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Assessment of the Electrochemical Synthesis Route to Silicones Starting from Silica as Feedstock

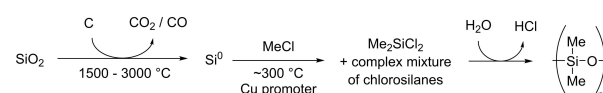Alexander D. Beck,[a, b] Lukas Schäffer,[b] Stefan Haufe,[a] and Siegfried R. Waldvogel*[b]

We successfully achieved methylation of various SiO_2 sources to cyclic methylsiloxanes via electroreduction reaction. Contrary to previous assumptions, the reaction does not start from methanol as methyl radical source, that results in methoxylation of the electrolyte solvent. Methylammonium cations were found to enable the direct conversion, strongly dependent on the radical intermediate stabilization by the electrolyte. THF/$Bu_4NCF_3SO_3$ is the sole applicable system with yields below 14% referred to the methylammonium cations for the highest amount of product obtained so far. Mechanistic insights show that methylation does not occur via the supposed hydrolysis of dimethoxydimethylsilane intermediate, but via a direct conversion reaction, as comparative studies of a Fenton-type procedure clearly indicate. Further, cyclic methylsiloxane products are prone to subsequent electrochemical equilibration, strongly directed by the electrolyte solvent.
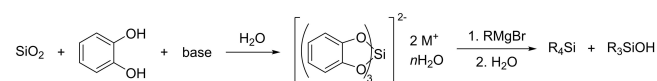
Introduction

Today's society is highly dependent on an important class of materials in numerous areas ranging from common household materials to industrial applications: Silicones. They enable our everyday life and can be found in a wide variety of fields, including appliances,[1,2] automotives and transport,[1,2] ceramics,[3] consumer goods,[1,2,4–6] electronics,[1,2,4,6] glass,[3] mechanical fluids,[1,2,7] medical solutions,[1,2,4–6,8,9] paints and coatings,[1,2,5,7] personal care products,[1,2,4–10] proceeding aids,[1,2,7] and textiles.[1,2] Currently, silicones, with polydimethylsiloxane as one of the most important compounds, are prepared exclusively via a highly energy-intensive route (Scheme 1, a).[11] In this process, SiO_2 is converted to elemental silicon by carbothermal reduction at 1500–3000 °C with the subsequent release of CO_2 and CO.[2,11,12] The metallurgical grade silicon is then reoxidized in the Rochow process with chloromethane under copper catalysis at about 300 °C to a mixture of methylchlorosilanes, mainly dimethyldichlorosilane.[2,3,11–15] Due to the low boiling temperature differences, elaborate distillation over several steps is required.[12] Finally, hydrolysis leads to the
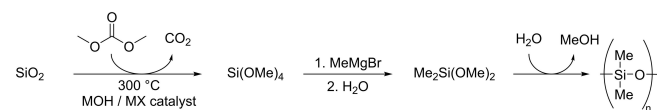
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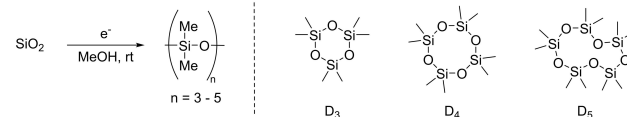   Consortium für elektrochemische Industrie
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Scheme 1. Synthetic strategies for polydimethylsiloxane starting from silica as raw material: a) current industrial process via carbothermic reduction of SiO_2,[2,11,12] followed by Rochow's direct synthesis of methylchlorosilanes and hydrolysis to silicone materials,[2,3,11–15] b) activation of SiO_2 in alkaline environment by catechol to form the respective dianionic hexacoordinated silicon complexes (with M as alkaline earth metal) and subsequent Grignard alkylation and hydrolysis to form silanols for further condensation to silicone materials,[16–18] c) direct alkoxylation of SiO_2 by a thermal carbonate route (with M as alkaline earth metal, X as halogenide) with subsequent Grignard alkylation followed by hydrolysis and condensation to form the respective silicone materials,[12,20–22] d) direct electrochemical reduction of silica as raw material to cyclic methylsiloxanes (D_3–D_5).[15,26–28]

desired polysiloxanes. The use of silica raw material (SiO_2) remains an excellent direct source of silicone feedstock chemicals, due to its high availability and extremely low cost. Yet, the high binding energy of Si–O bonds of 535 kJ/mol requires intense efforts to activate and convert SiO_2.[11]

