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New Aspects in the Electrochemical Polymerization of Organosilicon Compounds

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The replacement of sacrificial anodes by two new types of anodes—a silicon carbide and a hydrogen electrode—allows the electrochemical coupling of organohalosilanes without formation of metal chlorides. Methylated and phenylated mono- and dichlorosilanes were electrolyzed, using the new anodes in an undivided cell, with a constant current supply and with THF/HMPA/Et_4NBF_4 as the solvent/electrolyte system.

Introduction

The merit of polysilanes as precursors to silicon carbide based ceramics as well as starting materials for the production of photoresists and thermochromic materials[1] has stimulated research to find alternatives to alkali-metal reduction. Although we discovered the electrochemical polymerization of organohalosilanes in 1976,[2,3] only in the last 5 years has interest been growing for this new method for Si–Si bond formation. Several papers have now been published on this subject.[4–7] Up to now, however, the only possible anode reaction was the formation of metal chlorides by oxidation of a sacrificial anode, such as aluminum, magnesium, mercury, or copper. We now have succeeded in finding two new types of anodic reactions: the formation of chlorinated organic products by use of a silicon carbide rod and, more important, the generation of HCl by means of a modified hydrogen anode.

$$2R_3SiCl + H_2 \xrightarrow{\text{2 faradays}} R_3SiSiR_3 + 2HCl$$

Results and Discussion

Hengge and Litscher[2] carried out the first electrolyses in a divided, H-shaped cell, with a mercury anode, 1,2-dimethoxyethane (DME)/Bu_4NClO_4 as the solvent/electrolyte system, and trimethylchlorosilane as the substrate. Hexamethyldisilane was formed nearly quantitatively:

$$\text{cathode: } 2Me_3SiCl + 2e^- \rightarrow Me_3Si\text{–}SiMe_3 + 2Cl^-$$

$$\text{anode: } 2Cl^- + 2Hg \rightarrow Hg_2Cl_2 + 2e^-$$

To investigate the applicability of this new method, several other methylated and phenylated chlorosilanes were examined. They led to the corresponding di- and oligosilanes in high yield. Hengge and Firgo[3] continued this work and succeeded in the electrolysis of fluorine-containing chlorosilanes to obtain di- and oligosilanes without destruction of the C–F bond:

$$2(p\text{-F-}C_6H_4)_3SiCl \xrightarrow[-2Cl^-]{+2e^-} (p\text{-F-}C_6H_4)_3SiSi(p\text{-}C_6H_4\text{-F})_3$$

$$2(p\text{-F-}C_6H_4)_2CH_3SiCl \xrightarrow[-2Cl^-]{+2e^-} (p\text{-F-}C_6H_4)_2CH_3SiSiCH_3(p\text{-}C_6H_4\text{-F})_2$$

$$4(p\text{-F-}C_6H_4)_2SiCl_2 \xrightarrow[-8Cl^-]{+8e^-} [(p\text{-F-}C_6H_4)_2Si]_4$$

As shown by Dunoguès and his co-workers,[4] electrolysis in a simple, undivided cell with a stainless steel cathode and an aluminum or a magnesium anode simplifies the method while obtaining comparable results. We followed this method and carried out electrolyses with a mixture of THF and hexamethylphosphoric triamide (HMPA)—or HMPA alone—as the solvent and Et_4NBF_4 as the supporting electrolyte in a concentration of 0.02 mol/L. In accordance with Dunoguès we observed the formation of polymeric, completely insoluble polydimethylsilane when dimethyldichlorosilane was added to the solvent in a concentration of about 5 mol/L. However, decreasing the concentration of the starting material (0.5–0.8 mol/L) leads to the generation of decamethylcyclopentasilane and dodecamethylcyclohexasilane as the main reaction products. Diphenyldichlorosilane is different in that octaphenylcyclotetrasilane is the main reaction product, irrespective of the concentration in the reaction mixture, and polymeric material is formed only in negligible amounts. This is also remarkable, because the usual Wurtz synthesis always yields a mixture of four-, five-, and six-membered rings.

