Electrorefining of Silicon Using Molten Salt and Liquid Alloy Electrodes

T. Oishi, K. Koyama, and M. Tanaka

Environmental Management Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8569, Japan

A new Si refining process, which employs molten salt electrolysis and precipitation steps, is proposed and tested. In this process, impure Si is added to a Cu-Si liquid alloy anode, and the electrorefining of Si is conducted using an Al-Si liquid alloy cathode in a fluoride-based molten salt. From the obtained Si-enriched Al-Si alloy, purified Si is obtained by precipitation. A glow discharge mass spectrometry analysis revealed that the proposed process can effectively remove the dominant impurities such as Fe, Mn, Ti and V from metallurgical grade Si (98–99% purity). A preliminary electrolysis using Si cells recovered from a commercial photovoltaic module, of which the dominant impurities are Ag, Al and Na, showed that the present process is also applicable for Si recycling from waste photovoltaic modules.

In the past few decades, demands for photovoltaic (PV) cells have significantly increased. Although many types of PV cells have been invented and/or produced, crystalline silicon PV cells account for most of the produced PV cells at present, because of their high energy conversion efficiency, stability and safety. In addition, silicon is the second most abundant element in the earth’s crust by mass, which is really important when one considers the rapid spread of PV cells today and in the near future. On the other hand, one of the disadvantages of the crystalline silicon PV cells is economic cost, especially, the cost to produce pure silicon; solar-grade silicon (SoG-Si, 6N: 99,9999999999% purity) is regarded as one of the most serious problems. So far, SoG-Si has been supplied from the semiconductor industry, which uses higher purity silicon (SEG-Si, 11N: 99.9999999999% purity) commonly produced by the so-called Siemens process. Currently, SoG-Si is also produced independently by the Siemens-based process, which is specialized for the SoG-Si production. Although this process is advantageous for the purity of the Si product, it is rather costly and energy consuming. Thus, a more cost and energy-effective process to produce SoG-Si is required.

One of the other important issues we need to consider is how to handle the waste PV modules in the near future.1 As already mentioned, silicon itself is an abundant element, and the recycling of normal grade silicon might not seem to be important. The SoG-Si, however, requires huge economic and energy costs to produce, and it is better to recycle from this view point as well as the point of reducing environmental pollution due to the hazardous materials contained in the PV modules like Pb. Another aspect the authors focused on is the potential utilization of the Si cells recovered from waste PV modules as secondary resources for the SoG-Si production. Since the impurities in the Si cells are basically limited to intentionally added ones during the production steps, target elements which should be removed are also limited compared to that in the metallurgical grade Si (MG-Si, the feed material for the conventional SoG-Si production).

Based on this background, a number of new processes for SoG-Si production has been proposed and/or investigated, although most of them utilize natural resources like MG-Si and SiO2. Among the processes under investigation, molten salt electrolysis is one of the most extensively investigated ones,2-13 which allows reduction of the economic cost and energy consumption, and basically has a sufficient productivity. In most of these investigations, however, Si was electrodeposited in the solid state, which tends to cause contamination from the melt component. To avoid this problem, Mattei et al.7 attempted the Si electrodeposition at a temperature higher than the melting point of Si, around 1700 K, using a BaO/SiO2/BaF2 melt. Although this process was extensively investigated, it has not yet been commercialized. This is probably due to the contaminations from the used materials like the crucible, reaction chamber, electrodes, etc., which will be more dominant at such a high temperature. Focusing on the electrorefining of Si, which is more suitable than electrowinning for Si recycling from waste PV modules, the simplest process employs solid Si electrodes as the anode and cathode as Sharma et al. reported.8 Olsen and Carleton used a mixture of Si and a solid Cu-Si alloy as the anode.9 Recently, some research groups have employed the combination of a Cu-Si liquid alloy anode and solid Si cathode in a NaF-KF or CaCl2-based melt.11,12 Although CaCl2 is easily dissolved in water, the use of a fluoride melt makes it difficult to separate the Si product from the solidified melt. In addition, electrodeposition in the solid state is basically unsuitable for industrial electrolysis due to the risk of a short circuit and difficulty in realizing a continuous operation. From this viewpoint, the process that Olsen and Rolseth proposed might be one of the solutions in which a vertical stack of three molten layers with a Cu-Si alloy at the bottom, an intermediate fluoride melt, and liquid Si at the top are employed.10 Although this process has the potential to be operated in an industrial scale, like the electrorefining of Al, problems similar to the process Mattei et al. proposed might arise.7 That is, the use of liquid Si requires a higher temperature than 1700 K, which imposes severe limitations on the materials used as the components of the electrolytic cell and tends to cause some contamination from these materials.

