



Electrochemical decomposition of SiO₂ pellets to form silicon in molten salts

Emre Ergül, İshak Karakaya*, Metehan Erdoğan

Middle East Technical University, Engineering Faculty, Department of Metallurgical and Materials Engineering, İnönü Bulvarı, 06531 Ankara, Turkey

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ABSTRACT

Direct electrochemical reduction of porous SiO₂ pellets in molten CaCl₂ salt and CaCl₂–NaCl salt mixture was investigated by applying 2.8 V potential. The study focused on the effects of temperature, particle size of SiO₂ powder starting material and the behavior of cathode contacting materials during electrochemical reduction process. The starting materials and the electrolysis products were characterized by X-ray diffraction analysis and scanning electron microscopy mainly. The studies showed that smaller particle sizes and higher temperatures had slightly positive effects in increasing the reduction rate within the ranges covered in this study. The results were interpreted from variations of current and accumulative electrical charge that passed through the cell as a function of duration of electrochemical reduction under different conditions. Microstructures and compositions of the reduced pellets were used to infer that electrochemical reduction of SiO₂ in molten salts may become a method to produce silicon that could be used in solar energy utilization. Furthermore, X-ray diffraction analysis results indicated that the silicon produced at the cathode reacts with contacting materials; nickel, and iron in stainless steel to form Ni–Si and Fe–Si compounds due to very reactive nature of silicon especially at high temperatures.

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1. Introduction

Photovoltaic cells are considered as one of the promising solutions for energy and environmental issues. Clean and renewable energy can be produced by utilizing solar cells. As well as being an important part of the photovoltaic cells, solar grade silicon (SOG-Si) should be easily attainable for widespread usage of solar cells. The cost of conventional SOG-Si production is high due to processes which involve first conversion of raw Si into compounds such as; SiHCl₃, SiCl₄, SiH₂Cl₂, or SiH₄ and then transforming these silicon compounds back to high purity silicon [1]. Electrochemical methods have been considered as an alternative process, to reduce production cost of the solar grade silicon. Electrodeposition [2,3] and electrorefining [4] studies were carried out to obtain high purity silicon. However, feasible isolation of silicon with desired purity could not be achieved in these studies. Recently, a new study aiming at SOG-Si production was reported by Nohira et al. [5]. The study was based on electrodeoxidation of the oxide compound [6] in molten CaCl₂. After this report, several works related with the electrochemical reduction of SiO₂ to Si were reported [7–14]. A recent study [15] used a similar method with the addition of an yttria-stabilized zirconia oxygen ion conducting membrane in electrodeoxidation of SiO₂–TiO₂ mixture to form Si–Ti compounds by separating anode from molten electrolyte.

The reduction process of SiO₂ at the cathode is expressed as [8–10,12–14]:



A cyclic voltammetry study [16] showed the existence of above cathode reaction during decomposition of porous SiO₂. In addition, other cathode reactions, involving the formation of CaSi₂, Ca₂Si and Ca were reported at lower cathode potentials, corresponding to higher cell potentials.

Purity of the silicon is an important parameter for the production of SOG-Si. Therefore, particular attention should be given to the interactions between the cell components and the silicon. Silicon produced at the cathode is inevitably in contact with cathode contacting materials and the electrolyte. Molybdenum wire [5,8–10,13], nickel metal foil [7,11,12] and silicon plate [14] were used as the cathode contacting materials. Yet, the reported results do not comment adequately about the use of above metallic materials, except silicon, in the environments formed in these tests. Especially in the case of nickel and molybdenum that is in contact with elemental silicon, the formations of Ni_xSi_y and Mo_xSi_y intermetallics are inevitable [17,18]. In spite of this fact, only one study [11] mentioned that problem.

Furthermore, there are discrepancies about the rate of SiO₂ reduction in the literature. Only one of the reports [7] claims complete reduction of porous SiO₂ pellet to elemental Si. All other observations [5,8–14] give results of incomplete reductions. Although the reduction of bulk SiO₂ plates were claimed to be faster [10] than porous pellets, their reductions were still incomplete. In

* Corresponding author. Tel.: +90 3122102533; fax: +90 3122102518.
E-mail address: kkaya@metu.edu.tr (I. Karakaya).

addition, different colors reported for reduced products are; grey [7], red brick color [11], brown [16], and brownish as seen from reported photographs [5,8].