Variations of the solvent/electrolyte system (DME/Bu_4NBF_4, THF/$LiClO_4$) or the anode material (Cu, Ag, or Pt), were reported by several Japanese groups.[5–7] For example, Nonaka et al. electrolyzed dimethyldichlorosilane with addition of Me_3SiCl or Ph_3SiCl in a divided cell with DME/Bu_4NBF_4 as the solvent/electrolyte system and Pt plates as the anode and cathode. They obtained poly-

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Table 1. Electrolyses with the SiC Anode

chlorosilane	Cl trapping agent	product	% current yield
Me_3SiCl	THF/HMPA	$Me_3SiSiMe_3$	65
Me_3SiCl	cyclohexene	$Me_3SiSiMe_3$	52
Me_2SiCl_2	THF/HMPA	$-(Me_2Si)_n-$	27[a]
Ph_2SiCl_2	THF/HMPA	$[Ph_2Si]_4$	9
Me_2SiCl_2/Ph_2SiCl_2	THF/HMPA	$-[(Me_2Si)_{4.5}(Ph_2Si)]_n-$	13
$MePhSiCl_2$	THF/HMPA	$-(MePhSi)_n-$	10

[a] Partially siloxanized (oxygen content <3%).

(dimethylsilane) with R_3Si–terminal groups (R = Me, Ph).[7b] Replacing Pt by Al electrodes and using an undivided cell, they obtained polydimethylsilane in high current efficiency, even if no monochlorosilane was added.[7c] Electrolyses of $MePhSiCl_2$,[5,7a] Ph_2SiCl_2,[7a] and mixtures of various mono- and dichlorosilanes[6,7b] yielded the corresponding oligo- and polysilanes, depending on the silane concentration and the electrode/solvent/electrolyte system.

Silicon Carbide Anode. The technical applicability for all the aforementioned systems is rather restricted, as the formation of large amounts of metal chlorides raises the problem of their disposal. Therefore, we sought new anode materials. Hengge and Litscher[2] already reported that graphite is unsuitable because of passivation that occurs after a short time. As silicon was very interesting to us, we first tried silicon/aluminum alloys and silicon, doped with traces of different metals. However, the easily oxidizable components formed metal salts and the conductivity decreased continuously, whereas the silicon remained unchanged.

Searching for a silicon compound with good conductivity and high oxidation potential, we investigated silicon carbide. It turned out to be completely stable against oxidation, but in contrast to the case for sacrificial anodes, DME and dimethylformamide (DMF) are not suitable as solvents. On electrolysis without controlled potential, the SiC anode/stainless steel cathode system adapts to a different potential range and the solvent decomposes; no Si–Si bond formation is observed. However, with a mixture of THF and HMPA (or HMPA alone) several methyl- and phenyl-containing chlorosilanes were successfully electrolyzed (Table 1).

The cathodically formed chlorine now seaks a new reaction partner, which is the solvent, if no other chlorine trap is present. Thus, chlorinated products of THF and HMPA were detected by GC/MS analysis. Further isolation of these product mixtures was not carried out. However, to improve the method and to synthesize specific chlorinated products, we added cyclohexene as a chlorine trap in an electrolysis of trimethylchlorosilane (Table 1). Hexamethyldisilane now was formed in a lower yield (52%) due to the formation of 3-cyclohexenyltrimethylsilane as a byproduct (11%). Obviously, the chlorination of cyclohexene leads to two different products (Figure 1), and the 3-chlorocyclohexene formed reacts with the starting material to form 3-cyclohexenyltrimethylsilane, which was identified by GC/MS analysis.

Hydrogen Anode. These problems initiated the search for a reagent that would intercept the chlorine without formation of a reactive species. Finally, we found the proton—generated by anodic oxidation of hydrogen—to be ideal, forming easily removable HCl. Modification of the well-known normal hydrogen electrode led to the construction shown in Figure 2. The required precious metal (Pd or, more commonly, Pt) is coated on a cylindrical graphite block. Hydrogen is admitted into the center of the block by means of a copper tube. Due to the high porosity of the graphite, the hydrogen reaches the metal film well dispersed, thus having a maximum reaction surface. Although a small part of the generated hydrogen chloride is dissolved in the solvent—probably being reduced and thus diminishing the current yield—most of it is swept away with the excess hydrogen. The amount can easily be detected by absorption in a silver nitrate solution and subsequent determination of the silver chloride formed by potentiometric titration with KCl (Table 2).

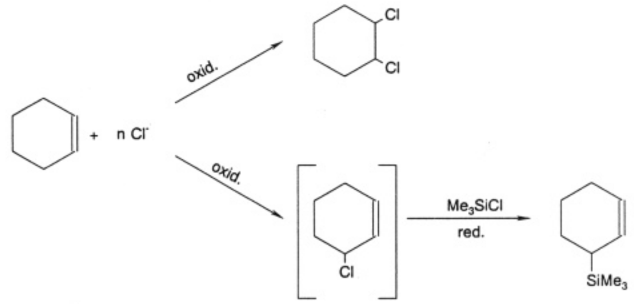

Figure 1. Reaction products of cyclohexene, detected by GC/MS analysis.

