst applied in a major chemical process in the production of oil additives, the hydroformylation reaction, was developed by the author's laboratory [*1–4*]. The electrochemical reaction pathway saves five synthesis steps compared to the classical route and doesn't require leaving groups in order to form the $C(sp^2)–C(sp^2)$ bond.

A noteworthy illustration of electrochemical synthesis applied to inorganic components is the anodic periodate synthesis. This is a common platform oxidizer in the chemical industry, which has already been scaled-up to generate several kilograms of product. Outstandingly, this method uses only electricity to synthesize periodate, without the need for external oxidizing agents.

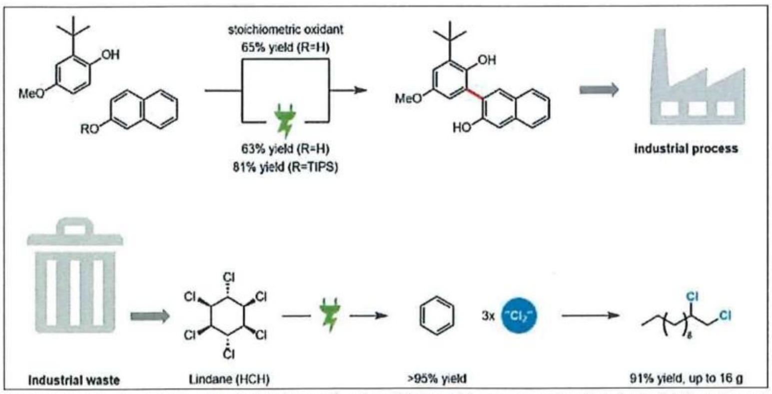


FIGURE 1. The reaction pathway for the synthesis of biphenol is an example of an industrially relevant electro-organic synthesis. The HCH upcycling reaction pathway is an example for an electro-organic driven circular economy [*3, 4, 10, 11*]

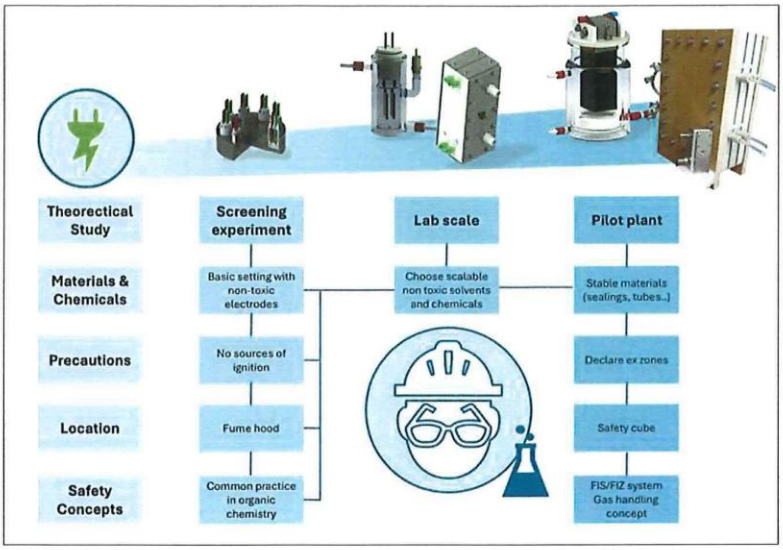


FIGURE 2. Consider safety aspects in the scaling process of an electro-organic synthesis process

COMMON ELECTROCHEMISTRY MYTHS AND CONCERNS

1. **Scaling up in electrochemistry is always done by numbering up.** Not true — some methods use different cell setups and special electrode designs
2. **Electrochemistry has its own distinct language.** Yes, but as in any scaling process, chemists and engineers must bridge their different languages
3. **Electrochemical equipment will cause sparks or shocks that are dangerous to operators.** Most electrochemical cells operate below 10 V d.c. However, stray current can be a problem in electrochemical plants
4. **Electrochemistry is expensive.** Although systems are often customized, electrochemical processes can compete economically due to lower carbon dioxide emissions

Moreover, iodo waste can be fed in, and the complete mineralization of organics results in periodination [5]. This approach exemplifies the resource- and chemical-efficient nature of electrochemical syntheses [*5–7*].

A method for the oxidative ring opening of cyclic hydrocarbons was also developed to eliminate the need for an oxidizer. By utilizing nickel oxide hydroxide anodes, a process was established for synthesizing substituted adipic acid derivatives from lignin-derived feedstock and was successfully scaled up to over 10 liters [*8–9*]. These examples epitomize the potential of electrosynthesis to enable conversions that are not only mild, resource-efficient, and sustainable, but also capable of being scaled up to meet industrial requirements.

Downstream processing

On top of classical synthesis, electrochemistry is also used for downstream processing. Applied electrochemical downstream methods are electrodialysis, wastewater treatment and electrostatic purification. An interesting example in electrochemical waste utilization is the upcycling of chlorinated persistent pesticides. This waste is not readily decomposed by nature and has been put into landfills on a multi-million-ton scale. In order to tackle this problem, researchers developed an electrosynthesis (e-shuttle) for upcycling this waste, which generated benzene and chlorine equivalents — both base chemicals that are highly relevant for the industry [*10*]. This example highlights the versatility of electrochemical processes in the search of a sustainable future.

Challenges

The innovation of electrosynthesis can lead to many approaches for optimizing chemical processes, but also poses challenges. Modern approaches do not focus on electrochemical stand-alone systems, but integrate electrochemical sub-steps as a part of a longer process chain. This enables the gradual implementation of electrochemical innovations in the industrial environment.

One of the biggest challenges when using electrochemistry in the chemical industry is the technical implementation. Unlike chlor-alkali electrolysis, which has been used on a technical scale for decades, most electrochemical syntheses and processes are completely new and have to be designed from scratch. There are almost no commercially available pilot systems for the examples mentioned above, and to the current authors' knowledge, there are no plants on an industrial scale that are commercially available. The lack of availability of these plants requires technical implementation within every company and their workshops, or highly individualized plants from the few available manufacturers (for electrodialysis, for example, Eurodia, MEGA, Fumatec).

It is even more difficult to find suppliers for large-scale plants in the field of organic electrosynthesis. Both options require knowledge of the hurdles and peculiarities of an electrochemical pilot plant and the ability to fix them internally. To dispel fears of implementing electrochemical processes, this article aims to avoid prejudices and typical mistakes from the outset [*12–13*].

Specific considerations

So let's dive into the possibilities of electrochemical processes and share with you our experience in scaling up

FIGURE 3. A proof of concept is typically started on the laboratory scale

A 2

FIGURE 4. After proving a concept in the laboratory, the next step in scaleup involves a mini plant like this electrosynthesis pilot plant

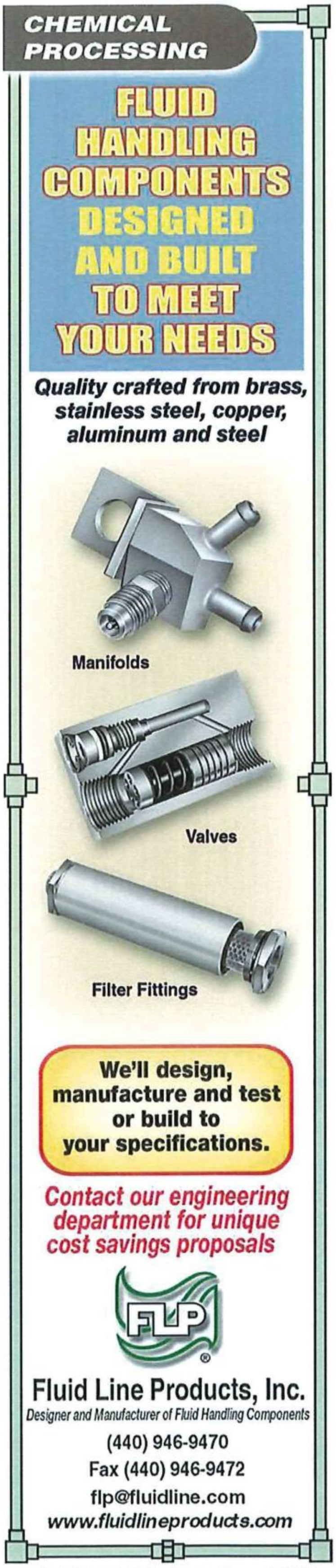
these processes. The next sections discuss the most important aspects that differ the most from classical chemical processes. These include: safety, material stability, impurities, suppliers and economics.

Safety. The safety of every reaction is of utmost importance in the chemical industry. The same applies to electro-organic reactions, where some peculiarities come into play. In scaling up an electrochemical reaction, several aspects must be considered, which can often be neglected in the laboratory on a screening scale, since working under standard laboratory conditions is sufficient for the safety concept (Figure 2).

The first aspect that distinguishes the electrochemical reaction from standard organic reactions is the most obvious one, namely the use of electricity. On the one hand, this aspect offers the advantage that ending unpredictable reactions is easily ensured by switching off the electricity. However, the use of electricity brings some challenges, especially on the pilot scale. The choice of materials can prevent some problems. For example, the use of stainless-steel pipes should be avoided due to so-called stray current. In addition, it should be ensured that safety signs with warnings of electrical risks, such as "caution electricity," are visibly displayed.

Another peculiarity in electrochemistry is the emission of gases. Typical gases formed in an aqueous solution are hydrogen at the cathode and oxygen at the anode. Since these gases can create an explosive atmosphere, especially in a mixture and when enriched, normal safety concepts, such as working in a fume hood and keeping all ignition sources away, are not sufficient at a larger scale. When working at the pilot scale, these gases must be diluted to lower than an explosive level. This can be achieved through complete inertization of the system or flushing concepts. To complete the safety concept and enable operation of the system without continuous monitoring of the flow, so-called flow-indication switch (FIS) shutdowns are used. These ensure that the power is shut off when the air flow decreases. If such a system is not sufficient, so-called explosive zones must be defined in plants. In addition to hydrogen and oxygen, toxic gases such as chlorine can also be emitted. Diluting the gas is not sufficient in this case, and neutralizing the gas is necessary.

Especially in organic electrochemistry, attention is also paid to the use of organic solvents and the use of alkylammonium salts as a supporting electrolyte, which are used in non-polar solvents. Therefore, the chemicals used should be safe in terms of their use in larger quantities (keywords are toxicity and flammability). The use of alkyl-



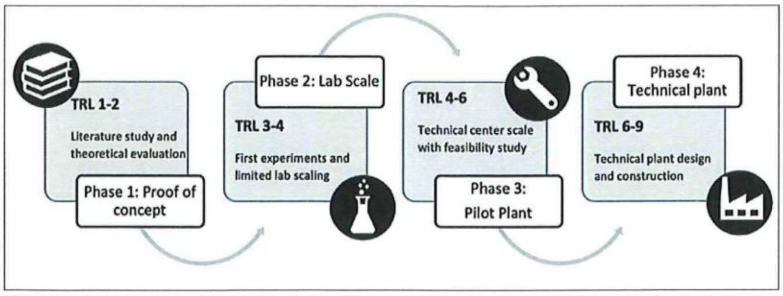


FIGURE 5. Technology readiness levels define the four phases of scaling an electro-organic reaction

ammonium salts must also be considered from a process engineering and economic perspective. These chemicals are not only expensive, but are also often toxic. Therefore, a recycling process must be implemented when using them.

Material stability and impurities. To ensure safety and prevent contamination in wastewater or products, attention must also be paid to the long-term stability of materials, such as electrodes. Electrode materials should also be carefully chosen to avoid toxic metals and contamination. A certain amount of instability must be expected, therefore toxic metals, such as mercury, lead or cadmium, are to be avoided. To design an economical process, long-term stability tests for materials like electrodes, sealings and membranes are crucial prior to scaling up. Membranes should be tested for at least 1,000 hours, with a focus on their stability towards organic media. The availability of robust membranes in the market is limited, so it is important to consider material stability and availability early on, especially in organic electrochemistry.

Laboratory-scale experiments often use high-grade chemicals, but in pilot- or industrial-scale plants, lower-purity grades are used. This can lead to issues not observed in the laboratory, such as particle blockages or damage of coated electrodes. Contamination can also result in gas emissions that need to be quenched to provide safety.

Process systems and economics. In addition to differences in the chemicals used and the stability of the materials employed, the general availability of pilot systems must also be considered. Electrochemical process systems require highly customized designs, making standardized package units impractical. This results in a complex and costly scaling process, even on pilot-plant scales. Developing custom concepts with manufacturers can slow down or prevent piloting. To ensure a smooth scaling process, it is important to consider pilot system design early on. For example, persulfate electrolysis requires individually developed and optimized cell types and electrode materials, with more than five unique installations worldwide. To establish electrochemistry as a competitive technology, economic competitiveness with optimized standard processes is crucial.

In addition to comparing operating costs (OPEX), carbon emission costs must also be considered. Long-term stability tests for electrode materials and membranes are important to control irregular operational costs. Regional differences in the cost of base chemicals, such as caustic soda, and restrictive wastewater guidelines can also affect economic efficiency.

Downstream processing and simplifying organic synthesis steps are also important factors to consider. Chemical parameters and environmental influences are not the only decisive factors in the industrial environment. One of the most important factors is the scalability and technical feasibility of processes. There are different examples of electrochemical processes that have been implemented on an industrial scale in the chemical industry. The production of Lysmeral by BASF is an example of organic electrochemistry on an industrial scale with about several tens of thousands of tons per year, in addition to chlor-alkali electrolysis [*14*].

Scaling up: step-by-step guide

This section illustrates the process of going from an initial idea to the development of a commercial process. Starting a proof of concept on a laboratory scale will likely result in a small scaleup with laboratory utensils (Figure 3). The next step is a mini plant or pilot-scale plant requiring a technical center (Figure 4). In this step, the scalability of the process is investigated and the influences of larger cells and requirements are unmasked. An industrial-scale plant is the last step of scaleup. The plant will be designed for the desired process, with larger equipment and numbering-up of electrochemical cells.

Technology readiness levels. Today, the process development steps are often expressed by technology readiness levels (TRLs). This is a scale for assessing the state of development of new technologies on the basis of a systematic analysis. On a scale of 1 to 9, it indicates how advanced a technology is. In Figure 5, the four phases of process development from feasibility to technical installation are depicted. The TRLs and the decisive properties of the phases are shown.

But how do you move from the current level into the next phase? When do you take the step out of the laboratory? What are the most crucial parameters to consider in each step? To answer these questions, you must first determine what you want to achieve in each of the scaling steps.

TRL 1–4. In the TRL 1–2 phase, a theoretical proof of concept is executed. Typically, you perform a literature study to represent the current state of the art and consider the feasibility of your idea. After the theoretical study, the next step includes performing experiments and evaluating the feasibility of the chemistry behind your idea. After proving the chemical viability and therefore reaching a TRL of 3–4, the next step is scaling.

Beyond TRL 4. To take the step toward a demonstration facility and thus prove the industrial feasibility, some parameters must first be precisely evaluated before reaching a

CHECKLIST FOR SCALEUP

- ✔ Safety
- ✔ Long-term stability
- ✔ Tests with original chemicals
- ✔ Supplier
- ✔ Economic feasibility
- → Are your parameters scalable?

TRL up to 6. The parameters mentioned in the earlier section, such as safety, long-term stability, chemical purity, supply source and economic viability for the process should be discussed. As part of the safety assessment, any potentially released gases should be examined and a plan must be developed for handling them. In addition, the scalability of the chemicals used in organic electrochemistry should be considered with regard to safety. Furthermore, the organic reaction should have been sufficiently studied so that any undesired reactions are known.

In the scaled-up process, the long-term stability of the selected materials is also an important safety consideration. In the laboratory, stable materials should have been identified for all components, such as pumps, hoses, seals, and similar items. In terms of scaling up, the same qualities of chemicals used in the pilot-scale should have been used in the laboratory. This results in circumventing unplanned events such as instabilities and leakage from the outset.

Suppliers. Once everything is ready to start scaling up, the search for suppliers starts. A pilot plant is often like a tailor-made suit that is precisely designed for the organic electrochemical reaction. It is important to pay attention to the commercial availability of materials, such as solvents, electrode materials, seals and more, and to clarify the question of in-house or outsourced engineering. Besides process and chemical parameters, the economic efficiency is decisive for scaleup.

Data generation. If the pilot plant phase is successful and you are able to transfer a laboratory reaction into a technical center, you have to start generating resilient data. These data will be the basis for calculations of operational and capital expenditures costs. Last but not least, you have to decide whether your process is not only chemically feasible, but also suitable for industrial implementation. ■

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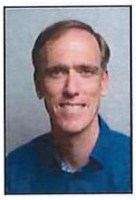

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Efficiency enhanced electrochemical treatment of industrial wastewater by quasi-division

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We present a novel method for treating real life industrial wastewaters containing different kind of organic contaminants, utilizing a quasi-divided cell setup that enhances total organic carbon (TOC) and chemical oxygen demand (COD) elimination efficiency. Three distinct wastewater streams were analyzed, containing various organic pollutants, including nitriles, amines, and dissolved cyanides. Degradation efficiencies of up to 99 % for both TOC and COD were achieved using a newly slit spacer that facilitates quasi-division, effectively reducing the hindrance of reductive back reactions by minimizing the cathode surface area. The innovative design of two plate electrodes, combined with the newly developed spacer, simplifies the scaling process for industrial applications by addressing the challenges of integrating quasi-division into conventional electrochemical flow systems with wires as the smaller electrode. Also the undivided cell setup simplifies the periphery infrastructure of a technical plant to one cycle. Additionally, we explored the impact of sulfate on treatment efficiency, finding that peroxodisulfate species generated in situ at boron-doped diamond anodes significantly enhance our degradation rates. This study introduces a promising approach for TOC elimination and cyanide oxidation simultaneously, demonstrating strong potential for industrial application due to its simplicity in regard to engineering the electrochemical reactor and periphery infrastructure.

1. Introduction

Almost every chemical process generates industrial wastewater, which often contains contaminants hazardous for both, nature and humans. One class of contaminants that needs to be eliminated from industrial wastewater are substances that are not biodegradable and may accumulate over time [1]. Therefore, treatment of industrial wastewater is often necessary prior to emission into the environment [2]. Commonly employed wastewater treatment processes revolve around microbiological degradation of contaminants. The biological treatment features are often limited in applicability, if organic pollutants are present in such wastewater [2]. In particular, organic species with high resistance to oxidative degradation require more aggressive treatment. There are various mature methodologies for wastewater treatment, which can be employed for the elimination of stable organic pollutants. These processes include membrane technology for separating pollutants from water, the Fenton technology and ozonolysis for the oxidative decomposition of organics, in addition to classical incineration among others [1–7]. All of these methods exhibit significant an distinct disadvantages: Membranes are prone to fouling and lose stability when exposed to aggressive chemicals [1,8,9]. Additionally, the membrane divides the wastewater stream into two sub streams, with the concentrate requiring further treatment, typically by incineration resulting in increased carbon dioxide emission [1]. Despite being comparably cost-effective in the elimination of poorly oxidizable substances, the Fenton process requires strict safety standards for H_2O_2 management and generates a high salt load including iron and other chemicals necessary for pH adjustements [4,10–13]. Lastly, ozonolysis entails the handling of hazardous gases and is comparably energy intensive. Thus, more sustainable processes are heavily sought after.

In the past years, electrochemistry has evolved to an emerging technology for sustainable chemical processes [14–18]. Electrochemistry has found widespread application in the production of organic

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Nomenclature

Abbreviations

BDD	Boron doped diamond
COD	Chemical oxygen demand
PP	Polypropylen
PTFE	Polytetrafluorethylen
RCS	Reactive chlorine species
RSS	Reactive sulfur species
TOC	Total of carbon

Symbols

A	*Ampere*
j	Current density
V	Voltage
Wh	Watt hour

compounds–known as electrosynthesis [19–21]. Additionally, electrochemistry can be utilized for highly efficient, oxidative decomposition of organic substances in aqueous media, a process, which can be extended to the treatment and disinfection of different kinds of wastewaters [4,12,13,15]. The electrochemical treatment of industrial wastewater involves the generation of highly reactive oxidizing species at the anode, which can eliminate various organic pollutants [3,6,22–25]. Boron-doped diamond (BDD) is the most efficient electrode material for this purpose, due to its high overpotential for oxygen evolution and its ability to generate highly reactive hydroxyl radicals in aqueous media [12,22–24,26–31]. Inorganic chlorides or sulfur species can be added to enhance the effect of the so-called cold combustion [24,26,27]. In this process, chloride is oxidized to reactive (oxo)chlorine species (RCS) and sulfur to reactive (per)sulfate species (RSS) [6]. Both species exhibit an utmost oxidizing power and support the degradation of organic pollutants [7,24,26–28,32–34]. Compared to other oxidative wastewater treatments, electrochemistry is more resource efficient and sustainable based on the in-situ generation of oxidizing species [7,15,32]. In the work of Canizares et al. [3], the three oxidative methods of Fenton, ozonolysis, and electrochemical treatment were compared regarding their efficiency in degrading various organic pollutants and in terms of operational and investment costs. The electrochemical approach proved to be the most efficient method, especially in heavily polluted wastewater, and was able to compete well with the operational costs of the Fenton process for many pollutants [3,26,35].

The experimental investigations presented here were conducted with the aim of developing a highly efficient, long-term stable and sustainable process for the treatment of industrial wastewater contaminated with organic pollutants resistant towards conventional biological treatment options. Therefore, the focus was on reducing environmentally harmful chemicals and ensuring the sustainability of the method. Additionally, the technology had to be amenable to varying wastewater composition from different industrial production plants and at various timepoints across the production lifecycle.

To enhance the applicability of our treatment system in industrial settings, we exclusively tested real effluent streams from chemical production. These wastewaters contained a diverse range of contaminants, including nitriles, amines, ketones, and free cyanides. Our objective was to develop a process that not only improves the biological degradability of these contaminants but also effectively removes residual cyanides. A key consideration was to maintain simplicity in reactor design, minimizing the peripheral infrastructure required for the treatment plant. Consequently, we conceived an undivided cell setup, streamlining the engineering requirements to a single cycle. This innovative approach addresses the challenge of maintaining sufficient oxidation power while suppressing undesirable reductive side or back reactions. By focusing on an uncomplicated system architecture, we aim to facilitate the integration of our treatment process into existing industrial frameworks, thereby enhancing its feasibility and operational efficiency. This study underscores the potential of our undivided cell design as a practical solution for the treatment of complex real life industrial wastewaters.

2. Materials and methods

2.1. General description of the experiments

The various wastewater samples (see Table 1) were tested in a laboratory facility using a semi-batch process. For this purpose, 300 mL of wastewater were continuously cycled through an electrochemical cell until the designated treatment time was achieved. During the treatment, samples were taken, and the volume was kept constant by addition of water. The samples were analyzed for COD, TOC changes, and, if applicable, cyanide content. Initial experimental investigations identified BDD as a suitable and long-term stable anode material, and a Pt strip welded onto tantalum as the best cathode material. For detailed information, please have a look at the supporting information.

2.2. Wastewater characterization

The real life industrial wastewater was provided by Evonik Operations GmbH and the main compounds are listed in Table 1. All Wastewaters had a caustic pH due to the inorganic bases.

3. Results

The experimental investigations were initiated with an attempt of treatment the different wastewater streams employing conventional electrochemical conditions. A classic flow cell with a BDD anode and a platinum on tantalum cathode was applied and very limited lowering (under 15 % TOC and COD elimination) in the contaminant concentration was obtained. Since a membrane for enhancing oxidation proved unfeasible, due to the limited stability of classic separators at the current densities required in wastewater treatment, a solution without a separator was required. In classical electrosynthesis, a technique called quasi-division was previously demonstrated to improve overall cell oxidative power. The basic concept of quasi-division is a kinetic limitation of undesired transformations occurring at the counter-electrode, thereby improving the overall cell-efficiency [36]. Generally, this is achieved by using a cell design with significant cell surface difference between the working and counter-electrode. Employing quasi-division was envisioned for the treatment of stable organic pollutants found in common industrial wastewater. With a tremendously undersized cathode surface area likely resulting in shielding of the electrode and restriction of undesired processes to the bulk. To test this concept, quasi-division was applied in wastewater treatment: Two plate electrodes were utilized in the optimized cell setup with restriction of the cathode surface by a polymer spacer with a slit (see Fig. 1). The plate electrode design allowed for simpler cell setup and the use of various electrode materials with easily available dimensions. The spacer material was either polypropylene or PTFE.

Table 1
Wastewater components: Listed are the main compounds of the wastewater originating from the production plant.