To circumvent these high bonding strengths and to find a less energy-intensive way, different approaches to activate SiO_2

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have been pursued. The preparation of organosilanes via the transformation of SiO_2 with catechol to dianionic hexacoordinated,[16–18] or ethylene glycol to anionic pentacoordinated silicon complexes,[11,19] was explored (Scheme 1, b). Subsequent alkylation via Grignard routes to silanes and silanols with further condensation led to the respective siloxanes. However, access to industrially relevant mono- and disubstituted silanes remains difficult.[11] Direct alkoxylation of SiO_2 by thermal conversion of carbonates catalyzed with alkali halides or hydroxides at 300 °C under the stoichiometric release of CO_2 has also been reported (Scheme 1, c).[12,20–22] Further, acid induced alkoxylation of silicate starting materials has been demonstrated.[14] While these synthetic protocols need stoichiometric amounts of oxidizers or reducing agents and elevated temperatures, electrochemistry provides an environmentally benign alternative.[23] Reagent waste and stoichiometric CO_2 emission are avoided and by the use of regenerative electricity as a green alternative, this key discipline for future synthesis applications becomes very sustainable.[24] Furthermore, due to simple switch-off, thermal runaway reactions can be prevented, making this technology inherently safe.[25] Using these principles, Chong and co-workers described an electrochemical pathway using methanol and SiO_2 under reductive conditions to afford hexamethylcyclotrisiloxane (D_3), octamethylcyclotetrasiloxane (D_4), and decamethylcyclopentasiloxane (D_5) (Scheme 1, d).[15] However, this publication was retracted due to intellectual property rights concerns, and several patent applications were published about this subject in the same year.[26–28] Since cyclosiloxanes can be further used for the synthesis of linear polydimethylsiloxanes,[5,12] applications and a need are already established. However, the carbothermic reduction and subsequent Rochow process is still the sole utilized industrial access to silicones. Therefore, in this comprehensive study, the crucial reaction conditions, mechanistic aspects, and challenges of the direct electrochemical process are described in more detail to add new insights to the previous concept of the route.

Results and Discussion

The electrochemical direct access to cyclic methylsiloxanes starting from silica as raw materials as described by Chong and co-workers is claimed to proceed via the reductive transformation of methanol (Scheme 2).[15] By a one-electron reduction, methanol is converted to a methyl radical or methoxide species **I**. These highly reactive intermediates lead to methylation or methoxylation of the SiO_2 raw material silica surface **II**. In consecutive steps dimethoxydimethylsilane (DMDMS) **III** as a stable intermediate is formed, which could be detected as a byproduct. Hydrolysis of DMDMS with water formed in situ via esterification of the silica surface or by deprotonation of methanol by the electrochemically generated hydroxide finally leads to the cyclic methylsiloxanes ($D_3–D_5$) **IV**.

Using a supporting electrolyte consisting of MeCN or THF with Bu_4NOTf, suitable electrode materials Pt, Ni–Cr, Ni or graphite were listed, and the silica as raw material is a quartz glass cuvette or quartz sand. Reproduction of the corresponding results has proven to be difficult independent of potentiostatic or galvanostatic reaction conditions, a problem discussed in the literature.[29] Especially, wrapping of the quartz cuvette allows for considerable tolerance of the distance between cathode and SiO_2 substrate, which seems to be crucial for the desired conversion. We therefore decided to change the original electrode arrangement from a vertical to a horizontal design and cover the cathode material with silica sand to achieve the closest possible distance allowing high reproducibility. Furthermore, insoluble materials as quartz sand, fumed silica and quartz wool could be used as SiO_2 source. An aliquot of pre- and post-electrolysis samples of every experiment was analyzed to ensure the influence of electrolysis. The concentrations of the products were calculated based on a GC-MS calibration curve. The yield was calculated based on the number of electrons used for the respective cyclic methylsiloxanes with the assumption of one electron per methyl moiety, due to the previously postulated radical conversion (see Supporting Information).[15]

