Determination of Cell Potential for Silicon Electrodeposition

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Electrowinning of Si from cryolite-based melts is a possible solution for mass production of high purity silicon. The required cell potential to deposit Si on a cathode of interest, copper, is fundamental information that needs to be measured for controlling the co-deposition of impurities. In this study, the potential was measured using cyclic voltammetry in a cryolite-6 pct SiO₂ melt. The deposited Si on copper forms a Cu-Si alloy in which the activity of Si affects the decomposition potential. The measurements were carried out in a range of Si concentrations, allowing the prediction of potential change during the actual deposition process, where the Si content changes constantly. The results were compared with the values obtained from cyclic voltammetry on an inert electrode, graphite, to investigate if the formation of Cu-Si alloy is responsible for decreasing the potential.

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I. INTRODUCTION

THERE is a great momentum to shift our fuel-based energy dependence towards the alternative renewable sources. One of the most abundant renewable energies is solar power with a potential to far surpass the total energy demand of the world. However, the high cost of this energy has been the main hurdle against its widespread usage. Silicon is the chief photovoltaic material that accounts for 25 to 50 pct of the cost of solar panels. Traditionally, the majority of silicon for solar industry was supplied from overcapacity, scraps, and rejects of the semiconductor industry. The semiconductor grade Si requires excessive purity (9 N) and costs around \$250 kg⁻¹.^[1] On the other hand, 6 to 7 N is the acceptable range of purity for solar application and further purification is not necessary. Therefore, a new type of silicon known as solar-grade silicon (SoG-Si) was introduced, for which the target price is \$10 to 15 kg⁻¹.^[2,3] The current price is about \$18 kg⁻¹,^[4] down from over \$200 kg⁻¹ in 2008.

The existing method for production of solar grade Si (SoG-Si) necessitates a two-step process: producing metallurgical-grade Si (MG-Si) by carbothermal reduction of SiO₂,^[5] followed by the CVD-based purification method (Siemens). Although this technique requires high energy consumption (120 to 200 kWh kg⁻¹) and massive environmental impacts (90 t CO₂/t Si),^[6] it is still utilized in producing 95 pct of SoG-Si in the market. Thus, the need for developing a technology with higher productivity and lower energy intensity is

important. The feasibility of developing this alternative method has been investigated by numerous research groups in the past two decades. However, their achievements are limited to laboratory and pilot scale^[7,8] and not successful in commercial scale. The electrolytic approach has been proven to be a successful silicon producing method due to its analogy with other elements in the periodic table namely aluminum; though this approach remains relatively understudied.

Decomposition potential is the minimum potential required for continuous electrolysis^[9] and is one of the parameters that has to be measured to predict the required cell voltage and the possibility and order in which other elements are reduced. The standard decomposition potential of SiO₂ has been calculated from the Nernst's equation as -1.75 V at 1313 K (1040 °C).^[3,10,11] In most of the researches, graphite has been used as the anode due to its resistance to the corrosive environment of molten salts. Graphite reacts with the evolved O₂ and results in the release of CO and CO₂ on the anode surface. The reactions decrease the theoretical decomposition potential to -0.73 and -0.57 V for CO₂ and CO release, respectively.^[11]

The experimentally measured deposition potentials^[12-20] are considerably different from these calculated values. For example, the decomposition potential on graphite cathode has been reported between -0.80 and -1 V,^[12-20] which is approximately 0.25 V larger than the predicted potential. According to Boe *et al.*,^[13] this difference is mainly due to the polarization and concentration overpotential. However, applying cyclic voltammetry by Boen *et al.*,^[20] Osen *et al.*,^[19] and Ming *et al.*^[21] revealed two-step reduction of Si⁴⁺ in the alkaline fluoride melts. This method also enabled measuring the deposition potential of Si on a graphite cathode that is reported to be approximately -0.8 V vs Ag electrode.^[20]

Cryolite-based salts have been reported as the most suitable electrolyte for electrolysis of the silicon with respect to the product purity and current efficiency.^[22-25] The main focus of this study is to determine the decomposition potential of Si, from cryolite-SiO₂ melt