Wastewater	Main compounds	Approximate TOC
1	Dinitrile, HCN, inorganic salts like phosphates	15,000 g/L
2	Cyclic diamine, HCN, sodium hydroxide, ammonia	2000 g/L
3	Cyclic nitriles, HCN, sodium hydroxide	4000 g/L

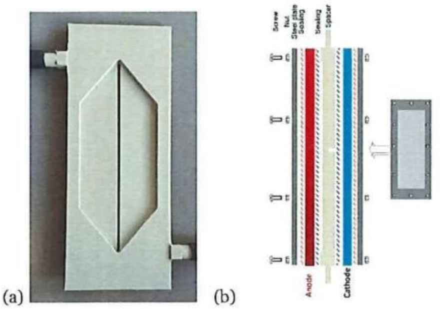

Fig. 1. (a) PP Slit spacer real imagine and (b) technical side view cell setup. Slit spacer (a)was used for all quasi-divided experiments and the technical sketch (b) shows the implementation within the cell setup.

3.1. *Efficiency test of the quasi division introduced by the spacer developed*

Evaluation of the impact by quasi-division on COD/TOC elimination was conducted by treatment of wastewater stream 1 in a comparative experiment with conventional electrolysis and a quasi-divided setup. The wastewater was electrolyzed at a BDD anode and platinum on tantalum as cathode for 2 h at 3 A (37,5 ma/cm^2). By using the quasi-division, the elimination of COD was increased from 14 % to 25 % and the elimination of TOC from 11 % to 20 %, respectively. This represents a 1.8-fold increase in efficiency displayed in Fig. 2, almost doubling the elimination. Consequently, quasi-division was used in all subsequent studies.

3.2. *Reaction time dependency of the electrochemical quasi-division elimination of TOC and COD*

Following initial optimization of the cell setup to boost the oxidation of the organic pollutants, the generality of the treatment process was evaluated using three different wastewater streams with varying levels of contaminants. Wastewater stream 1 contained a dinitrile as the main organic contamination; wastewater stream 2 contained cyclic diamines, and wastewater stream 3 contained a cyclic nitrile. All wastewater streams contain low levels of cyanide in the range of 3 to 72 ppm. Because of the presence of residual sodium hydroxide or ammonia, wastewater streams 1 and 3 exhibited sufficient conductivity and an alkaline pH. In case of wastewater stream 2 sodium hydroxide was added to enhance electrical conductivity without affecting the initial pH. To evaluate the relationship between the treatment duration and the degradation rate, samples were taken at different times. These samples were plotted in a graph of elimination rate against treatment time. A linear relationship between the treatment time and elimination of organic contaminants was found (see Fig. 3). Thus, the required treatment time can be determined via a linear function depending on the desired degree of elimination.

3.3. *Influence of the pH on the treatment efficiency in all three wastewater streams*

To investigate the effect of pH on treatment efficiency, concentrated sulfuric acid was added to the wastewater resulting in a pH of 7. In addition, sodium sulfate was included when necessary to increase conductivity. By adding small amounts of sulfuric acid until pH neutralization (up to 2 mL concentrated sulfuric in 300 mL wastewater to reach pH 7), the treatment efficiency was significantly improved (see Fig. 4). All other parameters, e.g. current density, voltage, treatment time and anode material were kept constant. Additionally, the same batch of wastewater was used as a reactant in both experimental series. The elimination rates were increased by approximately 300 %. In wastewater stream 1, the COD elimination was improved from 18 % to 97 %, and the TOC elimination from 13 % to 79 %. In wastewater stream 2, adding sulfuric acid resulted in an increase in COD elimination from 24 % to 85 %, and the TOC elimination efficiency was improved from 18 % to 78 %. In the wastewater stream 3, the COD elimination reached 98 % instead of 24 %, and the TOC elimination improved from 4 % to 98 %.

3.4. *Highest elimination rates of COD in the developed reactor*

Besides the significantly improved efficiency of the developed wastewater treatment process, the optimized conditions allowed for a reduction of the COD of all evaluated wastewaters below 100 ppm. Additionally, the process proved to be amenable to variations in the amount and type of organic pollution, as demonstrated by achieving below 100 ppm for both moderate initial COD of about 2000 ppm and heavily contaminated wastewater with a COD of 14,600 ppm, displayed in Fig. 5. Finally, it was demonstrated that electrochemical treatment is suitable as a single treatment option without requiring additional steps, e.g. biological degradation.

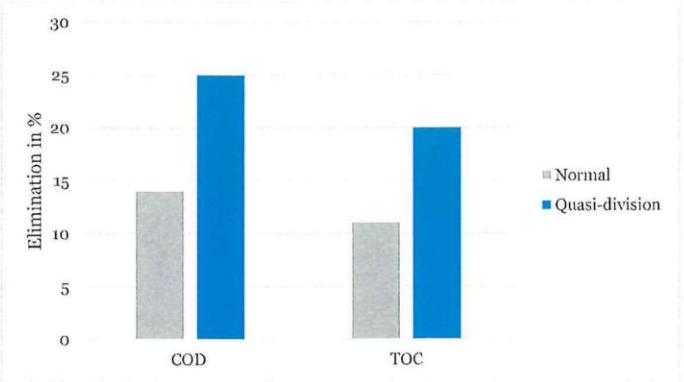

Fig. 2. Efficiency of the quasi-division: Comparison of TOC/COD elimination for wastewater stream 1 in a normal flow cell without quasi division and with a quasi-divided flow cell. Both experiments were executed with the same batch wastewater (300 mL) with a starting COD of 14,600 mg/l and a TOC of 5205 mg/l. As the anode BDD was used and as the cathode platinum on tantalum as support was employed.

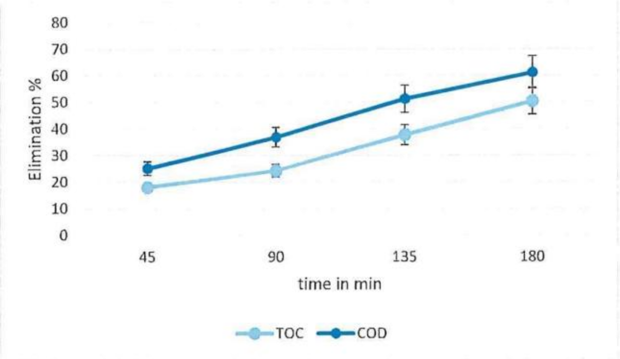

Fig. 3. Time dependent elimination: Treatment of wastewater stream 2 with added 50 mL 1 M NaOH with a BDD anode and cathode. The treatment was performed with 1 A (12,5 ma/cm^2) for over 180 min and samples were taken in the course of the electrolysis. Error range 10 % due to sample taking while the experiment.

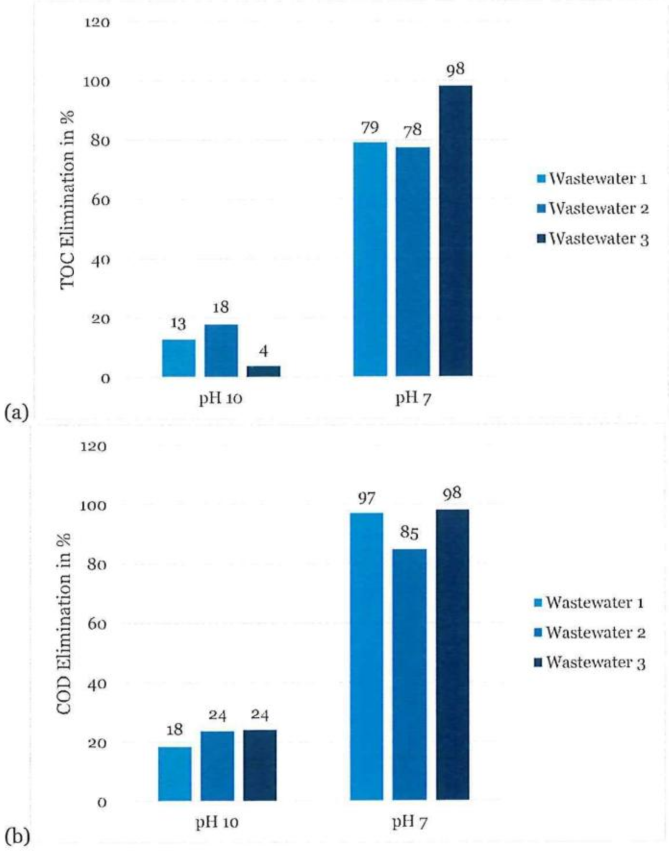

Fig. 4. Effect of neutralization prior to electrochemical wastewater treatment: The graphs show the TOC (a) and COD (b) elimination of all streams with pH 10 and 7. All wastewaters were treated with a BDD anode and either a BDD or tantalum supported platin cathode. The spacer was a vertical PTFE plate. 300 mL of: Wastewater 1 was treated in both cases 270 min with 3 A (62,5 ma/cm^2). Wastewater 2 was treated in both cases with 1 A (12,5 ma/cm^2) for 180 min. Wastewater 3 was treated with 1 A (12,5 ma/cm^2) 390 min. To adjust the pH concentrated sulfuric acid was added until a pH of 7 was reached. To remain the current density and voltage sodium sulfate was added to wastewater 2 until the same voltage was reached.

3.5. Examination of the role of peroxodisulfate as a mediator in the treatment

In order to delineate the origin of the improved electrochemical process efficiency under sulfuric acid addition, the effect of electrochemical peroxodisulfate formation in presence of sodium sulfate or sulfuric acid was investigated. Therefore, 10 g of peroxodisulfate per 10 mL wastewater was added to all three wastewater streams and the TOC was measured before and after treatment without applying a current. A lowering in TOC was observed in all streams (see Fig. 6).

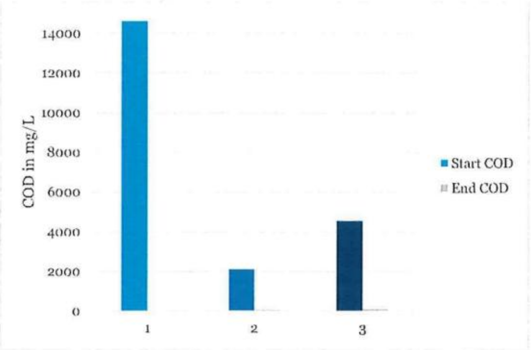

Fig. 5. Obtained elimination rates employing a quasi-divided cell setup under addition of sulfuric acid to improve treatment efficiency. All wastewaters were treated with a BDD anode, Tantalum supported Pt cathode and the vertical PTFE spacer. Wastewater 1 was treated for 390 min with 3 A (780 Wh/L, 62,5 ma/cm^2); Wastewater 2 was treated for 270 min with 1 A (180 Wh/L, 12,5 ma/cm^2); Wastewater 3 for 390 min with 1 A (220 Wh/L, 12,5 ma/cm^2).

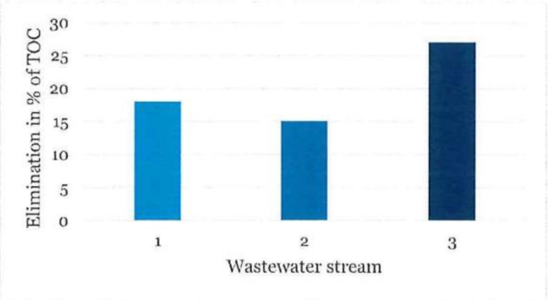

Fig. 6. TOC elimination achieved by peroxodisulfate treatment of wastewater streams 1–3 without electrolysis. 80 mL of the three wastewater streams were treated with 8 g of sodium peroxodisulfate and by stirring for 4 h.

Treatment with peroxodisulfate resulted in TOC elimination rates of 18 %, 15 % and over 25 % for wastewater streams 1, 2, and 3, respectively. This observation suggests the involvement of peroxodisulfate in the electrochemical wastewater treatment in the presence of sulfuric acid or sodium sulfate. The decrease in treatment efficiency compared to the electrochemical treatment with sulfuric acid addition results from the lack of peroxodisulfate recycling, which is achieved during the electrolysis by anodic oxidation of sulfate. Therefore, catalytic amounts of sulfate ions are sufficient to obtain high elimination rates in the electrochemical environment.

This hypothesis was confirmed by replacing sulfuric acid in the electrochemical treatment of wastewater stream 2 with sodium sulfate resulting in comparable TOC elimination (see Fig. 7, 57 % with sulfuric acid vs. 53 % with sodium sulfate). The slight decrease in elimination efficiency demonstrates the importance of controlling the pH during the electrolysis. However, sodium sulfate lowers the corresponding terminal voltage and therefore has a lower energy demand (50 Wh/L) compared to sulfuric acid as an additive (70 Wh/L).

3.6. *Proposed electrode reactions in the quasi-divided reactor with sulfate mediation*

With this result in hand we propose electrode reaction like shown in Fig. 8 [37]. A suppression of direct reductions of the oxidants, products or organic contaminants is achieved by the smaller surface area of the cathode. Since the wastewater is an aqueous solution we are proposing classic hydrogen evolution reaction here. We confirmed this by measuring the hydrogen qualitative with a sensor during some experiments. In the literature two main oxidative decomposition pathways of organic contaminants are proposed. The direct anodic mineralization from the organic contaminants to their oxidized products. The other pathway is the mediated oxidative mineralization via oxidants. The radial oxidants are generated from the water and the sulfate. These radicals can then either directly oxidize the organic contaminants or prior react to stable oxidants [37].

3.7. *Cyanide elimination in the developed reactor*

Lastly, the removal of cyanide from the wastewater samples was investigated. In particular, dissolved cyanide poses a significant challenge for chemical and biological treatment options. It was envisioned that the developed wastewater process can be tuned to allow for simultaneous TOC and cyanide elimination. Employing the developed setup, it was found that treating cyanide containing wastewater streams at basic to neutral pH resulted in almost complete removal of the cyanide (see Fig. 9). Staying at basic or neutral pH proved to be crucial in order to prevent emission of dissolved cyanide as hydrogen cyanide. Additionally, it was observed that the degree of cyanide removal was independent of the starting concentration (Fig. 9) with a reduction from 72 ppm to 1 ppm and 3 ppm to 0.1 ppm for wastewater streams 3 and 2,

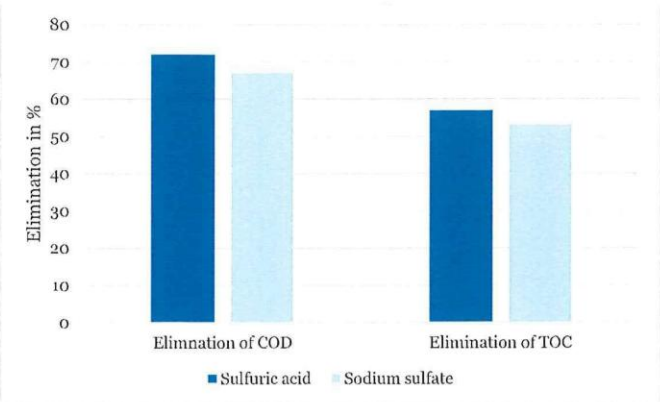

Fig. 7. Comparison of elimination in TOC and CSB with sodium sulfate and sulfuric acid as additive. The wastewater 2 was electrolyzed 2 h with 1 A (12,5 ma/cm^2) and the wastewater was taken from the same batch. The energy demand was 70 Wh/L with sulfuric acid and 50 Wh/L with sodium sulfate as an additive.

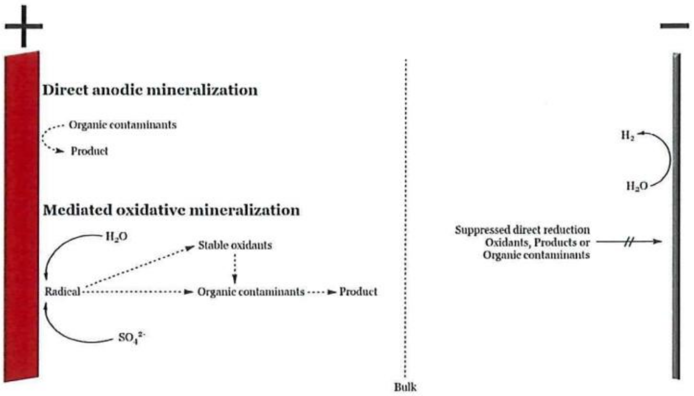

Fig. 8. Proposed electrode reactions: Shown is the BDD initiated radical generation and mediated mineralization of organic contaminants as well as the direct anodic mineralization in a quasi-divided cell setup, with sulfate additives [37]. Also the proposed suppressed reductive side reaction via the quasi division at the cathode is pictured.

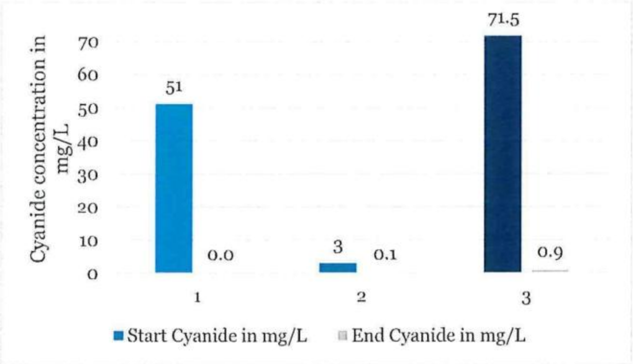

Fig. 9. Removal of cyanides: From wastewater stream 1–3 using the developed treatment process. All wastewater streams were treated at an alkaline pH to prevent the evaporation of HCN. At all experiments BDD was the anode and BDD or tantalum supported platin the cathode. Wastewater 1 270 min with 5 A (900 Wh/L, 62,5 ma/cm^2); Wastewater 2 was treated 180 min with 1 A (90 Wh/L, 12,5 ma/cm^2); Wastewater 3 270 min with 1 A (150 Wh/L, 12,5 ma/cm^2). This experiment was conducted in an alkaline pH with no additives in 1 und 3 and 50 mL of 1 M NaOH in 2, to avoid HCN release due to acidic pH.

respectively.

4. Conclusions

In conclusion, a highly efficient treatment method for diverse wastewater composition was established based on a quasi-divided cell setup with a newly designed spacer. Employing quasi-division was found to be crucial for allowing the elimination of highly stable organic pollutants with simultaneous removal of dissolved cyanide. By testing different concentrations of organic load and cyanide in addition to varying composition of different wastewater streams, the broad applicability of the quasi-divided setup developed was demonstrated. Optimizing the starting pH significantly improved the treatment efficiency. Given the necessity of neutralizing organically contaminated wastewater with sulfuric acid prior to biological treatment or emission to the environment, no additional additives were required. The established process demonstrates the suitability of electrochemistry employing quasi-division in combination with sulfate additives as a sustainable and efficient option for the treatment of diverse wastewaters streams allowing for the simultaneous elimination of organic contaminants and residual cyanide. This method enables compliance with environmental limits while lowering them to a minimum without the use of biological treatment processes.

CRediT authorship contribution statement

L. Lennartz: Investigation, Conceptualization, Visualization, Methodology, Data curation, Project administration, Writing – original draft. **J.B. Metternich:** Conceptualization, Visualization, Project administration, Writing – original draft. **T. Stadtmüller:** Investigation, Conceptualization, Visualization, Writing – review & editing. **L. Jonescheit:** Investigation. **P. Stenner:** Supervision, Conceptualization, Writing – review & editing. **S.R. Waldvogel:** Supervision, Conceptualization, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Siegfried R. Waldvogel reports was provided by Max-Planck-Institute for Chemical Energy Conversion. Siegfried R. Waldvogel reports a relationship with Max-Planck-Institute for Chemical Energy Conversion that includes: employment and funding grants. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2025.146422.

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Supporting Information - Efficiency enhanced electrochemical treatment of industrial wastewater by quasi-division

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1. Contents

2. General information

The wastewater was provided by Evonik industries. The main organic components are listed in the Table S1 below. All other chemicals were commercially available. The suppliers of the chemicals are listed.

2.1. *Wastewater*

The three tested wastewater were a aqueous solution with different kind of organic contaminants as well as inorganic salts and bases. All wastewaters were obtained from an Evonik site of three different processes and represent real life wastewaters.

TABLE S1: TREATED WASTEWATERS WITH THEIR MAIN COMPOUNDS AND THE APPROXIMATE TOC.

Wastewater	Main compounds	Approximate TOC
1	Dinitrile, HCN, inorganic salts like phosphates	15000 g/L
2	Cyclic diamine, HCN, sodium hydroxide, ammonia	2000 g/L
3	Cyclic nitriles, HCN, sodium hydroxide	4000 g/L

2.2. *Chemicals*

NaOH: Sodium hydroxide pellets for analysis provided by Merck

H_2SO_4: conc. Sulfuric acid for analysis provided by Merck

Na_2SO_4: Sodium sulfate anhydrous for analysis provided by Merck

Peroxodisulfate: Sodium peroxodisulfate >99% provided by Carl Roth

2.3. *Electrodes*

BDD electrodes were provided by Diaccon (support: Niob 2 mm with 12 microns diamond coating)

"Pt strips": Pt foil (99% Pt) on tantalum support welded. Was made in house by workshop.

3. Analysis

For the COD and cyanide analysis a Hach Lange Photometer DR3900 was used. The LT 200 from Hach Lange was used for the COD chemical breakdown prior analysis. The cuvettes for the COD analysis were LCK314 and for the cyanide analysis the LCK315.

For the TOC analysis a total organic analyzer from Shimadzu (TOC-L) was used.

Prior measurement the samples were diluted.

4. Materials and setup

4.1. *Cell setup*

The cell setup was designed as a sandwich arrangement. This frame and plate arrangement is fixed by screws and nuts through to stainless steel plates on the outer parts. To prevent a shortcut sealings are placed between stainless steel plate and electrode. Between anode and cathode the special spacer is placed. The material of the spacer was either polypropylene or Teflon. At the spacer the tubes are fixed for the inlet and outlet for the wastewater.

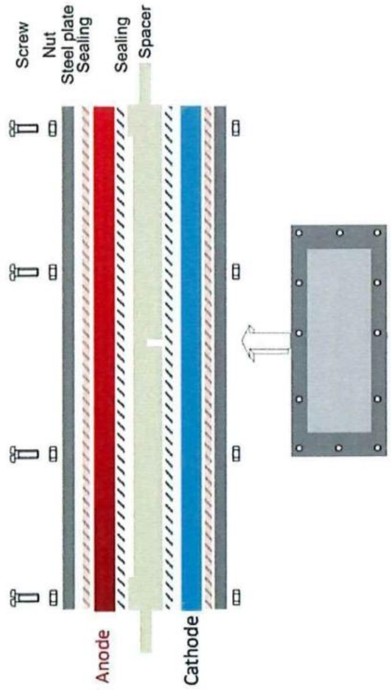

Figure S1: Schematic cell setup from the side.

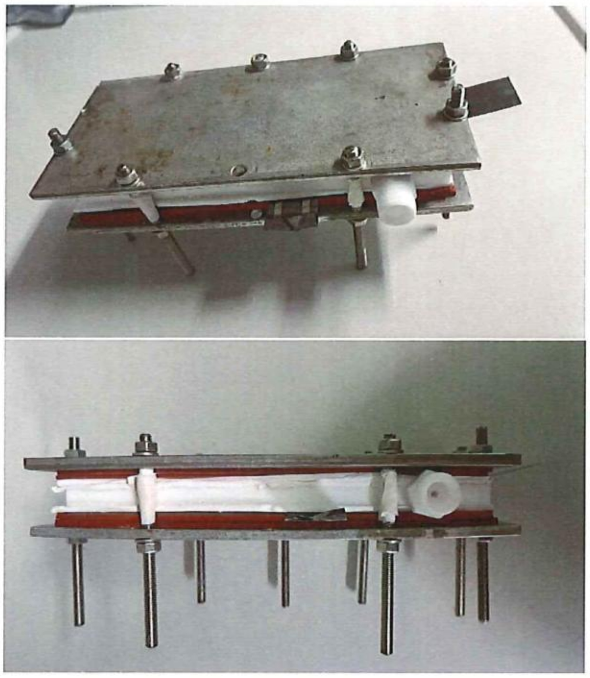

Figure S2: Pictures of the sandwich setup of the flow electrolysis cell (top: birds view, size of metal end plates 22 cm x 10 cm; bottom: side view with outlet).

4.2. Other setup components

As tubing for fluids PTFE tubes were used. For the connection of the tubes with *EM-technik* or Bola materials. The sealings were either by ePTFE or silicone. The used rotary pumps were either a Verder V-MD15 (max. flow 6 m^3/h) or a Fink F01-700-2,5.

