Silicon carbide was synthesized from mixtures of SiO2 and graphite by applying the concept of the FFC-Cambridge process and several fundamental aspects of the synthesis route were investigated. Porous disks composed of powders of SiO2 and graphite in molar ratios of 1:0.5, 1:1 and 1:1.5 were prepared by sintering in inert atmosphere and subjected to electro-deoxidization in molten CaCl2 at 1173 K under a range of experimental conditions. Disks of molar ratio 1:1.5, reduced at an applied voltage of 2.8 V for a duration of 6 h, yielded exclusively phase-pure SiC of nanowire morphology as the reaction product, while the other precursor compositions provided significant amounts of calcium silicides. Voltages lower than 2.8 V gave mixtures of SiC with elemental Si and graphite, and voltages higher than that gave CaSi alone. Shorter electro-deoxidation times led to incomplete reduction and allowed for the identification of CaSiO3 as a transient phase. Based on the experimental results a multipath reaction mechanism is proposed, consisting of the electrochemical reduction of SiO2 and CaSiO3 to Si and the subsequent in-situ carbonization of the Si formed to SiC. The effect of N2 at high temperature on the electrochemically synthesized SiC was investigated and the formation of nanowire Si3N4 was observed. Overall, the process presented was a facile single-step and low-temperature method for the synthesis of SiC with possible commercial prospects.

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depending on whether they are written in one step,

\[
\text{SiO}_2 + 4 \text{e}^- + \text{C} = \text{SiC} + 2\text{O}^2- \quad E_{1173K}^0 = 0.999 \text{ V vs. Ca/Ca}^{2+} \quad [2]
\]

or in two steps,

\[
\text{SiO}_2 + 4 \text{e}^- \rightarrow \text{Si} + 2\text{O}^2- \quad E_{1173K}^0 = 0.837 \text{ V vs. Ca/Ca}^{2+} \quad [3]
\]

\[
\text{Si} + \text{C} \rightarrow \text{SiC} \quad [4]
\]

The undesired cathodic reactions are characterized by the involvement of calcium from the electrolyte. These include the deposition of Ca, the in-situ reaction of Ca\(^{2+}\) ions with SiO\(_2\) to calcium silicides such as CaSi and Ca\(_2\)Si, and the in-situ reaction of Ca\(^{2+}\) ions with C to calcium carbide CaC\(_2\).

\[
\text{Ca}^{2+} + 2 \text{e}^- \rightarrow \text{Ca} \quad E_{1173K}^0 = 0 \text{ V vs. Ca/Ca}^{2+} \quad [5]
\]

\[
\text{SiO}_2 + \text{Ca}^{2+} + 6 \text{e}^- \rightarrow \text{CaSi} + 2\text{O}^2- \quad E_{1173K}^0 = 0.783 \text{ V vs. Ca/Ca}^{2+} \quad [6]
\]

\[
\text{SiO}_2 + 2 \text{Ca}^{2+} + 8 \text{e}^- \rightarrow \text{Ca}_3\text{Si} + 2\text{O}^2- \quad E_{1173K}^0 = 0.651 \text{ V vs. Ca/Ca}^{2+} \quad [7]
\]

Ca\(^{2+}\) discharge on a SiO\(_2\)-containing cathode will take place at potentials far less negative to that on an inert cathode such as W or Mo. Qualitatively, this has already been demonstrated by Jin et al.\(^{25}\) and Xiao et al.\(^{26}\) in cyclic voltammetric studies on the electro-deoxidation of pure SiO\(_2\), although there is only vague information about the precise voltages at which such reactions dominate. Ca\(^{2+}\) discharge on a pure containing cathode is also thermodynamically possible at potentials less negative than that on an inert cathode. This has been confirmed experimentally by Fan et al.\(^{13}\) and Peng et al.\(^{27}\) while it has been claimed by Dai et al.\(^{14}\) that graphite does not react cathodically with Ca\(^{2+}\). Fig. 1 illustrates schematically the competing reactions that are possible under cathodic polarization of SiO\(_2\)/C samples in a CaCl\(_2\) melt.

\[
\text{Si} + \text{Ca}^{2+} + 2 \text{e}^- \rightarrow \text{CaSi} \quad E_{1173K}^0 = 0.673 \text{ V vs. Ca/Ca}^{2+} \quad [9]
\]

\[
\text{Si} + 2 \text{Ca}^{2+} + 4 \text{e}^- \rightarrow \text{Ca}_2\text{Si} \quad E_{1173K}^0 = 0.464 \text{ V vs. Ca/Ca}^{2+} \quad [10]
\]

