Electrochemical Synthesis

Electrochemical Preparation of Silicon and Its Alloys from Solid Oxides in Molten Calcium Chloride**

*Xianbo Jin, Pei Gao, Dihua Wang, Xiaohong Hu, and George Z. Chen**

Silicon plays essential roles in the fabrication of solar cells, silicon chips, optical fibres, silicones, and is important as an element in lighter and stronger alloys, as well as hundreds of other advanced applications.[1,2] The industrial production of silicon is at present mainly through the carbothermic reduction of SiO_2 at 1700 °C, in which the oxygen is removed by the generation of CO_2.[3,4] This old-fashioned charcoal technology should be replaced by a more advanced process from the viewpoint of an environmentalist, in that the earth's climate is gradually becoming worse owing to the emission of greenhouse gases.[5] The world production of silicon in 2002 was about 4.1×10^6 tonnes,[6] equivalent to about 6.5×10^6 tonnes of CO_2 entering the atmosphere. A desired method of producing silicon may be the electrochemical reduction of SiO_2 in which the use of carbon reductant can be avoided and hence less environmental damage. In fact, electrolytic production of silicon began in 1854,[7] and silicon of 99.999 % in purity was later claimed[8] upon electrolysis of fluorosilicates in molten fluorides. DeMattei et al. in 1982 suggested[9] that the ideal raw material for silicon production should be SiO_2, and silicon metal with a purity of 99.97 % was produced in the $BaO/SiO_2/BaF_2$ system with the cell temperature being around 1450 °C. Recently, in molten $CaCl_2$ at about 900 °C, electrochemical deoxygenation of metals was investigated.[10–12] It was reported more recently[13–17] that when solid metal oxides are made into an electrode, regardless of their electron conductivities, they can be electroreduced (or electrodeoxidised) directly to the respective metals or alloys. This leads to a great possibility for the production of silicon directly from solid SiO_2. However, until now, there is only one relevant report that concerns the electroreduction of solid SiO_2, and only partial reduction of the SiO_2 electrode (quartz plate) was achieved.[18]

Herein, we report the fast, complete, and low energy electroreduction of a porous electrode prepared from SiO_2 powder. We also report an experimental observation that might indicate the existence of an optimal thickness of an insulating solid oxide, for example, SiO_2, through which the electroreduction can progress "quickly" to completion. Furthermore, two examples of silicon alloys have also been produced by the same electroreduction method.

Recently, Nohira et al. succeeded in removing oxygen from the surfaces of solid SiO_2 plates (quartz) in a molten $CaCl_2$ electrolyte at 850 °C.[18] Similar results were also obtained in our laboratory by using a different electrode design. In the experiments, a tungsten wire of 300 μm in diameter was sealed in a quartz tube by using a gas flame. The end face of the tungsten wire was revealed by grinding. The SEM image showed a very intimate contact between the quartz and the W wire (Figure 1 a). This W–SiO_2 electrode was then inserted into molten $CaCl_2$ at 850 °C and cyclic voltammetry was carried out by using a Pt wire and a graphite rod as the pseudoreference and counter electrodes, respectively. As shown in Figure 2 a, the reduction of SiO_2 began at −0.85 V, which led to a sharp increase in the current that reached a peak of about −12.5 mA at −1.0 V. The current then went through a slightly inclined plateau on which a couple of small peaks can be seen (Figure 2 a). These peaks are thought to correspond to the formation of the calcium and silicon compounds.[18,19] Upon reversing the potential sweep the current formed a typical stripping peak. When the sweep reached more positive potentials, a large poorly defined anodic peak occurred at about −0.7 V, thus suggesting that the reoxidation process may involve both pure and compounded forms of Si. A further study of the reaction mechanism is ongoing.

Figure 1 a–d shows the SEM images of the W-SiO_2 electrode before and after the first potential sweep cycle. After this sweep the central W disc was surrounded by a ring of porous product of about 200 μm in breadth (Figure 1 b).

