Electrodeposition of Solar Cell Grade Silicon in High Temperature Molten Salts

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Abstract. Silicon is the most common material used in solar cells. High cost of silicon restricts the widely use of PV power. In order to make solar cells more accessible and affordable, it is strongly needed to develop a new and low-cost production process of solar energy silicon (SoG-Si). Electrodeposition of SoG-Si films appears to be a cost saving technique since solidification and sawing steps which contribute significantly to the overall cost of solar cells will be bypassed. Electrodeposition of SoG-Si has been evaluated during the last three decades, and some of them have shown promising results. Thermodynamic and kinetic considerations which relate to the electrodeposition of silicon are discussed, and progresses towards the developments of the electrodeposition of silicon in high temperature molten salts are reviewed in this paper.

Keywords. Silicon, solar cell, electrodeposition, molten salts.

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1 Introduction

Photovoltaic technologies (PV) offer a potentially unlimited source of emission-free, renewable energy. In the last decade, PV has been the fastest growing renewable energy technology. Figure 1 presents the global annual PV market and global cumulative installed capacity from 2000 to 2010 (The data are from reference [1] and [2]). The world cumulative PV power installed was less than 3 GW in 2003 and increasing to almost 40 GW in 2010, and the annual market of PV has developed from less than 1 GW in 2003 to more than 16.6 GW in 2010 in spite of the difficult financial and economic circumstances.

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The most common semiconductor material used in photovoltaic cells is silicon, commanding about 80% of the market at present [2]. Although alternative technologies are developed, silicon is still expected to be the dominant PV technology for the foreseeable future due to the availability, the relatively inexpensive industrial production route and the non-toxicity of silicon. It should be noted that the operating hours of PV plants are lower than those of conventional plants today. Cost is the major factor, which limits the market of PV and prevents it from joining the energy mainstream. The high price of solar-cell modules is due to the high SoG-Si cost and significant wastage during ingot slicing. In order to make solar cells and modules more accessible and affordable, it is important to reduce the production costs. Much work has been focused on developing less expensive production routes of SoG-Si. Table 1 gives the comparative silicon cost produced by different technology (The data are from reference [6]).

Electrodeposition of silicon has received much attention since this technique has a number of unique and attractive features, such as lower operating temperature and applicability to large and irregular device areas. Probably most importantly, the electrodeposition process can be simply controlled by electrical parameters to facilitate precision in the film thickness and morphology [7–11], which appears to be cost saving technique since solidification and sawing steps which contribute significantly to the overall cost of solar cells will be bypassed.

It was reported that Ullik was the first one who successfully obtained silicon by electrodeposition in 1865 [12, 13]. Many attempts were done to improve the silicon electrodeposition process since then. The early work on silicon electrodeposition was reviewed by Elwell as seen in reference [13, 14]. However, in the past two decades, there

Technology	Purity	Production Cost	Market Share
Siemens process	9 N	\$35–\$50/ kg	≈ 78%
Fluidized bed reactors	6–7 N	\$25–\$45/ kg	≈ 16%
Upgraded metallurgical Si	≈ 5 N	\$20–\$60/ kg	≈ 6%

Table 1. Comparative cost analysis of different technology.

Figure 1. Evolution of global cumulative installed capacity and global annual PV market from 2000 to 2010.

have been many developments for silicon electrodeposition, i.e. new electrolyte systems and direct electro-reduction method. In this paper, we present a review on the development of silicon reduction by electrodeposition, especially after 1990 from the fundamental thermodynamic and kinetic consideration. Based on the different silicon precursor, the research works can be mainly divided into two aspects. One was using K_2SiF_6 as silicon precursor; the other was using SiO_2 as precursor.

2 K_2SiF_6 as Silicon Precursor

Fluorosilicic acid is a viable low-cost source of silicon for the silicon electrodeposition since the fluorosilicate may be obtained by the reaction of potassium fluoride and fluorosilicic acid, a byproduct of phosphate fertilizer production by acid treatment of rocks and has few uses at present [13, 15]. The Center for Materials Research at Stanford University was very active on the Si electrodeposition with K_2SiF_6 as silicon precursor in the 1970s and 1980s. They published many papers as seen in reference 16–25. Cohen and Huggins were probably the first to show that silicon could be electrodeposited from a molten alkali metal fluoride bath containing K_2SiF_6 in detail as seen in reference 7 and 10. There are many factors that influence the deposition of silicon, such as electrolyte composition, substrate, current density and so on.