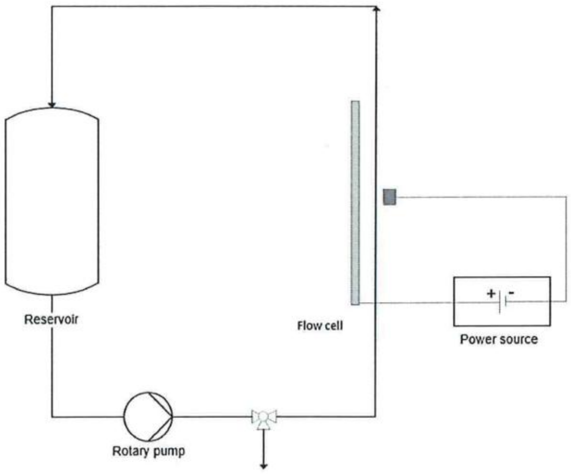

Figure S3: Schematic setup of the flow system.

Figure S4: Picture of the experimental setup in lab.

4.3. *Special spacer*

The spacer was made by the in-house workshop from polypropylene or PTFE plates. The slit was either horizontally or vertically located. By initial experiments the vertical version emerged superior, regarding the steadiness of the corresponding terminal voltage. Therefore, the vertical version (displayed below) was used in all experiments. Both materials exhibited no chemical instability or advantages over each other; for technical development, polypropylene was the preferred choice.

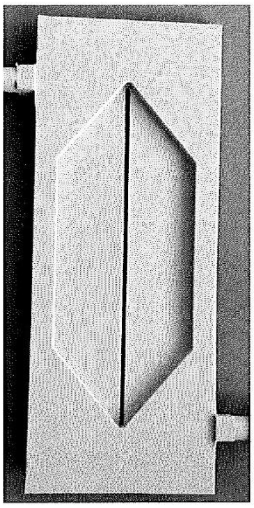

Figure S5: Picture of the special spacer (outer dimensions 20 cm x 8 cm, slit ~2 mm).

5. Experimental data

5.1. General protocol

The industrial wastewater (300 mL) was placed in the glass reservoir, and the rotary pump was activated. This specific volume was used to avoid air filled dead space in the reactor. If the experiment required an additive (sulfuric acid, sodium sulfate, or sodium hydroxide), it was added beforehand. The pH was monitored using pH paper strips. After briefly pumping the solution through the flow cell, electrolysis was initiated under galvanostatic conditions. In some experiments, 10 mL samples were collected during the process. The voltage was monitored over time and the noted voltages are average values. To not manipulate the measurements, water evaporation or electrolysis the volumes of the solutions were measured after electrolysis using volumetric control and refilled to 300 mL with water. Following each experiment, the setup was thoroughly cleaned by flushing with water and then with acetone or ethanol several times. The reactor, especially the electrodes were checked on a regular basis by opening and wiping the electrodes to avoid electrode fouling and check long-term stability. This was also done with the used sealings.

5.2. Material studies: Sealings and electrodes

To choose the best material regarding chemical stability and less cost intense solution, several materials for sealings and cathode materials were tested.

Sealings: EPDM was *not* chemically stable; silicone sealings were stable as well as ePTFE.

Cathode: In addition to platinum strips, BDD, and DSA were also tested as electrodes. However, after only a few experiments (fewer than 5), visible signs of wear occurred. This was attributed to a locally alkaline pH shift at the cathode, which attacked the coating of the electrodes.

5.3. *Reactor characterization*

For a better reactor characterization, we calculated the Reynolds number.

Because we didn't have a characteristic density or dynamic viscosity of our wastewater, we used the numbers for water a room temperature. For the flow velocity we used the highest flow rate of our pump (6 m^3/h) and the cross section of our reactor volume. As a characteristic length we choosed once the anode area surface and rechecked with the length of the reactor. In both cases we had an outcome of a turbulent flow, with a Reynolds number significantly over 4000.

$$Re = \frac{\rho v L}{\mu} = \frac{997\frac{kg}{m^3}*2{,}6\frac{m}{s}*xx}{1{,}001\ mPa*s} = >>4000\ (\sim 2.000.000)$$

The Schmidt number can be expressed as the ratio of the Prandtl number to the Reynolds number. Since the Prandtle number of water at room temperature is 6,99, the Schmidts number is really low (~0, 0.000003). A Schmidt number of 0.000003 is indicative of an extremely low value, suggesting that mass transport via diffusion occurs at a considerably faster rate compared to the fluid's viscosity. Typically, a Schmidt number below 1 implies that diffusion is the dominant mechanism, and a value on the order of 0.000003 reflects exceptionally high diffusion rates.

With the Schmidts number also the mass transport coefficient can be calculated. For that we used the ratio of the diffusion coefficient of water at room temperature ($2.3*10-9m^2/s$) and the calculated Schmidts number. The calculated mass transport coefficient k of approximately $6.58\times10-4m/s$ for these setting indicates a relatively high rate of mass transfer under the specified conditions. This value suggests that the transport of our targeted species through diffusion in the wastewater is efficient.

All numbers and formula are from the VDI Wärmeatlas edition 11.

5.4. *Analytical data with experimental tables*

All COD and TOC values are in mg/L, as well as the cyanide concentration. The costs for treatment are not included in this supporting information, because the electricity costs vary drastically depending on country and even on areas or sites within country. That's why we did not want the reader to be confused. If you want to check the costs in your region, just multiply the energy consumption per liter with the available electricity costs per kWh in your region.

Table S2: Highest Elimination rates of all Wastewaters. Obtained elimination rates employing a quasi-divided cell setup under addition of sulfuric acid to improve treatment efficiency. All wastewaters were treated with a BDD anode, Tantalum supported Pt cathode and the vertical PTFE spacer. Wastewater 1 was treated for 390 min with 3 A (780 Wh/L, 62,5 ma/cm²); Wastewater 2 was treated for 270 min with 1 A (180 Wh/L, 12,5 ma/cm²); Wastewater 3 for 390 min with 1 A (220 Wh/L, 12,5 ma/cm²).

No.	Time/min	Current/A	Voltage/V	j/ A/m²	Wh/L	Additive	pH	Cathode	Anode	Spacer	Start CSB	End CSB	Elimination CSB	Start TOC	End TOC	Elimination TOC
1	390	3	12	375	780	H_2SO_4	7	Pt	BDD	PTFE	14600	43	100	5205	23	100
2	270	1	12	125	180	H_2SO_4 + Na_2SO_4	7	Pt	BDD	PTFE	2088	73	97	688	37	95
3	390	1	10	125	217	H_2SO_4	7	Pt	BDD	PTFE	4520	89	98	1522	29	98

Table S3: Cyanide Elimination in all wastewaters. All wastewater streams were treated at an alkaline pH to prevent the evaporation of HCN. At all experiments BDD was the anode and BDD or tantalum supported platin the cathode. Wastewater 1 270 min with 5 A (900 Wh/L, 62,5 ma/cm²); Wastewater 2 was treated 180 min with 1 A (90 Wh/L, 12,5 ma/cm²); Wastewater 3 270 min with 1 A (150 Wh/L, 12,5 ma/cm²). This experiment was conducted in an alkaline pH with no additives in 1 und 3 and 50 mL of 1 M NaOH in 2, to avoid HCN release due to acidic pH.

	1	**2**	**3**
Start CN in mg/L	51	3	71,5
End CN in mg/L	0	0,1	0,9

Table S4: Effect on the pH adjustment on all three wastewaters. All wastewaters were treated with a BDD anode and either a BDD or tantalum supported platin cathode. The spacer was a vertical PTFE plate. 300 mL of: Wastewater 1 was treated in both cases 270 min with 3 A (62,5 ma/cm²). Wastewater 2 was treated in both cases with 1 A (12,5 ma/cm²) for 180 min. Wastewater 3 was treated with 1 A (12,5 ma/cm²) 390 min. To adjust the pH concentrated sulfuric acid was added until a pH of 7 was reached. To remain the current density and voltage sodium sulfate was added to wastewater 2 until the same voltage was reached.

Wastewater	pH	Time / min	Current / A	Voltage / V	Wh/L	j / A/m²	Additive	Spacer	Start CSB	End CSB	Elimination CSB	Start TOC	End TOC	Elimination TOC
1	10	270	3	7	315	375	None	PTFE	14600	11900	18	5205	4532	13
1	7	270	3	12	540	375	H_2SO_4	PTFE	14602	420	97	5205	1086	79
2	10	180	1	9	90	125	2M NaOH 25 mL	PTFE	2280	1738	24	713	585	18
2	7	180	1	11	110	125	H_2SO_4 + Na_2SO_4 20 g	PTFE	2279	344	85	713	160	78
3	10	390	1	10	217	125	None	PTFE	4520	3435	24	1522	1464	4
3	7	390	1	10	217	125	H_2SO_4	PTFE	4520	89	98	1522	29	98

Table S5: Treatment of wastewater 2 with the samples taken over the time; addition of 50 mL 1 M NaOH with a BDD anode and cathode. The treatment was performed with 1 A (12,5 ma/cm²) for over 180 min. Note an approx. 10% error on values, due to sample taking.

Sample	Time /min	TOC measured	Elimination TOC	COD measured	Elimination CSB
1	45	794	20	2340	28
2	90	723	27	1934	41
3	135	575	42	1392	57
4	180	440	56	1030	68

Table S6: Initial experiments for enhancing the elimination by the slit spacer and therefore a quasi-division. Both experiments were executed with the same batch wastewater (300 mL) with a starting COD of 14600 mg/l and a TOC of 5205 mg/l. As the anode BDD was used and as the cathode platinum on tantalum as support was employed.

Wastewater	Start COD	Start TOC	End COD normal	End TOC normal	End COD Slit	End TOC Slit
1	14600	5205	12500 (-14%)	4652 (-11%)	11000 (-25%)	4164 (-20%)

Table S7: Comparison of sulfuric acid and sodium sulfate as an additive for wastewater 2. It was electrolyzed for 2 h with 1 A (12,5 ma/cm²) and the wastewater was taken from the same batch. The energy demand was 70 Wh/L with sulfuric acid and 50 Wh/L with sodium sulfate as an additive.

	Original wastewater 2	**Wastewater 2 with H_2SO_4**	**Wastewater 2 with Na_2SO_4**
COD	2088	588	680
TOC	689	295	320
Elimination COD		72	67
Elimination TOC		57	53

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Simplified approach for an enhanced electrochemical hydrogenation of carbonyl compounds

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ABSTRACT

In this study, a method for the electrochemical hydrogenation of various carbonyl compounds was developed, with a particular emphasis on industrial applicability and scalability. Each parameter—including current density, solvent, solvent ratio, electrolyte, proton concentration, electrode material and structure, as well as substrate concentration—was systematically investigated for its impact on yield and selectivity. Isophorone served as a model compound, facilitating the transition from the corresponding enone to the ketone. Additionally, the applicability of the system was expanded to include the hydrogenation of other enones such as methacrylates, ketones, and aldehydes. The method employs nickel foam electrodes and a simple electrolyte mixture of water: methanol (1:1) with 0.5 M sulfuric acid. Notably, the current density used is relatively high at 90 mA/cm^2, enhancing the industrial attractiveness of the process.

1. Introduction

Hydrogenations reactions constitute one of the major classes of processes found in chemical manufacturing. Common hydrogenation methods are associated with energy intensive conditions, such as high pressure and elevated temperature [1]. Additionally, super stoichiometric amounts of hydrogen as well as the use of transition metal catalysts are typically necessary, e.g. ruthenium for the hydrogenation of ketones and enones [2]. The combination of harsh process conditions and precious metal catalysts results in high costs for state of the art hydrogenation processes. Given the utmost importance of hydrogenation technology for production of chemicals, more energy efficient and sustainable methods are strongly desired in chemical industry. The field of electro-organic synthesis is currently experiencing increased attention from both, academia and industry because it is considered as a green and cost-efficient future technology [3–5]. The combination of synthetic electrochemistry with catalytically active electrodes is ideally suited for combining the sustainability of electrochemical transformations with the potential of catalysis to control reactivity and selectivity. Therefore, electrochemistry provides a highly attractive waste-free alternative for such transformations as the electrons required for the redox process are directly supplied by the applied electrical current[6–9]. The inherent safety, scalability and unique reactivity make electrosynthesis to an outstanding approach [10–13]. An alternative to conventional hydrogenation processes is the electrochemical hydrogenation reaction. In electrochemical hydrogenations, hydrogen is generated in-situ by cathodic reduction of hydrogen sources such as hydrazine, ammonium chloride or water [14]. Water represents the optimal hydrogen source, due to inherent safety and low associated costs. The applicability of electrochemical hydrogenation processes has so far been limited by the necessity of employing complex electrodes modified with metal catalysts in addition to the need for hazardous and expensive additives, e.g., stoichiometric amounts of reducing agents. Commonly employed metal catalysts utilized in electrochemical hydrogenation reaction include manganese base-metal, Pt/Ru coatings, or Raney nickel. Additionally, substrate activation via organic catalysts has been reported, e.g. hexamethylphosphoramide [15–21]. One reported approach involves the hydrogenation of carbonyl compounds to secondary alcohols using carbon-based electrodes under potentiostatic conditions, with ammonia serving as the hydrogen source. Another study reports the hydrogenation of aldehydes employing manganese complexes, which enable the

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Nomenclature

Abbreviations

BDD	Boron-doped diamond
DSA	Dimensionally stable anode
GC	Gas chromatography
MS	Mass spectrometry
SEM	Scanning electron microscope

Symbols

A	Ampere
j	Current density
V	Voltage

electrochemical hydrogenation using phenol as proton donor [22]. The hydrogenation of cyclohexanone and enones derivatives in specific was demonstrated with a range of different electrochemical set-ups [19,23]. Mahdavi et al. reported a selective hydrogenation of the double bond in cyclic enones to the corresponding saturated ketones by the use of fractal-powder nickel or nickel boride cathodes in a divided cell setup [19]. The highest yield and selectivity were obtained at a current density of 3 mA/cm^2, using 0.1 M NaCl and H_3BO_3 as additives. Vilar et al. reported the hydrogenation of α,β-unsaturated ketones in an undivided setup using a sacrificial nickel-rod anode and NH_4Cl as supporting electrolyte [23]. By in-situ coating of several base cathode materials (Cu, Fe, Ni) with the dissolving nickel anode, saturated ketones were obtained in high yield and selectivity from the corresponding cyclic enones [23]. In a recent study by Tortajada et al., a combination of nickel foam electrodes with sulfuric acid as the electrolyte was found to convert enones to ketones selectively under potentiostatic conditions [24]. Additionally, significant advancements have been made in the electrochemical hydrogenation of nitriles to amines. Utilizing high current densities and a nickel foam cathode in a methanol-water mixture, high yields were achieved [25]. The aim of this work was the development of a simple, sustainable and efficient method for the selective hydrogenation of enones to saturated ketones and carbonyl compounds to the corresponding alcohols. The focus of this study is to enhance existing methods for the electrochemical hydrogenation of enones, prioritizing the practicality of the process. Initially, we examine the configuration of the electrochemical setup, aiming for a straightforward design that operates under galvanostatic conditions without the need for a third reference electrode, thereby simplifying the process. Additionally, we address the challenges associated with reaction parameters, advocating for the use of a practical and safe hydrogen source, such as water, and the implementation of readily available electrode materials like nickel foam. Noteworthy, nickel foam electrodes are common electrodes and used in alkaline media wherein they form at the surface NiOOH as active anode [26–30]. The study also aims to utilize high current densities, making the method more appealing for a straightforward industrial setting.

2. Materials and methods

2.1. Analysis

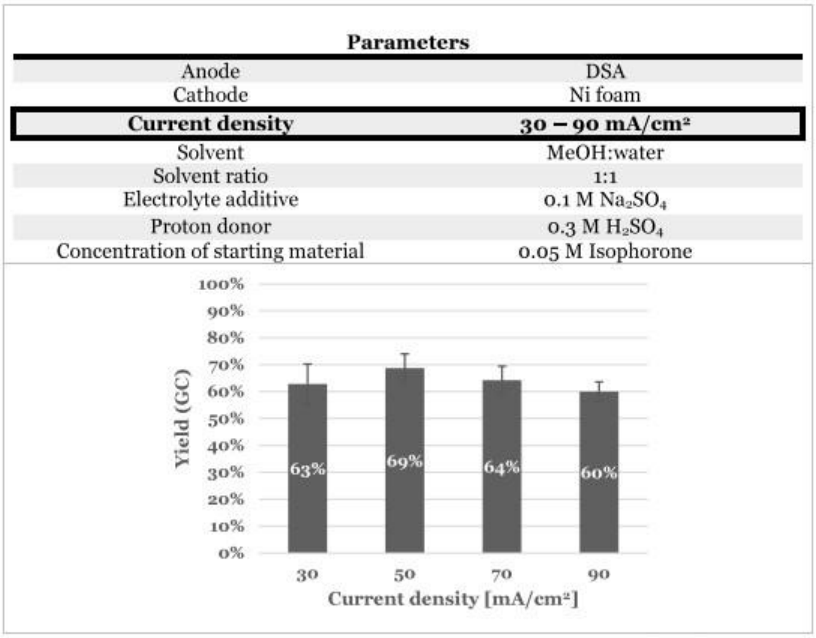
Analysis of the reaction mixtures was performed with GC–MS using internal standard calibration to determine the product yield. All reported results are the average of at least three repetitions with the standard deviation given as the margin of error.

2.2. Electrochemical cells

Electrochemical screening cells (divided) from IKA-Werke GmbH & Co. KG, Staufen, Germany, were utilized, along with the corresponding reaction setup for the magnetic stirrer. The screening cells are equipped with magnetic stir bars. The power supply used was the HMP4040 programmable laboratory power supply (32 V, 10A, 384 W) from Rohde & Schwarz GmbH & Co. KG, Munich, Germany. This set-up was described in detail before [31].

3. Results

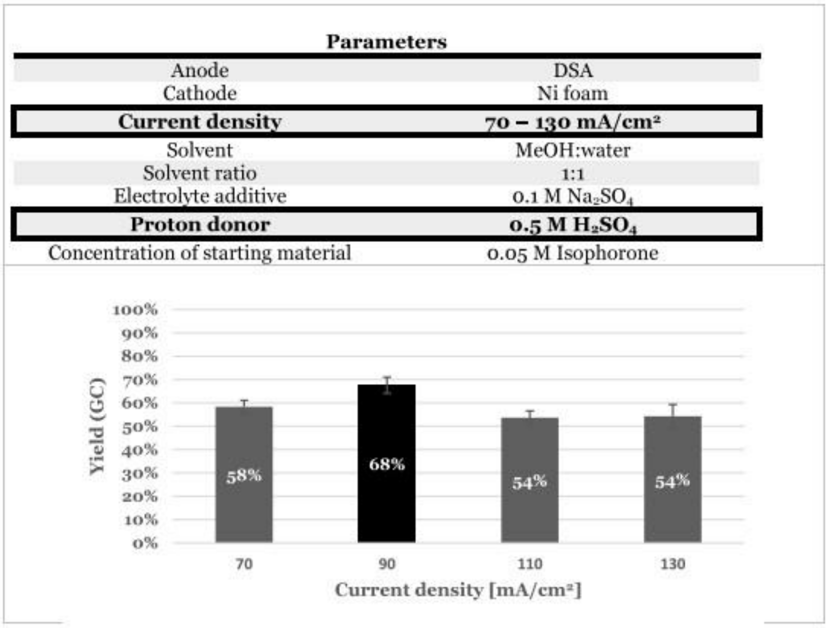
Following preliminary work by Tortajada et al., a method was envisioned allowing the electrochemical production of ketones from



Parameters

Anode	DSA
Cathode	Ni foam
Current density	**30 – 90 mA/cm²**
Solvent	MeOH:water
Solvent ratio	1:1
Electrolyte additive	0.1 M Na_2SO_4
Proton donor	0.3 M H_2SO_4
Concentration of starting material	0.05 M Isophorone

Fig. 1. Effect of the employed current density on the yield of 2. DSA was used as the anode and nickel foam as the cathode. Nafion^{TM} 424 served as a separator and the concentration of 1 was 0.05 M. The sulfuric acid concentration was 0.3 M.



Parameters	
Anode	DSA
Cathode	Ni foam
Current density	**70 – 130 mA/cm²**
Solvent	MeOH:water
Solvent ratio	1:1
Electrolyte additive	0.1 M Na_2SO_4
Proton donor	**0.5 M H_2SO_4**
Concentration of starting material	0.05 M Isophorone

Fig. 2. Effect of current density on the yield of 2 at higher sulfuric acid concentration (0.5 M). DSA was used as the anode and nickel foam as the cathode. Nafion^{TM} 424 served as a separator and the concentration of **1** was 0.05 M.

α,β-unsaturated enones with high selectivity [24]. Isophorone **1** was chosen as a test compound. A combination of sulfuric acid and sodium sulfate was used as the halogen-free electrolyte. Relying on halogen-free electrolytes prevents the generation of undesired process gases at the anode, e.g. chlorine. As the solvent, a methanol water mixture was selected to ensure sufficient solubility of the substrate in addition to providing sufficient amounts of activated hydrogen, with water being the best hydrogen source regarding economic and safety aspects. A Nafion^{TM} 424 membrane was selected as a separator to facilitate the transfer of protons generated at the anode to the cathodic compartment, thereby maintaining an acidic pH in the catholyte to provide sufficient protons for the hydrogenation reaction. As described above, readily available nickel foam exhibited an outstanding catalytic activity in electrochemical hydrogenation as observed in other reports [25]. High current density and galvanostatic conditions were applied to develop a practical electrochemical hydrogenation method.

3.1. *First optimization – influence of current density and concentration of sulfuric acid*

The first optimization started with the postulated methanol and water ratio of 1:1 and current density of 50 mA/cm^2. This current density refers to the geometric current density of the nickel foam. In every experiment 579 C were applied, which corresponds 8 *F*. Besides sulfuric acid (0.3 M), sodium sulfate was added in order to increase the conductivity for applying these high current densities[25]. Nickel foam was utilized as the cathode, while DSA served as anode. The study employed the proposed range of starting current densities from the literature as a baseline [25,27]. A yield of 69 % for **2** was observed in the initial trial (Fig. 1). To investigate the relationship between current density and yield, a lower current density of 30 mA/cm^2 was tested, resulting in a decrease to 63 % yield. Conversely, increasing the current density proved ineffective with 64 % and 60 % yield at 70 mA/cm^2 and 90 mA/cm^2, respectively.

Following the reaction, a caustic pH was observed in the catholyte for several of the conducted experiments. This observation is consistent with an imbalanced proton concentration in the electrolyte resulting in rapid proton consumption and too slow replenishment at the anode. In order to mitigate the loss in proton concentration at the cathode potentially resulting in losses of electrochemical activity, the current density screening was repeated with an increased concentration of sulfuric acid.

The obtained results with an increased sulfuric acid concentration are depicted in Fig. 2. At higher sulfuric acid concentration, the highest yield for **2** of 68 % was achieved at a current density of 90 mA/cm^2. The current density of 70 mA/cm^2 lead to 58 % yield. Notably, higher current densities of 110 and 130 mA/cm^2 exhibited a decreasing yield, with both yielding 54 %. With a higher availability of protons, the optimal current density for maximizing the yield of **2** is greater than observed at lower concentrations. Consequently, the decision was made to proceed with a current density of 90 mA/cm^2 in conjunction with a sulfuric acid concentration of 0.5 M.

To confirm the dependence of the reaction on applying an electrical current, an experiment was conducted without electrical current, utilizing the developed parameters. No conversion was observed, thus demonstrating the process depending on electrochemical activation.