Recently, the present authors proposed a new SoG-Si production process employing molten salt electrolysis and subsequent Si precipitation steps using an Al-Si liquid alloy.14 In this electrolysis, high purity SiO2, an Al-Si liquid alloy and carbon are used as the feed material, cathode and anode, respectively. One of the most important points is the use of the Al-Si liquid alloy as the cathode, which allows a good separation between the melt and cathode product at the relatively low temperature of 1000–1300 K. Another important advantage of this process is that continuous operation is easy due to the similarity to Al electrowinning called as the Hall-Héroult process. The use of high purity SiO2, however, is rather costly and makes it difficult to apply this process to the recycling of Si from waste PV modules. The authors now propose a new electrorefining process for Si, which employs an Al-Si liquid alloy and a Cu-Si liquid alloy as the cathode and anode, respectively. As shown in Fig. 1, Si is refined via the following steps; (a) low purity Si, such as Si cells from PV modules or MG-Si, is added to a liquid alloy anode like Cu-Si, (b) Si and these elements having a more negative redox potential than Si are dissolved from the anode into the melt, (c) Si and these elements having a more positive redox potential than Si are deposited on the liquid alloy cathode like Al-Si, (d) the liquid alloy having a high Si concentration is removed from the electrolytic cell and Si is obtained by precipitation or other

*Present address: Advanced Materials Science and Engineering, Faculty of Engineering, Chiba Institute of Technology, Narashino, Chiba 275-0016, Japan.

E-mail: tetsuo.oishi@aist.go.jp

© The Author(s) 2016. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0391614jes] All rights reserved.
techniques, and (e) the remaining liquid alloy is reused as the cathode for the electrolys.

The main reactions are as follows:

\[
\text{Anode: } \text{Si(liqui)} + \text{Cu-Si alloy} \rightarrow \text{Si(IV)} + 4e^- \quad [1]
\]

\[
\text{Cathode: } \text{Si(IV)} + 4e^- \rightarrow \text{Si(liqui)} + \text{Al-Si alloy} \quad [2]
\]

Precipitation: \( \text{Al-Si(liqui)} \rightarrow \text{Si + Al-Si(liqui)} \) [3]

In this study, we first observed the impurity behavior and current efficiencies during the proposed process using MG-Si as the feed material. Second, the Si cells were recovered from a commercial PV module and were used as the feed material for the preliminary experiment.

Structure of Crystalline Si PV Modules

The general structure of the crystalline Si PV module is shown in Fig. 2, in addition to a photograph of the PV module used for the present experiment. Although the Si used is originally p-type Si having a trace level of impurities, a certain amount of P is doped in the surface layer in order to make the p-n junction. In addition, Ag electrodes and anti-reflective coating(s) are mounted on the surface. The back side surface of the Si cell is usually coated with Al to make electrical contact. The Si cell and electric leads are encapsulated by ethylene-vinyl acetate (EVA), which has a high stability against moisture and ultraviolet radiation. The front and back surfaces are covered with a sheet of glass and a back film made from Al or a polymer.