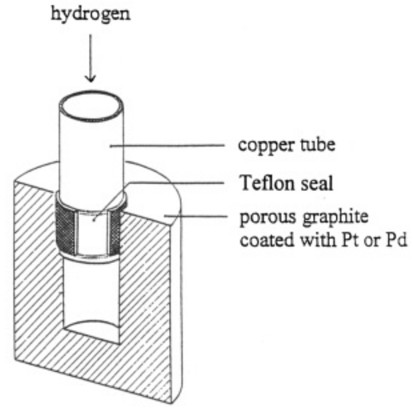

Figure 2. Hydrogen electrode.

Table 2. Electrolyses with the Hydrogen Anode

chlorosilane	solvent	product	% current yield
Me_3SiCl	THF/HMPA	$Me_3SiSiMe_3$	73
Me_2SiCl_2	THF/HMPA	$-(Me_2Si)_n-$	35

Cyclic Voltammetry. Electrolysis of a 1/1 mixture of Me_2SiCl_2 and Ph_2SiCl_2 with the SiC anode led to the formation of a polymer with a Ph/Me ratio of 1/4.5 (Table 1). This result was surprising in that Umezawa and his co-workers reported that Ph_2SiCl_2 can be reduced at a potential less negative than for Me_2SiCl_2.[7] Therefore, one would expect a Ph/Me ratio of the product >1, as electrolyses are carried out without controlled potential. In order to check this point, we thought cyclic voltammetry to be a suitable method. To determine the reliability of the chosen three-electrode system (platinum anode and cathode and a Ag/Ag^+ double-junction reference electrode) we recorded the well-known voltammogram of ferrocene. As the oxidation and reduction peaks (0.5 and 0.1 V vs. SCE) were in complete accordance with the literature,[8] we started to investigate several methyl- and phenyl

Table 3. Reduction Potentials E_p of Methyl- and Phenylchlorosilanes[a]

	Me_3SiCl	Ph_3SiCl	Me_2SiCl_2	$MePhSiCl_2$	Ph_2SiCl_2
E_p (V)	−0.1	−0.2	0.5/−0.7	0.4/−0.5	−0.2/−0.9

[a] Referenced to the saturated calomel electrode.

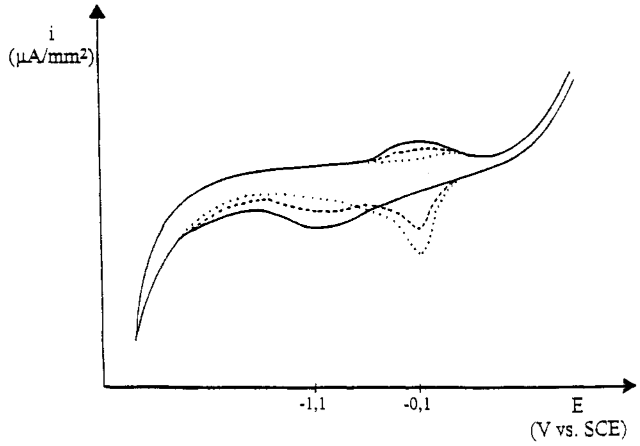

Figure 3. Cyclic voltammograms of Me_3SiCl before (···) and after the addition of 10^{-3} mol/L (- - -) or 6 × 10^{-3} mol/L (—) of water.

containing chlorosilanes (Table 3). To ensure that our measurements were not disturbed by water, HCl, or siloxane byproducts, all silanes were freshly distilled and freeze/thaw-degassed prior to use. The water content of the solvent was repeatedly checked by Karl Fischer titration to be below 20 ppm.

As the reduction potential of Me_3SiCl seemed rather high, we wanted to ensure that the observed voltammograms do not correspond to the reduction of HCl. Thus, we copied the experiment of Corriu[9] and added water to the solution of Me_3SiCl in DME. What we noticed was the appearance of a broad reduction peak at −1.1 V, whereas the peak at −0.1 V vanished. Obviously, this new peak corresponds to the reduction of HCl formed by hydrolysis, whereas the initial peak correlates with the reduction of the silane (Figure 3).

Our results (Table 3) showed that the phenylchlorosilanes are reduced at a potential more negative than for the methylchlorosilanes. This is in contrast to Umezawa's results, but he used steady-state voltammetry and a divided cell for his measurements.