3.2. *Investigation of the influence of electrolyte*

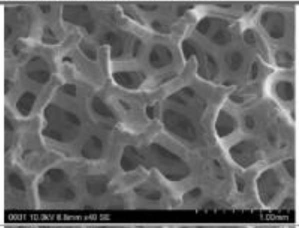
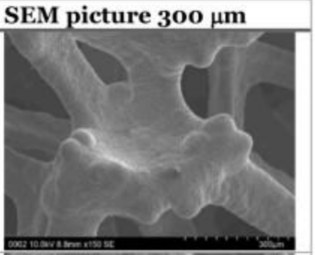
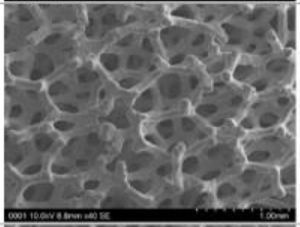
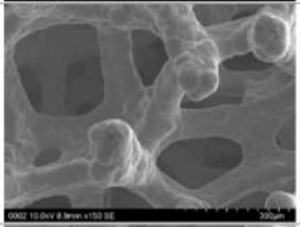
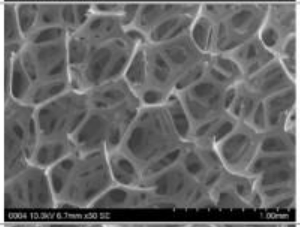
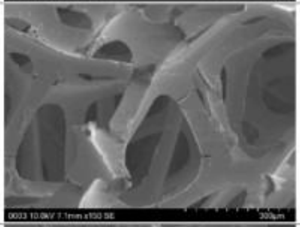
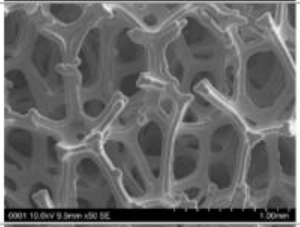
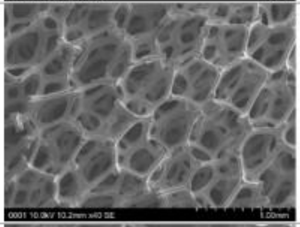
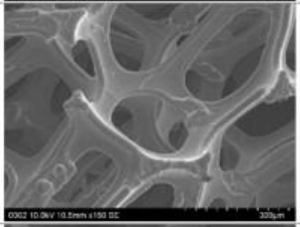
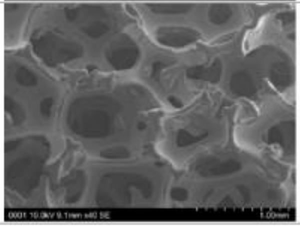
With basic process parameters in hand, the subsequent optimization aimed at increasing the yield of **2**. Additionally, the goal was to acquire sufficient knowledge about the reaction. Various parameters were investigated, e.g. the supporting electrolyte, co-solvents, solvent mixture and cathode material and structure.

To examine the influence of sodium sulfate as an additive, experiments were performed under the optimal conditions of 90 mA/cm^2 and a sulfuric acid concentration of 0.5 M, excluding sodium sulfate. No loss in yield was obtained when excluding sodium sulfate (68 % yield with sodium sulfate vs. 71 % without sodium sulfate). Consequently, sodium sulfate was removed as additional supporting electrolyte, simplifying the reaction conditions to three base chemicals.

The next step was to investigate the influence of the solvent on the reaction efficiency. A series of experiments were conducted using various organic co-solvents, e.g. acetonitrile, THF, and ethanol. The solvents were selected based on the miscibility with water as the hydrogen source. These experiments were conducted under conditions

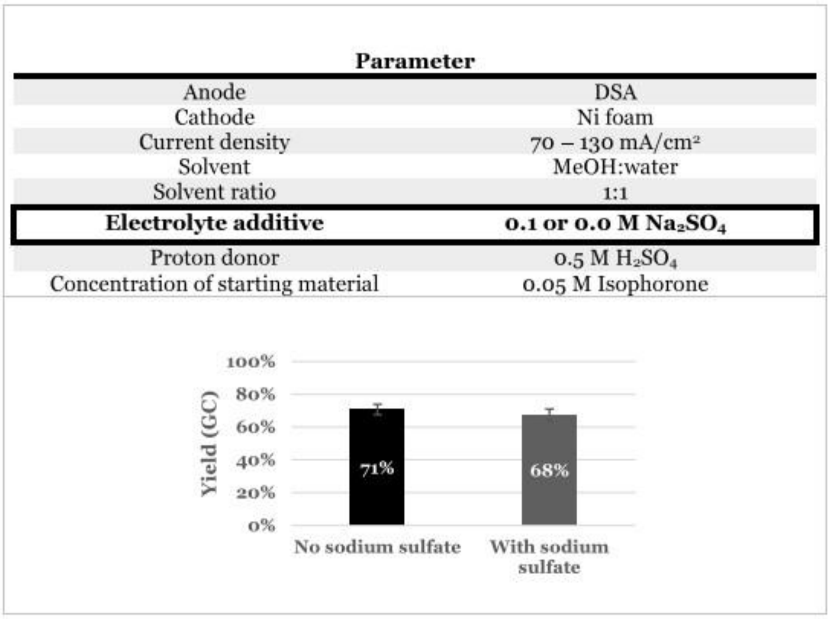
Table 1

SEM images of different nickel-foam electrodes at 1.00 mm and 300 microns magnification. Further information from the supplier can be found in the supporting information.

No.	SEM picture 1 mm	SEM picture 300 µm
1		
2		
3		
4		
5		
6		

of 90 mA/cm^2 and a concentration of 0.5 M sulfuric acid. As illustrated in Fig. 4, switching to other co-solvents resulted in a significant decrease in the yield of **2** compared to methanol. Ethanol emerged as the most promising alternative, yielding approximately 28 % of **2**. Additionally, it was observed that the use of the alternative co-solvents led to undesired side reactions in the cell, e.g. coating of the electrode. The overall recovery of reactants and products, assessed using a GC internal standard method, was found to be below 40 %. This observation highlights that methanol not only dramatically enhances the yield but also effectively suppresses side reactions like polymerizations.

To investigate the influence of the organic co-solvent in more detail, experiments were conducted varying the methanol content in the mixture. A decrease in yield was observed with any changes to the co-solvent concentration in the reaction mixture (see Fig. 5). Using a



Parameter	
Anode	DSA
Cathode	Ni foam
Current density	70 – 130 mA/cm²
Solvent	MeOH:water
Solvent ratio	1:1
Electrolyte additive	**0.1 or 0.0 M Na_2SO_4**
Proton donor	0.5 M H_2SO_4
Concentration of starting material	0.05 M Isophorone

Fig. 3. Effect of sodium sulfate as a secondary electrolyte on the yield of **2** at a current density of 90 mA/cm^2. DSA was used as the anode and nickel foam as the cathode. Nafion^{TM} 424 served as a separator and the concentration of **1** was 0.05 M. The sulfuric acid concentration was 0.5 M. Tested were conditions without sodium sulfate and sodium sulfate concentration of 0.1 M.

higher water content (1:2 methanol to water ratio) resulted in a yield of 56 % for **2**. The standard deviation was significantly higher compared to the initial mixture. This observation can be attributed to the insufficient solubility of isophorone (**1**) in the reaction mixture. Conversely, with an increased methanol concentration of 2:1 methanol:water, a yield of 46 % was obtained, showing that sufficient amounts of the hydrogen source water are crucial for the reaction. Additionally, a significant loss in reproducibility was found reflected by the significantly increased standard deviation across three experiments (see Fig. 5). Thus, the initial solvent system comprising a 1:1 mixture of methanol and water was confirmed as the optimal choice. The formulation provides the necessary solubility for the reactant while also delivering sufficient water to serve as the optimal hydrogenation donor.

3.3. *Influence of the used electrode material*

Copper was reported as suitable material for electrochemical hydrogenation reactions on other structural motives [32–34]. In addition to copper foam, copper mesh was tested to compare the geometric structures alongside the metallic properties. Using copper as the cathode material resulted in a significant loss in yield for **2** compared to nickel. Additionally, the copper mesh exhibited significantly inferior performance compared to copper foam, yielding 14 % versus 30 % of **2**.

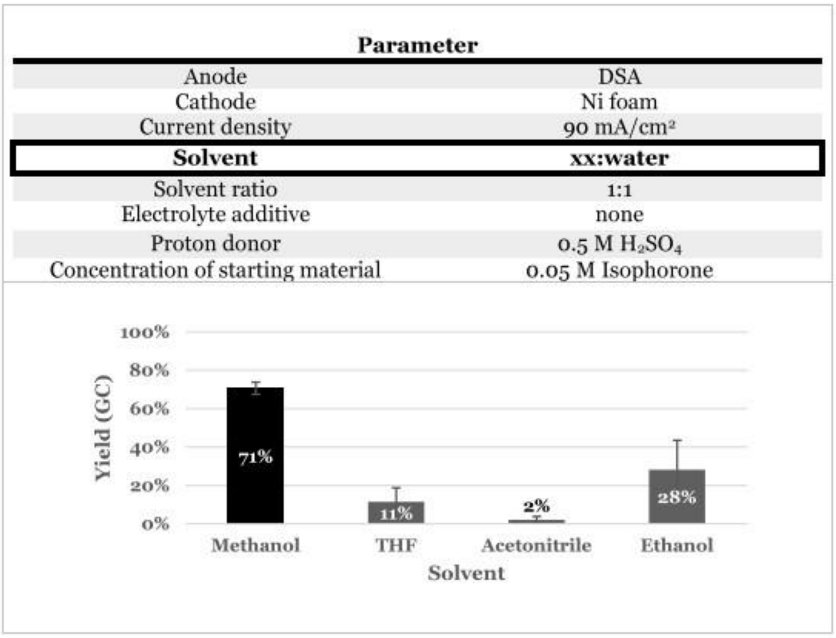
The observation suggests that the metal properties play an important role in the electrochemical hydrogenation reaction. Additionally, it highlights the importance of the surface activity. The hydrogenation reaction most likely occurs directly at the electrode rather than by hydrogen formation and subsequent hydrogenation reaction.

Given that copper proved to be inferior to nickel foam, the next experiments focused on cobalt as an alternative to nickel. Cobalt was selected due to the isoelectronic characteristics with nickel and overall strong redox-active catalytic properties of cobalt. Both cobalt foam and cobalt-nickel foam were evaluated to elucidate the performance dependence on varying nickel content in the cathode material. It was found that the performance improved with increasing nickel content in the cathode foam. Compared to pure cobalt foam yielding 46 % of **2**, use of the nickel-cobalt foam resulted in an increase in yield to 68 %, while the highest yield of 71 % was obtained with pure nickel foam. This suggests that nickel possesses superior features in catalysing the electrochemical hydrogenation reaction of **1**.

In order to delineate the effect of electrode morphology and surface properties, a series of different nickel foams were investigated, varying in mesh size, and nickel content. Additionally, SEM images were taken to analyse the geometric structure and surface properties. The SEM images show significant differences in both the surface structure, mesh size, and cavities (see Table 1, number supplied by IKA was used in previous optimization efforts). Typical for foam-type structures overlap of individual meshes was found. Type 1 (IKA) exhibits a smooth surface with round, bulky edges. The skeleton structures of Foam 3 are significantly more delicate and have a coarse surface with sharp-edges and cracks. The mesh size and cavities are tighter than those of the other foams. Foam 4 has a smooth, rounded surface. Furthermore, the edges of the skeleton structures protrude, creating a depression in the individual skeletons. The mesh size is larger than observed in the other foam materials.

Foam 5 has a similar surface structure to Foam 4. However, the skeletons are more delicate, resulting in smaller cavities. Foam 6 features a smooth, rounded surface structure and appears cartilaginous. The properties mentioned are derived from various manufacturing characteristics. For example, the difference between type 4 and 6 is the larger pore size of 6, 1.2 mm compared to 0.8 respectively. Details regarding the manufacturing process and additional characterization based on supplier information are provided in the supporting information.

The analysed nickel-foams were employed under optimized conditions to elucidate the impact of surface structure on reaction performance. Overall, comparable yields of **2** were obtained for the nickel-foams number 1, 2, and 4–6. Interestingly, nickel-foam number 3 with the coarse and cracked surface structure exhibited significantly lower performance with a yield of 30 % for **2**. The best results were obtained with nickel-foam number 6 yielding 77 % **2** under the optimized conditions. Given that hydrogenation likely occurs directly at the electrode surface, the surface properties determine the overall activity of the electrode material. Differences stemming from the manufacturing process, e.g. the coarse and cracked surface of electrode material 3, can have a direct impact on available surface area and thus efficiency of the



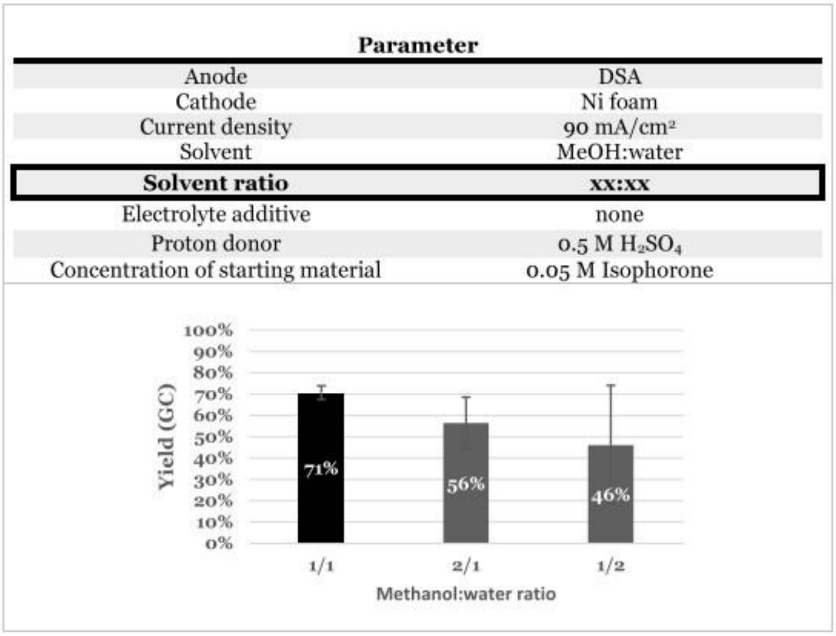
Parameter	
Anode	DSA
Cathode	Ni foam
Current density	90 mA/cm²
Solvent	**xx:water**
Solvent ratio	1:1
Electrolyte additive	none
Proton donor	0.5 M H_2SO_4
Concentration of starting material	0.05 M Isophorone

Fig. 4. Effect of the co-solvent on the yield of **2** at a current density of 90 mA/cm^2. DSA was used as the anode and nickel foam as the cathode. Nafion™ 424 served as a separator and the concentration of **1** was 0.05 M. The sulfuric acid concentration was 0.5 M. The investigated solvents were employed in a ratio of 1:1 with water.

electrochemical hydrogenation. As a last step we doubled the educt concentration of **1** from 0.05 to 0.1 M and investigate the influence. However, the yield was slightly decreased from 77 % to 71 % yield of **2**. A higher concentration was not investigated due to solubility issues of the educt.

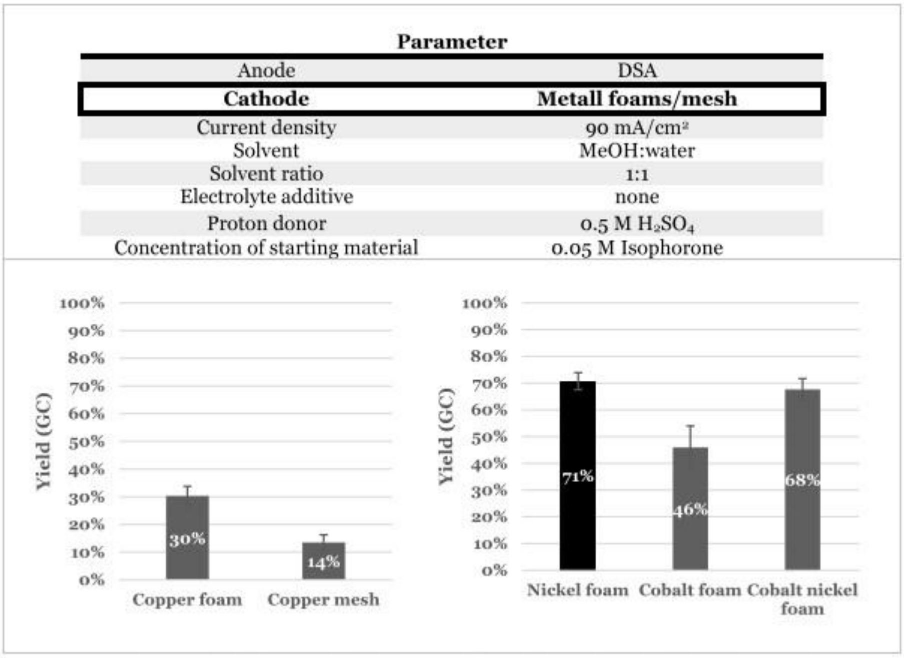
This observation prompted further investigations to elucidate the relationship between the electrode structure and the corresponding yield, specifically regarding the mechanism of electrochemical hydrogenation. CV measurements were conducted to determine whether substrate hydrogenation occurs directly at the electrode or is facilitated by hydrogen reduction. The CV results clearly indicate that direct reduction is feasible. However, the potential for proton reduction is significantly lower.

Based on these findings and insights from the literature, it is envisioned that the hydrogenation proceeds via metal hydride formation at the electrode surface [25,35]. This supports the conclusion that the electrode structure significantly influences the yield. For detailed information, please refer to the supporting information.



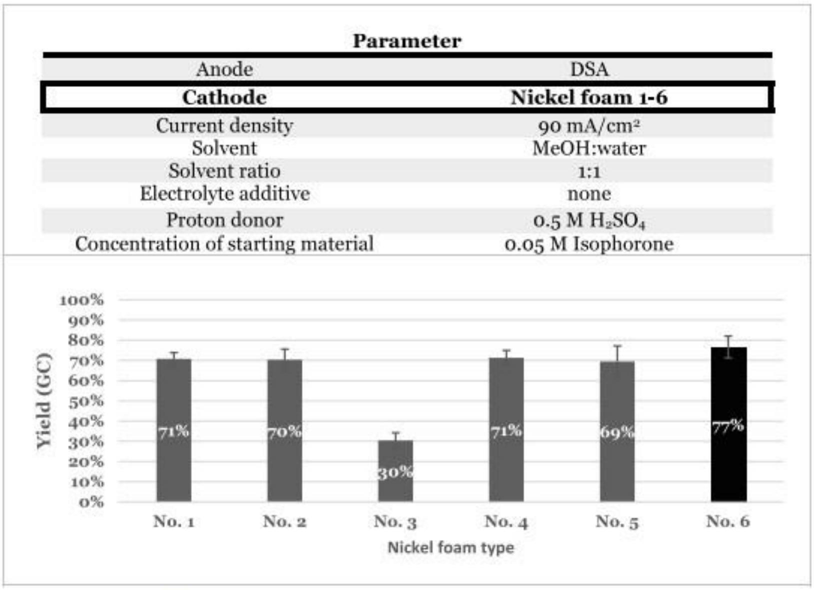
Parameter	
Anode	DSA
Cathode	Ni foam
Current density	90 mA/cm²
Solvent	MeOH:water
Solvent ratio	**xx:xx**
Electrolyte additive	none
Proton donor	0.5 M H_2SO_4
Concentration of starting material	0.05 M Isophorone

Fig. 5. Effect of the methanol concentration on the yield of **2** at a current density of 90 mA/cm^2. DSA was used as the anode and nickel foam as the cathode. Nafion™ 424 served as a separator and the concentration of **1** was 0.05 M. The sulfuric acid concentration was 0.5 M.



Parameter	
Anode	DSA
Cathode	**Metall foams/mesh**
Current density	90 mA/cm²
Solvent	MeOH:water
Solvent ratio	1:1
Electrolyte additive	none
Proton donor	0.5 M H_2SO_4
Concentration of starting material	0.05 M Isophorone

Fig. 6. Effect of the cathode material on the yield of **2** at a current density of 90 mA/cm^2. DSA was used as the anode. Nafion^{TM} 424 served as a separator and concentration of **1** was 0.05 M. The sulfuric acid the concentration was 0.5 M and a 1:1 methanol to water mixture was used as the solvent.



Parameter	
Anode	DSA
Cathode	**Nickel foam 1-6**
Current density	90 mA/cm²
Solvent	MeOH:water
Solvent ratio	1:1
Electrolyte additive	none
Proton donor	0.5 M H_2SO_4
Concentration of starting material	0.05 M Isophorone

Fig. 7. Effect of different Nickel-foam types (see Table 1) onto yield of **2** at a current density of 90 mA/cm^2. DSA was used as the anode. Nafion^{TM} 424 served as a separator and the concentration of **1** was 0.05 M. The sulfuric acid concentration was 0.5 M and a 1:1 methanol to water mixture was used as the solvent.

3.4. Transfer of the method developed to various carbonyl structural motifs

With the optimized conditions in hand, we turned our interests towards broadening the applicability of the developed electrochemical hydrogenation process. Therefore, the hydrogenation of a range of enones, ketones, and aldehydes was investigated. For this experiment row, the lower concentration of 0.05 M educt was chosen to avoid solubility issues. The method's effectiveness on other enone structures was demonstrated for cyclohexenone, which was converted to cyclohexanone in 51 % yield. To investigate other industrially relevant enones besides isophorone, two methacrylates were included in the study. Butyl methacrylate was hydrogenated to isobutyrate **13** in 58 % yield, while the corresponding benzyl derivative **14** yielded only 9 % of the hydrogenated product. This discrepancy may be attributed to the more lipophilic nature of the benzyl derivative, resulting in lower solubility in the polar mixture, corroborating the lower yields observed in isophorone experiments with higher water content. These findings demonstrate that ester-containing enone structures can be hydrogenated using the developed method. Based on the obtained results, it was

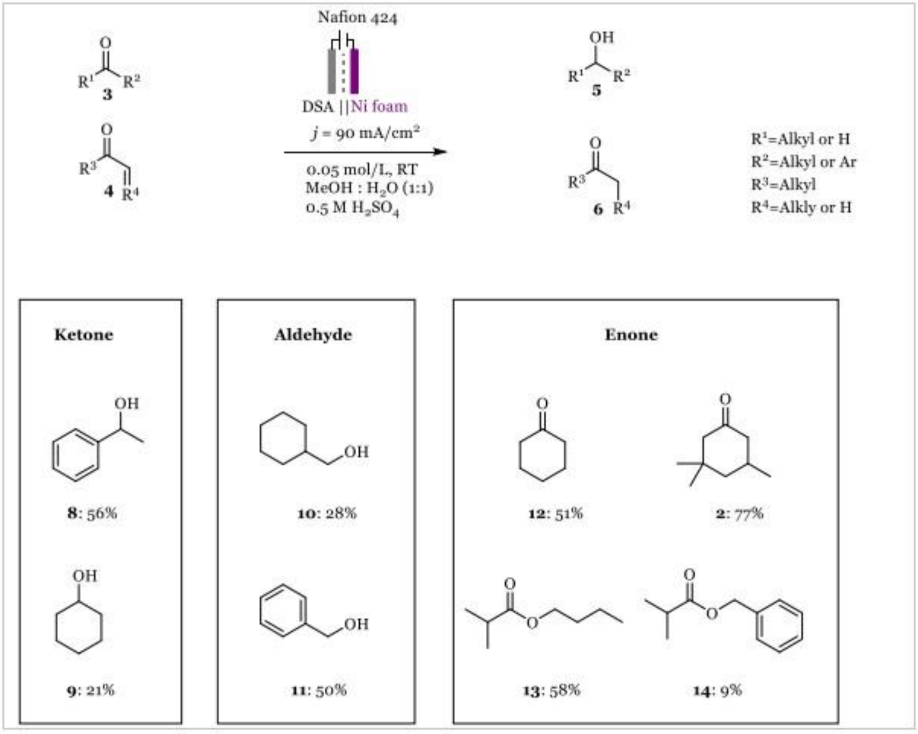


Fig. 8. The yields (GC) of different structure motifs are illustrated. The optimized conditions with 90 mA/cm^2, MeOH:water 1:1, 0.5 M H_2SO_4 and the type 6 nickel foam was used. Different carbonyl substrates were hydrogenated including ketones, enones and aldehydes.

hypothesized that the developed method can be extended to the hydrogenation of isolated carbonyl structures in the absence unsaturation. Testing cyclic non-conjugated ketones resulted in the formation of the corresponding alcohols **9** with lower yields of 21 %, respectively.

In contrast, aromatic conjugation of the ketone resulted in approved yields, e.g. 56 % for the hydrogenation of acetophenone to **8**. Similar results were obtained for aldehydes. The yield of benzaldehyde to benzylalcohol **11** was found to be higher at 50 %, compared to 28 % for the non-aromatic cyclohexancarboxaldehyde to **10** (Figs. 3, 6, 7 and 8)

4. Conclusions

In conclusion, a practical method for the electrochemical hydrogenation of carbonyl compounds including enones, aldehydes and ketones was established. The streamlined system is characterized by a high current density of 90 mA/cm^2 and galvanostatic conditions. Detailed understanding of the influence of proton concentration, additives, and the solvent combination on the process allowed for improvement of the hydrogenation and extension to a range of different substrates. Notably, methanol significantly affects the yield of the ketone and the selectivity of the reaction. Sulfuric acid emerged as the sole conductivity enabling material required in the electrolyte, with proton concentration being a critical parameter influencing both yield and increasing the optimal operating current density. The choice of cathode material was identified as a key factor not only for yield enhancement, but also for suppressing side reactions, such as the formation of polymer films, thereby increasing reaction selectivity. Additionally, the geometric structure of the electrodes was found to be crucial for improving the process efficiency. The obtained insights serve as a valuable takeaway for the design of future electro-organic processes that may occur directly at the electrode surface. Overall, a new electrochemical method for key structural motifs was developed. The method, based on a simplified two electrode system, demonstrates high efficiency through elevated current densities and the utilization of bulk chemicals as electrolytes. This approach is not only efficient but also serves as a valuable framework for the development of electrochemical hydrogenation techniques for other structures, highlighting the significance and impact of the investigated parameters.