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on a Cu cathode, using cyclic voltammetry. The reason for using copper as cathode is to form a liquid alloy with silicon, thus eliminating the possibility of forming powdery solid Si, also to increase the current density. The Si could then be recovered using methods described elsewhere.^[8] According to the Nernst equation the decomposition potential is a function of the activity of Si in cathode:

$$\text{SiO}_2(\text{s}) \rightarrow \text{Si}(\text{s}) + \text{O}_2(\text{g}) \quad \Delta G_{1313\text{K}(1040^\circ\text{C})}^\circ = 676.2 \text{ kJ}, \quad [1]$$

$$E_T = E_T^\circ - RT \ln \left(\frac{a_{\text{Si}} \cdot P_{\text{O}_2}}{a_{\text{SiO}_2}} \right). \quad [2]$$

During electrowinning, the deposited Si dissolves in molten Cu cathode and forms a Cu-Si alloy. Theoretically, increase in the concentration and as a result the activity of Si in the alloy pushes the required potential to more negative values. This means that for continuous electrolysis, the potential should be adjusted and larger overpotentials should be applied. This effect was investigated experimentally and the results are presented in this paper. These results are also compared with the deposition potential of Si on an inert cathode, graphite, where the activity of Si is equal to 1.

II. EXPERIMENTAL

A. Chemicals

Cyclic voltammetry was conducted in 100 gr of SiO_2 - Na_3AlF_6 electrolytes containing 6 wt pct of SiO_2 . Natural cryolite (supplied by Rio Tinto—Alcan) with Na:Al ratio of 3.3 and total impurity content of 0.6 wt pct was ground into fine powders to pass a 104 μm sieve. Silica with a purity of 99.5 pct and mean particle size of 2 μm was used. Both powders were heated in an oven to 423 K (150 °C) to eliminate moisture and other volatile impurities.

B. Cell Assembly

A schematic drawing of the complete cell assembly is presented in Figure 1. A vertical tube furnace equipped with a digital controller was used to heat up the cell to 1313 K (1040 °C). The cell was held in an alumina tube to protect the wall of the furnace and the heating elements from corrosive atmosphere. All the experiments were conducted under an inert atmosphere using dried argon gas. The flow rate of the inlet gas was 50 mL min^{-1} and similar flow rate was measured in the outlet to assure that the system is fully sealed.

The cell consists of two electrodes: a copper disk (25 mm diameter and 5 mm height) as the working electrode, and a graphite rod (6.35 mm diameter) as the counter electrode. All the electrodes were attached to Mo leads (wires of 2 mm diameter) that were extended out of the cell to be connected to the potentiostat. All the lead wires were sheathed in alumina tubes to prevent

Fig. 1—Schematic experimental setup.

short circuiting and protect them from corrosive gases. When the melt reached equilibrium, the counter electrode was lowered to touch the melt surface. The melt level was detected by chronoamperometry technique. Then, it was immersed 20 mm into the molten salt.

The electrode potentials were controlled with a 1287 Solartron Potentiostat connected to a computer with a CorrWare software. Cyclic voltammetry was performed for a potential range of -1.25 to 0.3 V, considering the reported decomposition potential for silica. Different scan rates (5-10-20-50-80-100 mV s^{-1}) were applied to investigate the kinetics of oxidation and reduction reactions. To study the effect of Si concentration on the deposition potential, the melt was electrolyzed twice, each time for 20 minutes at -1.2 V; resulting in changing the concentration of Si on the surface of Cu electrode. Then, cyclic voltammetry experiments were repeated after each deposition to study the shift of potential and the variation in kinetics. A blank test was first performed in pure cryolite melt to enable recognition of background peaks resulting from the electrolyte.

These results were compared with the measured deposition potential on a graphite electrode as an inert cathode. Finally, similar experiment was run on the surface of 5 gr Cu-8 wt pct Si alloy. This alloy in molten at 1313 K (1040 °C) and will provide the exact potential that is required for continuous deposition of Si on the surface of this alloy.