Screening of electrode materials, inter-electrode gap, type of SiO_2 source, applied current as well as possible supporting electrolyte combinations by galvanostatic conditions revealed, that cyclic methylsiloxanes ($D_3–D_5$) can be accessed by the direct electrochemical route especially by very high current densities (see Supporting Information). Non-stabilized THF needs to be used, due to the radical scavenging properties of butylated hydroxytoluene (as stabilizing component in the stabilized THF). In addition, butylated hydroxytoluene is easier to reduce electrochemically compared to MeOH.

The stabilization of radical species as vital intermediate combined with high cathodic stability, due to the irreversible reduction of methanol at −2.71 V vs. FcH/FcH^+ (Ferrocene/Ferrocenium) at a platinum electrode, show some of the faced requirements to the supporting electrolyte. Yet, calculated yields of the desired products are low and DMDMS could not be detected. The previously postulated supporting electrolyte THF/Bu_4NOTf ($OTf = CF_3SO_3^-$) is so far the sole combination leading to a successful formation of 1.9% yield of cyclic methylsiloxanes exclusively obtained via electrical current. Deviant solvents including the originally described MeCN as well as further cyclic and linear ethers like 1,4-dioxane or 1,2-dimethoxyethane do not yield cyclic methylsiloxanes. THF may be attributed a special role for the desired conversion, among others due to its excellent solubilization properties.[5] In

Scheme 2. The postulated mechanism by Chong and co-workers through the reduction of methanol via methyl radical or via methoxide species, consecutive reaction with silica surface (≡Si–OH) and subsequent reaction to form dimethoxydimethylsilane (DMDMS) as stable intermediate to further hydrolyze with water formed in situ to the respective cyclic methylsiloxanes ($D_3–D_5$).[15]

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addition, the combination with Bu$_4$NOTf is vital for a successful transformation. Further supporting electrolytes were investigated, such as Bu$_4$NClO$_4$, Bu$_3$MeNSO$_4$Me, Bu$_4$NBF$_4$ and Bu$_3$MeNNTf$_2$ (NTf$_2$ = [(CF$_3$SO$_2$)$_2$N]$^-$), which are electrochemically stable and exhibit weak to noncoordinating properties. However, in these cases, the formation of cyclic siloxanes could not be observed. High cathodic stability of the solvent in combination with low coordination of the anion seem to be only some of the requirements for the desired conversion. The stabilization of the reactive intermediate by hydrogen bonding via THF/OTf$^-$ as well as a suitable anodic process in the course of the reaction are needed.

