

## Electrochemical reduction behavior of granular SiO<sub>2</sub> in molten CaCl<sub>2</sub>

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### 1 Introduction

With the requirement for green renewable energy, solar power industry has been developing rapidly over the past decade. Since silicon (Si) is the most prevalent raw material for solar cells, there is a great demand for an innovative process for solar grade Si (SOG-Si) production with high yield and low cost.

The present authors had proved that solid silica (SiO<sub>2</sub>) can be electrochemically reduced to Si in molten salts [1-4]. Using high purity SiO<sub>2</sub> as the raw material, impurities in the produced Si can be controlled at low level [5]. A continuous electrochemical process was proposed to reduce powdery or granular SiO<sub>2</sub> to Si in molten CaCl<sub>2</sub> [6]. However, in order to scale up the laboratory experiment into an industrial production, an integrated understanding on the reduction process including mechanism and kinetics is still necessary.

This study aims to clarify the electrochemical reduction behavior of granular SiO<sub>2</sub> in molten CaCl<sub>2</sub>. The interfaces between the original SiO<sub>2</sub> and the produced Si after different electrolysis time were observed and analyzed. The effect of particle size of SiO<sub>2</sub> grains on reduction kinetics was also investigated.

### 2 Experimental

CaCl<sub>2</sub> (300 g) was charged in an Al<sub>2</sub>O<sub>3</sub> crucible. It was set inside a quartz vessel and heated to 850°C in a dry Ar atmosphere. A small graphite crucible filled with SiO<sub>2</sub> grains was used as the working electrode. A glassy carbon rod was used as the counter electrode and an Ag<sup>+</sup>/Ag electrode as the reference electrode.

As shown in Fig. 1, Al<sub>2</sub>O<sub>3</sub> tube was inserted into the inside of graphite crucible. A Ni wire was used as the current lead. Two kinds of high purity SiO<sub>2</sub> grains, 0.1-0.25 mm and 0.5-1 mm in diameter were charged to the inside of Al<sub>2</sub>O<sub>3</sub> tube. After immersing all the electrodes into the melt, the potential of 0.5 V vs. Ca<sup>2+</sup>/Ca was applied to the working electrode. After electrolysis for 2-300 min, the working electrode was taken out from the cell and cut vertically. The cross sections were directly observed. Then, they were also analyzed by SEM/EDX.

### 3 Results and discussion

Fig. 1 shows the cross sections of the working electrodes after electrolysis for 10, 60 and 300 min using SiO<sub>2</sub> grains of 0.5-1 mm in size. As can be seen, reduction proceeds from the crucible bottom to top. White SiO<sub>2</sub> grains were reduced to dark Si. As the electrolysis progresses with time, the thickness of the reduced layer increases.

Fig.2 shows the SEM images of the bottom of

graphite crucible after electrolysis for 2 min using the grains of 0.5-1 mm in size. The results of EDX analysis at positions in Fig.2 are listed in Table 1. The particle in the image was proved to be SiO<sub>2</sub> with Si-rich phase (Pos. 6 and 7) at the peripheral region. After electrolysis for even longer time, SiO<sub>2</sub> particles surrounded by Si-rich phases are still observed in the reduced layer. These results suggest that reduction starts at the SiO<sub>2</sub> particle periphery and proceeds to the core.

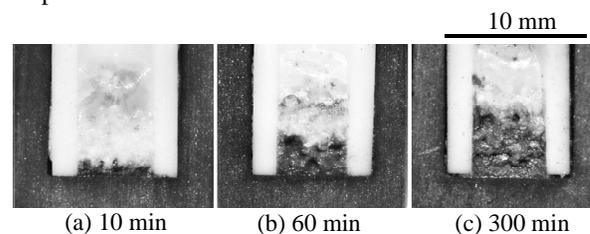


Fig. 1. Cross sections of the working electrodes after different electrolysis time. SiO<sub>2</sub> size: 0.5-1 mm.

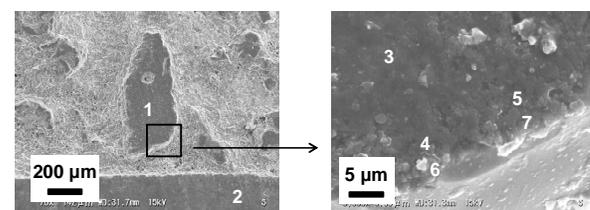


Fig. 2. SEM images near the bottom of graphite crucible after electrolysis for 2 min. SiO<sub>2</sub> size: 0.5-1 mm.

Table 1. Results of EDX analysis (at%).

| Position | Si   | O    | Ca  | Cl   | C    |
|----------|------|------|-----|------|------|
| 1        | 36.6 | 54.0 | 0.7 | 0.9  | 7.8  |
| 2        | 1.4  | 11.4 | 9.5 | 12.7 | 65.0 |
| 3        | 34.6 | 58.1 | 0.2 | 0.4  | 6.7  |
| 4        | 32.1 | 57.3 | 0.8 | 1.8  | 8.0  |
| 5        | 37.6 | 53.0 | 1.0 | 1.4  | 7.0  |
| 6        | 58.6 | 32.8 | 1.4 | 1.8  | 5.4  |
| 7        | 69.4 | 16.7 | 2.3 | 3.3  | 8.3  |

Accordingly, the overall reduction is considered to proceed in two different routes. One route is from the SiO<sub>2</sub> layer near the electrode to the distant SiO<sub>2</sub> layer along the particle surfaces. The other is from the particle periphery to the core in each grain. Further investigations suggest that the reduction from particle periphery to the core is the rate-determining step. In addition, the SiO<sub>2</sub> grains with smaller size were found to be favorable for faster electrochemical reduction.

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