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Reaction Behavior of Stratified SiO$_2$ Granules during Electrochemical Reduction

in Molten CaCl$_2$

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ABSTRACT

The electrochemical reduction behavior of stratified SiO$_2$ granules in molten CaCl$_2$ at 1123 K (850°C) was investigated to develop a new process for producing solar-grade silicon. The cross sections of the electrolyzed electrode prepared from a graphite crucible filled with SiO$_2$ granules were observed and analyzed. The visual and SEM observations indicate that the overall reduction proceeds via two different routes. In one route, the reduction proceeds along the granule surfaces from the SiO$_2$ near the conductor to the distant SiO$_2$. In the other route, the reduction proceeds from the granule surface to the core of each granule. The reduction along the granule surfaces is faster than that from the surface to the core. Fine SiO$_2$ granules are expected to be favorable for a high reduction rate.

**Key Words:** Solar-grade Silicon, Silica, Electrolysis, Molten Salt
I. INTRODUCTION

The established energy economy, fueled by oil, coal, and natural gas, is being replaced by an economy powered by renewable energies such as solar, wind, and geothermal energy. Of the renewable energy sources, the growth of the solar power industry in the past decade can be described as explosive. According to the latest data released by the European Photovoltaic Industry Association (EPIA), the global cumulative installed solar cell capacity has increased from 2.2 GW in 2002 to 102 GW in 2012.[1] The annual installation of solar cells in the world has reached 28.6 GW in 2012.[2]

Currently, crystalline silicon is the most prevalent raw material for solar cells on the market. Solar cells manufactured with silicon accounted for 88% of the global solar cell production in 2012.[2] It will take several decades before technologies based on other materials will become competitive from a business aspect. With the rapid growth of the solar power industry, the consumption of solar-grade silicon (SOG-Si; 6N purity) has grown dramatically and an average growth of 10–20% per year is estimated for the next decade.

The modified Siemens process, based on the hydrogen reduction and thermal decomposition of trichlorosilane (SiHCl₃), is currently the dominating process for SOG-Si production.[4] The productivity of this process is reinforced by the smaller number of distillations of SiHCl₃ and higher temperature of the reduction step compared to the conventional Siemens process. Even though the supply currently satisfies the market demand, the productivity limitation of this process will likely
causes a shortage of the SOG-Si supply after production of solar cells exceeds 50–60 GW per year.[4]

Moreover, the modified Siemens process has other disadvantages such as low reaction efficiency and high energy consumption. Therefore, development of an eco-friendly production process for SOG-Si with high yield and low cost is required.

Various processes have been developed with the aim of displacing the current SOG-Si production process.[3, 5-9] Electrochemical methods have been investigated as an alternative process for SOG-Si production.[10-13] Typically, silicon is electrodeposited on a cathode in molten salts, and a silicon compound is supplied as the raw material. In another method, silicon is produced on the cathode via electorefining using a low-purity Si anode as the raw material.

The authors have reported that solid silica (SiO2) can be electrochemically reduced to Si in CaCl2-based molten salts using the contacting electrode method.[14-21] In this method, SiO2 is reduced to Si by electrolysis at the three-phase zone of SiO2/CaCl2/electrode.[14, 15]

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

(1)

The byproducts of the O^{2-} ions are removed from the molten salt at the anode, where the COx gas evolution occurs when a carbon anode is employed. The electrochemical reaction proceeds mainly as a solid to solid reaction and only partly as a liquid to solid reaction in which Si is electrodeposited from silicate ions formed by dissolution of SiO2 in the molten salt.[19, 22] This type of method has also been reported by other groups.[23-29] The novelty and simplicity of this method may lead to a
new process for SOG-Si production by combining it with the use of high-purity silica and directional solidification refinement.\textsuperscript{[20]} The present authors have already proved that the impurities in the produced Si can be controlled at a low level when high-purity SiO\textsubscript{2} is used as the raw material.\textsuperscript{[30]}

Recently, the authors also proposed a semi-continuous electrochemical process of reducing powdery or granular SiO\textsubscript{2} to Si in molten CaCl\textsubscript{2}.\textsuperscript{[31]} In this process, SiO\textsubscript{2} powder or granules are supplied from the top of the electrolysis cell, stratified on the cathode placed at the bottom of the cell, and electrochemically reduced to Si. The produced Si granules are tapped out from the bottom of the cell as a slurry containing molten CaCl\textsubscript{2}. In a previous study, the reduction behavior of SiO\textsubscript{2} granules was estimated based on the current transient curve during electrolysis. The reduction front would spread much faster on the granule surface than in the inside of each granule. Therefore, the reduced SiO\textsubscript{2} granules, halfway through the electrolysis, should have a core(SiO\textsubscript{2})-shell(Si) structure. However, this reaction model needs to be confirmed by direct observation of the SiO\textsubscript{2} granules after electrolysis at different reduction stages. Moreover, such direct observation would allow for an integrated understanding of the reduction process, including the mechanism and kinetics, which is crucial to scale up the laboratory experiment for industrial production.