To gain deeper insights into the reaction mechanism and the species involved, we screened different methyl sources for the desired conversion referring to the patent applications.[26–28] Dimethyl carbonate, trimethoxymethane and dimethyl sulfoxide show high cathodic stability, exceeding the range of potential electrochemical stability of the used supporting electrolyte (see Supporting Information). Methyl trifluoromethanesulfonate is prone to hydrolysis with subsequent acidic catalyzed polymerization of the THF electrolyte, leading to exclusion even in strictly anhydrous supporting electrolytes. In presence of iodomethane (Table 1, entry 1) as well as trimethylsulfonium iodide (Table 1, entry 2) the cyclic methylsiloxanes could be detected although the yield is comparable to the results for methanol (Table 1, entry 3). This observation is surprising because the use of deuterated methanol did not lead to deuterated cyclic methylsiloxanes as one would expect (Table 1, entry 4). In fact, the product quantity, distribution, and species were identical to the use of non-deuterated methanol (Table 1, entry 3). The same results were achieved by application of further linear alcohols like ethanol. Instead of the formation of cyclic ethylsiloxanes, that should be accessible using the described direct pathway, cyclic methylsiloxanes were obtained (Table 1, entry 5). As the methanol content was reduced, the yield of cyclic methylsiloxanes increased to a maximum of 9.2 % yield in the absence of methanol (Table 1, entry 6). With the reasonable assumption that methanol does not serve as source of methyl for the desired product formation as initially claimed, also solvent decomposition was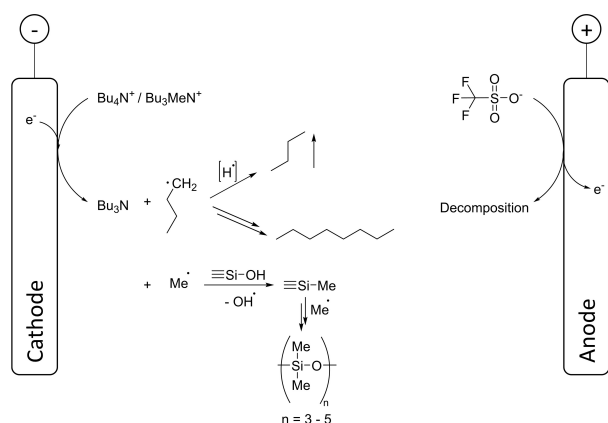 ruled out as a source of intermediates (Table 1, entry 7). Again, no deuterated cyclic methylsiloxanes were detected, which inevitably focuses attention on the supporting electrolyte. In fact, the amount of cyclic methylsiloxanes increases with higher concentration of the supporting electrolyte. This can be raised to a maximum of 0.4 M Bu$_4$NOTf, resulting in a yield of 13.7 % with D$_4$ as the main product (Table 1, entry 8).

In the presence of methanol, a comparable trend is obtained, yet the increase of (D$_3$–D$_5$) is considerably reduced, reaching 3.1 % yield for 0.4 M Bu$_4$NOTf. Methanol, instead of being the source of methyl radical for cyclic methylsiloxanes,[30] leads to the methoxylation of solvent, as the side reaction to 2-methoxytetrahydrofuran shows. Although methanol should be more easily reduced than the supporting electrolyte, due to the low selectivity of this process, Bu$_4$NOTf is still one of the main substrates reductively converted. So, by electrochemical reduction of Bu$_4$NOTf in THF-d$_8$ in the presence of 0.2 M methanol, Bu$_3$N with 24 % yield is obtained after application of 0.5 F. In the absence of methanol the yield of Bu$_3$N is raised to 30 %. Subsequent formation of butane and octane can be detected, indicating a butyl radical species to dimerize or abstract hydrogen (Scheme 3). Cyclic butylsiloxanes could not be traced, due to the increased steric requirements and lower stabilization by THF compared to methyl radicals. However, the dimerization reveals the access to radical species via the reduction of the supporting electrolyte. The formation of methyl radicals as essential intermediates result in the activation of the SiO$_2$ surface and subsequent conversion (see below), as can be implemented by the reductive conversion (Scheme 3). Analytical investigation of the supporting electrolyte Bu$_4$NOTf by multiple NMR techniques revealed contamination by a methylated ammonium cation. Bu$_3$MeN$^+$ appears to act as the methyl source for the electrochemical methylation with 4.3 %. The use of further ammonium triflate supporting electrolytes (R$_4$N$^+$ OTf$^-$), did not lead to the desired cyclosiloxanes, clearly indicating the necessity of methylated ammonium cations. However, attempts to increase the yield of cyclic methylsiloxanes using different methylated ammonium supporting electrolytes failed, due to the high requirements for the supporting electrolyte anions (see Supporting Information).