CRediT authorship contribution statement

Laura Lennartz: Writing – review & editing, Writing – original draft, Methodology, Investigation. **Vera Beier:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis. **Jan B. Metternich:** Writing – review & editing, Writing – original draft, Methodology. **Patrik Stenner:** Writing – review & editing, Writing – original draft, Supervision, Conceptualization. **Siegfried R. Waldvogel:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2025.147542.

Data availability

The data will be available in the supporting information.

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Supporting Information - Simplified Approach for an enhanced Electrochemical Hydrogenation of Carbonyl Compounds

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Contents

1. General information

1.1. *Materials*

1.1.1. Chemicals

TABLE S1: CHEMICALS USED WITH THEIR GRADE AND SUPPLIER.

Chemical	Grade	Supplier
1-Phenylethanol	97%	Thermo Fisher Scientific GmbH, Dreieich, Germany
3,3,5-Trimethylcyclohexanone	N/A	Evonik Industries AG, Essen, Germany
Acetonitrile	p.a., min. 99.5%	Carl Roth GmbH & Co. KG, Karlsruhe, Germany
Acetophenone	p.a., min. 98%	Carl Roth GmbH & Co. KG, Karlsruhe, Germany
Benzaldehyde	p.a., min. 99.5%	Carl Roth GmbH & Co. KG, Karlsruhe, Germany
Benzyl alcohol	p.a., +98 %	Thermo Fisher Scientific GmbH, Dreieich, Germany
Benzyl isobutyrate	p.a. min. 97%	Merck KGaA, Darmstadt, Germany
Benzyl methacrylate	98%, stab.	Thermo Fisher Scientific GmbH, Dreieich, Germany
Butyl isobutyrate	p.a. min. 97%	Merck KGaA, Darmstadt, Germany
Butyl methacrylate	99%, stab.	Thermo Fisher Scientific GmbH, Dreieich, Germany
cis-3,3,5-Trimethyl-cyclohexanol	p.a., >96%	TCI Deutschland GmbH, Heuchelheim, Germany
Cyclohex-2-en-1-one	97%	Thermo Fisher Scientific GmbH, Dreieich, Germany
Cyclohexane carboxaldehyde	97%	Merck KGaA, Darmstadt, Germany
Cyclohexanol	p.a., min. 99%	Carl Roth GmbH & Co. KG, Karlsruhe, Germany
Cyclohexanone	p.a., min. 99.5%	Th. Geyer GmbH & Co. KG, Höxter-Stahle, Germany
Cyclohexyl methanol	p.a.	Merck KGaA, Darmstadt, Germany
Ethanol	p.a., min. 99.5%	Merck KGaA, Darmstadt, Germany
Isophorone	97%	Merck KGaA, Darmstadt, Germany
Methanol	p.a., min. 99.9%	Merck KGaA, Darmstadt, Germany

Sodium hydroxide	97.0%, pellets	Merck KGaA, Darmstadt, Germany
Sodium sulfate	p.a., min. 99%, anhydrous	Carl Roth GmbH & Co. KG, Karlsruhe, Germany
Sulfuric acid	p.a., 95-97%	Merck KGaA, Darmstadt, Germany
Tetrahydrofuran	99+%, stab. with 250 ppm BHT	Th. Geyer GmbH & Co. KG, Höxter-Stahle, Germany

1.1.2. Electrodes

TABLE S2: ELECTRODE MATERIALS USED, LISTED BY TYPE WITH SPECIFICATIONS AND SUPPLIER.

Type	**Specifications**	**Supplier**
Cobalt foam	1200 g/m^2 Co, 1.6 mm width, 0.4 estimated average pore Ø mm	Alantum Europe GmbH, Munich, Germany
Cobalt nickel foam	1000 g/m^2 Co+Ni (280 g/m^2 Ni and 720 g/m^2), 1,7 mm width, 0.58 estimated average pore Ø mm	Alantum Europe GmbH, Munich, Germany
Copper foam	600 g/m^2 Cu, 1.5 mm width, 0.45 estimated average pore Ø mm	Alantum Europe GmbH, Munich, Germany
Copper mesh	ETP1 Ø 0.28 mm	Alantum Europe GmbH, Munich, Germany
Dimensional stable anode (DSA)	Titanium all-site coated with iridium mixed oxide 12 g Ir/m^2, 2 x 10 x 120 mm	METAKEM, Bad Homburg, Germany
Nickel foam (No.1)	no further manufacturer information	IKA-Werke GmbH & Co. KG, Staufen, Germany
Nickel foam (No.2)	Ni-4753, 0.6 estimated average pore Ø mm, 0.3 ... 0.6 density average gr/cm^3, 4.8 % relative average density, 95% average porosity, 5400 m^2/m^3 average specific surface, 1.2 x 10 x 120 mm	Recemat BV, Dodewaard, Netherlands
Nickel foam (No.3)	2 x 100 x 200 mm, trimmed into 2 x 10 x 120 mm	QUARKZMAN, Shenzhen, China
Nickel foam (No.4)	1100 g/m^2 Ni, 2.5 mm width, 0.8 estimated average pore Ø mm	Alantum Europe GmbH, Munich, Germany

Nickel foam (No.5)	480 g/m^2 Ni, 1,7 mm width, 0.58 estimated average pore Ø mm	Alantum Europe GmbH, Munich, Germany
Nickel foam (No.6)	1100 g/m^2 Ni, 0,3 mm width, 1.2 estimated average pore Ø mm	Alantum Europe GmbH, Munich, Germany

1.1.3. Chemicals Electrochemical Set-up

Electrochemical screening cells (divided) from IKA-Werke GmbH & Co. KG, Staufen, Germany, were utilized, along with the corresponding reaction block. The screening cells are equipped with magnetic stir bars. The power supply used was the HMP4040 programmable laboratory power supply (32V, 10A, 384W) from Rohde & Schwarz GmbH & Co. KG, Munich, Germany.

1.2. *Analytical methods*

1.2.1. Gas Chromatography-Mass Spectrometry (GC-MS)

GC/MS System: 7890A/5975C from Agilent Technologies Deutschland GmbH, Waldbronn, Germany.

Column: DB-35ms, 30 m, 0.32 mm, 0.25 µm, from Agilent Technologies Deutschland GmbH, Waldbronn, Germany.

Method: The temperature program begins at 50 °C for 1 minute and ramps up to 90 °C at a rate of 2 °C/min. The flow rate is set to 2 mL/min, with the inlet temperature maintained at 250 °C and the MSD transfer line temperature at 300 °C. Helium is used as the carrier gas, and an injection volume of 0.1 µL is applied in splitless mode, with ionization achieved through electron impact (EI).

Before each measurement, the samples were neutralized to a pH of 6-8 using an aqueous solution of sodium hydroxide.

For reference, cyclohexanone was added as an internal standard immediately after the reaction, directly into the reaction cell, prior to neutralization and transfer for measurement. Cyclohexanone was added in a molar ratio of 1:1 relative to the substrate. In the case of cyclohexanone as the substrate, isophorone was utilized as an internal standard following the same procedure. For substrate concentrations exceeding 0.05 mol/L, the sample was diluted to 0.05 mol/L with a methanol/water (1:1) solution prior to measurement. The Response Factor (RF) used for calculating substrate conversion and product yields was determined using Equation (1).

$$\mathbf{RF} = \frac{Counts \cdot s\ (Substrate)}{Counts \cdot s\ (Internal\ Standard)} \qquad (1)$$

The data for the Response Factor (RF) are substrate-specific and result from measurements of the substrate and the internal standard in a molar ratio of 1:1 in acetone, each at a concentration of 0.05 mol/L (Table s3).

TABLE S3: SUBSTANCE-SPECIFIC RESPONSE FACTOR (RF) IN GC-MS ANALYSIS, CALCULATED ACCORDING TO EQUATION (1), WITH REFERENCE TO AN INTERNAL STANDARD FOR YIELD DETERMINATION. A) INTERNAL STANDARD: CYCLOHEXANONE; B) INTERNAL STANDARD: ISOPHORONE.

Substance	**RF**
1-Phenylethanol	1.069568832$^{b)}$
3,3,5-Trimethylcyclohexanone	2.637078488$^{a)}$
Acetophenone	0.952636332$^{b)}$
Benzaldehyde	0.852638659$^{b)}$
Benzyl alcohol	0.805113841$^{b)}$
Benzyl isobutyrate	3.342286112$^{b)}$
Benzyl methacrylate	3.299796594$^{b)}$
Butyl isobutyrate	1.373341265$^{b)}$
Butyl methacrylate	1.208325606$^{b)}$
Cyclohexane carboxaldehyde	1.334429428$^{b)}$
Cyclohexanol	0.755808712$^{b)}$
Cyclohexanone	0.541487566$^{b)}$
Cyclohex-2-en-1-one	0.451096053$^{b)}$
Cyclohexyl methanol	1.566675824$^{b)}$
Isophorone	2.650928757$^{a)}$

To determine the yield in the reaction mixture, the Response Factor (RF) was multiplied by $Counts \cdot s\ (Internal\ Standard\ in\ reaction\ mixture)$ present in the reaction mixtures (Equation (2)).

$$\mathbf{Yield\%} = \frac{Counts \cdot s\ (Substrate\ in\ reaction\ mixture)}{\boldsymbol{RF}\ \cdot\ Counts \cdot s\ (Internal\ Standard\ in\ reaction\ mixture)} \tag{2}$$

Unless otherwise specified, each experiment was conducted three times, and the yields were subsequently averaged according to Equation (3). The error was determined from the standard deviation, as outlined in Equation (4) and (5).

$$\overline{Yield\%} = \frac{1}{3}\sum_{i=1}^{3} Yield\%_i \tag{3}$$

$$s = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N} (Yield\%_i\ -\ \overline{Yield\%})^2} \tag{4}$$

$$s = \sqrt{\frac{1}{2}\sum_{i=1}^{3} (Yield\%_i\ -\ \overline{Yield\%})^2} \tag{5}$$

1.2.2. Scanning electron microscope (SEM)

For the SEM images a FlexSEM 1000 II of the company Hitachi, Tokio (Japan) was used.

1.2.3. Cyclic voltammetry

The measurements were conducted using an Autolab PGSTAT204 potentiostat, with data acquisition and processing performed using Metrohm Autolab Nova version 42.1.10.4.1.11. The electrolyte mixture was a 0.1 M of n-Bu_4NBF_4 (supplied by TCI 98%+) as a supporting electrolyte in 3:1 MeOH-water at room temperature (ca. 298 K). The working electrode was a glassy carbon disc electrode (d = 3.0 mm, BSDi MF-2012), the counter electrode a platinum wire and the reference electrode a Ag/AgCl "leakless" reference electrode 'RE' (EDAQ). Before each measurement, the electrode was rinsed with distilled water and methanol, then dried. Cyclohex-2-en-1-one was utilized at a concentration of 10 mM, while sulfuric acid was added at a concentration of 1 mM. The solutions were purged with Ar prior to measurement. The scan rate was 100 mV/s.

2. General procedure

2.1. Membrane pretreatment

To separate the reaction sides of the anode and cathode, a Nafion®424 membrane from Ion Power GmbH, Munich, Germany, was consistently employed. The membrane was pretreated in a 0.7 mol/L aqueous sodium hydroxide solution for a minimum of 24 hours. It was oriented such that the smooth, glossy side faced the cathode.

2.2. Screening reactions

Initially, 7.5 mL of electrolyte solution was added to each of the two reaction sides. The electrolyte consisted of either 3.75 mL of methanol/ THF/ acetonitrile/ ethanol and 3.75 mL of deionized water, or 5.0 mL of methanol and 2.5 mL of deionized water, or 2.5 mL of methanol and 5.0 mL of deionized water, each with or without 0.11 g of sodium sulfate (0.00075 mol, 0.1 mol/L) and either 120.6 µL or 201.0 µL of sulfuric acid (0.00225 mol, 0.3 mol/L or 0.00375 mol, 0.5 mol/L). Subsequently, 56 µL, 113 µL, or 169 µL of isophorone (0.000375 mol, 0.05 mol/L or 0.00075 mol, 0.1 mol/L or 0.001125 mol, 0.15 mol/L) was added.

Following this, the electrodes (see **Fehler! Verweisquelle konnte nicht gefunden werden.**) were each immersed to a depth of 4.2 cm, corresponding to an immersed geometric surface area of 4.2 cm^2. A current of 126 mA, 209 mA, 295 mA, 380 mA, 460 mA, or 545 mA was applied, resulting in a current density of 30 mA/cm^2, 50 mA/cm^2, 70 mA/cm^2, 90 mA/cm^2, 110 mA/cm^2, or 130 mA/cm^2, and electrolysis was conducted for 1.28 h, 0.77 h, 0.55 h, 0.42 h, 0.35 h, 0.30 h, 0.85 h, or 1.27 h. This consistently corresponded to a charge amount of 16 F (578.91 C / 1157.82 C / 1736.74 C). The analysis was performed using an internal standard and GC-MS, as described in Section **Fehler! Verweisquelle konnte nicht gefunden werden.**. The specific experimental parameters and quantities can be found in Section **Fehler! Verweisquelle konnte nicht gefunden werden.**.

2.3. Synthesis of 3,3,5-trimethylcyclohexanone

The electrolyte solution was prepared by mixing 3.75 mL of methanol with 3.75 mL of deionized water. Following this, 201 µL of sulfuric acid (0.5 mol/L, 0.00375 mol) was added. Subsequently, 56 µL of isophorone (0.05 mol/L, 0.000375 mol) was introduced as the substrate for the synthesis of 3,3,5-trimethyl-cyclohexanone. The electrolysis was conducted at a current of 380 mA (90 mA/cm^2) for 0.42 hours, with the electrodes immersed to a depth of 4.2 cm (4.2 cm^2 immersed geometric surface area), resulting in a charge of 578.91 C, equivalent to 16 F. The product identification and yield determination was performed using 39 µL of cyclohexanone as an internal standard and GC-MS, as further described in Section **Fehler! Verweisquelle konnte nicht gefunden werden.**. This analytical method resulted in a yield of 77% ± 5% for 3,3,5-trimethyl-cyclohexanone. The faradaic efficiency is approximately 10% and the energy consumption per Mol product is approximately 6 kWh.

2.4. Synthesis of cyclohexanone

The electrolyte solution was prepared by mixing 3.75 mL of methanol with 3.75 mL of deionized water. Following this, 201 µL of sulfuric acid (0.5 mol/L, 0.00375 mol) was added. Subsequently, 36 µL of 2-cyclohexen-1-on (0.05 mol/L, 0.000375 mol) was introduced as the substrate for the synthesis of cyclohexanone. The electrolysis was conducted at a current of 380 mA (90 mA/cm^2) for 0.42 h, with the electrodes immersed to a depth of 4.2 cm (4.2 cm^2 immersed geometric surface area), resulting in a charge of 578.91 C, equivalent to 16 F. The product identification and yield determination was performed using 56 µL of isophorone as an internal standard and GC-MS, as further described in Section **Fehler!**

Verweisquelle konnte nicht gefunden werden.. This analytical method resulted in a yield of 51% for cyclohexanone. The reaction was performed only once, so no standard deviation can be provided.

2.5. Synthesis of benzyl isobutyrate

The electrolyte solution was prepared by mixing 3.75 mL of methanol with 3.75 mL of deionized water. Following this, 201 µL of sulfuric acid (0.5 mol/L, 0.00375 mol) was added. Subsequently, 64 µL of benzyl methacrylate (0.05 mol/L, 0.000375 mol) was introduced as the substrate for the synthesis of benzyl isobutyrate. The electrolysis was conducted at a current of 380 mA (90 mA/cm^2) for 0.42 h, with the electrodes immersed to a depth of 4.2 cm (4.2 cm^2 immersed geometric surface area), resulting in a charge of 578.91 C, equivalent to 16 F. The product identification and yield determination was performed using 56 µL of isophorone as an internal standard and GC-MS, as further described in Section **Fehler! Verweisquelle konnte nicht gefunden werden.**. This analytical method resulted in a yield of 9% for benzyl isobutyrate. The reaction was performed only once, so no standard deviation can be provided.

2.6. Synthesis of butyl isobutyrate

The electrolyte solution was prepared by mixing 3.75 mL of methanol with 3.75 mL of deionized water. Following this, 201 µL of sulfuric acid (0.5 mol/L, 0.00375 mol) was added. Subsequently, 60 µL of butyl methacrylate (0.05 mol/L, 0.000375 mol) was introduced as the substrate for the synthesis of butyl isobutyrate. The electrolysis was conducted at a current of 380 mA (90 mA/cm^2) for 0.42 h, with the electrodes immersed to a depth of 4.2 cm (4.2 cm^2 immersed geometric surface area), resulting in a charge of 578.91 C, equivalent to 16 F. The product identification and yield determination was performed using 56 µL of isophorone as an internal standard and GC-MS, as further described in Section **Fehler! Verweisquelle konnte nicht gefunden werden.**. This analytical method resulted in a yield of 58% for butyl isobutyrate. The reaction was performed only once, so no standard deviation can be provided.

2.7. Synthesis of cyclohexyl methanol

The electrolyte solution was prepared by mixing 3.75 mL of methanol with 3.75 mL of deionized water. Following this, 201 µL of sulfuric acid (0.5 mol/L, 0.00375 mol) was added. Subsequently, 45 µL of cyclohexane carboxaldehyde (0.05 mol/L, 0.000375 mol) was introduced as the substrate for the synthesis of cyclohexyl methanol. The electrolysis was conducted at a current of 380 mA (90 mA/cm^2) for 0.42 h, with the electrodes immersed to a depth of 4.2 cm (4.2 cm^2 immersed geometric surface area), resulting in a charge of 578.91 C, equivalent to 16 F. The product identification and yield determination was performed using 56 µL of isophorone as an internal standard and GC-MS, as further described in Section **Fehler! Verweisquelle konnte nicht gefunden werden.**. This analytical method resulted in a yield of 28% for cyclohexyl methanol. The reaction was performed only once, so no standard deviation can be provided.

2.8. Synthesis of benzyl alcohol

The electrolyte solution was prepared by mixing 3.75 mL of methanol with 3.75 mL of deionized water. Following this, 201 µL of sulfuric acid (0.5 mol/L, 0.00375 mol) was added. Subsequently, 38 µL of benzaldehyde (0.05 mol/L, 0.000375 mol) was introduced as the substrate for the synthesis of benzyl alcohol. The electrolysis was conducted at a current of 380 mA (90 mA/cm^2) for 0.42 h, with the electrodes immersed to a depth of 4.2 cm (4.2 cm^2 immersed geometric surface area), resulting in a charge of 578.91 C, equivalent to 16 F. The product identification and yield determination was performed using 56 µL of isophorone as an internal standard and GC-MS, as further described in Section **Fehler! Verweisquelle konnte nicht gefunden werden.**. This analytical method resulted in a yield of 50% for benzyl alcohol. The reaction was performed only once, so no standard deviation can be provided.

2.9. Synthesis of cyclohexanol

The electrolyte solution was prepared by mixing 3.75 mL of methanol with 3.75 mL of deionized water. Following this, 201 µL of sulfuric acid (0.5 mol/L, 0.00375 mol) was added. Subsequently, 39 µL of cyclohexanone (0.05 mol/L, 0.000375 mol) was introduced as the substrate for the synthesis of cyclohexanol. The electrolysis was conducted at a current of 380 mA (90 mA/cm^2) for 0.42 h, with the electrodes immersed to a depth of 4.2 cm (4.2 cm^2 immersed geometric surface area), resulting in a charge of 578.91 C, equivalent to 16 F. The product identification and yield determination was performed using 56 µL of isophorone as an internal standard and GC-MS, as further described in Section **Fehler! Verweisquelle konnte nicht gefunden werden.**. This analytical method resulted in a yield of 21% for cyclohexanol. The reaction was performed only once, so no standard deviation can be provided.

2.10. Synthesis of 1-phenyl ethanol

The electrolyte solution was prepared by mixing 3.75 mL of methanol with 3.75 mL of deionized water. Following this, 201 µL of sulfuric acid (0.5 mol/L, 0.00375 mol) was added. Subsequently, 44 µL of acetophenone (0.05 mol/L, 0.000375 mol) was introduced as the substrate for the synthesis of 1-phenyl ethanol. The electrolysis was conducted at a current of 380 mA (90 mA/cm^2) for 0.42 h, with the electrodes immersed to a depth of 4.2 cm (4.2 cm^2 immersed geometric surface area), resulting in a charge of 578.91 C, equivalent to 16 F. The product identification and yield determination was performed using 56 µL of isophorone as an internal standard and GC-MS, as further described in Section **Fehler! Verweisquelle konnte nicht gefunden werden.**. This analytical method resulted in a yield of 50% for 1-phenyl ethanol. The reaction was performed only once, so no standard deviation can be provided.

3. Experimental data

3.1. Cyclic voltammetry

For mechanistic investigations, we employed cyclic voltammetry to elucidate whether the substrate initially undergoes direct reduction or if the hydrogenation process occurs via metal hydrides.

The CV shows, that a direct reduction of the enone (red) is possible. However, the potential for proton reduction (blue curve) is significantly less negative compared to that of the substrate, suggesting that the hydrogen evolution reaction is the more favorable. The combination of sulfuric acid (1 equivalent) and the substrate (10 equivalents) appears to result in a lower pH, which facilitates the reduction of the substrate at a less negative potential. In this scenario, the hydrogen evolution reaction does not occur to the same extent as it does in the absence of the substrate, since the concentration of the substrate is way higher compared to the sulfuric acid. However, the parameters in our manuscript have 10 eq. sulfuric acid to 1 eq. substrate, resulting in an enhanced reduction of protons at the electrode surface.

Based on these results, it appears that the direct reduction of the carbonyl group is not the mechanism operating under our reaction conditions.

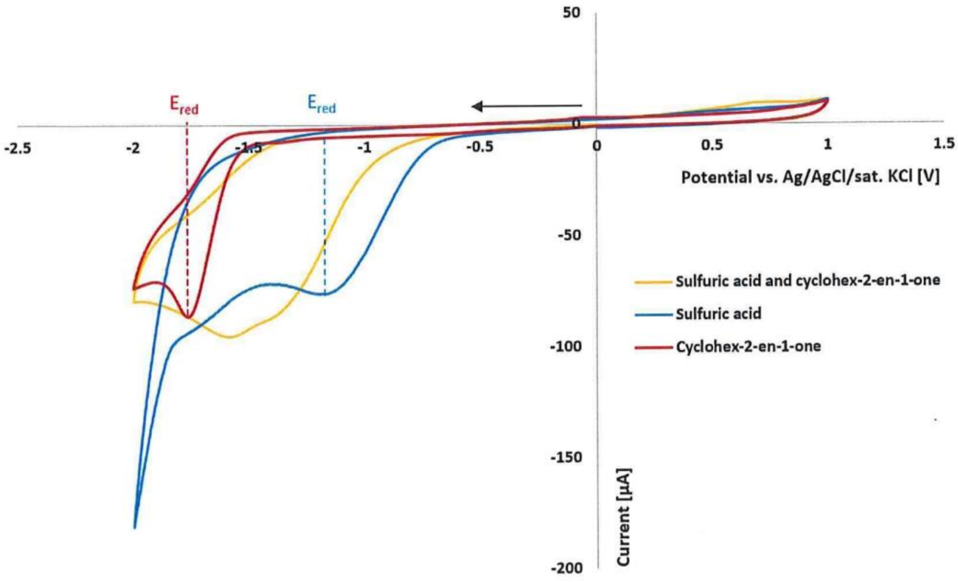

FIGURE S1: SEPARATELY MEASURED VOLTAMMOGRAMS OF CYCLOHEX-2-EN-1-ONE, SULFURIC ACID AND SULFURIC ACID WITH CYCLOHEX-2-EN-1-ONE.

In addition to the CV measurements, we made another observation regarding a trace by-product detected in some experiments, identified as the *trans*-diastereomer of the corresponding alcohol derived from isophorone.

Recent work by Yuan et al. has provided insights into the stereocontrol of electrochemical hydrogenation of carbonyl compounds, indicating that a *trans*-diastereomer is synthesized when the mechanism involves metal hydride formation at the electrode (hydrogen atom transfer, HAT). In contrast, the *cis*-diastereomer is produced via a proton-coupled electron transfer (PCET) mechanism.

Furthermore, a recent publication by Waldvogel et al. corroborates the hydrogenation mechanism at nickel foam, aligning with our findings that the yield is significantly influenced by the electrode structure. Based on these observations and the existing literature, we propose that the mechanistic understanding of the hydrogenation process is fundamentally linked to the formation of metal hydrides at the electrode surface.

