

Electrolytic Production of Silicon Using Liquid Zn Alloy Cathode in Molten CaCl₂

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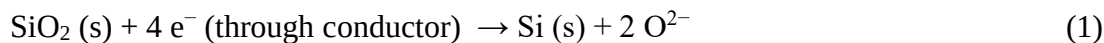
Abstract

A new electrolytic production process for solar-grade Si has been proposed utilizing a liquid Si–Zn alloy cathode in molten CaCl₂. The process consists of three major processes: electrolysis, precipitation, and refining. One of the advantages of the process is the attainability of high purity by application of a solidification refining from the liquid Si–Zn alloy. The residual zinc is easily removed afterwards due to its high volatility. To establish this process, the behavior of liquid Zn metal in molten CaCl₂ at 1123 K was investigated. Evaporation of Zn metal was largely suppressed by immersion into the molten salt, which enabled the use of a Zn electrode despite its high vapor pressure. Based on the results of cyclic voltammetry, the reduction of SiO₂ on a liquid Zn cathode was conducted by potentiostatic electrolysis at 0.9 V vs. Ca²⁺/Ca. Precipitated Si particles were recovered in the solidified Zn matrix.

Introduction

The rapid growth of photovoltaic (PV) industry has dramatically changed the industrial structure of high-purity polycrystalline Si. High-purity Si used for PVs is called as a solar-grade Si (SOG-Si; 5N~7N purity). SOG-Si was used to be supplied from an off-spec product as a product of semiconductor-grade Si of 11N~12N purity manufactured by the Siemens process utilizing the H₂ reduction/thermal decomposition of SiHCl₃. Nowadays, SOG-Si is manufactured as a main product in the Siemens plants, as a result of the increased demand for PV industry. For a next stage process of SOG-Si production, various types of production or refining processes of Si which can overcome the low productivity of the Siemens process are being investigated.

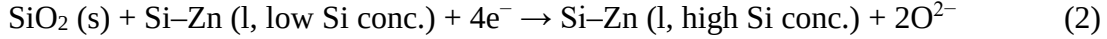
We have studied the direct electrolytic reduction of solid SiO₂ to Si in molten CaCl₂ at 1123 K as a new type of electrochemical reaction [1][2]. In this method, electrochemical reduction of insulating SiO₂ proceeds by the use of a SiO₂ contacting electrode which gives a three-phase interface between conductor/SiO₂/molten salt.



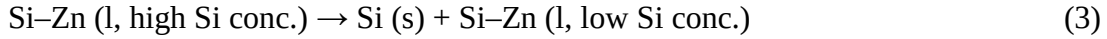
We also proposed that the combination of the electrolytic reduction of purified SiO₂ and a directional solidification refinement is a potential method to realize the low-cost production of SOG-Si [3]. Further, in order to increase the productivity of the process, we have studied the electrochemical reduction of SiO₂ granules set on the bottom cathode in molten CaCl₂ on the

analogy of the Hall-Héroult Al production process [4]. However, washing treatment using water or acid is necessary to recover the produced powdery Si from molten CaCl_2 and the residual SiO_2 . Since the separation between product and molten salt is an inherent problem for molten salt processes, in the practical manufacture of Li, Na, Mg, and Al metals, and rare earth alloys, the products are always produced in the liquid state for the easiness of the subsequent recovery.

Thus, we recently proposed an electrolytic process for SOG-Si production utilizing liquid Si-Zn alloy cathode as shown in Figure 1 [5]–[7]. The overall process is composed of three major processes: an electrolysis process, a precipitation process, and a refining process. In the electrolysis process, solid SiO_2 is reduced to form Si-Zn liquid alloy on the cathode.



Metallic Si is recovered in the precipitation process by lowering the temperature and the solubility of Si in the alloy.



The produced Si is further purified to SOG-Si by leaching, vacuum refining, and directional solidification. After the precipitation process, the Si-Zn alloy with low Si concentration is recycled for the cathode of the molten salt electrolysis.

In this study, fundamentals on the electrolysis process, namely, the evaporation of Zn metal in molten CaCl_2 and the electrochemical reduction of SiO_2 on Zn cathode were investigated at 1123 K.