In view of the above, Ca\(^{2+}\) discharge on a SiO\(_2\)-containing cathode will take place at potentials far less negative to that on an inert cathode such as W or Mo. Qualitatively this has already been demonstrated by Jin et al.\(^{25}\) and Xiao et al.\(^{26}\) in cyclic voltammetric studies on the electro-deoxidation of pure SiO\(_2\), although there is only vague information about the precise voltages at which such reactions dominate. Ca\(^{2+}\) discharge on a pure containing cathode is also thermodynamically possible at potentials less negative than that on an inert cathode. This has been confirmed experimentally by Fan et al.\(^{13}\) and Peng et al.\(^{27}\) while it has been claimed by Dai et al.\(^{14}\) that graphite does not react cathodically with Ca\(^{2+}\). Fig. 1 illustrates schematically the competing reactions that are possible under cathodic polarization of SiO\(_2\)/C samples in a CaCl\(_2\) melt.

Si\(_3\)N\(_4\)-bonded SiC composites are of considerable interest due to their attractive mechanical and thermal properties.\(^{28}\) Si\(_3\)N\(_4\) is conventionally produced by nitridation of a mixture of Si and SiC through heating in N\(_2\) gas at temperatures where the nitridation of silicon is thermodynamically favored over the nitridation of Si\(_3\)N\(_4\).\(^{28}\)

\[
3 \text{Si} (s) + 2 \text{N}_2 (g) = \text{Si}_3\text{N}_4 (s) \quad \Delta G_{1473K}^0 = -269.642 \text{ kJ/mol} \quad [11]
\]

\[
3 \text{SiC} (s) + 2 \text{N}_2 (g) = \text{Si}_3\text{N}_4 (s) + 3 \text{C} (s) \quad \Delta G_{1473K}^0 = -89.817 \text{ kJ/mol} \quad [12]
\]

The objective of the current study has been to investigate the electrochemical synthesis of SiC with the aims of optimizing precursor composition, understanding the cathodic reactions, and correlating product morphology with process conditions. A further goal has been to examine the nitridation behavior of the electrochemically prepared SiC and to identify the composition and morphology of the product.

**Experimental**

Powders of SiO\(_2\) (99% purity, 0.5–5 \(\mu\)m, Sigma Aldrich) and graphite (<20 \(\mu\)m, Sigma Aldrich) were mixed in the molar ratios of 1:0.5, 1:1 and 1:1.5. The mixtures were made into slurries by adding isopropanol together with 1 mass% of polyvinyl alcohol and 0.5 mass% of polyethylene glycol as binder and plasticiser. The slurries were ground in a ball mill and dried at 373 K in air. The process was repeated several times so as to attain a uniform powder mixture. The dry powder was uniaxially pressed into disks of 0.5 g in mass and 13 mm in diameter. The disks were sintered at 1523 K in a stream of Ar with 5 vol% H\(_2\) for 3 h to provide sufficient strength for further processing. The open porosities of the disks were measured by Archimedes’ method.

Anhydrous CaCl\(_2\) was obtained from CaCl\(_2\)·2H\(_2\)O (Sigma Aldrich) by drying at 423 K in air and then at the same temperature in vacuum for 48 h. The dried CaCl\(_2\) was loaded into an alumina crucible that was placed inside a gastight Inconel retort with provision for the insertion of electrodes from the top. The retort was brought to the operating temperature of 1173 K and constantly flushed with Ar. The CaCl\(_2\) melt was subjected to pre-electrolysis at 2.8 V for several hours, using a Ni coil as the cathode and a high-density graphite rod (Tokai Carbon, UK), degassed at 400 K in vacuum for 12 h, as the anode, until all redox-active impurities had been removed. A sintered SiO\(_2\)/graphite disk, tied with Ni wire, was employed as the cathode in the electro-deoxidation, using the same graphite anode as before. A Ni/NiO assembly was used to monitor the potentials of the individual electrodes.\(^{29}\) The SiO\(_2\)/graphite disks were subjected to electro-deoxidation under different experimental conditions, including (i) cathodes of three compositions as detailed above, (ii) applied voltages of 2.5, 2.8 and 3.1 V, and (iii) process durations of 20 min, 3 h and 6 h, all as compiled in Table I. Cyclic voltammetry was carried out with a W wire as an inert working electrode and with a graphite rod as a reactive working electrode. All potentials were quoted with respect to the Ca/Ca\(^{2+}\) potential. This was identified by extrapolating the linear region of the cathodic branch to zero current, thus eliminating any ambiguity originating from the gradual increase of the current prior to Ca deposition due to electronic conduction through the polarized melt.\(^{30}\)