Table 1. Screening of methyl sources for the direct electrochemical conversion of silica raw material to cyclic methylsiloxanes.
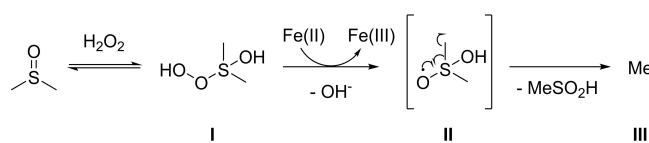
Entry	Conditions[a]	Methyl source[b]	Yield in [%] and [µmol] of		
			D$_3$[c]	D$_4$[c]	D$_5$[c]
1	Standard	MeI	0.0 (0.0)	0.6 (0.0)	0.5 (0.0)
2	Standard	Me$_3$S$^+$ I$^-$	0.8 (0.1)	1.7 (0.1)	1.4 (0.1)
3	Standard	MeOH	0.8 (0.1)	0.6 (0.0)	0.5 (0.0)
4	Standard	MeOH-d$_3$	0.8 (0.1)	0.6 (0.0)	0.5 (0.0)
5	Standard	EtOH	0.8 (0.1)	0.6 (0.0)	0.5 (0.0)
6	Standard	–	0.8 (0.1)	4.7 (0.3)	3.7 (0.2)
7	THF-d$_8$	–	0.8 (0.1)	4.7 (0.3)	3.7 (0.2)
8	Standard[d]	Bu$_4$NOTf (0.4 M)	2.9 (0.8)	6.3 (1.4)	4.5 (0.8)

[a] Reaction conditions: tetrahydrofuran as solvent with 0.1 M Bu$_4$NOTf supporting electrolyte, the anode is a platinum gauze, the cathode is a platinum wire emerged in 1.0 g quartz sand at room temperature, the inter-electrode gap is 2 mm, without stirring, current density of 6.6 A/cm^2, applied charge of 0.5 F, under argon inert gas atmosphere. [b] Concentration of substrates: 0.2 M, except otherwise noted. [c] Yield calculated based on the number of electrons used for the respective cyclic methylsiloxanes with the assumption of one electron per methyl moiety with Bu$_3$MeN$^+$ as methyl source, referenced to a GC-MS calibration curve. [d] The amount of supporting electrolyte differs from standard conditions, due to the application as methyl source, with an applied charge of 0.3 F.

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Scheme 3. Proposed mechanism for the methylation of SiO$_2$ raw material via the reduction of the supporting electrolyte cation (Bu$_4$N$^+$/Bu$_3$MeN$^+$) to a radical species and subsequent formation of butane and octane or methylation of the SiO$_2$ surface with following conversion to cyclic methylsiloxanes and simultaneous anodic decomposition of the supporting electrolyte anion.

Scheme 4. Mechanism for the formation of free methyl radicals by the Fenton-type oxidation of DMSO by H$_2$O$_2$/Fe(II).[34,35]

Especially halide ions show a disturbing effect on the desired conversion by slight oxidation and scavenging effects.[31] However, the low availability of the actual methyl source and the radical side reactions as observed for butyl radicals could be the reason for the poor yield of target substrates as well as an explanation for an optimal amount of applied charge in catalytic amounts. Chong and co-workers mentioned an ideal amount of applied charge well below 1.0 *F*, based on a presumably electrochemically initiated, subsequently catalyzed reaction.[15] Screening of the applied charge indicated 0.3 *F* as ideal for the desired conversion, which is consistent with the findings of Chong and co-workers, here due to the limited access of a suitable methyl source combined with the radical side reactions. It should be noted, that in the absence of methanol instead of the formation of 2-methoxytetrahydrofuran, anodic decomposition of the supporting electrolyte anion to a sulfur and fluorine containing brown solid occurs. Hence, reusability of the electrolyte for further inves-

tigations is prevented, rendering the ecological advantage of the desired process doubtful.

Analogue to the electrochemical conversion, we investigated possibilities to initiate the generation of free methyl radicals via chemical routes. The corresponding activation and conversion of SiO$_2$ raw materials should achieve conversion to cyclic methylsiloxanes comparable to the electrochemical route. Using Fenton-type reaction conditions, the generation of free methyl radicals via the oxidation of dimethyl sulfoxide (DMSO) by a H$_2$O$_2$/Fe(II) system has been reported.[32–35] It is supposed that in the course of the reaction DMSO is oxidized by H$_2$O$_2$ to the peroxo intermediate **I**, subsequently reduced by Fe(II) with elimination of hydroxide to the respective radical species **II**, to yield the free methyl radical species **III** (Scheme 4).