2.1 Electrolyte Composition

Molten fluorides were first used as the electrolyte for the silicon deposition based on their attractive properties such as

high conductivity, low viscosity, high decomposition voltage, and fluxing agents for surface oxides. Cohen et al. described that high quality epitaxial layers of silicon could be deposited upon single crystalline silicon substrates from a $KF-LiF$ (1 : 1) bath, with 5 mole% K_2SiF_6 as a solute in a vacuum tight-chamber filled with an atmosphere of purified helium [7]. Elwell et al. and other groups studied several fluoride solvent systems [16–38]. However, they found that only the binary $LiF-KF$ eutectic or the ternary $LiF-NaF-KF$ eutectic melt gave acceptable quality deposit. Beside the research work of using the molten fluoride as electrolyte, molten chloride has also been used as electrolyte [26, 27, 34, 35].

According to the familiar Nernst equation (Equation 1), electrodeposition of M can occur at potentials more negative than the equilibrium potential E_M . This difference in potential is the overpotential (η^M).

$$E_M = E_M^\varphi + (RT/nF) \ln[(\alpha_{M^{m+}})/\alpha_M], \quad (1)$$

where E_M^φ is the standard potential for the reduction to form M , R is the gas constant, T is the absolute temperature, m is the number of electrons required for the reduction, F is the Faraday constant, and $\alpha_{M^{m+}}$ and α_M are the activities of M^{m+} in the electrolyte, and of M in the deposit, respectively. The more positive of E_M value, the easier it is to reduce metal ions, and the more negative of E_M value, the more difficult it is to reduce the metal ions.

When there are some impurities (N^{n+}) in the electrolyte, N may codeposit with M if their deposition potentials are more positive than silicon, as Equation 2 shows.

$$E_N + \eta^N \geq E_M + \eta^M. \quad (2)$$

To obtain high quality silicon deposit, it is important to control the purity of the electrolyte and concentration of silicon electroactive species. Pre-electrolysis at little positive potential than the deposited potential of silicon is an effective procedure to remove impurities which have higher deposition potential than the applied potential for pre-electrolysis. Cohen [7] confirmed that silicon purity was improved by pre-electrolysis. Boen and Bouteillon [26, 27] noticed that only discrete silicon nuclei were obtained on the electrode surface when using a partially purified solvent, and they pointed out that it was impossible to obtain electrolytic silicon on graphite or silver electrodes using a non-purified solvent. Moore et al. [31] also concluded that high-quality silicon could be obtained by pre-electrolysis treatments before deposition.

However, impurities with a lower deposition potential than the applied potential for pre-electrolysis still remain in the solution after pre-electrolysis. If the subsequent applied potential for the deposition of silicon is more negative than their deposit potential, they will codeposit with silicon. So it is important to carefully choose the concentration of electroactive species and the applied potential to obtain high purity of silicon.

2.2 Electroactive Species Concentration

As mentioned above, the concentration of the electroactive species should not be too low in order to avoid codeposition of impurity elements because of the cathodic shift of the reversible potential when the concentration decreases. But more important is the effect of the concentration on the limiting current density for silicon deposition, since electrodeposition near the limiting current density gives rough and dendritic deposits. However, too high concentration of electroactive species increases the melting point of the bath, which leads to volatilization of the salts as well as to inter-diffusion of the substrate and the Si film. So it is very important to choose a proper concentration of electroactive species. Elwell et al. concluded that 4–15 mol% K_2SiF_6 concentrations were desirable to obtain continuous inclusion-free silicon layers [13]. Abbar et al. [36] indicated that the purity of deposited silicon increased with decreasing K_2SiF_6 concentration. Moreover, they suggested that concentrations lower than 10% were not suitable because the current decreased rapidly.

2.3 Substrate

The substrate material is a very important parameter for determining the deposited coatings structure and properties. It is well-known that the nature and surface characteristics of the substrate play a very important role on the initial formation of any electrodeposits [39]. Cohen [8] used Ag, W or Nb as the substrate for silicon deposition. It was found that

the deposited layer was more uniform and had better adherence with Ag substrate than W and Nb. Cohen pointed out that the reason for the better uniformity of the deposit on Ag is probably due to the easier nucleation on Ag. The better adherence to the Ag substrate is probably due to the lack of an underlying diffused silicide alloy with Ag (W and Nb form WSi_2 and $NbSi_2$, respectively). Also, Ag is more ductile and may easily accommodate the stresses created by non-matching thermal expansion coefficients. Elwell et al. [17, 20] confirmed that graphite substrate was also suitable for the silicon deposition. Electrodeposited silicon could be stripped more easily as a sheet from the graphite substrate than from the silver substrate. Compared with silver substrate, graphite is relatively inexpensive.