After completion of each experiment, the electrodes were lifted above the melt and cooled to room temperature. The products were thoroughly rinsed with distilled water until free from salt and dried in vacuum at room temperature. The crystallographic phases, microstructures and elemental compositions of the samples before and after electro-deoxidation were identified by X-ray diffraction analysis (XRD) (Phillips PW 1830), scanning electron microscopy (SEM) (FEI Nova NanoSem 450) and energy-dispersive X-ray spectroscopy.
Table I. Electro-deoxidation experiments of SiO2/graphite disks carried out in CaCl2 melt at 1173 K under argon.

| Experimental conditions | Voltage and time | Residual oxygen |
|-------------------------|------------------|-----------------|
| SiO2:graphite (in moles) |                  | Phases formed   |
| 1:1                     | 2.5 V for 6 h    | graphite (M), Si (SH), SiC (m) 16,300 ppm |
| 1:1                     | 2.8 V for 6 h    | SiC (M), Si5C3, CaSi, Ca2Si - |
| 1:1                     | 3.1 V for 6 h    | CaSi - |
| 1:1.5                   | 2.5 V for 6 h    | graphite (M), SiC (SH) 81,400 ppm |
| 1:1.5                   | 2.8 V for 6 h    | SiC - |
| 1:1.5                   | 3.1 V for 6 h    | CaSi 13.20 % |
| 1:0.5                   | 2.8 V for 6 h    | CaSi (M), SiC (SH), Ca2Si (trace) - |
| 1:1.5                   | 2.8 V for 20 min | graphite (M), SiO2 (M), CaSiO3 (SH) - |
| 1:1.5                   | 2.8 V for 3 h    | graphite (M), SiO2 (M), SiC, CaCO3 (m) - |

M - major, SH - second highest, m - minor.

Figure 2. Cyclic voltammograms with W as the working electrode on the cathodic side and with high-density graphite as the working electrode on the anodic side in CaCl2 melt at 1173 K at a scan rate of 20 mV/s. Graphite rods and Ni coils were used as the counter electrodes in the former and latter cases, respectively. Ni/NiO was used as the reference electrode.

(EDX) (Bruker X Flash 61100). In selected cases, the reduced samples were further characterized by transmission electron microscopy (TEM) (FEI Tecnai G2-F20). The residual oxygen content of the reduced samples was determined with the hot extraction method (ELTRA ONH 2000).

The effect of N2 at elevated temperature on the electrochemically prepared SiC was investigated by heating a SiC sample of about 20 mg under a continuous flow of N2 of 100 mL/min at 1473 K for 8 h, and subsequently studying the phase composition and morphology of the reaction product. The thermokinetic behavior was examined by subjecting a SiC sample of 200 mg to simultaneous thermogravimetric analysis and differential scanning calorimetric analysis (TA Instruments) using a heating rate of 20 K/min from 298 to 1473 K in a stream of N2.

Results and Discussion

Electrochemical behavior of graphite during cathodic polarization in CaCl2 melt.—Fig. 2 shows cyclic voltammograms recorded in a CaCl2 melt, with a W working electrode on the cathodic side, and with a high-density graphite working electrode on the cathodic and anodic sides. The reduction of Ca2+ on W was found to begin at 0.00 V, which confirmed its inertness. In contrast, appreciable reduction on graphite progressed from +1.059 V onwards. The Ca2+ discharge on graphite at potentials less negative to that on W may be attributed to the formation of Ca-C compounds, most likely CaC2, as expressed in Eq. 8. Based on the present results, graphite has to be considered a reactive electrode when polarized cathodically in a CaCl2 melt. Comparing the linear regions of the cathodic branches of the cyclic voltammograms, the electrochemical window of CaCl2 in the presence of a graphite electrode is lower by ∼450 mV than in the presence of an inert electrode.

In line with the observations of the present study, Fan et al.13 and Peng et al.27 likewise suggested the formation of CaC2 from graphite and Ca2+ during cathodic polarization in a CaCl2 melt. In contrast, Dai et al.14 found in cyclic voltammetry studies with a metallic cavity electrode at 1123 K that graphite did not react with Ca2+ during cathodic polarization in CaCl2 but behaved more like an inert electrode.

Sintering behavior and microstructure of SiO2/graphite mixtures.—SiO2/graphite disks, made from mixtures of the SiO2 and graphite powders in the molar ratios of 1:0.5, 1:1 and 1:1.5 and sintered at 1523 K in Ar with 5 vol% H2 for 3 h, possessed open porosities of about 40%. Figs. 3a–3c show the XRD patterns of the SiO2 and graphite powders along with that of a sintered SiO2/graphite disk of molar ratio 1:1.5. The peaks at 20 = 20.95°, 26.73° and 50.20° seen in the XRD patterns for the pure SiO2 and the sintered SiO2/graphite mixture originate from the diffractions of the (100), (011) and (112) planes of quartz, and those at 26.5° and 54.6° in the XRD pattern for the pure graphite and the sintered SiO2/graphite mixture are from the (002) and (004) planes of graphite. The XRD analysis confirms that the starting materials were phase pure and that, in line with thermodynamic expectations, they underwent no reaction during sintering.