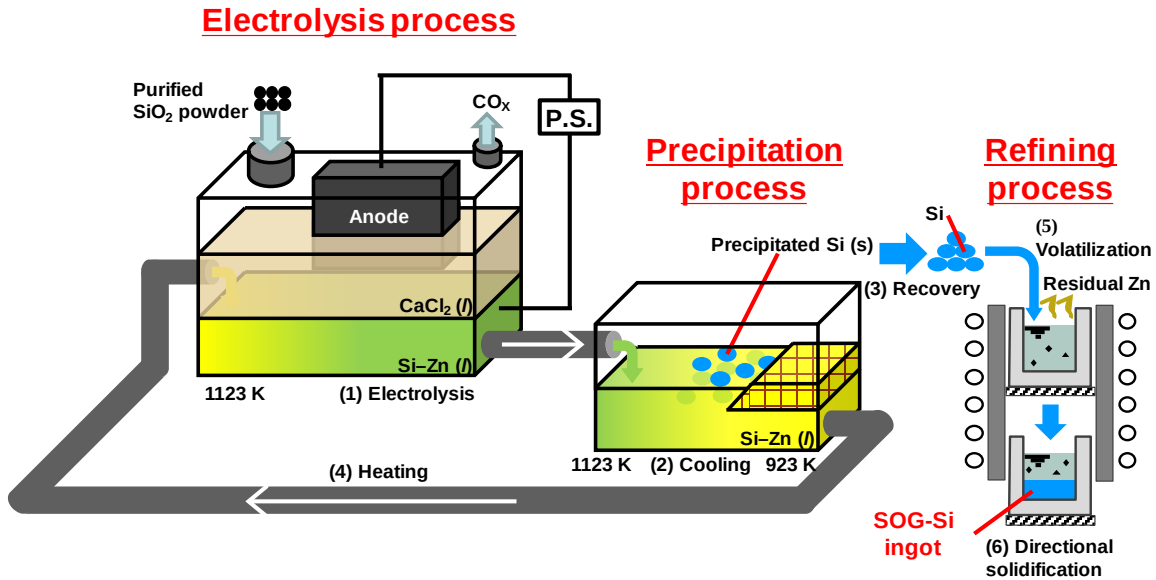


Figure 1 A schematic drawing of solar-grade Si production utilizing the electrochemical reduction of SiO_2 powder on liquid Si-Zn alloy cathode in molten CaCl_2 [5]–[7].

Experimental

The evaporation rate of Zn in an Ar atmosphere at 1123 K was measured by the weight change of Zn metal (5.4~5.6 g) set at the bottom of a silica tube (10.5 mm inner diameter). Experiments were conducted with/without the presence of molten CaCl_2 .

For investigation on electrochemical behavior, all the electrochemical experiments were carried out in a dry Ar atmosphere at 1123 K. High-purity CaCl_2 was charged in an alumina crucible and dried under vacuum at 773 K for 24 hours. Electrochemical behavior was investigated by cyclic voltammetry and potentiostatic electrolysis using a newly designed liquid Zn electrode. The counter electrode was a carbon rod. An Ag^+/Ag electrode was used as a reference electrode. Potentiostatic electrolysis was carried out for the liquid Zn electrode with SiO_2 granules on it.

Results and discussion

Figure 2 shows the relationship between reaction time and weight loss of Zn metal in the experiments with/without the presence of molten CaCl_2 over liquid Zn. In both cases, the weight of Zn metal linearly decreases with time. The graph obviously shows that the evaporation is significantly suppressed by the presence of molten salt. The evaporation rate determined by the slope of the plot is $4.45 \times 10^{-3} \text{ g cm}^{-2} \text{ h}^{-1}$ for the case with the presence of molten salt, which corresponds to the evaporation rate of 0.18 mm day^{-1} depth of Zn cathode. Thus, the evaporation of Zn metal covered with molten CaCl_2 is found to be negligibly small for the electrolysis process, even though the vapor pressure of Zn is as high as 0.54 atm at 1123 K [8].