III. RESULTS AND DISCUSSION

A. Cyclic Voltammetry on Graphite

Initially, cyclic voltammetry was conducted on an inert cathode (graphite) to measure the required potential at which the cathodic half reaction commences at graphite electrode. The deposition potential was measured vs Pt as a quasi-reference electrode. The

experimental setup was similar to what was explained for copper cathode. The only differences in the setup were the working electrode, which was a graphite rod (6.35 mm diameter), the counter electrode, which was graphite crucible, and the concentration of SiO₂ in cryolite. The detailed experimental procedure is provided in previous publications.^[10,26] A typical voltammograms recorded with two different scan rates, in cryolite-5 wt pct SiO₂ at 1313 K (1040 °C), is shown in Figure 2. Major cathodic and corresponding anodic peaks form due to Si deposition and re-oxidation. At lower scan rate, Figure 2(a), the reduction reaction starts at -0.65 V and reach its maximum at -1 V. The presence of the corresponding anodic peak at around -0.1 V indicates that silicon can be cathodically deposited and anodically oxidized. The shape of the voltammogram confirms that this reaction is not reversible. However, the major cathodic peak is a combination of two small peaks, indicating multi-stage reduction of Si on graphite, which is also confirmed by the formation of an anodic shoulder on the main peak. According to Ming *et al.*^[21] the main peak is due to:

and the post-peak is due to the actual silicon formation:

These two peaks have a similar current intensity that corresponds to similar rate constant of the reactions at scan rate as low as 20 mV s⁻¹. While the recorded voltammogram at higher scan rate, 50 mV s⁻¹ shown in Figure 2(b), illustrates two completely separate peaks: the first peak at -0.7 V is elongated and the second one at -1 V is hindered. This brings the conclusion that the second reaction has a slow kinetics and is likely the rate determining step. At higher scan rates (50 mV s⁻¹); the progress of this reaction is very limited. Whereas, at lower

scan rates (20 mV s⁻¹), this reaction has enough time to proceed and the two steps occur at a comparable rate.

B. Voltammetry Measurements on Copper

In the following sections, the effect of changing cathode to Cu will be discussed. Cu will form a liquid cathode with Si that is expected to change the kinetics of electrolysis, as well as the deposition potential by decreasing the activity of Si.

C. Cyclic Voltammetry in Cryolite

As a blank test and to eliminate possible background peaks later, cyclic voltammogram were recorded before any Si⁴⁺ were introduced to the system as SiO₂. The potential was varied in the cathodic direction from 0.5 V and was reversed at -1.2 V to determine the electrochemical behavior of the melt. The recorded voltammograms are shown in Figure 3.

From the figure it is seen that decomposition of cryolite starts approximately at -0.6 V. This peak is attributed to irreversible Na deposition as no broad oxidation peak is observed in the oxidation cycle. As the working temperature of the cell was above the boiling temperature of Na 1156 K (883 °C), evaporation of the deposited Na occurs and the oxidation peak is less prominent.^[21,27] Deposition of Al is also reported in cryolite,^[21,27] and can be a reason for the serration of the graph at larger overpotential. Oxidation of copper was observed at around 0.4 V, which dictated the anodic range of the potential window.

D. Cyclic Voltammetry in Cryolite-6 wt pct SiO₂ Melt

Cyclic voltammogram for deposition and subsequent dissolution of Si on a copper electrode were recorded within the potential range of 0.3 to -1.4 V. Cyclic voltammetry in of molten cryolite on a copper electrode shows that copper oxidation starts at 0.3 V, Figure 3(a),

Fig. 2—Typical voltammogram recorded on a graphite cathode vs Pt reference in cryolite-5 wt pct SiO₂ melt at 1313 K (1040 °C); (a) scan rate 20 mV s⁻¹, (b) scan rate 50 mV s⁻¹.