Experimental

**Electrorefining of Si in a cryolite-based melt.**—The experimental setup for the electrorefining is schematically shown in Fig. 3. Although a three-layer electrolysis is more suitable for commercialization, it is unsuitable as a preliminary experiment due to the strict limitation in the setup and the difficulty in avoiding the influence of possible volatile substances on the cathode reaction. Thus, the anode and cathode were located at the bottom of the crucible and a cryolite-based melt was selected as one of the typical and inexpensive fluoride melts. Compared to the potential electrolyte of the BaF\(_2\) and/or CaF\(_2\)-based melt for the three-layer electrolysis, the use of a cryolite-based melt probably has a negative effect on the purity of the refined Si because Na and Al could be electrodeposited on the cathode at more positive potential compared to Ba and Ca. A Cu-Si (17 wt%) alloy was initially prepared from a MG-Si of 98% purity and Cu particles of 99.99% purity. These were weighed, vacuum sealed in a quartz tube, kept at 1523 K for 2.5 hours to form a homogeneous liquid phase, then cooled in the air. A total 350 g of the NaF-AlF\(_3\) melt, of which the NaF/AlF\(_3\) molar ratio was 2.7 and typically containing 1 wt% of SiO\(_2\) and 9 wt% of Al\(_2\)O\(_3\), was used as the electrolyte. A 70–90 g sample of the Cu-Si alloy and 12 g of Al (99%) were placed in boron nitride (BN) crucibles of I.D. 30 mm \(\times\) 35 mm (h). These were placed in a carbon crucible of I.D. 70 mm \(\times\) 140 mm (h), and the entire sample was positioned in a reaction chamber, then heated by an electric furnace at 773 K under vacuum for 20 hours in order to remove the adsorbed water and gases. The reaction chamber was then filled with 1 atm Ar and further heated to 1273 ± 5 K under flowing Ar.

Galvanostatic electrolysis was carried out using the fused Cu-Si and Al-Si (initially, pure Al) alloys as the anode and cathode, respectively, at current densities of 0.3, 0.5 and 0.6 A/cm\(^2\) (from 2 to 4 A) for 6.4 hours. Carbon rods of 5 mm diameter covered with BN tubes were used as the electric leads. After the electrolysis, Si precipitation was conducted by slowly cooling the entire sample in a reaction chamber, which was stored in the electric furnace with no power supply. In the examined condition, it took around 15 hours to cool to room temperature. The solidified cathode, anode and melt were separated from each other and weighed. The whole of the Al-Si cathode was dissolved in a hydrochloric acid solution and the electrodeposited Si on the cathode was collected as Si powder. The Al content of the Al-Si alloy was measured by ICP-AES using the filtrate of the above solution. Around 0.5 g of the obtained Si powder and MG-Si used were ground separately to homogenize and were measured by GD-MS (glow discharge mass spectrometry; the diameter of the analyzing area was 10 mm) in order to evaluate the impurity content.

**Si cell recovery from a PV module and preliminary electrorefining.**—In order to evaluate the effectiveness of the present process on the Si recycling from PV modules, the Si cell was recovered from a commercial PV module by burning off of the EVA after removal of the Al frame. The Si cell was then collected from the mixture of glass, back sheet, interconnector and Si cell. The obtained Si cell was further treated by a gas burner in order to remove the attached organic carbon. Thus obtained Si cell was ground and subjected to the electrorefining under essentially the same conditions as described.
in Electrorefining of Si in a cryolite-based melt section. Based on the result of the electrorefining using MG-Si, the SiO₂ concentration increased from 1 to 2 wt%, and electrolysis was conducted at the current density of 0.3 A/cm² for 10 hours. Parts of the Si cell, purified Si and Al-Si alloy cathode after the electrorefining were subjected to GD-MS.

Results and Discussion

Electrorefining of Si in a cryolite-based melt.—The resultant anode was weighed in order to evaluate the anodic current efficiency. Since our preliminary examination indicated that the weight loss of the anode is attributed to reaction 1 and the contribution of Cu oxidation is negligible, the anodic current efficiency was evaluated using the following equation:

\[
ε_a = \frac{Δw_a}{A_0} \frac{4F}{Δw} \quad [4]
\]

where \(ε_a\) represents the anodic current efficiency, \(Δw_a\) is the weight loss of the anode, \(A_0\) is the atomic weight of Si, \(Q\) is the amount of electricity passed and \(F\) is Faraday’s constant. As for the cathode, the Al-Si alloy was dissolved in a hydrochloric acid solution and Si in the alloy was collected as Si powder as described in the Experimental section. Although a part of the Si dissolved in the solution, it was negligible because the mass of the dissolved Si was three orders of magnitude lower than that of the Si powder. The partial cathodic current efficiencies for the Al and Si electrodeposition were calculated using the following equations:

\[
ε_{c(Al)} = \frac{3F}{A_{Al}} \frac{Δw_{Al}}{Q} \quad [5]
\]