Of interest is the appearance of two reduction peaks in the case of the dichlorosilanes, which may be assigned to the consecutive reactions of the two chlorine atoms (Figure 4). A more detailed study of this is currently in progress.

Experimental Section

General Methods. Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) (Fluka "purum") were dried by refluxing over sodium/potassium alloy or potassium, respectively, for several days. (The water content of DME was checked by Karl Fischer titration to be below 20 ppm.) Hexamethylphosphoric triamide (HMPA) (Aldrich) was purified by refluxing over CaO for several hours and subsequently distilling from sodium at about 4 mm pressure. Et_4NBF_4 (Fluka "purum") and Bu_4NClO_4 (Fluka "purissimum") were dried under vacuum at 50 °C for 2 days. The silanes, supplied by Wacker Chemie GmbH, were distilled prior to use.

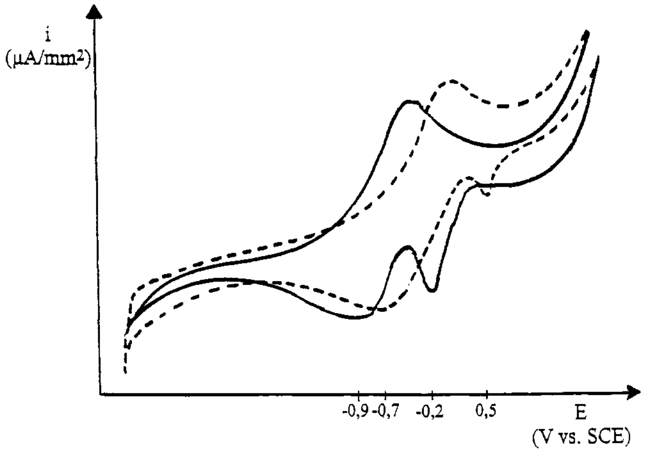

Figure 4. Cyclic voltammograms of Me_2SiCl_2 (- - -) and Ph_2SiCl_2 (—) (scan rate 100 mV/s).

Cyclic Voltammetry. All voltammograms were performed with a Wenking POS 73 potentioscan and recorded with a Kipp and Zonen BD8 flatbed recorder. The three-electrode system consists of a platinum anode and cathode and a double-junction reference electrode (0.001 M $AgClO_4$ (0.1 M Bu_4NClO_4) in DME/Ag wire). A 25-mL portion of a 0.1 M solution of Bu_4NClO_4 in DME is introduced into the cell, and the silane is added in a concentration of 2 × 10^{-3} mol/L by means of a syringe.

General Procedure for the Electrolysis. A constant current supply was afforded by a Wenking ST 72 potentiostat. Electrolysis is carried out in an undivided cell with the anode in the center and a cylindrical cathode, made of stainless steel, around it. Et_4NBF_4 is dissolved in a concentration of 0.02 mol/L in a 1/1 mixture of THF and HMPA, and 100 mL of this solution is introduced into the cell under a dry nitrogen atmosphere. After addition of the silane in concentrations of 5–10 mol/L, electrolysis is carried out at a constant current density of 0.5–1 mA/cm² for a certain period, thus defining the amount of electricity passed. The current yield was calculated as reported by Dunoguès[10] and is given in parentheses.

(a) In the case of the aluminum electrode, we examined the influence of the concentration of the starting material on the reaction products. Decreasing the silane concentration to 0.5–0.8 mol/L, we obtained cyclic compounds instead of polymeric material.

(b) In the case of the SiC anode, the chlorination products of THF, HMPA, and cyclohexene were not isolated but were detected by GC/MS analysis.

(c) In the case of the hydrogen anode, HCl is detected as follows: to remove traces of silicon compounds, the escaping H_2/HCl mixture is cooled to about −60 °C and subsequently led into 0.1 M $AgNO_3$. The amount of the AgCl precipitate formed is determined by potentiometric titration with 0.1 M KCl.

Trimethylchlorosilane. Method b_1. A 0.79-mol amount was electrolyzed for 24 h; i = 75 mA. Repeated distillation of the reaction mixture yielded 3.19 g of hexamethyldisilane (65%).

Method b_2. After addition of 20 mL of cyclohexene, 0.70 mol of Me_3SiCl was electrolyzed for 24 h; i = 75 mA. GC/MS analysis showed a disilane/cyclohexenylsilane ratio of 5/1; repeated distillation yielded 2.55 g of hexamethyldisilane (52%). Isolation of 3-cyclohexenyltrimethylsilane was not carried out.