According to the cyclic voltammograms of liquid Zn electrode with/without SiO_2 granules, the production of Si–Zn was suggested to occur in the potential range of 0.9~1.25 V vs. Ca^{2+}/Ca . Therefore, potentiostatic electrolysis was conducted for a liquid Zn electrode with SiO_2 granules having a diameter of 0.1 mm at 0.9 V for 5.5 h in molten CaCl_2 at 1123 K. The sample was observed after cross-sectioning in the vertical direction. In the upper part of the Zn electrode, precipitated particles were found by the optical microscope observation. Figure 3 shows a cross-sectional SEM image of the particles after the electrolysis. EDX analysis conducted at a cross mark in Figure 3 confirmed that Si particles with a diameter of 10~20 μm were deposited in Zn matrix. According to the Si–Zn phase diagram [9], solubility of Si in liquid Zn metal/Si–Zn alloy is ca. 6 at% at 1123 K that becomes negligibly small in solid Zn at room temperature. These

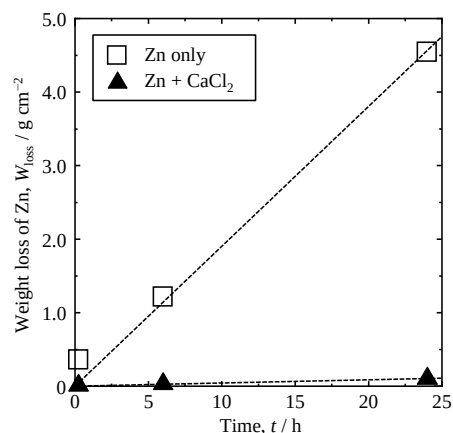


Figure 2 Time dependence of the weight loss of Zn at 1123 K with/without the presence of molten CaCl_2 [7].

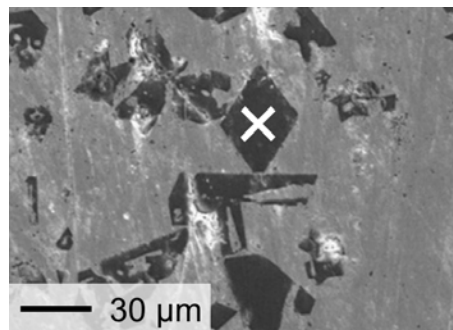


Figure 3 A cross-sectional SEM image of the Zn cathode after potentiostatic electrolysis at 0.9 V vs. Ca^{2+}/Ca for 5.5 h in molten CaCl_2 at 1123 K [7].

results indicated that SiO₂ was reduced to form liquid Si–Zn alloy and then Si particles were precipitated during the cooling process.

Conclusions

The electrolytic production process of SOG-Si utilizing liquid Si–Zn alloy in molten CaCl₂ was proposed. A liquid Zn cathode works even at 1123 K because the evaporation of Zn is effectively suppressed by the presence of molten salt. The formation of Si–Zn alloy was confirmed after the electrochemical reduction of SiO₂ granules on the Zn cathode at 0.9 V vs. Ca²⁺/Ca for 5.5 h.

Acknowledgements

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References

- [1] T. Nohira, K. Yasuda, and Y. Ito: *Nature Materials*, 2003, vol. 2(6), pp. 397-401.
- [2] K. Yasuda, T. Nohira, K. Amezawa, Y. H. Ogata, and Y. Ito: *J. Electrochem. Soc.*, 2005, vol. 152(4), pp. D69-D74.
- [3] K. Yasuda, T. Nohira, R. Hagiwara, and Y. H. Ogata: *Electrochim. Acta*, 2007, vol. 53(1), pp. 106-110.
- [4] T. Toba, K. Yasuda, T. Nohira, X. Yang, R. Hagiwara, K. Ichitsubo, K. Masuda, and T. Homma: *Electrochemistry*, 2013, vol. 81(7), pp. 559-565.
- [5] K. Yasuda, T. Nohira, R. Hagiwara, and T. Homma: *Abst. 45th Symp. Molten Salt Chemistry, Japan*, 2013, pp. 49-50. (in Japanese)
- [6] K. Yasuda: *Yoyuen Oyobi Koon Kagaku*, 2015, vol. 58(1), pp. 20-27. (in Japanese)
- [7] K. Yasuda, T. Shimao, R. Hagiwara, T. Homma, and T. Nohira, *J. Electrochem. Soc.*, 2017, vol. 164(8), pp. H5049-H5056.
- [8] M. W. Chase Jr.: *NIST-JANAF thermochemical tables fourth edition. J. Phys. Chem. Ref. Data*, 1998.
- [9] R. W. Olesinski and G. J. Abbaschian: *J. Phase Equilib.*, 1985, vol. 6(6), 545-548.