\[
ε_{c(Si)} = \frac{4F}{A_{Si}} \frac{w_{Si depo}}{Q} \quad [6]
\]

where \(ε_{c(i)}\) represents the partial cathodic current efficiencies for \(i\), \(Δw_{Al}\) is the weight gain of Al in the cathode, and \(w_{Si depo}\) is the weight of the Si powder. The calculated current efficiencies are summarized in Fig. 4. As for the anodic current efficiency, \(ε_a\), it ranged from 1.1 to 1.3. This is essentially consistent with the results that Olsen and Rolseth reported. According to them, the higher \(ε_a\) than unity is attributable to the initial dissolution of the impurities. Although similar phenomenon might have occurred under the present condition, our additional experiment suggested another possibility of a non-faradaic reaction. That is, when the Cu-Si alloy was exposed to the melt under the same condition as the electrolyzed anode with no current flow, the weight loss of 1 wt% was observed, which is attributed to the oxidation and dissolution of Si in the Cu-Si alloy possibly caused by the residual water or oxygen in the melt. Because of the existence of reactive metals, Al in the cathode and Si in the anode, this oxidation probably proceeds immediately just after the fusion of the melt. In other words, the contribution of the non-faradaic reaction could be assumed to be constant regardless of the current density. Based on this assumption, \(Δw_a\) in Equation 4 could be substituted by the total weight loss minus 1% of the initial weight of the Cu-Si alloy, and \(ε_a\) decreases from 1.1–1.3 to 0.9–1.1. Concerning the partial cathodic current efficiency for the Al electrodeposition, which is explained by reaction 7, it increased with the current density. This is basically due to the negative shift of the cathode potential during the electrolysis at the higher current densities.

\[
Al(III) + 3e^- → Al(liq)_{in Al-Si alloy} \quad [7]
\]

The partial cathodic current efficiency for the Si electrodeposition showed the highest and lowest values at the current density of 0.5 A cm⁻² and 0.6 A cm⁻², respectively, when the SiO₂ concentration was fixed at 1 wt%. Such a complex tendency is attributable to the fact that the present cathode reaction is controlled by a variety of reactions like a substitution reaction between Al and Si, formation of monovalent Al ions, divalent Si ions and Na metal fog, etc. Although the reason why \(ε_{c(Si)}\) decreased at 0.6 A cm⁻² is unclear at present, one of the possible explanations is indirect reduction of Si(IV) by reducing reagent like Na metal fog, which is formed on the cathode at a high current density due to the negative shift of the cathode potential. The formed Na metal fog could reduce Si(IV) species in the melt and decrease the Si(IV) concentration near the cathode surface. This might consequently decrease the \(ε_{c(Si)}\) value. Actually, an XRD analysis indicated the existence of crystalline Si in the solidified melt taken from the part near the cathode and intermediate point between the anode and cathode, as shown in Figs. 5a and 5c. The presence of crystalline Si at a point distant from the cathode strongly suggests that the crystalline Si was not formed by direct reduction on the cathode.

![Figure 4](image1.png)  
**Figure 4.** Anodic current efficiency and partial cathodic current efficiencies plotted versus the current density. The closed and open symbols represent the results obtained in the 1 wt% and 2 wt% SiO₂ containing melt, respectively.

![Figure 5](image2.png)  
**Figure 5.** XRD patterns of the solidified melt obtained from the part (a) near the cathode, (b) near the anode and (c) distant from both electrodes, after the galvanostatic electrolysis at 0.46 A/cm².
but formed by indirect reduction of Si(IV) species by reducing reagent like Na metal fog. The other peaks shown in Fig. 5 correlated to the melt components of cryolite (Na₃AlF₆) and chiolite (Na₅Al₃F₁₄), reflecting the NaF/AlF₃ molar ratio of 2.7. As for Fig. 5b, which is the result of the solidified melt located near the anode surface, the strongest peak appeared at 2θ = 28.5° (Cu-Kα). Although this might correspond to the peak of crystalline Si, other peaks that coincided to Si were weak or difficult to be recognized. Thus, the presence of Si in this part is doubtful at present.