In the present study, the electrochemical reduction of SiO\textsubscript{2} granules in molten CaCl\textsubscript{2} at 1123 K (850\textdegree C) was investigated using a different approach from the previous studies. The cross sections of the electrolyzed electrodes prepared from a graphite crucible filled with SiO\textsubscript{2} granules were
observed and analyzed. An integrated explanation of the reduction behavior of SiO$_2$ granules in molten CaCl$_2$ was proposed by combining the present results with the previously proposed mechanism for the reduction of an SiO$_2$ plate$^{[15]}$ and SiO$_2$ granules.$^{[30]}$
II. EXPERIMENTAL

An Al$_2$O$_3$ crucible (Nikkato Corp., o.d. 90 × i.d. 80 × height 100 mm) charged with 300 g of CaCl$_2$ (Kojundo Chemical Lab. Co., Ltd., 99%) was set inside an SiO$_2$ vessel and heated to 1123 K (850°C) in a dry Ar atmosphere. The CaCl$_2$ salt was pre-dried under vacuum at 453 K (180°C) for several days and 773 K for one day. A small graphite crucible (Toyo Tanso Co., Ltd., o.d. 13 × i.d. 8 × height 8 mm) was used as the working electrode. As shown in Figure 1, an Al$_2$O$_3$ tube (Nikkato Corp., o.d. 8 × i.d. 5 × height 9 mm) was inserted into the graphite crucible to avoid electrical contact between the wall of the crucible and the sample. The crucible and tube were fixed with a nickel wire (Nilaco Corp., dia.1.0 mm, 99%) by threading it into a drilled hole with 1.2 mm in diameter. The nickel wire acts as a current lead as well. Approximately 0.07 g of high purity SiO$_2$ granules (Taiheiyo Cement Corp.) with two kinds of granule sizes; 0.10–0.25 mm and 1.0–2.0 mm, were charged in the crucible. Electrical contact to SiO$_2$ was only available through the bottom of the graphite crucible. A glassy carbon rod (Tokai Carbon Co., Ltd., dia. 5.2 mm) was used as the counter electrode.

The reference electrode was an Ag$^+/Ag$ electrode in which a silver wire (Nilaco Corp., dia.1.0 mm, 99%) was immersed in a CaCl$_2$ melt containing 0.5%AgCl (Wako Pure Chemical Co., Ltd., 99.5%) in a mullite tube (Nikkato Corp., o.d. 6 × i.d. 4 × height 450 mm). The potential of this reference electrode was occasionally checked against a Ca$^{2+}$/Ca dynamic reference electrode.
galvanostatically prepared on a Mo wire (Nilaco Corp., dia.1.0 mm, 99.95%).[21] All the potentials are given with reference to the Ca$^{2+}$/Ca potential.

After immersing the working electrode in the CaCl$_2$ melt, the potential of the working electrode was set at 0.5 V vs. Ca$^{2+}$/Ca. After electrolysis for 2 min to 150 min under a dry Ar atmosphere, the working electrode was taken out from the melt and vertically cut into two exact halves with a diamond wheel saw (SBT 650, Meiwafosis Co., Ltd.). The cross sections were photographed by a digital camera (Pentax Ricoh Imaging Co. Ltd., K100D). After washing the cut samples in 1M hydrochloric acid for 8 h to remove the remaining CaCl$_2$, the cross sections were analyzed by SEM (Keyence Corp., VE-8800) and EDX (AMETEK Co., Ltd., EDAX Genesis APEX2). In some cases, the samples were recovered from the crucible after electrolysis, washed in 1M hydrochloric acid for one day, and then successively washed in distilled water for one day. The obtained powdery samples were characterized by XRD (Rigaku Corp., Ultima IV, Cu-K$_\alpha$ line).
III. RESULTS AND DISCUSSION