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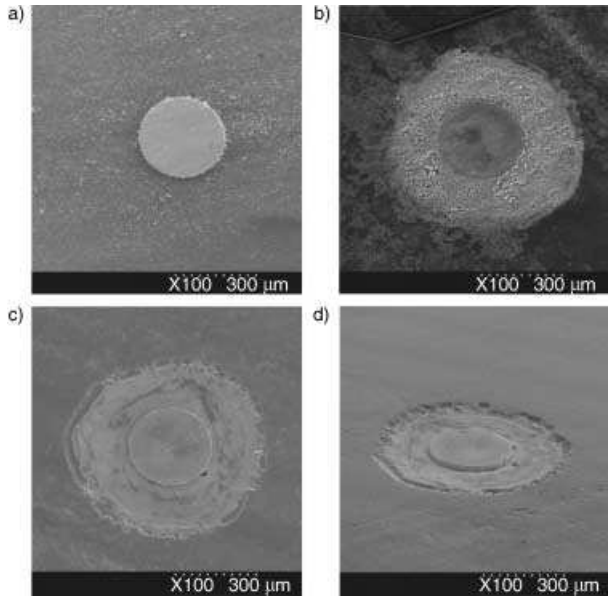

Figure 1. SEM images of the W–SiO2 electrode a) before and b) after one cycle of potential sweep between 0.5 and −1.7 V, and c) after washing the electrode shown in (b) in an ultrasonic water bath. d) A side view of the situation in (c).

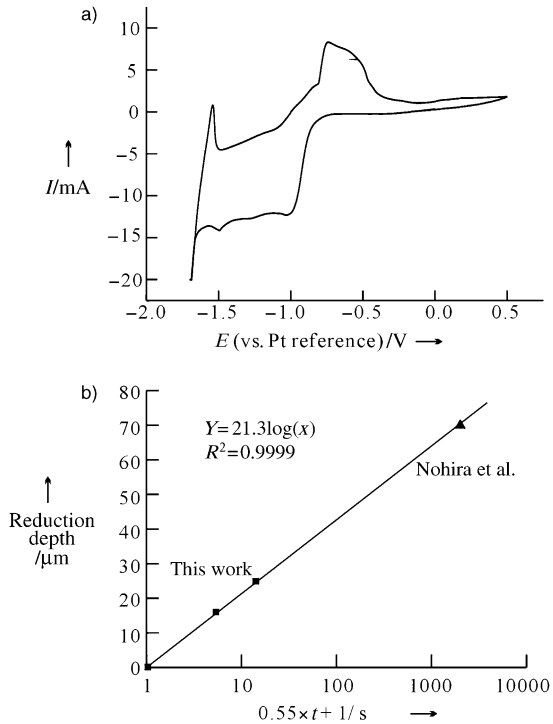

Figure 2. a) Cyclic voltammogram of the W–SiO_2 electrode in molten $CaCl_2$ (200 mV s^{-1}, 850 °C), b) the relationship between the depth and time of reduction of solid SiO_2.

The product was removed by immersing the electrode in an ultrasonic water bath, thus resulting in a circular cave in the shape of a flat-bottom pan. By using the depth (16 µm), the top (200 µm) and bottom breadths (150 µm) of the cave (Figure 1 c, d), the volume of the reacted SiO_2 was estimated to be about 4.2×10^{-6} cm^3. Considering the density of quartz (2.2 g cm^{-3})[19] and the molecular mass of SiO_2 (60 g/mol), we estimate that about 1.54×10^{-7} moles of SiO_2 were reduced, which is equivalent to a total charge of about 59.4 mC if four electrons were transferred. This value can be compared with the total charge of about 61.5 mC passed during the negative and positive sweep between −0.85 V and −1.7 V (Figure 2 a). The good agreement between the two charge values is strong evidence that the reduction product between −0.85 and −1.7 V was mainly silicon.

By using the average current of the plateau between −1.0 V and −1.7 V, the reaction rate was estimated to be higher than 80 A cm^{-2} with reference to the revealed side surface of the tungsten wire, which is 1.41×10^{-4} cm^2 (Figure 1 d). This value is even higher than that usually observed in the electrodeposition of metals from liquid electrolytes. Such a high current density suggests a great potential of the electroreduction of solid SiO_2 for the industrial production of silicon. However, it should be pointed out that this high reaction rate was observed at the very beginning of the electroreduction, and the affected volume of the quartz was very small. The question is whether this high reaction rate could be achieved if the volume of quartz were significantly increased.