In order to observe the influence of the SiO₂ concentration, galvanostatic electrolysis was also carried out at SiO₂ and Al₂O₃ concentrations of 2 and 8 wt%, respectively. As shown in Fig. 4 by the open symbols, the increase in the SiO₂ concentration lead to an increase in the partial cathodic current efficiency for Si electrodeposition, while that for the Al electrodeposition was reduced. This improvement is attributable to the increase in the partial current used for the Si electrodeposition, which consequently suppressed the competitive reaction of the Al electrodeposition. In addition, dendritic Si was found around the cathode, which is probably formed by a faradaic reaction and was not obtained in the liquid alloy due to the comparatively high deposition rate versus the low diffusion rate of Si inside the liquid alloy. Figure 6 shows a photograph of the cathode and dendritic Si after solidification. Similar solid Si deposition was observed in the other conditions, and it was most significant when the SiO₂ concentration increased to 2 wt%, where the highest n(Si) was obtained. Since it is quite difficult to collect the dendritic Si because of the low solubility of the solidified melt in aqueous solutions, the amount of the dendritic Si was not considered as part of cathodic current efficiency. This is probably the main reason why the total cathodic current efficiency was much less than unity in all cases.

The impurity content of the Si powder obtained from 1 wt% SiO₂ containing melt at 0.5 A/cm² was measured by GD-MS in order to roughly evaluate the purification effect of the present process. Note that the GD-MS is a quasi-quantitative measurement and that the purification effect for the minor impurities has no meaning because of the presence of such impurity elements in the original melt, Al cathode and the other materials used in the electrolysis. It should also be taken into consideration that a part of obtained Si was originated from the SiO₂ added to the melt. The GD-MS result of the obtained Si powder and MG-Si used in the present experiment are shown in Table I. Although the purification effect could be discussed from the results of GD-MS, it contains contributions of both the electrorefining and precipitation steps. Thus, the purification effect of the present electrorefining was evaluated using the following equations:

\[ k_{i,\text{electrolysis}} = k_{i,\text{electrolysis}}^\ast \times k_{i,\text{prec}} = \frac{C_i,\text{in Purified Si}}{C_i,\text{in MG-Si}} \]  
\[ k_{i,\text{prec}} = \frac{C_i,\text{in Precipitated Si}^\ast}{C_i,\text{in Impure Si}^\ast} \]

where \( k_{i,\text{electrolysis}} \), \( k_{i,\text{electrolysis}}^\ast \), and \( k_{i,\text{prec}} \) represent the purification effect of the total process, the electrorefining step, and the precipitation step for element \( i \). \( C \) is the concentration of element \( i \) in the following materials:

- \( C_i,\text{in Purified Si}^\ast \): purified Si obtained in the present work
- \( C_i,\text{in MG-Si}^\ast \): MG-Si used in the present work
- \( C_i,\text{in Precipitated Si}^\ast \): purified Si obtained in the literature
- \( C_i,\text{in Impure Si}^\ast \): impure Si used as the feed material in the literature

On the assumption that \( k_{i,\text{prec}} \) in the present work was identical to that in the literature, \( k_{i,\text{electrolysis}} \) values for some elements were calculated using Equation 8, present GD-MS results and the data reported by Yoshikawa and Morita. In addition to the obtained \( k_{i,\text{electrolysis}} \) values, the redox potential calculated from the Gibbs Free Energy of the fluoride compound at 1273 K is also listed in Table I as a reference to the Si(IV)/Si redox potential under standard conditions. From a thermodynamic point of view, noble elements in comparison to Si, that is, Fe, V, Ni, etc., are not oxidized and remain in the anode alloy. Concerning the ignoble metals like Na and Ca, these are supposed to be oxidized and remain in the melt. These elements having redox potentials close to that of Si(IV)/Si, i.e., Mn, Ti, P and B, are difficult to be removed by the present electrorefining. Based on the theoretical consideration, the low \( k_{i,\text{electrolysis}} \) value for Fe and the high purification effect for the noble metals like Fe, V and Ni shown in Table I are attributed to the anode process. On the other hand, the low \( k_{i,\text{electrolysis}} \) value for Ti and relatively high purification effect for Mn and Ti seems inconsistent with the thermodynamic calculation. One of the possible explanations is that the activities of these metals in the Cu-Si alloy were much lower than unity, which shifted the redox potential in the positive direction according to the Nernst equation. As for P, the \( k_{i,\text{electrolysis}} \) value was 5 and higher than unity, which might mean that the present electrorefining cannot effectively remove P. This point will be further discussed in the following section.