A. Reduction from the Bottom of the Crucible to the Top of the SiO₂ Layer

During the potentiostatic electrolysis, the recorded current stayed around -0.2 A in all cases, which was similar to the blank electrolysis test without SiO₂ granules. Since the total surface area of the graphite crucible (ca. 51.2 cm²) was much larger compared with the valid surface area (ca. 0.2 cm²) for SiO₂ reduction, the current corresponding to the SiO₂ reduction was difficult to be distinguished from the background current. The large background current is mainly contributed by the electrochemical reaction relevant to the residual moisture in the melt. The cross sections of the working electrodes after electrolysis for (a) 2 min, (b) 10 min, (c) 60 min, and (d) 150 min using SiO₂ granules 0.10–0.25 mm in size are shown in Figure 2. A dark layer is observed at the bottom of the crucible for each sample. It grows up from the bottom as the electrolysis time increased. The XRD patterns of the samples, before and after electrolysis for 150 min, shown in Figure 3, confirm that crystalline Si is formed by electrolysis. Thus, the dark layer consists of Si converted from colorless SiO₂. The thickness of the original SiO₂ layer (δ₀) is ca. 4.5 mm, as indicted in Figure 2 (a). The thickness of the reduced dark layer (δ_R) for each electrolysis time is also given in the figure. Only a very thin dark layer is noticed after 2 min of electrolysis, while the layer extends to the top of the original SiO₂ layer after 150 min of electrolysis. The growth of the dark layer from the bottom to the top indicates that SiO₂ granules in contact with the bottom are reduced to Si at the beginning of
electrolysis. As the new electron pathways of the reduced Si are extended,[15] the reduction proceeds from the bottom of the crucible to the top of the SiO$_2$ layer.

Figure 4 shows an SEM image of the cross section of the working electrode that appeared in Figure 2(b) after electrolysis for 10 min. The reduced layer (at least the surface of the granule), as indicated in the figure, is easily identified by the morphology of the granules. Three regions, (a) unreduced layer, (b) interlayer between the reduced and unreduced layers, and (c) reduced layer, are magnified in Figure 5. The results of EDX analysis at the positions designated in Figure 5 are listed in Table I. As shown in Figure 5 (a), a granule in the unreduced layer has a dense and rather smooth surface. At the interlayer (Fig. 5 (b)), the morphology is different. The lower part (Pos. 3) of the granule is porous and the upper part is dense. EDX analysis implies that the surface of the lower part has been reduced to Si while the upper part has not. In accordance with the previous studies using SiO$_2$ plate electrodes,[14] [15] SiO$_2$ with a dense surface became porous after electrochemical reduction, and a vacant space was formed because of the significant volume decrease from SiO$_2$ to Si (SiO$_2$: 27.3 cm$^3$ mol$^{-1}$ at 1123 K (850°C),[32] Si: 12.1 cm$^3$ mol$^{-1}$ at 1123 K (850°C).[33]). In the reduced layer (Fig. 5(c)), only porous particles are found, indicating that the granule has been reduced to some extent. The different granule appearances in the three regions suggest propagation of the reduction from the bottom of the crucible directed to the top of the SiO$_2$ layer. Since both SEM and EDX are surface analysis methods, the reduction degree inside the granules can only be
analyzed after cutting them.

B. Reduction inside the SiO$_2$ Granule

In order to investigate the reduction inside the granules, SiO$_2$ granules with the size of 1.0-2.0 mm were used. Figure 6 shows the cross sections of the working electrodes after electrolysis for (a) 60 min and (b) 150 min. Propagation of the reduction from the bottom of the crucible to the top of the SiO$_2$ layer is also observed. Figure 7 shows an SEM image of the cross section of the working electrode after electrolysis for 60 min. The cross section was slightly polished before the observation. In Figure 7, several granules are found to have dense cores, and they were proven to be SiO$_2$ by EDX. Two regions, (a) and (b) in Figure 7, are magnified to observe the reaction interface. The magnified images are shown in Figure 8 and the results of the EDX analysis at the positions designated in Figure 8 are listed in Table II. In both SEM images, a core-shell structure is observed. EDX analysis indicates that the shells are rich in Si (Pos. 2, 3, 4, and 5), and the cores remain SiO$_2$ (Pos. 1 and 6).