3.2. Mass spectra table of the products

TABLE S4: MASS SPECTRA DATA OF THE PRODUCTS.

	TMCon			Benzylisobutyrat			Butylisobutyrat			Cyclohexanalcohol	
m/z	**Abundance**	**Abundance %**	**m/z**	**Abundance**	**Abundance %**	**m/z**	**Abundance**	**Abundance %**	**m/z**	**Abundance**	**Abundance %**
83.1	4839424	100	91.1	8388096	100	87.1	6824960	100	55.1	4389376	100
69	2225152	45.98	108.1	2809344	33.49	69.1	6822912	99.97	83.1	3285504	74.85
55.1	1481728	30.62	178.1	1963520	23.41	56.1	3220480	47.19	81.1	3064320	69.81
140.1	1405952	29.05	65.1	1211904	14.45	55.1	725440	10.63	67.1	2249216	51.24
56.1	1260544	26.05	92.1	964288	11.5	59.1	569920	8.35	82.1	1382912	31.51
125.1	672256	13.89	71.1	871552	10.39	57.1	550592	8.07	96.1	1124864	25.63
84.1	466560	9.64	77.1	849664	10.13	70.1	475392	6.97	68.1	705408	16.07
57.1	305600	6.31	90.1	748928	8.93	88	378752	5.55	54.1	609280	13.88
97.1	280384	5.79	79.1	595328	7.1	86.1	365568	5.36	53.1	398656	9.08
53.1	230656	4.77	89.1	532352	6.35	113.1	165312	2.42	56.1	250944	5.72
67.1	183360	3.79	51.1	441600	5.26	53.1	111400	1.63	84.1	232768	5.3
98.1	175808	3.63	107.1	408704	4.87	74	107496	1.58	66.1	224192	5.11
70	168704	3.49	63.1	299264	3.57	99	95848	1.4	95.1	216960	4.94
141.1	146304	3.02	179.1	244608	2.92	58.1	87696	1.28	79.1	200832	4.58
96.1	128552	2.66	109.1	221056	2.64	71	80656	1.18	57	175296	3.99
82.2	125112	2.59	105.1	219776	2.62	100	77736	1.14	77.1	143616	3.27
107.1	106600	2.2	78.1	180992	2.16	73.1	70752	1.04	65.1	132352	3.02

112.1	97432	2.01	50.1	152384	1.82	85	70504	1.03	51.1	131968	3.01
81.1	77264	1.6	52.1	126336	1.51				69.1	104952	2.39
51	76936	1.59	64.1	93608	1.12				97.1	104888	2.39
79.1	76040	1.57							50.1	64640	1.47
54.1	74480	1.54							52.1	61328	1.4
85	65576	1.36									
77.1	59120	1.22									
126.1	57592	1.19									
65	57112	1.18									

TABLE S5: MASS SPECTRA DATA OF THE PRODUCTS.

	Cyclohexanon			Phenylethylalcohol			Benzylalcohol	
m/z	**Abundance**	**Abundance %**	**m/z**	**Abundance**	**Abundance %**	**m/z**	**Abundance**	**Abundance %**
55	5110784	100	82.1	8388096	100	79.1	4373504	100
98.1	3365376	65.85	138.1	2919424	34.8	108.1	3842560	87.86
69	1805824	35.33	54.1	1257984	15	77.1	2823168	64.55
70	1318400	25.8	95.1	883904	10.54	107	2743296	62.73
83	693760	13.57	83.1	681024	8.12	51	963584	22.03
56	603840	11.82	53.1	637952	7.61	91.1	751616	17.19
54.1	421952	8.26	67.1	637184	7.6	78.1	562816	12.87
80.1	341504	6.68	55.1	481280	5.74	80.1	427840	9.78
99.1	257088	5.03	77.1	425344	5.07	89.1	398720	9.12
53.1	235968	4.62	79.1	390976	4.66	90	358144	8.19

97.1	228032	4.46	139.1	313664	3.74	63	331072	7.57
51.1	152256	2.98	51.1	277056	3.3	65	317952	7.27
50.1	129168	2.53	123.1	232832	2.78	109	300288	6.87
79.1	104576	2.05	65.1	182592	2.18	53.1	262784	6.01
71	103344	2.02	91.1	172096	2.05	52.1	260480	5.96
67	86984	1.7	52.1	150912	1.8	74	200832	4.59
68.1	78200	1.53	110.1	129008	1.54	105	182080	4.16
57	72408	1.42	69.1	127560	1.52	62	159040	3.64
65.1	54384	1.06	50.1	126512	1.51	76.1	98000	2.24
52.1	53960	1.06	93.1	125528	1.5	75	92312	2.11
			78.1	93608	1.12	61	71672	1.64
			63.1	85464	1.02	64.1	68720	1.57
						92.1	58944	1.35
						73.1	48008	1.1

3.3. All experiments listed in table

For all experiments if not otherwise declared following conditions were used:

TABLE S6: CONDITIONS IN EVERY EXPERIMENT.

Anode	DSA 4.2 cm^2
Amount of Applied Charge	16 F
Geometric cathode surface	4.2 cm^2

TABLE S7: EXPERIMENT LIST OF THE SULFURIC ACID CONCENTRATION AND CURRENT DENSITY SCREENING.

	GC analytics			*Co-solvent*		*Solvent*		*Cathode*	*H_2SO_4*	*Na_2SO_4*	*Electrolysis*	
No.	**2**	**1**	**Conversion**	**V [mL]**	**Type**	**V [mL]**	**Type**	**Type**	**c [mol/L]**	**c [mol/L]**	**Current [mA]**	**Current density [mA/cm²]**
1	70%	3%	84%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.3	0.1	126	30
2	55%	26%	57%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.3	0.1	126	30
3	63%	18%	77%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.3	0.1	126	30
M	***63%***	***15%***	***73%***									
SD	***7%***	***12%***	***14%***									
4	74%	9%	86%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	0.1	126	30
5	**50%**	**37%**	**56%**	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	0.1	126	30
6	73%	0%	93%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	0.1	126	30
M	***66%***	***15%***	***78%***									
SD	***14%***	***19%***	***20%***									
7	65%	6%	79%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.3	0.1	209	*50*
8	75%	4%	89%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.3	0.1	209	*50*
9	66%	11%	76%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.3	0.1	209	*50*
M	***69%***	***7%***	***82%***									
SD	***5%***	***3%***	***7%***									
10	66%	14%	73%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	0.1	209	*50*
11	35%	55%	35%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	0.1	209	*50*

12	61%	8%	75%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	0.1	209	50
M	***54%***	***25%***	***61%***									
SD	***17%***	***26%***	***22%***									
13	63%	21%	73%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.3	0.1	295	70
14	60%	7%	76%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.3	0.1	295	70
15	70%	0%	88%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.3	0.1	295	70
M	***64%***	***9%***	***79%***									
SD	***5%***	***11%***	***8%***									
16	57%	30%	61%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	0.1	295	70
17	56%	15%	69%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	0.1	295	70
18	61%	11%	73%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	0.1	295	70
M	***58%***	***18%***	***68%***									
SD	***3%***	***10%***	***6%***									
19	63%	18%	72%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.3	0.1	380	90
20	56%	2%	70%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.3	0.1	380	90
21	61%	3%	80%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.3	0.1	380	90
M	***60 %***	***8%***	***74%***									
SD	***4%***	***9%***	***5%***									
22	70%	20%	79%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	0.1	380	90
23	69%	7%	84%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	0.1	380	90

24	64%	18%	71%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	0.1	380	90
M	***68%***	***15%***	***78%***									
SD	***3%***	***7%***	***7%***									
25	56%	14%	69%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	0.1	460	110
26	51%	39%	51%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	0.1	460	110
27	54%	16%	68%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	0.1	460	110
M	***54%***	***23%***	***63%***									
SD	***3%***	***14%***	***10%***									
28	58%	21%	66%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	0.1	545	130
29	49%	37%	53%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	0.1	545	130
30	56%	25%	61%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	0.1	545	130
M	***54%***	***28%***	***60%***									
SD	***5%***	***8%***	***7%***									

TABLE S8: CO-SOLVENT SCREENING.

	GC analytics			***Co-solvent***		***Solvent***		***Cathode***	**H_2SO_4**	***Electrolysis***	
No.	**2**	**1**	**Conversion**	**V [mL]**	**Type**	**V [mL]**	**Type**	**Type**	**c [mol/L]**	**Current [mA]**	**Current density [mA/cm²]**
31	67%	16%	77%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	380	*90*
32	72%	0%	90%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	380	*90*
33	73%	23%	84%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	380	*90*

M	**71%**	**13%**	**84%**							
SD	**3%**	**12%**	**6%**							
34	7%	10%	7%	3.75	THF	3.75	Deionized water	Ni foam (No. 1)	0.5	380	*90*
32	7%	15%	7%	3.75	THF	3.75	Deionized water	Ni foam (No. 1)	0.5	380	*90*
33	20%	12%	20%	3.75	THF	3.75	Deionized water	Ni foam (No. 1)	0.5	380	*90*
M	**11%**	**12%**	**11%**							
SD	**7%**	**3%**	**7%**							
34	0%	27%	0%	3.75	Acetonitril	3.75	Deionized water	Ni foam (No. 1)	0.5	380	*90*
35	3%	39%	3%	3.75	Acetonitril	3.75	Deionized water	Ni foam (No. 1)	0.5	380	*90*
36	3%	45%	3%	3.75	Acetonitril	3.75	Deionized water	Ni foam (No. 1)	0.5	380	*90*
M	**2%**	**37%**	**2%**							
SD	**2%**	**9%**	**2%**							
37	42%	28%	42%	3.75	Ethanol	3.75	Deionized water	Ni foam (No. 1)	0.5	380	*90*
38	12%	38%	12%	3.75	Ethanol	3.75	Deionized water	Ni foam (No. 1)	0.5	380	*90*
39	30%	18%	30%	3.75	Ethanol	3.75	Deionized water	Ni foam (No. 1)	0.5	380	*90*
M	**28%**	**28%**	**28%**							
SD	**15%**	**10%**	**15%**							

TABLE S9: EXPERIMENT LIST OF THE SOLVENT RATIO ANALYSIS.

	GC analytics	*Co-solvent*	*Solvent*	*Cathode*	H_2SO_4	*Electrolysis*

No.	2	1	Conversion	V [mL]	Type	V [mL]	Type	Type	c [mol/L]	Current [mA]	Current density [mA/cm²]
31	67%	16%	77%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	380	*90*
32	72%	0%	90%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	380	*90*
33	73%	23%	84%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	380	*90*
M	**71%**	**13%**	**84%**								
SD	**3%**	**12%**	**6%**								
43	63%	30%	73%	5.00	Methanol	2.50	Deionized water	Ni foam (No. 1)	0.5	380	*90*
44	42%	58%	42%	5.00	Methanol	2.50	Deionized water	Ni foam (No. 1)	0.5	380	*90*
45	64%	19%	73%	5.00	Methanol	2.50	Deionized water	Ni foam (No. 1)	0.5	380	*90*
M	**56%**	**36%**	**63%**								
SD	**12%**	**20%**	**18%**								
46	67%	5%	78%	2.50	Methanol	5.00	Deionized water	Ni foam (No. 1)	0.5	380	*90*
47	14%	5%	14%	2.50	Methanol	5.00	Deionized water	Ni foam (No. 1)	0.5	380	*90*
48	57%	30%	57%	2.50	Methanol	5.00	Deionized water	Ni foam (No. 1)	0.5	380	*90*

TABLE S10: EXPERIMENT LIST OF THE EXPERIMENTS FOR THE INFLUENCE OF SODIUM SULFATE.

	GC analytics			***Co-solvent***		***Solvent***		***Cathode***	***H_2SO_4***	***Na_2SO_4***	***Electrolysis***	
No.	**2**	**1**	**Conversion**	**V [mL]**	**Type**	**V [mL]**	**Type**	**Type**	**c [mol/L]**	**c [mol/L]**	**Current [mA]**	**Current density [mA/cm²]**
31	67%	16%	77%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5		380	*90*

32	72%	0%	90%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5		380	*90*
33	73%	23%	84%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5		380	*90*
M	**71%**	**13%**	**84%**									
SD	**3%**	**12%**	**6%**									
40	70%	20%	79%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	0.1	380	*90*
41	69%	7%	84%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	0.1	380	*90*
42	64%	18%	71%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	0.1	380	*90*
M	**68%**	**15%**	**78%**									
SD	**3%**	**7%**	**7%**									

TABLE S11: TESTS OF DIFFERENT COPPER CATHODES.

	GC analytics			***Co-solvent***		***Solvent***		***Cathode***	***H_2SO_4***	***Electrolysis***	
No.	**2**	**1**	**Conversion**	**V [mL]**	**Type**	**V [mL]**	**Type**	**Type**	**c [mol/L]**	**Current [mA]**	**Current density [mA/cm²]**
49	30%	57%	30%	3.75	Methanol	3.75	Deionized water	Copper foam	0.5	380	*90*
50	27%	45%	37%	3.75	Methanol	3.75	Deionized water	Copper foam	0.5	380	*90*
51	34%	43%	41%	3.75	Methanol	3.75	Deionized water	Copper foam	0.5	380	*90*
M	**30%**	**48%**	**36%**								
SD	**3%**	**8%**	**5%**								
52	15%	83%	15%	3.75	Methanol	3.75	Deionized water	Copper mesh	0.5	380	*90*
53	10%	92%	10%	3.75	Methanol	3.75	Deionized water	Copper mesh	0.5	380	*90*
54	16%	82%	16%	3.75	Methanol	3.75	Deionized water	Copper mesh	0.5	380	*90*
M	**14%**	**86%**	**14%**								
SD	**3%**	**6%**	**3%**								

TABLE S12: EXPERIMENTS WITH DIFFERENT COBALT. COBALT NICKEL AND NICKEL FOAMS.

	GC analytics			*Co-solvent*		*Solvent*		*Cathode*	*H_2SO_4*	*Electrolysis*	
No.	**2**	**1**	**Conversion**	**V [mL]**	**Type**	**V [mL]**	**Type**	**Type**	**c [mol/L]**	**Current [mA]**	**Current density [mA/cm²]**
40	67%	16%	77%	3.75	Methanol	3.75	Deionized water	Ni foam	0.5	380	90
41	72%	0%	90%	3.75	Methanol	3.75	Deionized water	Ni foam	0.5	380	90
42	73%	23%	84%	3.75	Methanol	3.75	Deionized water	Ni foam	0.5	380	90
M	**71%**	**13%**	**84%**								
SD	**3%**	**12%**	**6%**								
55	55%	4%	67%	3.75	Methanol	3.75	Deionized water	Cobalt foam	0.5	380	90
56	40%	48%	46%	3.75	Methanol	3.75	Deionized water	Cobalt foam	0.5	380	90
57	42%	61%	50%	3.75	Methanol	3.75	Deionized water	Cobalt foam	0.5	380	90
M	**46%**	**37%**	**55%**								
SD	**8%**	**30%**	**11%**								
58	70%	5%	91%	3.75	Methanol	3.75	Deionized water	Cobalt nickel foam	0.5	380	90
59	63%	21%	73%	3.75	Methanol	3.75	Deionized water	Cobalt nickel foam	0.5	380	90
60	70%	25%	83%	3.75	Methanol	3.75	Deionized water	Cobalt nickel foam	0.5	380	90
M	**68%**	**17%**	**82%**								
SD	**4%**	**11%**	**9%**								

TABLE S13: EXPERIMENTS WITH DIFFERENT NICKEL FOAMS.

	GC analytics			*Co-solvent*		*Solvent*		*Cathode*	H_2SO_4	*Electrolysis*	
No.	**2**	**1**	**Conversion**	**V [mL]**	**Type**	**V [mL]**	**Type**	**Type**	**c [mol/L]**	**Current [mA]**	**Current density [mA/cm²]**
31	67%	16%	77%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	380	90
32	72%	0%	90%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	380	90
33	73%	23%	84%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 1)	0.5	380	90
M	**71%**	**13%**	**84%**								
SD	**3%**	**12%**	**6%**								
61	69%	16%	73%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 2)	0.5	380	90
62	76%	0%	96%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 2)	0.5	380	90
63	66%	0%	87%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 2)	0.5	380	90
M	**70%**	**5%**	**85%**								
SD	**5%**	**9%**	**12%**								
64	27%	34%	27%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 3)	0.5	380	90
65	30%	49%	37%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 3)	0.5	380	90
66	34%	34%	37%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 3)	0.5	380	90
M	**30%**	**39%**	**34%**								
SD	**4%**	**8%**	**6%**								
67	68%	15%	68%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 4)	0.5	380	90
68	75%	0%	90%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 4)	0.5	380	90

69	70%	8%	83%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 4)	0.5	380	90
M	**71%**	**8%**	**80%**								
SD	**4%**	**7%**	**11%**								
70	63%	36%	63%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 5)	0.5	380	90
71	78%	0%	98%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 5)	0.5	380	90
72	68%	39%	73%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 5)	0.5	380	90
M	**69%**	**25%**	**78%**								
SD	**8%**	**22%**	**18%**								
73	81%	8%	88%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 6)	0.5	380	90
74	71%	0%	88%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 6)	0.5	380	90
75	78%	6%	95%	3.75	Methanol	3.75	Deionized water	Ni foam (No. 6)	0.5	380	90
M	**77%**	**5%**	**90%**								
SD	**5%**	**4%**	**4%**								

TABLE S14: ALL EXPERIMENTS WERE CONDUCTED WITH NI FOAM 6 AS CATHODE, DSA AS ANODE WITH 90 MA/CM2, 0.05 M EDUCT, MEOH:H_2O 1:1 AND 0.5 M H_2SO_4.

No.	Educt	Educt %	Product %
76	Butyl methacrylate	0	58
77	2-Cyclohexen-1-one	0	51
78	Cyclohexane carboxaldehyde	57	28
79	Benzyl methacrylate	11	9
80	Benzaldehyde	7	50
81	Cyclohexanone	48	21
81	Acetophenone	38	56

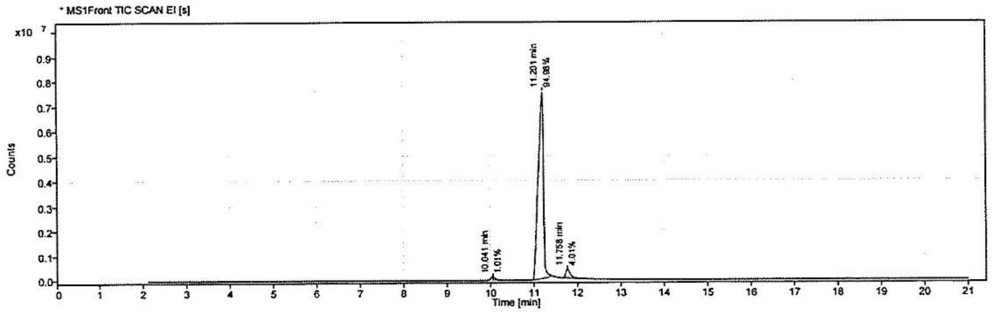

FIGURE 22: *CIS*-TRIMETHYLCYCLOHEXANONE.

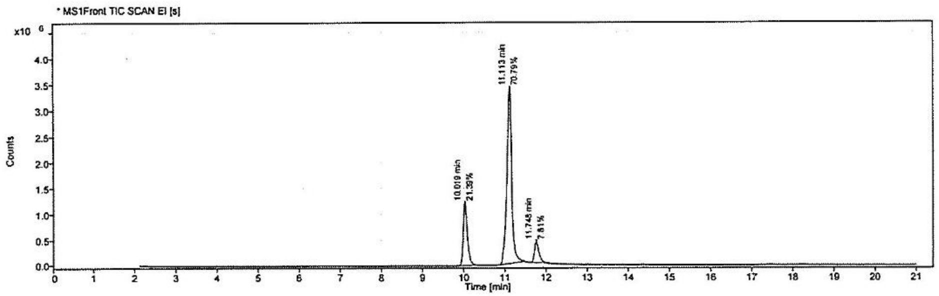

FIGURE 33: MIXTURE OF *TRANS*- AND *CIS*-TRIMETHYLCYCLOHEXANOL (20:80 %).

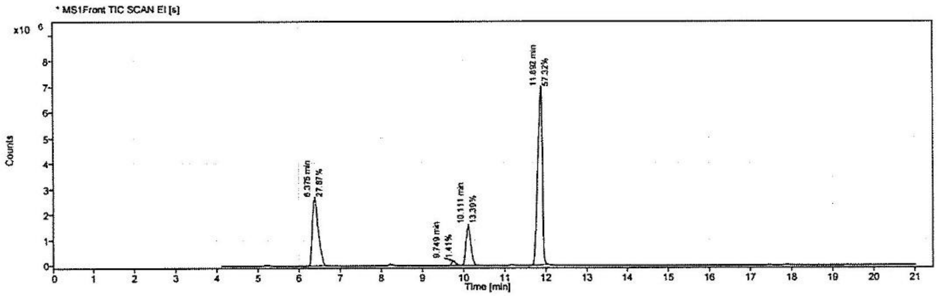

FIGURE 44: EXAMPLE OF ONE REACTION WITH BYPRODUCT.

TABLE 15: LIST OF RETENTION TIME IN MIN OF CYCLOHEXANONE AND BOTH DIASTEREOMER ALCOHOLS.

Substance	**Retention time in min**
Cylohexanone	6.3
Trans-trimethylcyclohexanol	10.1
Cis-trimethylcyclohexanol	11.2

Trimethylcylcohexanone	11.8

Electrochemical Treatment of Industrial Wastewater Degrading Tetrabutylammonium Bromide Using a Quasi-Divided Cell Design

Laura Lennartz, Tobias Stadtmüller, Sebastian Arndt, Patrik Stenner, Siegfried R Waldvogel*

Abstract: A robust, simple, and safe anodic treatment of an industrial wastewater was developed containing tetrabutylammonium salts. The use of a quasi-divided electrolysis cell set-up proved to be the key to success. Quasi-division enabled the generation of oxidizing mediators without the necessity of an expensive and/or fragile membrane as separator. Screening experiments with significantly different current densities between anode and cathode revealed a higher efficiency compared to similar current densities at both electrodes. Furthermore, acidification of the wastewater prior to electrolysis improved the degradation efficiency by prevention of sulfurous electrode coatings (electro-fouling). Under optimized conditions, the concentration of tetrabutylammonium cations was diminished to levels (<1 ppm) far below those required by environmental guidelines. 99% of the tetrabutylammonium species were depleted in total with a degradation rate of around 1 mmol tetrabutylammonium bromide/100 min with an energy consumption of 2.5 kWh/L. The developed processes is applicable to wastewater with a varying composition.

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

1. Introduction

Tetrabutylammonium bromide (TBABr) is a frequently used chemical in industrial processes and academic research. It serves as phase transfer catalyst, pH regulator, or as supporting electrolyte, amongst others.[1] The advantage of superior stability even towards bacterial degradation compared to similar classes of substances, turns into a clear detriment when it comes to disposal and waste treatment.[1b] Studies from 2018 indicate a persistent biocidal impact on water organism, and teratogenic effects on the unborn child.[1c]

As result, TBABr disposal is an increasingly subject of environmental regulations restricting the use and requiring increasingly thorough removal thereof.[1c] TBABr is classified as a Category 3 chronic aquatic chemical according to CLP classification and ECHA guidelines.[2] Therefore, it should not be discharged into sewage systems without prior treatment.[2] Treatment of wastewater is an important and contemporary topic in the chemical industry.[3] A common method is the Fenton-type oxidation process using iron catalysts and hydrogen peroxide.[4] However, the emission of iron species into the environment is also legally regulated. Therefore, the generated iron sludge must be appropriately disposed of, resulting in a secondary off plant waste stream. Another often used approach is the incineration of the wastewater, which has an high energy demand rendering it uneconomical and unecological.[5] A third and sophisticated approach is the removal of the targeted pollutants by membrane filtration.[6] However, the stability of such membranes is limited by organic pollutants and the resulting concentrate has to be incinerated.[6] Only the amount of waste that needs to be incinerated is minimized.