Method c. A 0.57-mol amount was electrolyzed for 40 h; i = 50 mA. Distillation led to 3.99 g of hexamethyldisilane (73%).

MS and ^{29}Si data were identical with those reported in the literature.

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Dimethyldichlorosilane. Method a. A 0.080-mol portion was electrolyzed for 40 h; *i* = 50 mA. GC/MS analysis showed a 3/1 ratio of dodecamethylcyclohexasilane (Si_6Me_{12}) and decamethylcyclopentasilane (Si_5Me_{10}). After removal of the solvent and excess Me_2SiCl_2 under vacuum, the brownish, oily residue was mixed with 50 mL of acetone; filtration, washing, and drying yielded 0.25 g of white Si_6Me_{12} (15%). NMR and MS data were identical with those reported in the literature. Isolation of Si_5Me_{10} was not effected.

Method b. A 0.66-mol portion was electrolyzed for 23 h; *i* = 150 mA. The yellow precipitate was filtered, washed with THF and MeOH, and dried to obtain 1.02 g of white, insoluble poly(dimethylsilane) (27%). IR: 1247, 1035 (Si–O), 830, 740, 722, 628, 358 cm^{-1}. Anal. Calcd for $(SiC_2H_6)_n$: Si, 48.29; C, 41.31; H, 10.40. Found: Si, 46.93; C, 39.93; H, 10.72. The oxygen content of the polymer is less than 3%.

Method c. A 0.51-mol portion was electrolyzed for 12 h; *i* = 58 mA. After filtration, washing, and drying 0.26 g of white, insoluble poly(dimethylsilane) was isolated (35%). IR: 1240, 830, 740, 730, 625, 350 cm^{-1} (no Si–O). Anal. Calcd for $(SiC_2H_6)_n$: Si, 48.29; C, 41.31; H, 10.40. Found: Si, 47.49; C, 41.25; H, 10.46.

Diphenyldichlorosilane. Method b. A 0.60-mol portion was electrolyzed for 40 h; *i* = 75 mA. The yellowish precipitate was filtered, washed with THF, and dried to obtain 0.91 g of white octaphenylcyclotetrasilane (9%), identified by IR spectroscopy.[11] MS data were also identical with those reported in the literature.

Methylphenyldichlorosilane. Method b. A 0.56-mol portion was electrolyzed for 38 h; *i* = 61 mA. The volatile components were removed under vacuum, the residue was added to 500 mL of MeOH, and the precipitate was filtered, followed by reprecipitation from 2-propanol and THF to yield 0.51 g of white poly(methylphenylsilane) (10%). The product is soluble in toluene, $CHCl_3$, and CCl_4. ^{29}Si NMR (δ; $CDCl_3$): −34.53 (SiMe), −39.10, −39.69, −40.99 (SiPh). ^{13}C NMR (δ; $CDCl_3$): 137.13, 135.75, 134.01, 133.73, 130.02, 128.45 (phenyl ring carbons), −5.68 (br, SiMe). IR data were identical with those reported by Trujillo.[12]

Coelectrolysis of Dimethyl- and Diphenyldichlorosilane. Method b. A 100-mL portion of a 1/1 mixture (v/v) of Me_2SiCl_2 and Ph_2SiCl_2 was electrolyzed for 44 h; *i* = 80 mA. After removal of the volatile compounds MeOH was added; filtration and reprecipitation yielded 0.68 g of poly(dimethylsilane-*co*-diphenylsilane) (13%). The overall Me/Ph ratio was calculated from the relative intensities of the H_{alkyl} and H_{aryl} peaks of the ^{1}H NMR spectrum, thus leading to a stoichiometric form of $[(Me_2Si)_{4,5}(Ph_2Si)]_n$. ^{29}Si NMR (δ; $CDCl_3$): −32.3 (SiMe), −36.3, −37.2 (SiPh). ^{13}C NMR (δ; $CDCl_3$): 136.3, 135.7, 128.5, 127.8 (phenyl ring carbons), −3.7 to −2.1 (br, SiMe). ^{1}H NMR (δ; $CDCl_3$): 7.27 (phenyl ring protons), 0.4 to −0.2 (SiMe). Anal. Calcd for $(SiC_{3.81}H_{6.72})_n$: Si, 34.84; C, 56.76; H, 8.40. Found: Si, 32.00; C, 54.58; H, 8.22. IR data were comparable to those reported by Sartori et al.[13]

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