Fig. 3—(a) Voltammogram in molten SiO₂-free cryolite; 20 mV s⁻¹, (b) Voltammogram in molten SiO₂-free cryolite; 50 mV s⁻¹.

Fig. 4—Voltammogram for deposition of Si on copper in molten cryolite-6 wt pct SiO₂; 10 mV s⁻¹.

therefore the anodic potential limit was set below this value to avoid the oxidation of the copper electrode. The cathodic limit was set to observe a deposition peak and tolerate the current limit of the potentiostat.

Figure 4 shows a typical cyclic voltammogram obtained on the copper electrode for Si⁴⁺ reduction in a cryolite system with 6 wt pct SiO₂ at 1313 K (1040 °C). This voltammogram is compared with the recorded voltammogram in cryolite at the same scan rate, 10 mV s⁻¹. As seen, bulk deposition of Si (C₁) commences from -0.6 V with a maximum rate at -1 V. This potential is less cathodic than the equilibrium potential predicted by the Nernst equation. However, it is in good agreement with the presented potential by Grjotheim *et al.*^[13] His results reports -1.1 V as the cell potential for deposition of Si on Cu. Peak identified as A₁ in the reverse cycle corresponds to the stripping of electrodeposited Si. The charge consumed for the current rise at -1 V is much greater than the corresponding anodic peak. This difference in current

indicates that considerable amount of current is consumed by irreversible solvent decomposition (as seen in Figure 3).

Two minor reversible peaks (C₂ and A₂) are also observed at potentials below that for bulk deposition of Si. These peaks are related to the under-potential deposition (UPD) and subsequent oxidation of Si. UPD is mainly because of adsorption of Si ions on Cu substrate ($\text{Si}_{\text{solv}}^{4+} + 4\text{e}_{\text{Cu}} = \text{Si}_{\text{ad,Cu}}$).^[28,29] This phenomenon can only happen if the activity of the product in the cathode is less than unity. Besides the bulk deposition and UPD peaks, another cathodic peak (C₃) also exists in this voltammogram. The most plausible explanation for this neighbor peak seems to be interaction between Cu and Si, and formation of Cu-Si alloy. As soon as Si deposits on the surface of Cu electrode a molten layer of Cu-Si alloy forms on the surface. At 1313 K (1040 °C), to form a liquid, approximately 4 pct Si must be present in the cathode, which can be achieved at the surface rather quickly. In the anodic scan, a very small reduction peaks (A₃) appears, which corresponds to de-alloying of Si from the surface before stripping of Si.

E. Effect of Scan Rate

To investigate the kinetics of the reduction reaction, the reaction was studied over a wide range of scan rates. The potential was swept with different rates (20, 50, 80, and 100 mV s⁻¹) in the cathodic direction from 0.3 V. The recorded voltammograms are presented in Figure 5. The bulk deposition potentials independent of the scan rate indicate that the reaction is reversible. However, the potentials for UPD and alloying are influenced by this increase. The two cathodic peaks C₂ and C₃ merge to become one peak with larger current intensity at the scan rate of 100 mV s⁻¹. The merge is accompanied by a shift toward more cathodic potentials. This shift reveals that adsorption is controlled by diffusion. At low scan rates, the ions have sufficient time for diffusion, whereas this is not possible at faster scan rates.

A cyclic voltammogram recorded under the same condition as Figure 5, but with a lower scan rate (5 and 10 mV s^{-1}) is provided in Figure 6. As can be seen, the currents for both reduction and corresponding oxidation peaks increase from the first to the second cycle. In the first cycle, Si deposits on the surface of solid copper, forming a shallow melt, which enhances both adsorption and bulk deposition occurring in the second cycle.

F. Effect of Si Concentration

As discussed earlier, the deposition potential is a function of Si activity in the product. According to the results of cyclic voltammetry the deposited Si interacts with the Cu cathode and forms a Cu-Si alloy. During the deposition process, the concentration of Si in the alloy constantly changes, which results in continuous change in the deposition potential. To investigate this effect, Si was deposited from cryolite-6 wt pct SiO_2 on the surface of Cu at -1.2 V in two 20 minutes intervals and cyclic

voltammetry was conducted on the surface of the formed alloy after each step. The recorded voltammograms at 20 and 50 mV s^{-1} scan rates are presented in Figure 7.