A modern method for wastewater treatment is the "cold combustion" by electrolysis.[3b, 3c, 7] The general process has been known since 1889, but the use of electricity instead of chemicals has recently become attractive by the expansion of the renewable energy production.[3b, 8] The electrochemical wastewater treatment is based on the in-situ generation of strongly oxidizing species at the anode that are capable of eliminating various organic pollutants in industrial wastewaters.[3a, 3b, 9] The most efficient electrode material to date is boron-doped diamond (BDD) due to its high overpotential for oxygen evolution and its preference to produce extremely reactive hydroxyl radicals in aqueous media.[3a, 3b, 9-10] Hydroxyl radicals are capable of mineralizing organics up to CO_2.[3b, 9a, 10b] In addition, BDD is a sustainable choice compared to other commonly used anode materials, such as IrO_x/RuO_x on titanium or PbO_2, since it is fabricated from methane and poses no risk of leaching highly toxic heavy metals into solution.[3b, 9-10, 10i, 11] The effect of the cold combustion may be enhanced by adding inorganic chlorides or sulfur species, among others.[9a, 12] Chloride is oxidized to reactive (oxo)chlorine species (RCS) and sulfur to reactive (per)sulfate species (RSS).[3b, 9a, 10b, 13] Both are mediators with a high oxidizing power supporting the degradation of organic pollutants.[3b, 9a, 10b, 10j, 14] Another effect of such additives is the improvement of the electrical conductivity. The applied voltage decreases versus the overpotentials for hydrogen and oxygen evolution reaction (HER, OER), which diminishes water splitting as the primary parasitic side reaction.[3a] Consequently, higher current densities can be applied and allow a more compact electrolysis cell. An advantage of electrochemical treatment compared to conventional methods is the flexible adjustment of the degree of elimination of the targeted pollutant.[3c] The correlation between reaction time and degradation level is predominantly mathematical in nature. While the reaction time is a significant factor influencing the degradation rate, it is not the sole variable that can be manipulated. The number of reactors employed also plays a crucial role. Given that electrochemical plants are frequently designed using a modular reactor system, increasing the number of modules can enhance the elimination rate as required. This approach allows for an improved degradation process without necessitating the complete construction of an additional facility. Levels below <1 ppm can be reached without alteration in the setup. If required, the pollution is eliminated beyond this amount by a complementary electrolysis cell with an adapted geometry. This is called water polishing. Amended environmental guidelines can be met by numbering up the electrolysis cells or by prolonged electrolysis time.

In the following paragraphs, TBABr will be referred to as TBA (tetrabutylammonium cation), as our objective is to provide a treatment method applicable to the broader spectrum of tetrabutylammonium and tetraalkylammonium cations. Additionally, there are several established methods for reducing salt concentrations, including the remaining inorganic bromide-containing salts, such as ion exchange processes. TBA or other tetraalkylammonium containing wastewaters accrue, when it cannot be substituted. Typically, such TBA concentrations are in the range of 4.000 to 12.000 ppm with impurities of sodium chloride and sulfide. Our ambition for an electrochemical treatment of wastewater was decreasing the TBA concentration below 5 ppm in agreement with concurrent environmental guidelines. We envisioned a simple, flexible, robust, and cost-effective system, without the necessity for additional reagents. Importantly, the biodegradability of the treated wastewater was a central requirement for this approach. Our study aimed to propose a treatment option for TBA-contaminated wastewater in general not only TBABr by testing the method on actual industrial effluent demonstrating its applicability in an industrial context.

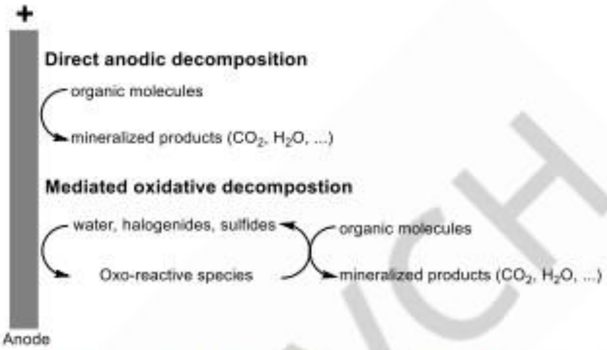

Figure 1: Oxidative degradation pathways of organic molecules at the anode (directly or mediated).[8, 15]

2. Results and Discussion

2.1. Materials and methods

Batch-type electrolysis trials were performed in a flow cell operated in cycling mode. The flow-electrolysis cell had a plate-electrode design and was tailor-manufactured in our workshop on site. The sandwich of sealings in frame design (e.g. Viton; red), spacers (PP, brown), and electrodes (e.g. BDD; grey) and were pressed by two steel plates (dark grey), steel screws, and screw nuts at the edge of the plates

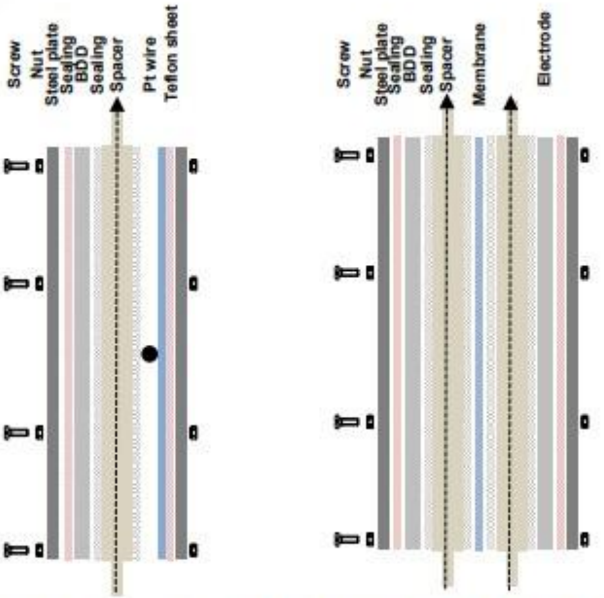

Figure 2: Cross-section drawing of the undivided and the divided flow-electrolysis cell set-up (left, right) and frontal view (middle).

2.2. Experimental Results

Preliminary experiments were conducted at standard electrolytic conditions using electrolysis cells equipped with a planar BDD anode and a platinum cathode. The beaker or H-cells were operated either undivided or divided using a cation-exchange or an anion-exchange membrane (CEM, AEM). The electrolysis conditions were varied in respect to current density, surface area difference, pH, and electrolysis time. However, in all examples no sufficient decrease or no decrease in TBA (= TBA+) concentration was detected via HPLC-MS confirming the outstanding stability of TBA towards oxidative degradation.

Interesting results were observed when experiments were conducted in a cycling batch mode utilizing a divided flow cell. (see **Figure 4**). Only limited degradation of about 20% was observed when using the AEM setup (Table 1, entry 2). When using Nafion 424 as a separator the observation was made, that the TBA permeated partially from the anolyte into the catholyte due to the positive charge. The remaining TBA in the anodic compartment was almost completely removed with only a residual concentration of 67 ppm left upon electrolysis (Table 1, entry 1). The TBA in the cathodic compartment remained unconverted. About half of the TBA was depleted in total (4640 ppm down to 2516 ppm). More experiments besides the listed in **Table 1** conducted in the divided flow cell are listed in the supporting information.

Based on these preliminary results, the setup was changed to a *quasi*-divided electrolysis cell to avoid the necessity of a membrane and the accumulation in the catholyte.[16] *Quasi*-division means that the electrode surfaces differ strongly in area while operating in a undivided setup, which limits the mass transport kinetically at the smaller electrode, in our case the cathode.[16a-d, 17] The electrode reaction is thus mostly restricted to the bulk solvent.[16a-d] The corresponding flow-electrolysis setup was equipped with a BDD anode (active surface: 80 cm^2) and a platinum cathode (employed surface of 15.6 cm^2, tantalum supported) and was operated in cycling mode. The wastewater (300 mL) was kept in a reservoir and pumped through the flow electrolysis cell. The electrolysis was performed with a difference in surface area ($\Delta s.a$) between anode and cathode of $\Delta s.a = 5.1:1$ for 345 min. The use of a *quasi*-divided setup affected the TBA degradation significantly. The experiment resulted in a total TBA degradation of 2825 ppm (44%) (Table 2, Entry 1), in comparison to no degradation for the undivided experiment in batch-type operation. Due to the obviated accumulation in the catholyte, we envisioned a complete oxidative degradation below 5 ppm with the quasi-divided setup. With this result in hand, a series of screening experiments were performed on the difference in surface area between anode and cathode and the electrolysis time (Table 2, entry 2+3).

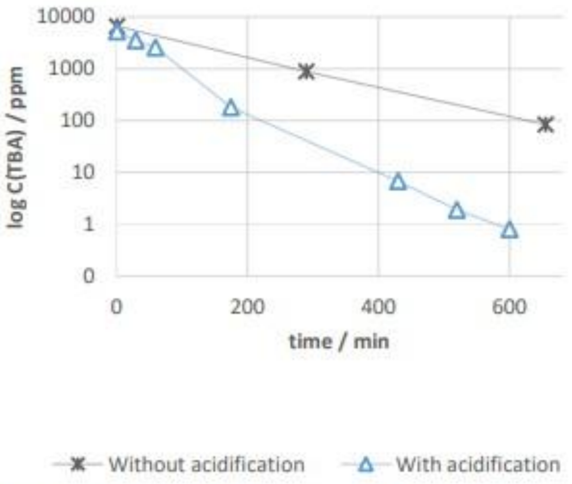

Figure 3: Anodic degradation versus time plot for acidified and non-acidified wastewater. Experiments with the same electrolysis conditions were compared (Table 2, Entry 3 and

Table 1: The catholyte was 0.1 M NaOH. In all experiments, BDD was the anode and tantalum supported platin sheet the cathode. Average terminal voltage range was 5-16 V. The current applied was 1.2 A.

No.	Membrane	Electrolysis time / min	Anode area/ cm^2	Cathode area/ cm^2	Starting TBA concentration/ ppm	TBA concentration in anolyte/ ppm	TBA concentration in catholyte/ ppm	Total degradation/ ppm
1	CEM	290	80	15.6	4640	67	1453	2516 (54%)
2	AEM	405	80	15.6	5967	4885	23	1059 (18%)

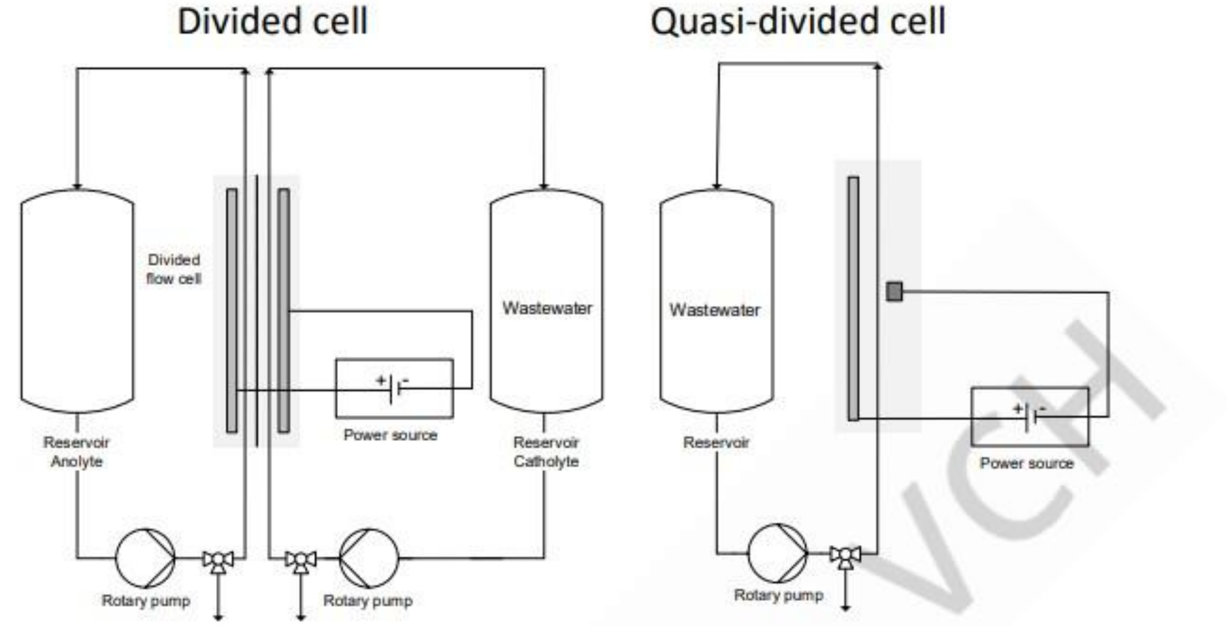

Figure 4: Flow scheme of divided flow cell (left) and a quasi-divided flow cell (right) operated in cycling mode.[16d]

A beneficial effect was observed for higher differences in surface area, which was even more pronounced when going to smaller cathode surfaces (Table 2 Entry 2+3), in the range from 80 cm^2 (anode) compared to 6 cm^2 to 3 mm^2 (cathode). A surface area difference $\Delta s.a$ = 13.3:1 in surface area gave a lowering of the TBA concentration by about 99% from 6870 ppm to 40 ppm (Table 2 Entry 2). With an even higher difference in surface area of $\Delta s.a$ = 2666:1 and a prolonged electrolysis time of 1060 min, the TBA concentration was reduced to 19 ppm (Table 2, Entry 3). However we still not met our initial goal with an end TBA concentration of under 5 ppm. Throughout our experiments, we observed that sulfur contaminations in our wastewater disturbed the electrolysis by forming insulating coatings (electro-fouling) at the anodic surface. For this reason, the effect of acidification as a pretreatment to electrolysis was examined. A low pH generally increases the oxidation potential in the electrolysis promoting the targeted degradation. The acidification of the wastewater prior to the electrolysis successfully removed the sulfur species by liberation as gaseous hydrogen sulfide. Three experiments were carried out subsequently using the optimized parameters, i.e. (Table 2: Entry 4-6) a very small cathodic surface (3 mm^2) creating a significant difference in surface area of $\Delta s.a.$ = 2666:1 and prolonged electrolysis times from 395 to 710 min using acidified wastewaters. The targeted concentration of less than 5 ppm of TBA was achieved in all three experiments, reaching even a concentration below 1 ppm for TBA. The treatment efficiency was reproducible despite varying composition and homogeneity of the evaluated wastewater batches (Table 2: Entry 6).

The beneficial effect of acidification on the current efficiency was clearly demonstrated by the rate of the degradation that was determined by taking samples over the course of electrolysis (Figure 4). A three times faster degradation rate for the acidified wastewater (before pH=8; after acidification pH=2) was found compared to the non-acidified. The preclusion of sulfurous coating and a higher stability of the applied potential was observed. To understand TBA destruction mechanisms, we analyzed total organic carbon (TOC), organic acids, total nitrogen (TN), ammonia, nitrite, and nitrate levels before and after treatment as well as performing HR-MS analysis. We observed an 80% decrease in TOC but only a 30% reduction in organic acids, indicating carbon is primarily oxidized to carbonic acid. No increase in nitrate or nitrite suggests nitrogen from TBA remains in solution, while the decrease in TN implies nitrogen is released as gas. Additionally, ammonia levels increased, supporting the hypothesis of butyl chain oxidation and nitrogen elimination, resulting in ammonia release. Only traces (range of ppb) of chlorinated and or oxidized butyl chain derivates of the TBA were detected via HPLC-HR-MS. The analysis indicates that the butyl chains of the TBA are oxidized, while the nitrogen remains as ammonia. For further information look in the supporting information. Finally, the stability of the applied materials was evaluated. Alternative, less costly cathode materials than platinum or BDD were investigated with regard to their stability and performance. Stainless-steel (1.4401) and graphite as cathode were unstable within the applied range of conditions. Thus, platinum remained the cathode material of choice.

3. Conclusion

An electrolyzer setup was developed and optimized for the cold combustion of TBABr containing wastewater. The cation TBA is a highly challenging substrate in terms of electrolysis as it is often used as cation as a supporting electrolyte. However, superior degradation efficiencies were reached by employing a quasi-divided electrolysis cell and by prior acidification with hydrochloric acid. TBA concentrations were reproducibly depressed below 5 ppm, and even below 1 ppm, were achieved in agreement with environmental guidelines. The degradation rate corresponded to 1 mmol/100 min specifically, 6 mmol TBA/615 min with an energy consumption of 2.5 kWh per liter. The results were well reproducible, and stable materials were identified.

Considerations should be directed towards addressing secondary components in the wastewater and the emitted exhaust gases. The emitted hydrogen sulfide from acidification can be captured using an activated carbon filter. The chlorine gas emitted during electrolysis can be converted into sodium chloride through the use of sodium hydroxide. This can then either be disposed, used as brine, or recycled into hydrochloric acid and sodium hydroxide through electrodialysis, thus allowing it to be recovered for the treatment process. The present study can be extended beyond cold combustion topic to organic electrosynthesis. In the future besides the feasibility of permeating Nafion 424 membranes, especially organic electrochemists should be aware of the possible instability within high current densities as an supporting electrolyte.

Table 2: Wastewaters were electrolyzed in a quasi-divided setup with BDD as anode. Wastewaters were acidified with aqueous HCl to pH 2. The average terminal voltage ranged from 5 V to 16 V.

No.	Pretreatment	Reaction time / min	Cathode area	Anode area	Δs.a.	Δj/ A/m2	Starting/ ppm	Result / ppm	Total degradation/ ppm
1	none	345	15,6 cm^2	80 cm^2	5.1:1	5	6463	3638	2825 (44%)
2	none	360	6 cm^2	80 cm^2	13.3:1	13	6910	40	6870 (99%)
3	none	1060	3 mm^2	80 cm^2	2666:1	250	6584	19	6565 (99%)
4	acidification	710	3 mm^2	80 cm^2	2666:1	250	5346	2	5344 (99%)
5	acidification	395	3 mm^2	80 cm^2	2666:1	250	5385	4	5381 (99%)
6	acidification	615	3 mm^2	80 cm^2	2666:1	250	5208	<1	5207 (99%)

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Keywords: Industrial wastewater • Cold combustion • Quasi-Divison • Tetrabutylammonium • Boron-doped diamond

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Supporting Information

Electrochemical treatment of industrial wastewater degrading tetrabutylammonium bromide using a quasi-divided cell design

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1 Contents

2 General information

The wastewater was provided from Evonik industries and the major compounds were sodium chloride, sodium sulfide and tetrabutylammonium bromide in varying concentrations. All other chemicals were commercially available.

Chemicals

HCl: Hydrochloric acid fuming 37% for analysis provided by Merck

NaOH: Sodium hydroxide pellets for analysis provided by Merck

H_2SO_4: conc. Sulfuric acid for analysis provided by Merck

Electrodes

BDD electrodes were provided by Diaccon (Niob 2 mm with 12 ym diamond coating)

"Pt strips": Pt on Ta welded; were provided by an in house workshop

Analysis

The LC Analysis were performed on an device from Agilent technologies (series 1260, quadrupole detector) with an RP 18 column. The quantitative analysis was done with an external calibration of tetrabutylammonium and determined via retention time and mass spectrometry.

We also tried GC-MS analysis, whether we detect any byproducts after treatment. However, we did not found any detectable compounds in the GC-MS.

For the cuvette tests following cuvettes from Hach were used:

Analysis	Cuvette type
Organic acid	LCK365
Ammonia	LCK305 and LCK 304
Nitrite	LCK341
Nitrate	APC339

For the analysis the Hach Lange Photometer DR3900 was used. The LT 200 from Lange was used for chemical breakdown prior analysis. For the TOC and TN analysis a total organic analyzer from Shimadzu was used.

Prior to measurement the samples were diluted with water.

Summarized interpretation

Since no significant concentrations of side products were detected in the initial samples, the analysis was conducted in SIM mode for TBA^+. However, in the quasi-divided optimized experiments, the samples were reanalyzed without SIM mode to verify the absence of oxidative side products. In all optimized experiments no detectable amounts of oxygenated or chlorinated forms of TBA were found.

Only one sample (Table S2 experiment No. 3) revealed the presence of chlorinated and oxygenated products of TBA. The detected amount were in all side products below 50 ppm. The ESI-HRMS spectra are attached in the document.

To gain a deeper understanding of the mechanism underlying TBA destruction, we analyzed the total organic carbon (TOC) and organic acid levels for carbon elimination, as well as total nitrogen (TN), ammonia, nitrite, and nitrate content before and after treatment. Our observations revealed an approximate 80% decrease in TOC, contrasted with only a 30% reduction in organic acids. This suggests that carbon is oxidized primarily into carbonic acid.

We found no increase in nitrate or nitrite levels, indicating that the nitrogen from the TBA molecule does not undergo oxidation and remains in solution. However, the observed decrease in TN suggests that nitrogen is emitted as a gaseous compound. Additionally, we noted an increase in ammonia levels. This combination of results, along with the relative increase in organic acids compared to TOC, supports the hypothesis of butyl chain oxidation and the elimination of nitrogen, resulting in ammonia being released.

Since no byproducts or oxidative degradation products of TBA were detected in the optimized experiments, we hypothesized the presence of gaseous oxidation products of TBA. Our proposed process implementation involves the thermal afterburning of gas emissions, a method commonly employed at chemical production facilities to convert gas emissions into energy. Given that hydrogen is invariably produced as a byproduct of electrochemical reactions in aqueous solutions, we considered utilizing this hydrogen while addressing the potential issue of hazardous oxidative byproducts associated with TBA. Consequently, we propose to combust our gas emissions in a thermal afterburner, thereby harnessing the generated hydrogen as an energy source. Additionally, the thermal afterburning system incorporates filtration mechanisms to manage pollutants such as nitrogen oxides (NOx) and carbon monoxide (CO). For the chlorine gas emission a gas scrubber with sodium hydroxide is utilized. The sodium chloride can then be upcycled again into HCl and NaOH. The HCl can be reused for acidification and the sodium hydroxide for the gas scrubber.

3 Materials and setup

3.1 Cell setup: schematic scheme

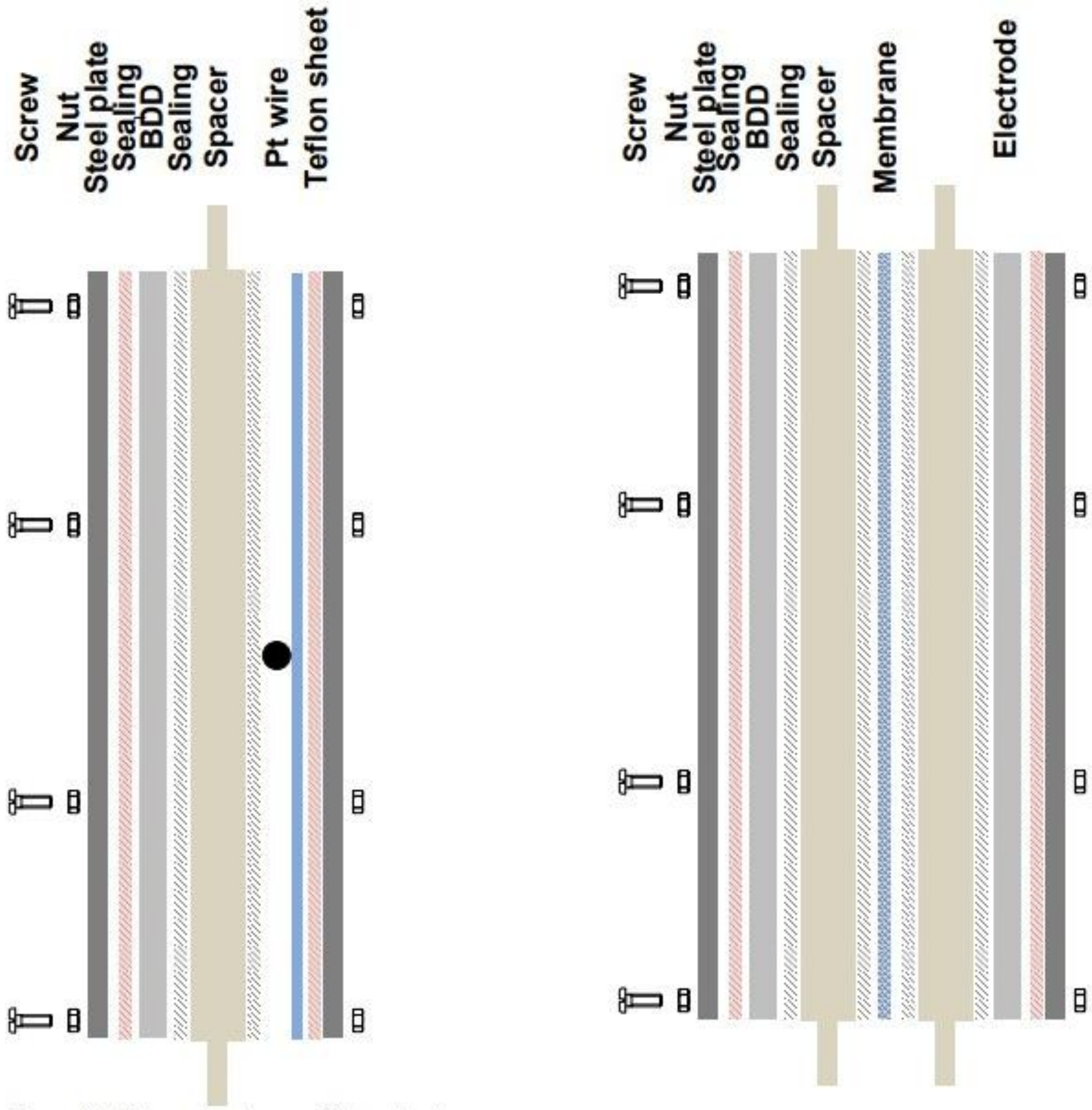


Figure S1: Schematic scheme of the cell setups.