Figs. 3d–3i show SEM images and EDX spectra of the SiO2 and graphite powders. The micrographs reveal that the SiO2 consisted of particles of irregular morphology with size in the range of 0.15–5 μm, while the graphite consisted of particles of flaky morphology with size in the range of 2–12 μm; and the elemental analysis confirmed that there were no significant impurities. Figs. 4a–4f show SEM images of the cross-sections from the sintered SiO2/graphite disks of the three different compositions. The two types of particles can be clearly identified by their morphologies and compositions, evidencing that they formed an intimate near-uniform mixture. Elemental maps for Si, O and C of selected regions from the cross-sections are given in Fig. S1 (Supplementary Material).

Electro-deoxidation of SiO2/graphite mixtures.—Electro-deoxidation of SiO2/graphite of molar ratio 1:1 at different voltages.—SiO2/graphite disks of molar ratio 1:1 were subjected to electro-deoxidation at applied voltages of 2.5, 2.8 and 3.1 V for durations of 6 h in order to investigate the effect of polarization. The current vs. time curves are shown in Fig. S2. The results of the XRD analysis of the three products are compiled in Table 1. At 2.5 V, Si and SiC were observed together with unreacted graphite. At 3.1 V, only CaSi was found. At the intermediate voltage of 2.8 V, SiC was

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Figure 3. XRD patterns of (a) as-received SiO_2 powder, (b) as-received graphite powder, and (c) SiO_2/graphite disk (molar ratio 1:1.5) sintered at 1523 K in Ar with 5 vol% H_2 for 3 h. (d) SEM image and (e) high-resolution SEM image of SiO_2 powder with (f) corresponding EDX analysis. (g) SEM image and (h) high-resolution SEM image of graphite powder with (i) corresponding EDX analysis.

the major phase, but minor amounts of Si_5C_3, CaSi and Ca_2Si were also present.

The XRD analysis thus demonstrates that, at the low voltage, all SiO_2 was electro-deoxidized, and even though some SiC was formed, its rate of formation was low so that not all graphite was consumed. At the high voltage, undesired reactions involving Ca prevailed. At the intermediate voltage, the complete consumption of the graphite was achieved, but Ca-based by-products were formed. The results therefore indicate that equal quantities of SiO_2 and graphite are insufficient to arrive at a stoichiometric SiC product, presumably because some graphite is lost due to side reactions.

Electro-deoxidation of SiO_2/graphite of molar ratio 1:1.5 at different voltages.—Based upon the above findings, SiO_2/graphite disks of molar ratio 1:1.5 were subjected to electro-deoxidation at applied voltages of 2.5, 2.8 and 3.1 V for durations of 6 h. The current vs. time and cathode potential vs. time curves are shown in Figs. 5a, 5b. In all three cases, the currents initially peaked and then declined toward stable residual values, thus indicating the progression of the cathodic reactions. As expected, the current was higher at higher voltage, while the main characteristics of the curves were similar. The cathode potentials vs. Ca/Ca^{2+} evolved with distinct features that could be directly correlated with the current behavior. The potentials shifted in the more negative direction with increasing reaction time, with stable values reached faster at higher voltage.

The three products obtained after electro-deoxidation were all in the form of powder, as seen from the insets of Fig. 5a. The XRD patterns of the products are shown in Figs. 5c–5e and the phases identified are given in Table I. At 2.5 V, the product was a mixture of SiC and graphite, and at 3.1 V, the product was again pure CaSi. At 2.8 V, however, phase-pure SiC was now obtained. The SiC existed in its cubic β modification, with the peaks at 35.5°, 41.1°, 60.0° and...
Figure 4. SEM images of cross-sections of SiO$_2$/graphite disks of molar ratios (a) 1:0.5 (b) 1:1 and (c) 1:1.5, sintered at 1523 K in Ar with 5 vol% H$_2$ for 3 h, showing SiO$_2$-rich and graphite-rich regions. (d), (e), (f) High-resolution SEM images with EDX analyses of the indicated areas.

