

Direct Electrolytic Reduction of Porous SiO₂ in Molten CaCl₂

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Silicon solar cells are indispensable to solve the energy and environmental issues. The demand for solar grade Si (SOG-Si) is expected to monotonically increase in the future. Thus, low-cost mass production of SOG-Si is essential to meet such a growing demand.

The authors have proposed a novel reduction process of SiO₂,¹⁻³ in which solid-state SiO₂ is electrochemically reduced to Si directly, as represented by



At the operation temperature (1123 K), Si behaves as an electric conductor. Hence, the electrochemical reaction described in Eq. (1) continuously proceeds as far as the produced O²⁻ is removed from the reaction sites. More importantly, the Si produced in this process is expected to have the same purity as the starting SiO₂. So far, the authors have succeeded in electrochemically reducing SiO₂ plates and clarified the reduction mechanism.¹⁻³ For practical and industrial applications, it is essential to use SiO₂ powder as a starting material.

It is reported that solar grade SiO₂ (SOG-SiO₂) powder can be easily and economically obtained by refining SiO₂ in acidic and basic solution processes, compared with the same-purity silane gases for the current Siemens process.^{4,5} Importantly, the SiO₂ powder refined in the solution processes is amorphous and has a peculiar porous shape, which may invoke the high reduction rate of SiO₂. The authors have reported the reduction of fumed SiO₂ powder⁶ and the SiO₂ powder refined in the solution processes.⁷

In this study, the authors studied the effect of microscopic properties (structure, porosity, etc.) on the electrolytic reduction of SiO₂ in molten CaCl₂ at 1123 K.

Experimental

All electrolysis was conducted in molten CaCl₂ at 1123 K under an Ar atmosphere. The working electrode was a SiO₂ pellet wound by a Mo wire as an electron-conducting material. The porous SiO₂ pellet was made by compressing amorphous SiO₂ powder refined in the above-mentioned solution processes. The counter electrode was a graphite rod, and the reference electrode was made by immersing a Ag wire in CaCl₂ containing 0.5 mol% AgCl set in a mullite tube. The Ca²⁺/Ca electrode was produced by electrochemically forming Ca on a Mo wire. Hereafter, all potentials were reported with reference to that of the Ca²⁺/Ca electrode.

Samples were prepared by the electrolysis at 1.00 V based on the previous cyclic voltammetric studies.¹ They were characterized by X-ray diffraction (XRD).

Results and Discussion

Figure 1 shows photographs of a SiO₂ pellet before and after the electrolysis at 1.00 V for 10 minutes. The electrolysis produced the circular parts whose color had been changed from white to dark brown, centered at pellet–Mo contacting points. From the pellets with different electrolysis duration, it was confirmed that the dark brown parts radially propagate from the contacting points with the progress of electrolysis.

The electrolyzed SiO₂ pellets were then characterized by XRD. Figure 2 shows XRD patterns of a SiO₂ pellet before and after the electrolysis at 1.00 V for 60 minutes. The XRD patterns confirm that a porous pellet made of amorphous SiO₂ powder is electrolytically reduced to form crystalline Si in molten CaCl₂.

In the symposium, more detailed discussion will be made for the enhancement of the reduction reaction as well as for the shape control.

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References

1. T. Nohira, K. Yasuda, and Y. Ito, *Nat. Mater.*, **2**, 397 (2003).
2. K. Yasuda, T. Nohira, and Y. Ito, *J. Phys. Chem. Solids*, **66**, 443 (2005).
3. K. Yasuda, T. Nohira, K. Ameszawa, Y. H. Ogata, and Y. Ito, *J. Electrochem. Soc.*, **152**, D69 (2005).
4. H. A. Aulich, K. H. Eisenrith, and H. P. Urbach, *J. Mater. Sci.*, **19**, 1710 (1984).
5. M. Bessho, K. Umehara, T. Takaura, T. Nishiyama, and H. Shingu, *J. Min. Mater. Process. Inst. Jpn.*, **117**, 736 (2001).
6. K. Yasuda, T. Nohira, K. Takahashi, R. Hagiwara, and Y. H. Ogata, *J. Electrochem. Soc.*, **152**, D232 (2005).
7. Y. Nishimura, T. Nohira, K. Yasuda, Y. Fukunaka, and R. Hagiwara, *Trans. MRS-J*, submitted.

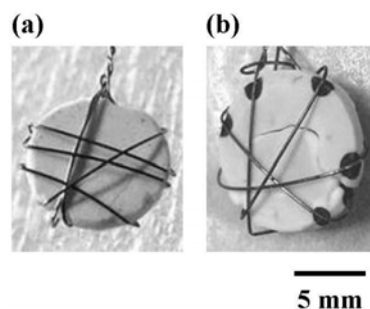


Figure 1. Photographs of a SiO₂ pellet (a) before and (b) after the electrolysis at 1.00 V for 10 minutes in molten CaCl₂ at 1123 K.

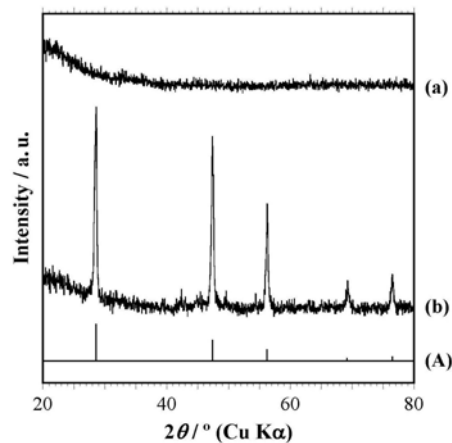


Figure 2. XRD patterns of a SiO₂ pellet (a) before and (b) after the electrolysis at 1.00 V for 60 minutes in molten CaCl₂ at 1123 K. The reference XRD pattern of (A) Si (JCPDS no. 27-1402) is also shown for comparison.