3.1.1 Cell setup 1: Divided flow cell

The compartments of the cell are layered like a sandwich and are pressed together by two screwed steel plates. To isolate the electrodes from the steel plates a sealing (material: Viton, color: red) is used. On this sealing the electrode is placed. A small metal sheet (tantalum sheet with Pt strips) serves as a contact for the planar electrodes. Before and after the spacer (material: PP; color: brown) a sealing (material: EPDM or ePTFE; color: grey lines) is placed. Between the two sealings the membrane (color: blue) is fixated. Both types of membranes (material: Nafion 424 and AEM provided by Ralex) were inlayed a minimum of two days before use in water. After the membrane the sandwich replicates similar.

3.1.2 Cell setup 2: Quasi-divided flow cell

The same sandwich type flow cell is used, despite the double layered spacer and membrane is missing. An ePTFE sheet (color: blue) conduces as an inert back part of the cell and sealing, if a platin wire is used.

3.3 Constitution setup

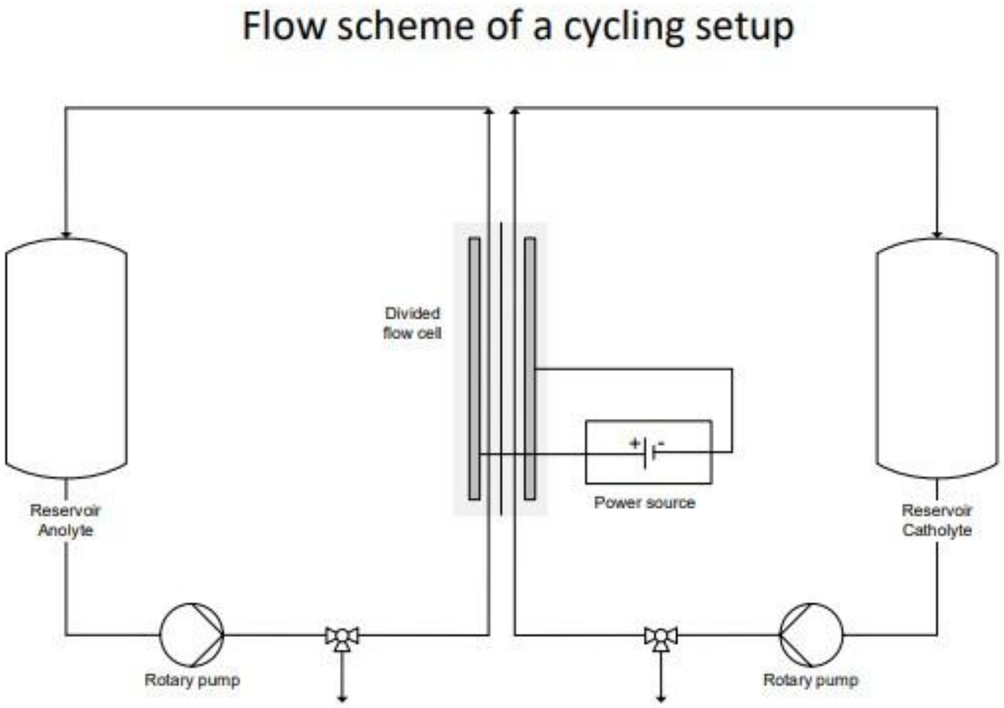


Figure S2: R&D scheme of the experimental setup.

For plumbing 6 mm teflon tubes were used. The rotary pump was a centrifugal pump provided by verder serie V-MD15. The three-way-valve was provided by EM-Technik (material: PP). As a reservoir an open glass vessel was used. The connection of the vessel and Teflon tube was provided from EM-Technik. The connection of rotary pump, Teflon tubing and also cell and Teflon tubeing, was a flexible EPDM tubing fixed by two hose clamps. The power source was provided from Rhode&Schwarz (R&S®HMP4000). As cables standard connectors were used and as clamps served standard clamps.

4 General procedure

4.1 General procedure 1: divided flow setup

The catholyte solution (300 mL of 3% H_2SO_4 or 0.1 M NaOH) was filled in the catholyte reservoir. In the anolyte reservoir the provided industrial wastewater (300 mL) was filled. After starting the rotary pumps, the fluid level on the vessel was marked. If the fluid level got below this level during electrolysis, the difference was refilled with distilled water. After a short time pumping the solution through the chamber, the electrolysis was started. While electrolysis the voltage was checked regularly and noted. In some experiments samples were taken while the experiment in an amount of 2 mL. The volume of both solutions was checked after electrolysis, either by volumetric control or weighting. After every experiment the setup was cleaned by flushing with water and ethanol serval times.

No	Pretreatment	time / min	Anode	cathode	anode area / cm²	cathode area / cm²	applied current	Current density anode A/m2	Average voltage / V	Membrane	anolyte	catholyte	Result catholyte /ppm	Result Anolyte/ ppm	Starting ppm	Difference
1	none	315	BDD	Steel	80	80	1.2 A	150	15	Nafion 424	Wastewater	3% H_2SO_4	8033	102	~10000-12000	
2	none	355	BDD	Steel	80	80	5.0 A --> 1.0 A in 5 steps	625 --> 125	12	Nafion 424	Wastewater	3% H_2SO_4	12384	74	~10000-12000	
3	none	905	BDD	Steel	80	80	5.0 A	625	12	Nafion 424	Wastewater	3% H_2SO_4	9988	10	~10000-12000	
4	none	535	BDD	Steel	80	80	5.0 A --> 1.2 A drop after 2 h	625 --> 150	12	Nafion 424	Wastewater	3% H_2SO_4	7705	88	10000-12000	
5	none	290	BDD	Steel	80	80	1.2 A	150	10	Nafion 424	Wastewater	0.1 M NaOH	1076	4348	6744	1320
6	add NaOH to anolyte before	395	BDD	Steel	80	80	1.2 A	150	9	Nafion 424	Wastewater	0.1 M NaOH	1076	3817	6325	1432
7	add NaOH to anolyte before	345	BDD	Steel	80	80	5.0 A	625	15	Nafion 424	Wastewater	0.1 M NaOH	4397	52	4941	492
8	none	260	BDD	Platin strips	80	15,6	5.0 A	625	13	Nafion 424	Wastewater	0.1 M NaOH	782	576	6287	4929
9	none	775	BDD	Platin strips	80	15,6	5.0 A	626	13	Nafion 424	Wastewater	0.1 M NaOH	1883	1	6728	4844
10	none	290	BDD	Platin strips	80	15,6	1.2 A	150	12	Nafion 424	Wastewater	0.1 M NaOH	1453	671	4640	2516
11	none	400	BDD	Platin strips	80	15,6	1.2 A	150	7	AEM	Wastewater	0.1 M NaOH	41	5180		-5221
12	none	405	BDD	Platin strips	80	15,6	1.2 A	150	7	AEM	Wastewater	0.1 M NaOH	23	4885	5967	1059

Table S1: All divided experiments are listed.

4.2 General procedure quasi divided flow setup

The industrial wastewater (300 mL) was filled into the reservoir and the rotary pump was started. After starting the rotary pumps, the fluid level on the vessel was marked. If the fluid level got below this level during electrolysis, the difference was refiled with distilled water. After a short time pumping the solution through the chamber, the electrolysis was started. While electrolysis the voltage was checked regularly and noted. In some experiments samples were taken while the experiment in an amount of 2 mL. The volume of both solutions was checked after electrolysis, either by volumetric control or weighting. After every experiment the setup was cleaned by flushing with water and ethanol serval times.

Table S2: All undivided (quasi divided) experiments are listed. The listed current density are the current densities of the anode as the working electrode.

No	Pretreatment	Time / min	Anode	Cathode	Anode area / cm^2	Cathode area	Applied current	delta s.a	Current density anode A/m^2	Average voltage / V	Result / ppm	Starting ppm	Difference
1	none	345	BDD	Pt strips	80	15.6 cm^2	2.0 A	5.1:1	250	5,5	3638	6463	2825
2	none	50	BDD	Pt strips	80	6 cm^2	5.0 A	5.1:1	625	7,7	5744	6827	1083
3	none	360	BDD	Pt strips	80	6 cm^2	5.0 A	13.3:1	625	10	40	6910	6870
4	none	1065	BDD	Pt wire	80	3 mm^2	0.5 A	13.3:1	62.5	5	2778	6440	3662
5	none	1060	BDD	Pt wire	80	3 mm^2	5.0 A	13.3:1	625	11	19	6584	6565
6	none	260	BDD	Graphite	80	1 cm^2	5.0 A	80:1	625	16	323	7185	6862
7	acidification with HCl	710	BDD	Pt wire	80	3 mm^2	5.0 A	2666:1	625	11	2	5346	5344
8	acidification with HCl	395	BDD	Pt wire	80	3 mm^2	5.0 A	2666:1	625	12	4	5385	5381
9	acidification with HCl	615	BDD	Pt wire	80	3 mm^2	5.0 A	2666:1	625	12	1	5208	5207
10	acidification with HCl	850	BDD	BDD	80	1 cm^2	5.0 A --> 1.0 A	80:1	625 --> 125	10	286	6318	6032
11	acidification with HCl	850	BDD	BDD	80	1 cm^2	5.0 A --> 1.0 A	80:1	625 --> 125	11	117	6296	6179

5 Pictures of the cell

5.1 Spacer

Figure S3: Front view (left) and side view (right) of the spacer. In and outlets are at the top and the bottom and connected to the pump and vessel; outer dimension 20 cm x 8 cm.

5.2 Stainless steel frame

Figure S4: Stainless steel frame as backbone for the sandwich setup. Holes are for screws and nuts to tighten the setup; outer dimension 22 cm x 10 cm.

6 Analysis

To investigate the mechanism of the mineralization of the tetrabutylammonium further, analyses were performed. Besides the reduction of TBA as such, analyses were performed to watch out for species which could be harmful to the environment.

6.1. Carbon: TOC and organic acids

To determine whether only the TBA content decreases or if there is also a reduction in the total organic content (TOC), an analysis of our Experiment No. 7 from Table S2 was conducted. The results are shown in This description is primarily a well-informed hypothesis, as organic acids are known to undergo reactions during electrolysis, such as in the Kolbe reaction, leading to the formation of carbon dioxide. Consequently, these acids are more likely to react and diminish in concentration during our experiment compared to other carbon structures. However, it is important to note that this remains an assumption.

Table S3. There is a total reduction in the total organic content (TOC) from 20953 mg/L to 4027 mg/L, representing an elimination rate of 80%. This result suggests that not all carbon compounds are converted to carbon dioxide or other gaseous forms. To explore whether the mechanism for the degradation of the butyl chains involves the oxidation of the alkane chains to form organic acids, we also measured the content of organic acids. The results indicate a decrease from 2292 mg/L to 1621 mg/L, reflecting a 30% elimination rate compared to the 80% observed in the TOC. This suggests a degradation mechanism in which the alkane chains are oxidized to organic acids. This finding is promising, as organic acids are generally more biologically degradable than alkane chains. However, there is no certainty that the organic acids detected in the sample at the conclusion of the experiment are not merely the residual organic acids present from the initial conditions. This description is primarily a well-informed hypothesis, as organic acids are known to undergo reactions during electrolysis, such as in the Kolbe reaction, leading to the formation of carbon dioxide. Consequently, these acids are more likely to react and diminish in concentration during our experiment compared to other carbon structures. However, it is important to note that this remains an assumption.

Table S3: Measurements of TOC and organic acids before and after treatment.

Sample	TOC in mg/L	Organic Acids in mg/L
Prior treatment	20953	2292
After treatment	4027	1621

6.2. Nitrogen: TN, NH_4^+, NO_2^-, NO_3^-

To investigate the fate of nitrogen, given that TBA is a quaternary ammonium salt, we measured the same sample for total nitrogen (TN), ammonia, nitrate, and nitrite. The results indicate a total reduction in TN from 287 mg/L to 153 mg/L, reflecting an elimination rate of approximately 50%. This suggests that about 50% of the nitrogen content is emitted during the experiment.

To determine whether nitrogen is released as NOx gases, ammonia, or other forms, we also analyzed ammonia, nitrate, and nitrite levels. While we were unable to conduct an inline gas analysis due to limitations in our laboratory's analytical capabilities, we did not observe any significant increase in nitrite or nitrate after treatment. This finding suggests that a high amount of nitrous gases is not being emitted, which is beneficial for wastewater treatment, as nitrate and nitrite are hazardous compounds in water. The ammonia content increased from 0.5 mg/L to 2.9 mg/L. Although this is a modest increase, it provides insight into the degradation mechanism of the TBA molecule. It indicates that the butyl chain is oxidized to organic acids, while ammonia remains as the nitrogen byproduct, suggesting that carbon may be oxidized first in the process.

Table S4: Measurements of TN, NH_4^+, NO_2^-, NO_3^- before and after treatment.

Sample	TN in mg/L	NH_4^+ mg/L	NO_2^- mg/L	NO_3^- mg/L
Prior treatment	287	0,5	0,05	3,2
After treatment	153	2,9	0,08	3,4

6.3. ESI-HRMS data

Here are the spectra of the detected side products of experiment No.3 of table S2 attached. The range of concentration is in all cases below 50 ppm. The mass 276,24525 and 310,20628 were also detected in normal HPLC-MS measurements. All other masses were not detectable without high resolution mass spectrometry indicating a concentration range in ppb for these side products. In all optimized quasi divided experiments no side products were detected via standard HPLC-MS.

The substance of Figure S6 with the composition $C_{16}H_{36}N_1O_1$ indicates a mono-oxidized form of a intact tetrabutylammonium species. The substances of Figure S7, Figure S9, Figure S11 and Figure S13 with the composition $C_{16}H_{36}N_1Cl_x$, with x=1,2,3 or 4 reveals, that and intact tetrabutylammonium besides oxidation, also gets chlorinated. The substances detected in Figure S8, Figure S10, Figure S12 and Figure S14 with the composition of $C_{16}H_{36}N_1O_1Cl_x$, with x=1,2,3 or 4 shows a intact tetrabutylammonium with a single oxidation and mono or multiple chlorination's. This indicate, that the oxidation and chlorination of the tetrabutylammonium is not selective. The chlorination reaction may result due to the high sodium chloride concentration in the wastewater and radical chlorination reactions. The isotopic ratio appears to be normal, specifically 3:1 for 35Cl to 37Cl.

The majority of substances, apart from those shown in Figure S7 and Figure S11, were not detectable through standard HPLC-MS analysis and were identified only in this unoptimized experiment. Therefore, we assert that these minor traces do not pose a significant environmental impact. However, if such a wastewater treatment is implemented, it is essential to monitor these traces and discuss them with the environmental department.

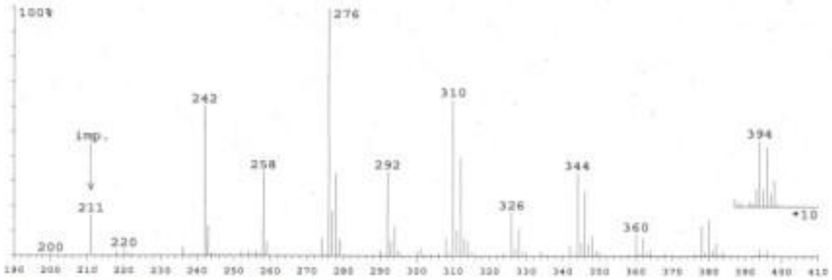


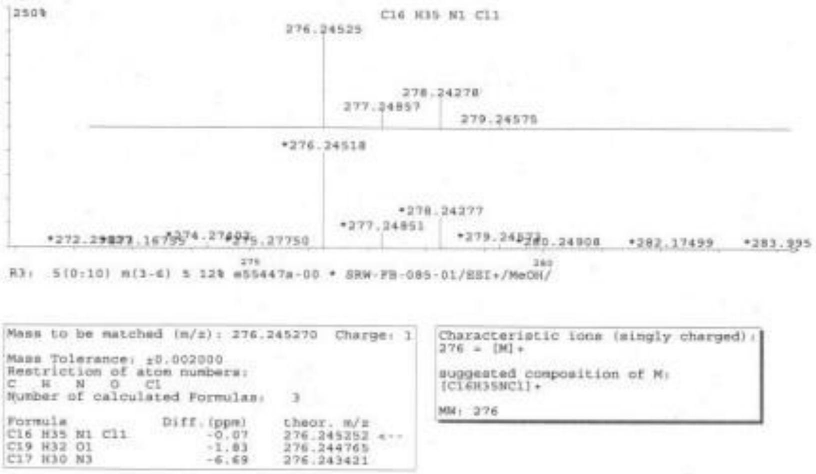
Figure S5: Mass spectra of the HR-ESI-MS.

```
K3:  5(0:10) m(3-6) 5 12% e55447a-00 * SRW-FB-085-01/ESI+/MeOH/
```

```
Mass to be matched (m/z): 258.279170  Charge: 1

Mass Tolerance: ±0.001000
Restriction of atom numbers:
C   H   N   O   Cl
Number of calculated Formulas:   1

Formula              Diff.(ppm)    theor. m/z
C16 H36 N1 O1           -0.12      258.279139 <--
```

```
Characteristic ions (singly charged):
258 = [M]+

suggested composition of M:
[C16H36NO]+

MW: 258
```

Figure S6: Mass spectra of 258,27914.



```
R3:  5(0:10) m(3-6) 5 12% e55447a-00 * SRW-FB-085-01/ESI+/MeOH/
```

```
Mass to be matched (m/z): 276.245270  Charge: 1

Mass Tolerance: ±0.002000
Restriction of atom numbers:
C   H   N   O   Cl
Number of calculated Formulas:   3

Formula            Diff.(ppm)    theor. m/z
C16 H35 N1 Cl1          -0.07    276.245252 <--
C19 H32 O1              -1.83    276.244765
C17 H30 N3              -6.69    276.243421
```

```
Characteristic ions (singly charged):
276 = [M]+

suggested composition of M:
[C16H35NCl]+

MW: 276
```

Figure S7: Mass spectra of 276,24525.

```
R3:  5(0:10) m(3-6) 5 12% e55447a-00 * SRW-FB-085-01/ESI+/MeOH/
```

```
Mass to be matched (m/z): 292.240230  Charge: 1

Mass Tolerance: ±0.001000
Restriction of atom numbers:
C   H   N   O   Cl
Number of calculated Formulas:   2

Formula               Diff.(ppm)    theor. m/z
C16 H35 N1 O1 Cl1          -0.22    292.240167 <--
C19 H32 O2                 -1.88    292.239680
```

```
Characteristic ions (singly charged):
292 = [M]+

suggested composition of M:
[C16H35NOCl]+

MW: 292
```

Figure S8: Mass spectra of 292,24017.

```
R3:  5(0:10) m(3-6) 5 12% e55447a-00 * SRW-FB-085-01/ESI+/MeOH/
```

```
Mass to be matched (m/z): 310.206300   Charge: 1

Mass Tolerance: ±0.002000
Restriction of atom numbers:
C    H    N    O    Cl
Number of calculated Formulas:    4

Formula              Diff.(ppm)    theor. m/z
C16 H34 N1 Cl2            -0.07    310.206279 <--
C19 H31 O1 Cl1            -1.63    310.205793
C9 H26 N8 O4               2.74    310.207150
C17 H29 N3 Cl1            -5.97    310.204449
```

```
Characteristic ions (singly charged):
310 = [M]+

suggested composition of M:
[C16H34NCl2]+

MW: 310
```

Figure S9: Mass spectra of 310.20628.

```
R3:  5(0:10) m(3-6) 5 12% e55447a-00 * SRW-FB-085-01/ESI+/MeOH/
```

```
Mass to be matched (m/z): 326.201260   Charge: 1

Mass Tolerance: ±0.001000
Restriction of atom numbers:
C    H    N    O    Cl
Number of calculated Formulas:    3

Formula              Diff.(ppm)    theor. m/z
C16 H34 N1 O1 Cl2         -0.20    326.201195 <--
C19 H31 O2 Cl1            -1.69    326.200708
C9 H26 N8 O5               2.47    326.202064
```

```
Characteristic ions (singly charged):
326 = [M]+

suggested composition of M:
[C16H34NOCl2]+

MW: 326
```

Figure S10: Mass spectra of 326,20120.

```
R3:  5(0:10) m(3-6) 5 12% e55447a-00 * SRW-FB-085-01/ESI+/MeOH/
```

```
Mass to be matched (m/z): 344.167360   Charge: 1

Mass Tolerance: ±0.002000
Restriction of atom numbers:
C    H    N    O    Cl
Number of calculated Formulas:   10

Formula              Diff.(ppm)    theor. m/z
C16 H33 N1 Cl3            -0.15    344.167308 <--
C12 H22 N7 O5              0.96    344.167691
C13 H28 O10                0.99    344.167700
C19 H30 O1 Cl2            -1.57    344.166821
C9 H25 N8 O4 Cl1           2.38    344.168178
C11 H26 N3 O9             -2.92    344.166356
C10 H20 N10 O4            -2.94    344.166347
C13 H18 N11 O1             4.84    344.169026
C14 H24 N4 O6              4.87    344.169035
C17 H28 N3 Cl2            -5.47    344.165477
```

```
Characteristic ions (singly charged):
344 = [M]+

suggested composition of M:
[C16H33NCl3]+

MW: 344
```

Figure S11: Mass spectra of 346,16451.

```
Mass to be matched (m/z): 360.162320  Charge: 1

Mass Tolerance: ±0.001000
Restriction of atom numbers:
C   H   N   O   Cl
Number of calculated Formulas:   6

Formula                Diff.(ppm)    theor. m/z
C16 H33 N1 O1 Cl3           -0.27    360.162223 <--
C26 H20 N2                  -0.62    360.162097
C12 H22 N7 O6                0.79    360.162606
C13 H28 O11                  0.82    360.162615
C19 H30 O2 Cl2              -1.62    360.161736
C9 H25 N8 O5 Cl1             2.14    360.163092
```

```
Characteristic ions (singly charged):
360 = [M]+

suggested composition of M:
[C16H33NOCl3]+

MW: 360
```

Figure S12: Mass spectra of 362,15945.

```
Mass to be matched (m/z): 378.128420  Charge: 1

Mass Tolerance: ±0.001000
Restriction of atom numbers:
C   H   N   O   Cl
Number of calculated Formulae:   8

Formula                Diff.(ppm)    theor. m/z
C16 H32 N1 Cl4              -0.22    378.128336 <--
C15 H18 N6 O6               -0.50    378.128232
C14 H12 N13 O1              -0.52    378.128223
C12 H21 N7 O5 Cl1            0.79    378.128719
C13 H27 O10 Cl1              0.81    378.128728
C19 H29 O1 Cl3              -1.51    378.127849
C29 H16 N1                  -1.84    378.127724
C9 H24 N8 O4 Cl2             2.08    378.129206
```

```
Characteristic ions (singly charged):
378 = [M]+

suggested composition of M:
[C16H32NCl4]+

MW: 378
```

Figure S13: Mass spectra of 380,12550.

```
R3:  5(0:10) m(3-6) 5 12% e55447a-00 * SRW-FB-085-01/ESI+/MeOH/
```

```
Mass to be matched (m/z): 394.123290  Charge: 1

Mass Tolerance: ±0.001000
Restriction of atom numbers:
C   H   N   O   Cl
Number of calculated Formulas:  11

Formula                  Diff.(ppm)    theor. m/z
C16 H32 N1 O1 Cl4           -0.10      394.123251 <--
C15 H18 N6 O7               -0.36      394.123147
C14 H12 N13 O2              -0.39      394.123138
C26 H19 N2 Cl1              -0.42      394.123125
C12 H21 N7 O6 Cl1            0.87      394.123634
C13 H27 O11 Cl1              0.90      394.123643
C19 H29 O2 Cl3              -1.33      394.122764
C29 H16 N1 O1               -1.65      394.122639
C9 H24 N8 O5 Cl2             2.11      394.124121
C11 H25 N3 O10 Cl1          -2.51      394.122299
C10 H19 N10 O5 Cl1          -2.54      394.122290
```

```
Characteristic ions (singly charged):
394 = [M]+

suggested composition of M:
[C16H32NOCl4]+

MW: 394
```

Figure S14: Mass spectra of 394,12325.