**Table I. Summary of GD-MS results of the purified Si and MG-Si along with the calculated redox potentials.**

| Unit | Fe (ppmw) | Al (ppmw) | Mn (ppmw) | Ti (ppmw) | V (ppmw) | Ni (ppmw) | P (ppmw) | B (ppmw) |
|------|-----------|-----------|-----------|-----------|----------|-----------|----------|----------|
| MG-Si| 3000      | 500       | 200       | 100       | 100      | 50        | 50       | 5        |
| Purified Si| 2        | 400       | 0.2       | 0.3       | 0.1      | 0.3       | 4        | 300      |
| \( \epsilon \) vs. Si(IV)/Si| V = 0.9 | -0.36     | 0.16      | -0.06     | 1.06     | 1.33      | 0.11     | 0.05     |
| Redox couple| Fe(II)/Fe| Al(III)/Al| Mn(II)/Mn| Ti(IV)/Ti| V(IV)/V | Ni(II)/Ni| P(II)/P  | B(III)/B  |
| \( k_{i,\text{electrolysis}} \) | 9 × 10⁻² | 7 × 10⁻²  | 7 × 10⁻²  | 7 × 10⁻²  | 7 × 10⁻² | 7 × 10⁻²  | 7 × 10⁻² | 7 × 10⁻² |
orders of magnitude and became less than 1 ppmw. Since Ag is a much more noble metal compared to Si, the result suggests that almost all of the Ag remained in the anode. This is one of the advantages of the present process, because Ag seems to be completely separated during the anode process, and Ag in a Cu-based alloy could be easily recovered by a copper smelter. Concerning the other major impurities, most of them were removed with some exceptions like Al, B and Fe. The reason for the increase of Fe content is attributed to the relatively high Fe content in the Al used, because Fe is known as a major impurity in Al due to the presence in bauxite as the oxide state. In fact, the Fe contents in the purified Si shown in Tables I and II are nearly the same, which strongly suggests that the detected Fe originated mainly from the used Al. The removal ratio of P is similar to the result shown in reference [10].

This is because the purification effect during the precipitation step was carried out under the appropriate conditions. Thus, purification effect during the precipitation step from Al-Si alloy, $k'_{\text{prec}}$ was calculated using the impurity content of Al-Si alloy instead of that in the impure Si.

$$k'_{\text{prec}} = \frac{C_{i, \text{in Precipitated Si}}}{C_{i, \text{in Al-Si alloy}}} [10]$$

where $C_{i, \text{in Al-Si alloy}}$ represents impurity contents of the Al-Si alloy. The calculated values are also listed in Table II. On the one hand, the calculated values from the literature were on the order of 10$^{-2}$ or less for Fe, Ti, B and P, which experimentally clarified the effectiveness of this precipitation step. On the other hand, obtained values in the present work were $1.5 \times 10^{-2}$, 30, 1 and 2.5 for Fe, Ti, B and P, respectively, which were much higher (less) except for Fe. These results indicate that there is room for further improvement, if the precipitation step was carried out under the appropriate conditions. This result also suggests that actual $k_{\text{electrolysis}}$ values for Ti and P were much lower than those listed in Table I.

Although the impurity content of the purified Si is still high to meet the standard of SoG-Si, and an Al removal process that Saegusa etc. proposed, for example, is essentially indispensable, the data obtained in the present study indicated the possibility of the proposed process in refining impure Si like MG-Si and Si cells obtained from waste PV modules. In the present study, however, the behavior of B was not clarified because of the use of BN crucible. In addition, in order to discuss the impurity behavior on the order of 1 ppm or less, special attention should be paid to the materials used in the electrolysis. These will be the major subjects in a future study.