As shown in both graphs, increase in Si concentration due to longer deposition time shifts the reduction peaks to more cathodic potential or toward the predicted standard potential. This shift should be considered during the deposition process either by adjusting potential in a certain period of time or applying larger overpotential.

Besides the change in potential, both anodic and cathodic currents increase with higher Si concentration. This change in the kinetics can be due to transformation of solid Cu to molten Cu-Si alloy.

G. SEM Analysis

The feasibility of depositing Si was studied by analyzing the cathode after two-step deposition at -1.2 V. The surface of the cathode was cleaned from solidified electrolyte and was studied under SEM. The image of the sample as well as the elemental mapping is presented in Figure 8. The elemental mapping verifies deposition of Si particles, which are uniformly distributed in Cu. This distribution confirms that the deposited Si dissolves in copper and forms an alloy. The formed Cu-Si alloy is molten at this temperature resulting in formation of a liquid layer on the surface. This surface melting is responsible for change in the shape of the cathode from cylindrical to semi hemispherical shape.

H. Voltammetry Measurements on Copper-8 wt pct Si Alloy

The electrochemical behavior of the melt on the surface of a Cu-8 wt pct Si alloy was investigated. The recorded voltammogram is presented in Figure 9. Comparing these two voltammograms reveals the UPD and alloying at 0.15 and 0.04 V. Bulk deposition starts at lower potential of -1.1 V compared to pure copper cathode (Figure 4). One other main difference between

Fig. 5—Effect of scan rate on the recorded voltammogram in cryolite-6 wt pct SiO_2 melt, scan rates 20,50,80, 200 mV s^{-1} .

Fig. 6—Recorded voltammogram in cryolite-6 wt pct SiO_2 melt at scan rates of 5 and 10 mV s^{-1} .

Fig. 7—Cyclic voltammogram recorded in cryolite-6 wt pct SiO_2 after two-deposition steps of 20 min; (a) scan rate 20 mV s^{-1} , (b) scan rate 50 mV s^{-1} .

Fig. 8—SEM image and elemental mapping of cathode after 40 min electrolysis at -1.2 V .

Fig. 9—Voltammogram on Cu-8 wt pct Si in molten cryolite-6 wt pct SiO_2 ; 50 mV s^{-1} .

this graph and Figure 4 is the anodic peaks (A_2 and A_3) corresponding to dealloying and stripping of adsorbed Si does not happen on the surface of Cu-Si alloy indicating that these reactions are not reversible. Cu-Si

alloy is molten at this working temperature, which means that the deposited silicon dissolves in the bulk of cathode immediately, whereas in the experiments involving pure Cu cathode, the deposited Si forms a monolayer or solid layer that later strips off in the reverse cycle.

IV. CONCLUSIONS

The deposition potential of Si on graphite electrode was measured at approximately -1 V . This is the required potential that has to be applied to graphite vs Pt for the continuous deposition of Si. It was found that the kinetics of Si deposition on graphite is slow, so electrodeposition in molten cathode was considered as a possible solution. Copper was chosen as the candidate cathode, expecting the formation of a liquid Cu-Si alloy. The results showed that UPD of Si and formation of Cu-Si alloy take place. This was associated to the lower activity of Si due to its dissolution in Cu. The bulk deposition of Si on Cu occurs approximately at -1 V . Increase in Si concentration did not change the bulk deposition potential, while shifted the underpotential

peaks toward the predicted standard potential, possibility as a result of increase in silicon activity. SEM analysis on the cathode after 40 minutes deposition confirmed uniform distribution of Si at the Cu surface. The voltammetry on the surface of molten Cu-Si alloy confirms -1.1 V as the bulk deposition potential of Si. Both underpotential and alloying effect are also observed on this cathode but these reactions are irreversible.

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