In the present study, electrochemical reduction of porous SiO₂ pellets was performed to examine the behavior of cathode materials and resolve the conflicts over the rate of reduction and the color of the products. Furthermore, the effects of reduction temperature and particle size of the SiO₂ powder starting material on the reduction of porous SiO₂ pellets in molten CaCl₂–NaCl salt mixture were investigated.

2. Experimental

The experimental set-up used in this study is a modified form of apparatus used before [19]. Detailed information about the experimental set-up and the procedure can be found elsewhere [20]. Brief information about the set-up and procedure is given below. Porous SiO₂ pellets were prepared by compressing about 1.20 grams of SiO₂ powder (Fluka 00653 purum p.a.; ≤230 mesh) into a cylindrical form under 1.5 t of load. Sintering at 1300 °C for 2 h resulted cylindrical pellets that had average diameters of 15 mm and heights of 5 mm. Silicon dioxide pellet, sandwiched between two contacting metal plates formed the cathode assembly. Plates were stainless steel, except in experiments that involved the study of the behavior of nickel cathode plate. One of the plates was welded to the end of the stainless steel wire (Ø: 3 mm, height: 60 cm) and placed under the pellet. The other plate was placed on top of the pellet. To hold this sandwiched structure together, a wire (Kanthal D, Ø: 0.15 mm) was wrapped around the plates. Two different procedures were employed to place the SiO₂ pellets in to the cathode assembly. Silica pellets were directly used in one, they were covered with a Kanthal wire (Kanthal D, Ø: 0.15 mm) mesh in the other procedure. The tests to examine the behavior of cathode contacting materials were done by using pellets without the wire mesh to have contact surface between the pellet and the contacting materials as much as possible. The wire mesh was used to decrease the contact surface between the pellet and contacting metal plates at the same time increase the electrolyte volume at SiO₂–cathode metal conductor–electrolyte interface. This procedure was expected to increase oxygen transport from the cathode and yield higher reduction rates.

The anode was prepared by connecting a 15 cm long and 13 mm diameter graphite (Alfa Aesar A10134) rod to a stainless steel wire (Ø: 3 mm, height: 45 cm). This assembly was covered with quartz to prevent short-circuiting of electrodes and undesired interactions with the gases formed inside the cell vessel. Both anode and cathode wires were extended out of the quartz cell vessel (50 mm outer diameter and 50 cm height) to enable easy connection to the power source. A Teflon lid was used to cover the quartz vessel at the top.

CaCl₂ (Riedel-de-Haën 12022) salt was dried before experiments under the vacuum by heating at a rate of 8 °C/h up to 400 °C to remove moisture. In some of the experiments CaCl₂ (70 mole%)–NaCl (Riedel-de-Haën 13423) (30 mole%) salt mixture was used as the electrolyte. About 100 g of salt was used in each experiment.

An alumina crucible with 4.5 cm outer diameter and 10 cm height filled with dried salt(s) was placed to the bottom of the cell vessel. The Teflon lid together with the anode and the cathode assemblies was then placed to the top of the vessel. The quartz vessel containing parts of the cell was placed into a Lindberg LHTF3226 vertical furnace. Argon inlet and gas outlet connections were established. A Eurotherm 818P unit was used to control the furnace temperature. It took about 2 h to attain a temperature around 800 °C. The whole heating processes and the electrolysis experiments were conducted under continuous flow of argon. When the cell reached the desired temperature, electrodes were immersed into the electrolyte. Sufficient period of time was given for the temperature and the composition to homogenize before the electrical connections to the cell were made. An Agilent N6700B low profile MPS main frame with N6773A direct current (DC) power module, power supply was used to apply 2.8 V potential between the cathode and the anode. The current passing through the cell was collected by a computer connected to the power supply via a visual basic code.