Using analogue reaction conditions to previous studies,[34,35] we were able to convert quartz sand as silica source to the desired cyclic methylsiloxanes at room temperature via the formation of free methyl radicals. However, Fe(II) and a concentrated H$_2$O$_2$ solution (30%) were mandatory as well as the SiO$_2$ source for the favored activation and conversion, yielding the cyclic methylsiloxanes (Table 2, entries 1–4). The yield could be increased by using fumed silica, due to the very high surface area of 130–170 m^2/g and the hydrophobic properties enabling easier access for methyl radicals. As has been mentioned in literature, the surface of SiO$_2$ is a key aspect to stabilize methyl radicals,[36] simplifying the consecutive reaction to cyclic methylsiloxanes. Since the surface of the used fumed silica is modified by dimethylsiloxy groups, an additional positive influence through "pre-methylation" is conceivable. Yet, the yield remains low with 1.2% D$_3$–D$_5$ (Table 2, entry 5).

Table 2. Chemical conversion of SiO$_2$ via the free methyl radical pathway using the DMSO/peroxide/Fe(II) system.

Entry	Conditions[a]	Peroxide[b]	Yield in [%] and [μmol] of		
			D$_3$[c]	D$_4$[c]	D$_5$[c]
1	No Fe(II)	H$_2$O$_2$	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
2	No SiO$_2$	H$_2$O$_2$	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
3	Standard	None	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
4	Standard	H$_2$O$_2$	0.1 (0.9)	0.3 (2.1)	0.1 (0.5)
5	Standard[d]	H$_2$O$_2$	0.2 (1.8)	0.8 (5.3)	0.2 (1.1)
6	Standard	K$_2$S$_2$O$_8$	0.1 (0.9)	0.2 (1.4)	0.1 (0.5)
7	Standard[d]	K$_2$S$_2$O$_8$	0.1 (0.9)	0.4 (2.7)	0.2 (1.1)
8	Standard	*t*BuOOH	0.1 (0.9)	0.1 (0.7)	0.1 (0.5)
9	Standard[d]	*t*BuOOH	0.1 (0.9)	0.2 (1.4)	0.1 (0.5)
10	Standard[e]	H$_2$O$_2$	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)

[a] Reaction conditions: anhydrous FeCl$_2$ (0.5 mmol, 63 mg, 0.5 equiv.) and quartz sand (1.0 g) in 3 mL anhydrous DMSO under argon inert gas atmosphere, peroxide is added under stirring and extraction of cyclic methylsiloxanes with n-pentane after 24 h at room temperature. [b] Addition of H$_2$O$_2$ (30%, 5 mmol, 511 μL, 5 equiv.), K$_2$S$_2$O$_8$ (anhydrous, 5 mmol, 1352 mg, 5 equiv.) or *t*BuOOH = *tert*-butyl hydroperoxide (anhydrous in decane, 5 mmol, 250 μL, 5 equiv.). [c] Yield calculated based the amount of peroxide referenced to a GC-MS calibration curve. [d] Fumed silica (Wacker HDK H-15) was used instead of quartz sand. [e] TEMPO = (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (5 mmol, 781 mg, 5 equiv.) is applied.

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Side reactions to the favored generation of cyclic methylsiloxanes could be detected. Due to the locally high radical concentration, dimerization of methyl radicals occurred at the beginning of the reaction as well as subsequent oxidation of DMSO to the stable dimethyl sulfone. In addition to the H_2O_2 approach in aqueous media, anhydrous systems could be used by the implementation of appropriate peroxides. Potassium persulfate and tert-butyl hydroperoxide, as anhydrous solution in decane, resulted cyclic methylsiloxanes, although the yield of the H_2O_2 system remains the highest so far (Table 2, entries 6, 8). Again, the use of fumed silica leads to a slightly increased yield compared to quartz sand as the SiO_2 source (Table 2, entries 7, 9). The product distribution indicates the formation of D_4 as the main product, independent of the used peroxide and the source of SiO_2. This is explained by the lower ring tension of the formed cyclic system and the higher Si–O bond energy in comparison to D_3,[37] which is in agreement with previous electrochemical experiments. There,[32,34,35] the use of TEMPO for scavenging of free methyl radicals leads to disruption of the desired reaction pathway (Table 2, entry 10) confirming the free radical pathway.