71.6° stemming from the diffractions of its (111), (200), (220) and (311) planes. It has been reported that β-SiC forms preferentially at process temperatures below 1973 K while the α-type prevails at higher temperatures.$^{31}$

Figs. 6a–6f show SEM images of the three products. The microstructure of the product at 2.5 V contained wire-like entities with lengths from a few tens to a few hundreds of nanometers (Figs. 6a, 6d). EDX analysis revealed that they were composed of Si and C, thereby suggesting them to be SiC. In addition, some flaky particles with diameters of a few micrometers were observed that were similar to those in the SiO$_2$/graphite precursor before processing (Figs. 6a, 6d, Fig. S3). EDX analysis confirmed them to be from carbon, thereby identifying them as unreacted graphite. The microstructure of the product at 3.1 V contained comparatively bulky particles with diameters in the range of several micrometers (Figs. 6c, 6f, Fig. S4). EDX analysis showed them to consist of primarily Ca and Si, thus identifying them as CaSi. Neither SiC nanowires nor graphite flakes were present, and the significant charging during imaging was because of the sample’s poor electronic conductivity. Significant levels of O were found (Fig. S5), which were likely due to absorption of and reaction with water in the washing step. The microstructure of the product at 2.8 V was very different (Figs. 6b, 6e), featuring exclusively SiC nanowires. Fig. 7 shows a low-magnification SEM image of the sample, along with the EDX elemental maps for Si and C and a typical EDX analysis. A small quantity of oxygen of about 2.7 mass% was found too. Fig. 8 shows a high-resolution TEM image that clearly indicates the nanoscopic nature of the SiC with good crystallinity and an average particle size of about 20–30 nm. The lattice spacing was measured as approximately 0.25 nm for the SiC (111) plane (inset in Fig. 8) which is coincident with literature values.$^{21,22}$

The occurrence of the different reaction products can be readily understood in view of Eqs. 2 to 8. An applied voltage of about 2.8 V is required to ensure a sufficiently fast formation of the SiC, including the electro-deoxidation of the SiO$_2$ to Si and its in-situ reaction with the graphite in the cathode. However, at this voltage the formation of CaC$_2$ through the reaction of the graphite in the cathode with Ca$^{2+}$ ions from the electrolyte is not negligible, and this leads to a partial consumption of the graphite. The arising Si surplus then manifests itself in the formation of Si$_5$C$_3$ as a carbon-deficient silicon carbide and of CaSi and Ca$_2$Si, as seen with the SiO$_2$/graphite disks of molar ratio 1:1. This notion was further corroborated by electro-deoxidation experiments with SiO$_2$/graphite disks of molar ratio 1:0.5 under otherwise the same conditions (Fig. S6). In such a cathode, the carbon deficit exists straight from the beginning, and the main compound found in the reduced samples was CaSi (Table I). Consequently, to achieve stoichiometric SiC, a sufficient excess of graphite in the SiO$_2$/graphite precursor is necessary to compensate for its partial loss as CaC$_2$. Usefully, CaC$_2$ reacts with water in the washing step and does not accrue as a by-product in the cathode.
Figure 5. (a) Current vs. time curves and (b) cathodic potential vs. time curves during electro-deoxidation of SiO2/graphite disks (molar ratio 1:1.5) in CaCl2 melt at 1173 K for 6 h at 2.5, 2.8, and 3.1 V. Insets in (a) show photographs of the three products. (c), (d), (e) XRD patterns of the products obtained at the three different voltages.

The above would also explain the observation of a carbon loss, or the need of a carbon surplus, in related studies. For example, in the preparation of ZrC from ZrO2, an excess of carbon was required to achieve a phase-pure product, and in the preparation of HfC from HfO2, a small loss of carbon happened during the process. The effect may be further compounded by the large difference in particle size of the SiO2 and the graphite in the present case, as this leads to longer diffusion distances in the in-situ reaction of Si with carbon and enhances the possibility of carbon loss via side reactions. For example, in the preparation of Cr7C3 from Cr2O3, the use of large carbon particles led to a slow rate of carbonization, while in the preparation of NbC from Nb2O5, the use of carbon nanoparticles improved the extent of carbonization.

Electro-deoxidation of SiO2/graphite of molar ratio 1:1.5 for different durations.—In order to investigate the nature of any transient phases occurring in the course of the reduction of SiO2 in the presence of graphite, partially reduced samples were prepared, by subjecting SiO2/graphite disks of molar ratio 1:1.5 to electro-deoxidation at an applied voltage of 2.8 V for durations of only 20 min and 3 h. Figs. 9a, 9b show the current vs. time and the cathodic potential vs. time curves from these experiments along with curves from a 6 h run.

The product obtained after 20 min was in the form of a disk, and that after 3 h was a powder, as seen from the insets of Fig. 9a. Figs. 9c, 9d show the XRD patterns of the 20 min and 3 h samples, respectively, and demonstrate that the main transient phase was CaSiO3 and that its amount diminished as the amount of SiC product grew.