Considering the morphology of the reduced SiO$_2$ granules in Figure 8, the reduction progress in an SiO$_2$ granule is schematically illustrated in Figure 9. The reduction first starts at a certain point on the granule surface (Fig. 9(a)), and later proceeds via two routes: along the surface ($R_{surf}$), or from the surface to the core ($R_{ins}$) of the granule. The lengths of the solid arrows in Figure 9 represent the reduction rate. The reduction rate is faster along the granule surface than in the core, i.e. the reaction
front (three-phase zone) spreads faster at the surface compared to the core (Fig. 9(b)). After the entire surface is reduced and the porous Si shell is formed, as shown in Figure 9 (c), the reduction only proceeds inside the granule.

As reported in previous studies using an SiO$_2$ plate,$^{[15]}$ or pellets,$^{[21]}$ the reduction rate is thought to be closely related to the diffusion of the O$^{2-}$ ions. The observed reduction behavior is explained by the diffusion rate of O$^{2-}$ ions as follows. As shown in Figure 9, O$^{2-}$ ions are formed both at the granule surface (O$^{2-}_{\text{surf}}$) and inside (O$^{2-}_{\text{ins}}$). The widths of the open arrows in Figure 9 represent the diffusion rate of the O$^{2-}$ ions. For the reduction along the granule surface, the formed O$^{2-}$ ions immediately diffuse into the bulk CaCl$_2$. For the reduction inside, the formed O$^{2-}$ ions initially diffuse through the crevice of Si shell where CaCl$_2$ penetrates and successively to the bulk CaCl$_2$. As explained in the previous study,$^{[15]}$ the O$^{2-}$ ions accumulate in the CaCl$_2$ in the crevice, leading to an increase in the viscosity of CaCl$_2$ and the decrease in the diffusion coefficient of the O$^{2-}$ ions. Consequently, the diffusion of O$^{2-}$ ions decelerates inside the granule compared to the granule surface, resulting in a faster reduction along the granule surface than in the core. Accordingly, the reduction rate is expected to be higher for the smaller SiO$_2$ granules with a larger total surface area and shorter diffusion path. A detailed explanation of the effect of SiO$_2$ granule size on the reduction rate will be given in another paper.
**C. Reduction Mechanism**

By combining the present results with the previously reported mechanism for the reduction of an SiO$_2$ plate$^{[15]}$ and the predicted mechanism for SiO$_2$ granules,$^{[31]}$ an integrated explanation of the reduction behavior of SiO$_2$ granules stratified on the conductor in molten CaCl$_2$ was summarized and is shown in Figure 10.

(a) The granule surfaces in contact with the conductor are reduced to Si. The initial interface becomes porous because of the volume shrinkage from SiO$_2$ to Si. Molten CaCl$_2$ penetrates into the formed crevices, and the byproduct O$^{2-}$ ions diffuse away towards the anode. The produced Si with a high electric conductivity at 1123 K (850 °C)$^{[34]}$ forms new three-phase (SiO$_2$/CaCl$_2$/Si) zones.

(b) With the creation of new three-phase zones, the reduction proceeds both along the SiO$_2$ granule surface and into the core. The reduction is faster in the surface region compared to the inside region because of the difference in the diffusion rate of the O$^{2-}$ ions.

(c) A porous shell of Si is formed while the core remains unreacted for the SiO$_2$ granules in contact with the conductor. Since electrons are supplied through the porous Si shell, the reduction also proceeds at the SiO$_2$ granules second neighbor to the conductor.

(d) The reduction proceeds via two routes: (1) from the SiO$_2$ granules near the conductor to the top of the SiO$_2$ layer along the granule surfaces, and (2) from the surface to the core in partially...
reduced granules.
IV. CONCLUSIONS

The electrochemical reduction behavior of SiO$_2$ granules stratified on the current collector graphite in molten CaCl$_2$ at 1123 K (850°C) was investigated. The results show that the overall reduction proceeds via two different routes. One route is from the SiO$_2$ granules near the conductor to the distant ones along the granule surfaces. The other is from the surface to the core in partially reduced granules. The results also indicate that the reduction is faster via the former route rather than the latter one. The overall reduction rate is expected to improve using fine SiO$_2$ granules.

ACKNOWLEDGMENTS

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REFERENCES


1750-1758.


Caption List

Table I. Results of the EDX analysis of the positions in Fig. 5.

Table II. Results of the EDX analysis of the positions in Fig. 8.

Figure 1. Schematic illustration of the working electrode structure.