These investigations clearly support the hypothesis of a free methyl radical reaction pathway. However, DMDMS could not be detected, neither in the course of the electrochemical synthesis, nor by the chemically initiated radical methylation. In the preparation of cyclic siloxanes via the DMSO route in anhydrous conditions, the hydrolysis of DMDMS can be excluded, yet cyclic methylsiloxanes are obtained. To further support this theory, we added different concentrations of water to DMDMS as a substrate in the electrolyte at room temperature. Regardless of the water concentration, no cyclic siloxanes could be detected that should form due to the hydrolysis reactions (see Supporting Information). Therefore, the process involves direct methylation of the SiO_2 surface and conversion toward cyclic methylsiloxanes (Scheme 3), the thermodynamic optimum of which determining the ring size.

As mentioned before the cyclic methylsiloxanes D_4 and D_5 represent the thermodynamic optimum of this product class, due to the low ring tension and the high Si–O bond energy (see above).[37] However, in the course of our investigations, we discovered that the cyclic systems, especially D_3 can be electrochemically equilibrated to elongated ring structures. The

catalytic effects of electrolyte, platinum surfaces and temperature, could be excluded by boiling D_3, D_4 and D_5 in the electrolyte under current-less conditions. The equilibration occurred only via electrochemical conversion. A cathodic process could be observed by using divided cells, although the reductive stability of cyclic methylsiloxanes exceeds that of the supporting electrolyte (see Supporting Information). Furthermore, the amount of applied charge needed for the respective equilibration is in the range of 0.2–1.0 F, indicating catalytic activity and an influence on the reaction by the supporting electrolyte. As expected D_4 and D_5, as the most stable substrates, show only minor conversion (Table 3, entries 1, 2). D_3 is converted to D_4–D_6 (Table 3, entry 3). While the equilibration to D_4 and D_5 is anticipated, D_6 is the main product starting from D_3, contra intuitive to its stability, due to the ring tension. This finding might involve a radical process of the cyclic methylsiloxane further dimerizing to D_6. This trend can be similarly observed with further supporting electrolytes, generating D_6 as the main product. A direct influence by intermediate species generated via the decomposition of the supporting electrolyte anion can be ruled out (Table 3, entries 4, 5). However, the role of the solvent used for the electrochemical conversion is vital for the stabilization of the intermediates. Using MeCN as solvent, similarly to the direct methylation of SiO_2 raw materials, the stabilization of radical species is significantly reduced, shifting D_6 to a side product and favoring the formation of D_4 (Table 3, entries 6–8).

Conclusion

We critically investigated the direct electrochemical conversion of silica as raw materials to silicones regarding reaction conditions, mechanistic aspects, and challenges. The direct methylation of SiO_2 materials has been achieved via electrochemical conversion, however, the desired pathway demands specific requirements of the used supporting electrolyte. High electrochemical stability, good stabilization of methyl radical species and low coordination by the supporting electrolyte anion are crucial. Methanol does not result in the release of methyl radicals during conversion as claimed by previous studies, but in the methoxylation of THF electrolyte solvent.

Table 3. Equilibration of the cyclic methylsiloxanes D_3–D_5 via the electrochemical conversion.[a]