Fig. 10a shows a low-resolution SEM image of the cross-section of the sample obtained after 20 min of electro-deoxidation, and Fig. 10b shows SEM image of a smaller area of this cross-section, in which the interface between two separate regions can be clearly discerned. As seen from Figs. 10c, 10d, one region had bulky morphology with particles of SiO2 and carbon similar to that in the starting material, indicating that practically no reduction had taken place here, while the other region had SiC nanowires together with large particles and flakes, indicating that reduction had commenced but remained incomplete. Separate SEM images of these regions with their dissimilar microstructures are shown in Fig. S7, and an EDX analysis further indicated that the partially reduced regions still had significant quantities of oxygen. Figs. 10e, 10f show the microstructure of the sample.
obtained after 3 h of electro-deoxidation. The individual particles were identified as SiO2, graphite and CaSiO3, and the amount of SiC nanowires had increased compared with the shorter experiment. Further SEM images and an EDX analysis are shown in Fig. S8.

**Mechanistic considerations.**—Ideas about the reaction mechanism of the electro-deoxidation of SiO2 in the presence of graphite in a CaCl2 melt can be derived from the transient phases, Si and CaSiO3, found in some of the experiments. The following reaction sequences are conceivable.

**Direct reduction of SiO2.**—The transient presence of free elemental Si in the cathode, in combination with an amount of SiC, in the experiments at low applied voltage indicates that the electro-deoxidation of SiO2 directly to Si is one of the reactions occurring. This is then followed by the in-situ reaction of the Si with C to SiC.

\[
\text{SiO}_2 + 4 e^- \rightarrow \text{Si} + 2 \text{O}^{2-}
\]

\[E^0_{1173K} = 0.837 \text{ V vs. Ca}/\text{Ca}^{2+}\] [13]

\[
\text{Si} + \text{C} \rightarrow \text{SiC}
\]

[14]

The reduction of SiO2 to Si, with the temporary formation of other phases, has also been reported to happen in the absence of C.\textsuperscript{32} Such direct conversions are likewise known for the reduction of Fe\textsubscript{2}O\textsubscript{3}\textsuperscript{33} and UO\textsubscript{2}\textsuperscript{34}

**Reduction of SiO2 via electrochemical formation of CaSiO3.**—The transient presence of CaSiO3 in the cathode in the short experiments at intermediate applied voltage may indicate a two-step reduction process, which involves the combined formation of Si and CaSiO3, followed by the electro-deoxidation of the CaSiO3.

\[3\text{SiO}_2 + 2\text{Ca}^{2+} + 4e^- \rightarrow \text{Si} + 2\text{CaSiO}_3\]

\[E^0_{1173K} = 1.308 \text{ V vs. Ca}/\text{Ca}^{2+}\] [15]

\[\text{CaSiO}_3 + 4e^- \rightarrow \text{Ca}^{2+} + \text{Si} + 3\text{O}^{2-}\]

\[E^\text{O}_{1173K} = 0.602 \text{ V vs. Ca}/\text{Ca}^{2+}\] [16]

\[
\text{Si} + \text{C} \rightarrow \text{SiC}
\]

[17]

The reduction of SiO2 to Si, with the temporary formation of CaSiO3, has indeed been reported when only small amounts of electrolyte were present.\textsuperscript{35} Reaction sequences of this kind are also well known from the reduction of TiO\textsubscript{2}\textsuperscript{36}, Cr\textsubscript{2}O\textsubscript{3}\textsuperscript{30}, and Nb\textsubscript{2}O\textsubscript{5}\textsuperscript{29}. It is noted that Ca metallates tend to give very strong peaks in the XRD pattern, so that those of the corresponding metals or suboxides are sometimes obscured.
Figure 7. (a) SEM image with EDX elemental maps and (b) EDX spectrum of the SiC product obtained from SiO\textsubscript{2}/graphite (molar ratio 1:1.5) by electro-deoxidation in CaCl\textsubscript{2} melt at 1173 K for 6 h at 2.8 V.

Reduction of SiO\textsubscript{2} via chemical formation of CaSiO\textsubscript{3}.—The transient presence of CaSiO\textsubscript{3} in the cathode may also be due to its chemical formation from SiO\textsubscript{2} and CaO dissolved in the CaCl\textsubscript{2}. The CaO originates from insufficient drying of the CaCl\textsubscript{2} and forms in the melt during the electro-deoxidation process.

\begin{equation}
\text{SiO}_2 + \text{CaO} \rightarrow \text{CaSiO}_3 \quad [18]
\end{equation}
\begin{equation}
\text{CaSiO}_3 + 4 \text{e}^- \rightarrow \text{Ca}^{2+} + \text{Si} + 3 \text{O}^{2-} \\
E^{0}_{1173K} = 0.602 \text{ V vs. Ca/Ca}^{2+} \quad [19]
\end{equation}

\begin{equation}
\text{Si} + \text{C} \rightarrow \text{SiC} \quad [20]
\end{equation}

The chemical formation of Ca metallates with CaO from the electrolyte has also been found in the reduction of Ta\textsubscript{2}O\textsubscript{5}.\textsuperscript{37}