It was proposed that the electroreduction of insulating solid oxides could proceed at the three-phase boundary linking the conductor, oxide and electrolyte.[14] This principle was advocated and demonstrated with an elegantly designed experiment for the reduction of a quartz plate.[18] In our experiment, before reduction had occurred, there was a W/SiO_2/$CaCl_2$ three-phase boundary at the edge of the central W disc (end of wire). Upon electron transfer, the SiO_2 next to the W disc was converted into silicon which has a reasonably high electronic conductivity (50 Ω^{-1} cm^{-1}).[20] Therefore, further reduction may occur at the newly formed Si/SiO_2/$CaCl_2$ three-phase boundary. In theory, the continuation of this change should lead to the propagation of the three-phase boundary in a 3D manner. However, Figure 1 c, d tells a different story and shows a transverse reaction width of 200 µm, but a reaction depth of only 16 µm. While this is an indication of a greater reaction resistance along the depth direction than the transverse direction, the phenomenon may be broadly understood by the accessibility of the molten salt to the reaction sites that are directly in touch with the molten salt along the transverse direction, but in a different situation along the depth direction.

However, if the volume remains the same, the removal of oxygen from SiO_2 should result in a porosity of about 56.2 % if the density difference between SiO_2 and Si is considered (2.2 and 2.33 g cm^{-2},[19] respectively). Therefore, the transverse propagation of the Si/SiO_2/$CaCl_2$ three-phase boundary opens up the solid phase by creating pores/channels for the molten salt to access the SiO_2 phase behind the porous Si layer.[18] This explanation agrees well with the porous product shown in Figure 1 b. Nonetheless, it can be reasonably considered that the mass transfer within the formed porous silicon layer is slower than that at the SiO_2/molten salt interface, thus leading to a slower reaction rate along the depth direction than the transverse direction.

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The observation of a flat bottom in the cave (Figure 1c) suggests that the electroreduction of the insulating SiO_2 might be limited to a certain distance in the depth direction, which is less dependent on the time of the applied potential. This depth limit as shown in Figure 1d may be mainly attributed to the limit of mass transfer through the porous silicon layer formed on the surface.

We would like to highlight the practical significance of this finding of different reaction rates along the transverse and depth directions. For industrial production, the use of bulk solid quartz as the electrode is obviously not practical. Instead, a process is likely to involve the use of readily available SiO_2 powder to fabricate a porous SiO_2 electrode, on the analogy of the reports by Chen and co-workers.[13,14] However, it can be anticipated that, if the oxide particles are too large, the same situation would occur to the individual oxide particles, as observed in our electroreduction of the bulk solid quartz electrode. That is, within a practically tolerable time, the reduction would take place only on the surface of the oxide particle with the inner part being unaffected. To the best of our knowledge, there has not been any report in the literature giving an accurate account, either experimental or theoretical, of the effect of powder particle size on the efficiency of the electro-reduction. On the basis of our findings and that of Nohira et al.,[18] a logarithm relation could be approximated between the reduction depth and time (see Figure 2b). It can then be estimated that, for example, the complete reduction takes place within 0.1 s, 1.3 s and 403 s of three SiO_2 particles of 1 μm, 10 μm and 100 μm in diameter, respectively.

The above estimation was found to agree broadly with the result from the electrolysis of the SiO_2 powder, with particle sizes ranging from 2 to 7 μm (Figure 3a). The powder was manually pressed into a porous pellet (1.3 cm in diameter,

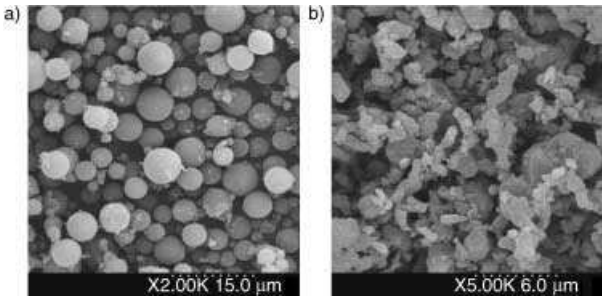

Figure 3. SEM images showing a) the SiO_2 powder electroreduced in molten $CaCl_2$ (2.8 V, 850 °C, 4 hrs) into b) the Si powder.