At the end of the experiments electrodes were lifted out of the electrolyte. After the system was cooled down, reduced pellets were taken out from the cathode. The product was washed in the ultrasonic water bed for 10 min to remove the remaining electrolyte from the pellet. Then, the reduced powder was put into about 200 ml hydrochloric acid solution that had 0.1 M concentration. The mixture was stirred for 20 min at room temperature to remove the calcium carbonate which was found in the reduced pellets. Characterization of the electrolysis products before and after the HCl treatment and the materials formed on the cathode contacting materials were done by XRD (Rigaku D/MAX2200/PC) and SEM (Nova NanoSEM 430, FEI) analysis.

3. Results and discussion

Electrochemical reduction of porous SiO₂ pellets were performed at 850 °C in CaCl₂ and 750 °C, 800 °C and 850 °C in

CaCl₂–NaCl molten salt electrolytes. Two different particle sizes: smaller than 64 μm and smaller than 38 μm, were used. Fig. 1(a) shows the current versus time graphs of these reduction experiments. In order to show these results in a different way, and associate them with the amount of reduction, *W*, accumulative (total) charge, *Q*, passing through the cell, was calculated (shown in Fig. 1(b)) from;

$$Q = \int_0^t I dt = \frac{100WzF}{AX} \quad (2)$$

where *I* is the current in amperes, *t* is the time in seconds, *F* is the Faraday constant, *z* is the valence, *A* is the molecular weight of silicon dioxide and *X* is the percent current efficiency. The theoretical total charge required for the complete reduction of 1.2 g of SiO₂ was 7720 Coulombs (As) as calculated from Eq. (2) by taking 100% current efficiency. Effects of temperature, electrolyte composition and particle size on the current and total charge that passed through the cell, shown in Fig. 1, were confirmed by repeated runs. As it is apparent from this figure, complete reduction of the pellets could not be achieved in any of the experiments. The highest total charge was observed during the experiment at 850 °C in CaCl₂ salt. Addition of NaCl decreased the value of *Q* at the same temperature of 850 °C. All experiments, except the one conducted at 850 °C in CaCl₂–NaCl salt mixture for 175 min, were conducted for 350 min.

The plots presented in Fig. 1(b) may be used to compare reduction rates of different runs when the same current efficiency is assumed. The CaCl₂ (70 mole%)–NaCl (30 mole%) salt mixture was used as the electrolyte to investigate the effect of temperature, for the first time. The experiments were conducted at 750 °C, 800 °C and 850 °C at 2.8 V. According to the graphs given in Fig. 1, temperature increase has a small positive effect in increasing the reduction rate in the temperature range studied. This increase was thought to be due to the increase in the diffusion of O²⁻ ions with increase in temperature. This result is consistent with the reported rate determining step of the electrodeoxidation process of SiO₂ [8], which is the diffusion of O²⁻ ions at the cathode. In the graphs of Fig. 1, it can also be seen that the reduction rate slightly increased with decreasing the particle size from sub-64 μm to sub-38 μm at 750 °C. This is in accord with the expectations, because smaller particle size yields condensed pellets that decrease the diffusion and the conduction paths.

The result of the test employing SiO₂ pellet with the Kanthal wire mesh is compared with SiO₂ pellet without the wire mesh in Fig. 2. Both data are from the experiments involving the same electrolyte composition, temperature, particle size and applied voltage. Since the reaction always starts where the contacting lead contacts the SiO₂ and the electrolyte, there are likely more contacts when Kanthal wire is wound round the sample. It is clear that employment of the Kanthal wire mesh increased the reduction rate by increasing oxygen transport from the cathode.

3.1. The rate of electrochemical reduction of porous SiO₂

Jin et al. [7] reported complete reduction of porous SiO₂ pellets to silicon at the end of 4 h of electrolysis. Contrary to this study, complete reduction of porous SiO₂ pellets with similar geometry and dimensions under the same applied DC potential, could not be achieved in 4 h in the present study. Only about half of the pellet was reduced at 850 °C, as deduced from Fig. 1. In the study of Pistorius and Fray, reduction of the porous SiO₂ pellets (Ø: 13.1 mm, height: 7.1 mm) to Si was achieved, but unreduced CaSiO₃ was reported. Their experiment probably continued for at least 16 h as can be deduced from their current versus time graphs. The presence of CaSiO₃ in their study may be the result of the reaction between the pellet and CaO.

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