Reduction of CaSiO\textsubscript{3} via dissolution and deposition.—In the above reaction sequences, the reduction of the CaSiO\textsubscript{3} has been written as a solid-state reaction. However, there is significant solubility on the percent level of CaSiO\textsubscript{3} in CaCl\textsubscript{2} melts with CaO additions.\textsuperscript{38} Therefore, it is possible that at least a portion of the CaSiO\textsubscript{3} may have entered into the CaCl\textsubscript{2} melt during the experiment, from which the Si was then electro-deposited back onto the cathode.

\begin{equation}
\text{CaSiO}_3 \rightarrow \text{Ca}^{2+} + \text{SiO}_4^{2-} \quad [21]
\end{equation}
\begin{equation}
\text{SiO}_4^{2-} + 4 \text{e}^- \rightarrow \text{Si} + 3 \text{O}^{2-} \\
E^{0}_{1173K} = 0.602 \text{ V vs. Ca/Ca}^{2+} \quad [22]
\end{equation}
This type of SiO₂ reduction has been considered to be the dominant one by Xiao et al.³⁸ and Zou et al.²² Overall, the electro-deoxidation of SiO₂ in the presence of graphite in a CaCl₂ melt is highly complex and likely to progress via several parallel reaction sequences. These are dependent on the precursor morphology and on the applied voltage and may therefore differ between individual experiments. This highlights the necessity of empirical process optimization as has been done in the present study.

Nitridation of SiC nanowires.—Fig. 11a shows the XRD pattern of the material obtained after heating the electrochemically prepared SiC in N₂ at 1473 K for 8 h. The product contained Si₃N₄O together with the cristobalite phase of SiO₂. Figs. 11b–11d show SEM images and an EDX analysis of the product, notably demonstrating that it had retained its nanowire morphology. The present study is therefore believed to be the first report on the synthesis of nanowire-type Si₃N₄O.

Fig. 11e shows the mass change and heat flow vs. temperature curves recorded in the TG/DSC experiments of the electrochemically made SiC in N₂ atmosphere. The TG curve presents two distinct stages, one involving mass loss (stage I), and one involving mass gain (stage II). The curve begins with a mass loss, which is quite steep from 25 to about 710 K and then becomes rather insignificant. The minimum mass of 99.98% of the original is reached at 870 K. This is followed by a mass gain, which is rather slow up to 1120 K and then becomes quite steep.

Tishchenko et al.³⁹ studied the thermokinetic behavior of SiC in air by TG/DSC and reported that the mass loss from room temperature to about 467 K was due to the presence of moisture. In line with that, the small endothermic mass loss of the SiC sample up to 475 K may be attributed to the removal of adsorbed moisture. Roy et al.⁴⁰ reported that the subsequent oxidation of SiC has two components, active oxidation with oxygen at low activity according to Eq. 23, involving a net mass loss, and passive oxidation with oxygen at high activity according to Eq. 24, involving a net mass gain.

\[
\text{SiC} + 2 \text{O} (\text{residual in SiC}) \rightarrow \text{SiO} (g) + \text{CO} (g) \quad [23]
\]

\[
\text{SiC} + 2 \text{O}_2 (\text{surrounding gas}) \rightarrow \text{SiO}_2 (s) + \text{CO}_2 (g) \quad [24]
\]

Due to the high level of residual oxygen in the electrochemically prepared SiC material (Table I), the mass loss of the SiC up to 870 K may be attributed to active oxidation, with the oxygen evolving in the form of CO and SiO gases.

The endothermic mass gain above 870 K may be ascribed to the reaction of the SiC with N₂. This must involve the formation of Si₃N₄O, as evidenced by the XRD analysis of the nitrided sample. Mechanistically, the formation of Si₃N₄O may include both the residual oxygen...
Figure 10. (a) SEM images of the product obtained from SiO$_2$/graphite (molar ratio 1:1.5) by electro-deoxidation in CaCl$_2$ melt at 1173 K for 20 min at 2.8 V, with (b) enlargement of the indicated area in (a) showing the interface of regions with no reduction and with commencing reduction. High-resolution image of (c) region with no reduction, and (d) region with commencing reduction. (e) SEM images of the product obtained from SiO$_2$/graphite (molar ratio 1:1.5) by electro-deoxidation in CaCl$_2$ melt at 1173 K for 3 h at 2.8 V, with (f) enlargement of the indicated area in (e).

in the SiC as well as the trace oxygen in the N$_2$ gas.

\[
2 \text{SiC} + \text{CO} (g) + \text{N}_2 (g) \rightarrow \text{Si}_2\text{N}_2\text{O} + 3 \text{C} \\
\Delta G^0_{1473 K} = -109.577 \text{kJ/mol} \tag{25}
\]

\[
2 \text{SiC} + \frac{1}{2} \text{O}_2 (g) + \text{N}_2 (g) \rightarrow \text{Si}_2\text{N}_2\text{O} + 2 \text{C} \\
\Delta G^0_{1473 K} = -351.029 \text{kJ/mol} \tag{26}
\]

Munro and Dapkunas$^{41}$ reported that when pure SiC is heated in the presence of pure N$_2$, it slowly converts into Si$_3$N$_4$. They further reported that the additional presence of CO would lead to the formation of oxynitrides. This is in line with the current findings where CO is thought to be released in the active oxidation.