Entry	Educt	Electrolyte	Yield in [%] and [mmol] of			
			D_3[b]	D_4[b]	D_5[b]	D_6[b]
1	D_5	THF, Bu$_4$NOTf	0 (0.0)	7 (0.1)	93 (1.9)	0 (0.0)
2	D_4	THF, Bu$_4$NOTf	0 (0.0)	98 (2.0)	2 (0.0)	0 (0.0)
3	D_3	THF, Bu$_4$NOTf	46 (0.9)	15 (0.3)	8 (0.2)	31 (0.6)
4	D_3	THF, Bu$_4$NClO$_4$	34 (0.7)	14 (0.3)	15 (0.3)	37 (0.7)
5	D_3	THF, Bu$_4$NBF$_4$	57 (1.1)	13 (0.3)	6 (0.1)	24 (0.5)
6	D_3	MeCN, Bu$_4$NOTf	0 (0.0)	66 (1.3)	24 (0.5)	10 (0.2)
7	D_3	MeCN, Bu$_4$NClO$_4$	47 (0.9)	30 (0.6)	8 (0.2)	15 (0.3)
8	D_3	MeCN, Bu$_4$NBF$_4$	61 (1.2)	21 (0.4)	5 (0.1)	13 (0.3)

[a] Reaction conditions: 5 mL of anhydrous solvent with 0.1 M supporting electrolyte, cyclic methylsiloxanes (2 mmol, 0.4 M, 1.0 equiv.), anode and cathode are platinum, at room temperature, inter-electrode gap is 5 mm, without stirring, current density of 10 mA/cm², applied charge of 0.2 F, under argon inert gas atmosphere. [b] Yield determined by NMR referenced to TMS.

Contrary, methylated ammonium cations can be used as a methyl source for the methylation of SiO_2 via cathodic transformation. Similarly, the methylation of SiO_2 is achieved by the direct chemical access via Fenton-type conditions using a DMSO/Fe(II)/peroxide mixture to obtain cyclic methylsiloxanes in low yields. Dimethoxydimethylsilane is not a prerequisite intermediate for the desired conversion as anticipated. Methylation of the SiO_2 surface occurs via direct activation with subsequent conversion to the cyclic methylsiloxanes. However, cyclic methylsiloxanes can be easily electrochemically equilibrated, with the used solvent determining the product ring size.

Experimental Section

Synthesis of material: All described experiments were performed under argon inert gas atmosphere (< 0.1 ppm O_2 and < 0.1 ppm H_2O content). For screening experiments an undivided (25 mL) glass cell for the electrolysis was used. The active surface of the respective used platinum wire cathode was $0.009\,cm^2$, the geometric measurements of the platinum gauze anode were 20 mm in diameter. The separation of the electrode surfaces could be varied and was screened in the course of the project. The software used was IKA Labworldsoft 6.0. The glass cell compartment of the horizontal design was charged with 10 mL of a 0.1 M solution of Bu_4NOTf in THF (not stabilized by butylated hydroxytoluene). Methanol (81 µL, 2.0 mmol, 1.0 equiv.) was added and the cathode was placed in the glass cell compartment. The cathode was covered by quartz sand (1.0 g, 40–80 µm diameter), the anode was added, and both connected to the IKA power supply. As a blank sample, 0.3 mL of the reaction mixture was taken and filtered with n-pentane over silica gel and analyzed by a calibrated GC-MS method. Afterwards the reaction was conducted at room temperature without stirring. After termination of the electrolysis ($j = 6.6$ A/cm^2, 0.5 F), a second aliquot of the reaction mixture was taken and filtered with n-pentane over silica gel and analyzed by a calibrated GC-MS method.

Characterization

NMR Spectroscopy of ^{1}H, ^{13}C and ^{29}Si spectra were recorded at 25 °C, using a Bruker Avance 500 (500 MHz, Analytische Messtechnik, Karlsruhe, Germany). Chemical shifts (δ) are reported in parts per million (ppm). Traces of CH_2Cl_2 in the corresponding deuterated solvent, or tetramethylsilane for ^{29}Si spectra were used as internal standard for calibration.

GC-MS measurements were carried out on an Agilent GC-A6890N using a HP-5 column (Agilent Technologies, Santa Clara, California), length: 30 m, inner diameter: 0.25 mm, film: 0.25 µm, carrier gas: helium. The chromatograph was coupled to a mass spectrometer Agilent MSD 5975C (Agilent, Santa Clara, California, USA).

Detailed information on general procedures, electrochemical conversions, cyclic voltammetry measurements and product characterization can be found in the Supporting Information.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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