0.5 cm in thickness, 1.5 g in weight). A manually operated press was used for making the pellets and hence the actual pressure was unknown but was sufficient to form a strong pellet. After sintering at 1000 °C, the pellet was pressed and sandwiched between two porous nickel foils. Then, constant-voltage (2.8 V) electrolysis was performed, under argon, on the assembled cathode in molten $CaCl_2$ at 850 °C with a graphite rod as the anode. The recorded current was very high (about 4 A) during the first few minutes but declined thereafter (within 2 h) to the background value, ≈0.2 A. After electrolysis, which usually lasted for 4 h to ensure complete reduction, the cathode was removed from the molten salt. Upon washing the cathode (pellets) in distilled water in an ultrasonic bath, a grey powder was collected.

The obtained powder was dried and analyzed by XRD (Figure 4), thus confirming the product to be dominated by pure silicon. In addition to the pure silicon phase, the XRD spectrum also exhibited some small but distinguishable sundry peaks which are likely due to $MgSiO_3$. This was tracked down to an $MgCl_2$ impurity (about 0.3 %) contained in the $CaCl_2$ used in this work.

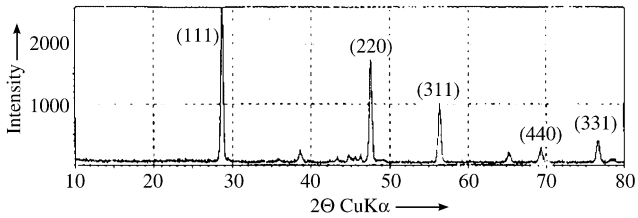

Figure 4. The XRD spectrum of the Si powder obtained from the electroreduction of pellets of the SiO_2 powder in $CaCl_2$ molten salts.

When inspected under SEM (Figure 3b), the silicon powder particles were observed to be 1–3 μm in diameter, which is in accordance with the theoretical prediction from the density difference between Si and SiO_2. Because both SiO_2 and Si are almost insoluble in $CaCl_2$, the output rate should be very high. These results prove that the silicon powder can be mass produced from the SiO_2 powder by the electroreduction method. It is worth mentioning that in our experiments complete reduction of the SiO_2 pellets took a much shorter time than the reduction of TiO_2 (≈15 h) under similar conditions as reported in literature.[13] This difference may be due to the fact that oxygen is highly soluble in solid titanium but not in solid silicon.

By mixing powders of different metal oxides, alloys can be produced by the electroreduction method.[13,14,21] Because fine powders of oxides can be prepared easily and mixed uniformly, the electroreduction of such a mixture leads to an alloy, the composition of which is precisely controlled. Indeed, in our experiments, Si–Fe and Si–Cr alloy powders with a particle size of 2–3 μm were also prepared.

In conclusion, we have demonstrated, for the first time, that porous pellets of the SiO_2 powder or its mixture with other metal oxide powders can be electroreduced to pure silicon or the respective silicon alloy powders in molten $CaCl_2$. Furthermore, cyclic voltammetry revealed that the electroreduction of SiO_2 could proceed very quickly, with the current density reaching beyond 80 $A\,cm^{-2}$ with reference to the surface area of the conducting substrate. Although such a high current density may be difficult to achieve on an industrial scale, it may be used as a fundamental reference for the design of an industrial process for the mass production of silicon powder by electrolysis. Furthermore, we found that the relation between the reduction depth and time of solid SiO_2 may be approximated by the logarithm law. This finding may be used to select the particles sizes of the SiO_2 powder so

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that complete reduction of the electrode prepared from the SiO_2 powder can be achieved within a practically tolerable time. This work shows that when the particle size is in the range of 2–7 μm, complete reduction of a 0.5 mm thick porous pellet at 2.8 V and 850 °C could be less than 4 h with the energy consumption being within 13 kWh (kg of Si)$^{-1}$ which is expected to decrease further upon optimization. This can be compared with the energy consumption, 13–16 kWh (kg of Si)$^{-1}$, of the carbothermic method used by the industry in China.[22]

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