Overall, the observed mass changes and the formation of Si$_2$N$_2$O and SiO$_2$ can be explained by the oxidation and nitridation of the electrochemically made SiC. Some stoichiometric considerations to corroborate this notion are given in the Appendix.

Conclusions

Silicon carbide with nanowire morphology was electrochemically synthesized from SiO$_2$/graphite mixtures in a CaCl$_2$ melt. Three competing reactions were found to occur in cathodically polarized SiO$_2$/graphite, (i) the electro-deoxidation of SiO$_2$ to Si and the subsequent in-situ reaction of the Si with graphite to form SiC, (ii) the reaction of Si with Ca$^{2+}$ ions to form calcium silicides such as CaSi and Ca$_2$Si, (iii) the reaction of graphite with Ca$^{2+}$ ions to form CaC$_2$.

The successful synthesis of pure SiC requires an optimized combination of the composition of the SiO$_2$/graphite precursor, the magnitude of the applied voltage, and the duration of the polarization, while deviations from such conditions lead to the incomplete reaction of the Si with the graphite or to the preferential formation of calcium silicide. A significant excess of graphite in the starting material is required to compensate for the loss of carbon through inevitable side reactions. Partially reacted SiO$_2$/graphite samples contained Si or CaSiO$_3$, which enabled detailed considerations of possible reaction paths.

Nitridation experiments of the electrochemically made SiC at elevated temperature showed the formation of Si$_2$N$_2$O. TG/DSC studies with the SiC in N$_2$ atmosphere indicated distinct stages, attributable to the loss of moisture, the partial oxidation with residual oxygen in the material, and the reaction with N$_2$.

Notably, the SiC is in its β-phase and has nanowire morphology, and the Si$_2$N$_2$O retains this nanowire morphology. This may make possible the application of the materials in the energy and other sectors as will be elaborated in future reports.
Figure 11. (a) XRD pattern of the Si$_2$N$_2$O/SiO$_2$ product obtained from SiO$_2$/graphite (molar ratio 1:1.5) by electro-deoxidation in CaCl$_2$ melt at 1173 K for 6 h at 2.8 V and subsequent heat-treatment in N$_2$ flow at 1473 K for 8 h. (b) SEM image and (c) high-resolution SEM image of the same sample with (d) corresponding EDX analysis. (e) TG/DSC curves of a 200 mg sample of SiC in N$_2$ flow of 100 mL/min at a scan rate of 20 K/min.

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Appendix: Stoichiometric Calculations on the Formation of Si$_2$N$_2$O from SiC

It is suggested that the formation of Si$_2$N$_2$O from SiC can progress via parallel reaction paths.

One reaction path is based on information from the literature concerning the mechanisms of active oxidation with residual oxygen and nitridation with gaseous N$_2$, as discussed in the main text, and can be expressed as follows.

$$\text{SiC} + 2\text{O} \text{(residual in SiC)} \rightarrow \text{SiO} \text{(g)} + \text{CO} \text{(g)} \quad [A1]$$

$$2\text{SiC} + \text{CO} \text{(g)} + \text{N}_2 \text{(g)} \rightarrow \text{Si}_2\text{N}_2\text{O} + 3\text{C} \quad [A2]$$

Each experiment involved 20 mg of electrochemically prepared SiC, with a residual oxygen content of 2.7 mass%. The mass of oxygen in the SiC was 0.54 mg, corresponding to 0.27 mg of oxygen present in the CO and the other half in the SiO. This would have allowed for the formation of 1.7 mg of Si$_2$N$_2$O.
The purity of the technical N₂ used in the nitridation experiments was specified at 99.999%, with 5 ppm of O₂ and 3 ppm of H₂O as the main impurities. With a flowrate of 3.4 mg of Si₂N₂O.

A further source of oxygen may have been adsorbed O₂ and H₂O in the SiC reactant. Now the mass of oxygen in the SiC of 0.54 mg would have allowed for the formation of 5.2 mg of Si₂N₂O.

Overall, the formation of milligram quantities of Si₂N₂O from the SiC is consistent with the experimental conditions applied in the nitridation experiments. The results there-