Figure 2. Photographs of the cross sections of the working electrodes after electrolysis at 0.5 V vs. \( \text{Ca}^{2+}/\text{Ca} \) for 2 min to 150 min in molten \( \text{CaCl}_2 \) at 1123 K (850°C). \( \text{SiO}_2 \) size: 0.10–0.25 mm. (\( \delta_R \)—thickness of the reduced dark layer; \( \delta_O \)—thickness of the original \( \text{SiO}_2 \) layer)

Figure 3. XRD patterns of (a) raw \( \text{SiO}_2 \) and (b) the sample after electrolysis at 0.5 V vs. \( \text{Ca}^{2+}/\text{Ca} \) for 150 min in molten \( \text{CaCl}_2 \) at 1123 K (850°C).

Figure 4. SEM image of the cross section of the working electrode after electrolysis at 0.5 V vs. \( \text{Ca}^{2+}/\text{Ca} \) for 10 min in molten \( \text{CaCl}_2 \) at 1123 K (850°C). \( \text{SiO}_2 \) size: 0.10–0.25 mm.

Figure 5. Magnified SEM images of the regions shown in Fig. 4.

Figure 6. Photographs of the cross sections of the working electrodes after electrolysis at 0.5 V vs. \( \text{Ca}^{2+}/\text{Ca} \) for 60 min and 150 min in molten \( \text{CaCl}_2 \) at 1123 K (850°C). \( \text{SiO}_2 \) size: 1.0–2.0 mm.

Figure 7. SEM image of the cross section of the working electrode after electrolysis at 0.5 V vs.
Ca$^{2+}$/Ca for 60 min in molten CaCl$_2$ at 1123 K (850°C). SiO$_2$ size: 1.0–2.0 mm.

Figure 8. Magnified SEM images of the regions shown in Fig. 7.

Figure 9. Schematic illustration of the reduction progress in an SiO$_2$ granule. (R$_{\text{surf.}}$—reduction along the surface, R$_{\text{ins.}}$—reduction from the surface to core, O$^{2-}_{\text{surf.}}$—O$^2$ ions formed at the granule surface, O$^{2-}_{\text{ins.}}$—O$^2$ ions formed inside the granule)

Figure 10. Schematic illustration of the mechanism of electrochemical reduction of SiO$_2$ granules in molten CaCl$_2$. 
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Table II. Results of the EDX analysis of the positions in Fig. 8.

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Fig. 1 Schematic illustration of the working electrode structure.
Fig. 2 Photographs of the cross sections of the working electrodes after electrolysis at 0.5 V vs. Ca\(^{2+}\)/Ca for 2 min to 150 min in molten CaCl\(_2\) at 1123 K. SiO\(_2\) size: 0.10–0.25 mm. (\(\delta_R\)—thickness of the reduced dark layer; \(\delta_O\)—thickness of the original SiO\(_2\) layer)
Fig. 3 XRD patterns of (a) raw SiO$_2$ and (b) the sample after electrolysis at 0.5 V vs. Ca$^{2+}$/Ca for 150 min in molten CaCl$_2$ at 1123 K.
Fig. 4 SEM image of the cross section of the working electrode after electrolysis at 0.5 V vs. Ca$^{2+}$/Ca for 10 min in molten CaCl$_2$ at 1123 K. SiO$_2$ size: 0.10–0.25 mm.
Fig. 5 Magnified SEM images of the regions shown in Fig. 4.
Fig. 6 Photographs of the cross sections of the working electrodes after electrolysis at 0.5 V vs. Ca\textsuperscript{2+}/Ca for 60 min and 150 min in molten CaCl\textsubscript{2} at 1123 K. SiO\textsubscript{2} size: 1.0–2.0 mm.
Fig. 7 SEM image of the cross section of the working electrode after electrolysis at 0.5 V vs. Ca\(^{2+}/Ca\) for 60 min in molten CaCl\(_2\) at 1123 K. SiO\(_2\) size: 1.0–2.0 mm.
Fig. 8 Magnified SEM images of the regions shown in Fig. 7.
Fig. 9 Schematic illustration of the reduction progress in an SiO$_2$ granule.

($R_{\text{surf}}$—reduction along the surface, $R_{\text{ins}}$—reduction from the surface to core, $O^{2-}_{\text{surf}}$—$O^{2-}$ ions formed at the granule surface, $O^{2-}_{\text{ins}}$—$O^{2-}$ ions formed inside the granule)
Fig. 10 Schematic illustration of the mechanism of electrochemical reduction of SiO$_2$ granules in molten CaCl$_2$. 

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