### Table II. Summary of GD-MS results of the Si cell recovered from a commercial PV module, Al-Si alloy cathode and purified Si, along with the calculated redox potentials.

| unit     | Ag   | Al  | Na  | Ca   | P   | Sn | Ti | B  | Fe | Mn |
|----------|------|-----|-----|------|-----|----|----|----|----|----|
| Acid treated Si cell | ppmw | 10000 | 500$^*$ | 100  | 70 | 50 | 50 | 30 | 3  | 1  | 0.01 |
| Al-Si alloy | ppmw | 2 | matrix | 0.2 | 0.1 | 2   | $<0.5$ | 5 | $<0.5$ | 30 | 3 | 0.04 |
| Purified Si | ppmw | 0.4 | 500 | 0.6 | $<0.5$ | 5 | $<0.5$ | 30 | 3 | 0.04 |

* 10 wt% before the acid treatment.
** Calculated from the experimental data reported by Yashikawa and Morita.

### Conclusions

As a new SoG-Si production process or Si recycling process from waste PV modules, molten salt electrorefining using Al-Si and Cu-Si liquid alloy electrodes combined with a Si precipitation step from an Al-Si liquid alloy has been proposed, and the following results and conclusions were obtained.

a) The GD-MS result of the purified Si indicated that the present process has certain purification effects in both cases that the metallurgical grade Si and the Si cells recovered from a commercial PV module were used as the feed material.

b) As for Fe, Ti and P, the purification effect during the electrorefining and precipitation from the Al-Si alloy steps were separately evaluated, and it was confirmed that the present electrorefining is effective to separate Fe and Ti.

c) The cathodic current efficiency varied with the current density and was much lower than unity, while the anodic current efficiency was close to unity. This is partly attributed to the solid Si electrodeposition near the Al-Si alloy cathode.

d) The behavior of B was not clarified in the present study. Thus, further investigation is needed.

### Acknowledgment

This research was supported in part by a grant from the Environment Research and Technology Development Fund (RFP-I-1101) of the Ministry of the Environment, Japan. The authors gratefully acknowledge the helpful discussions with Dr. Saegusa, Dr. Sawabe and Dr. Hata of Sumitomo Chemical Co., Ltd.

### References

1. N. C. McDonald and J. M. Pearce, *Energy Policy*, **38**, 7041 (2010).
2. D. Ellwell and R. S. Feigelson, *Solar Energy Mater.*, **6**, 123 (1982).
3. D. Ellwell and G. M. Rao, *J. Appl. Electrochem.* **18**, 15 (1988).
4. E. J. Frazer and B. J. Welch, *Electrochem. Acta*, **22**, 1187 (1979).
5. J. M. Olson and K. L. Carleton, *J. Electrochem. Soc.*, **128**, 2698 (1981).
6. G. M. Rao, D. Ellwell, and R. S. Feigelson, *J. Electrochem. Soc.*, **128**, 1708 (1981).
7. R. C. De Mattei, D. Ellwell, and R. S. Feigelson, *J. Electrochem. Soc.*, **128**, 1712 (1981).
8. K. H. Stern and M. E. Mccollum, *Thin Solid Films*, **124**, 129 (1985).
9. I. G. Sharma and T. K. Mukherjee, *Metall. Trans. B*, **17B**, 395 (1986).
10. T. Nohira, K. Yasuda, and Y. Ito, *Nat. Mater.*, **2**, 397 (2003).
11. E. Olsen and S. Rolseth, *Met. Mat. Trans. B*, **41B**, 295 (2010).
12. J. Cai, X.-c. Luo, G. M. Haarberg, O. E. Kongstein, and S.-l. Wang, *J. Electrochem. Soc.*, **159**, D155 (2012).
13. L. Massot, A. L. Bieber, M. Gibilaro, L. Cassayre, P. Taxil, and P. Chamelot, *Electrochim. Acta*, **96**, 97 (2013).
14. T. Oishi, M. Watanabe, K. Koyama, M. Tanaka, and K. Saegusa, *J. Electrochem. Soc.*, **158**, E93 (2011).
15. T. Yoshikawa and K. Morita, *ISIJ Int.*, **45**, 967 (2005).
16. P. Wang, H. Lu, and Y. Lai, *J. Cryst. Growth*, **390**, 96 (2014).
17. A. Roine et al., HSC Chemistry 7, Outotec Research Oy, Finland, 2009.
18. K. Saegusa, T. Megumi, and H. Tabuchi, Japanese patent disclosure 2010-257714 (2010).