2.4 Current Density/Potential Control

The nature and morphology of the deposit are influenced by the rate of the electron transfer reaction and concentration. The nucleation rate of crystals is a function of the current density/overpotential. Lower current density/overpotential causes a low deposition rate of silicon, and the deposits are rougher and dendritic. The rougher and dendritic microstructure leads to the adsorption of electrolyte in the deposits surface. Increased current density was found to contribute to more uniform growth [7]. But deposition at higher current densities was found to result in powdery or dendritic deposits on top of a thin, coherent layer. Elwell [13] suggested that the current density on a silver cathode should not exceed 20 mA/cm^2 . They attributed the noncoherent or spongy deposits to a secondary reaction between deposited silicon and Si^{4+} from the melt as the following reaction [18],

Under normal current density and concentration, layers produced during electrolysis for short periods are often spongy and less crystalline, but prolonged electrolysis leads to densification. Generally, the upper layers of the thick deposits are porous [17]. Cohen [8] suggested that the Alternating Square Wave Pulse (ASWP) technique could help to improve the uniformity and growth rate of polycrystalline Si. Boen and Bouteillon [26, 27] found that DC current lead to dendritic growth and the texture irregularity increased with increasing current density. However, it was found that the deposits on silver and graphite using pulsed current were non-dendrites.

Stern and Mccollum [29] noticed that the morphology of the deposits depends primarily on the applied voltage. At the lowest voltages the coating consisted of densely packed small crystals, but the coating structure consisted of a densely packed network of lacy rounded crystals at a slightly higher voltage. A small increase in voltage resulted in a separation of the network into individual crystals.

2.5 Deposit Quality

The typically deposit purity obtained at potential closed to the deposition potential was more than 99.98% by using 99–99.5% purity starting materials and running pre-electrolysis process [16, 17, 20]. The impurities were Al, B, Cr, Fe, Mg and Ni. The best sample obtained was 99.999% purity silicon obtained by Rao et al. with 10 ppm level of impurity concentration in the electrodeposits, including 2 ppm B, 5 ppm Cr, 0.6 ppm Cu, 0.3 ppm Pt, and 1 ppm Ag [16].

2.6 Deposit Morphology

The typical morphology of deposits on silver and graphite was polycrystalline. The grain structure of the deposited silicon was columnar, and the grain size in range from 60–100 μm was typical for silicon films deposited for 8–10 h [18]. Individual grains of a polycrystalline layers for use in photovoltaic cells should be at least 100 μm to yield an efficient of photovoltaic energy conversion great than 10% [17]. It is known that the grain size will be larger by prolonging the deposition time or in electrolysis involving large charge densities. Carleton and Olson et al. [28] found that the grain size was different by control different initial current-time profiles to the same final current density from zero. The grain size of the material can be controlled independently of the final growth conditions by controlling the initial current-time profile. Also, the authors pointed out that there were areas where the nuclei did not coalesce; leaving voids in the material if the initial current density was too low.

Carleton and Olson et al. [28] studied the electrochemical nucleation and growth of silicon on vitreous carbon and graphite in molten KF-LiF-K₂SiF₆. The results indicated that the nuclei were hemispherical and were also all of equal size which indicating that the growth was three dimensional and the nucleation process was instantaneous, which was also pointed out by Stern and Mccollum [29].

2.7 Current Efficiency

High current efficiency, as well as high quality of deposit, is an important target for electrolysis process. The optimum current efficiency affected by such factors as electrolyte composition, electrolyte temperature, electrode spacing, and addition agents etc. Sharma and Mukherjee [30] studied the effect of cathode current density, electrolysis temperature and K₂SiF₆ concentration on the cathode current efficiency respectively. The results were as follows:

- (1) By properly increasing the current density, the current efficiency could increase, while too higher current density may lower the efficiency. This is presumably because the deposit become more and more powdery in nature and consequently less adherent.

- (2) 750°C was found to be the optimum temperature as any change from this value decreased the current efficiency quite sharply. The decrease of current efficiency at higher temperature (800°C) is presumably due to volatilization, which lower the K₂SiF₆ concentration. The authors also reported that the deposits obtained at higher temperatures were difficult to remove from the electrode.
- (3) The current efficiency improved progressively when the K₂SiF₆ concentration was increased from 6 to 15 mol%, but it started to decrease when the K₂SiF₆ concentration was beyond 15 mol%. Chemical dissolution of deposited silicon in the electrolyte at higher concentration may be a possible reason for such reduction in current efficiency.

The current efficiency was normally 30–50% for electrodeposition silicon in LiF-KF and LiF-NaF-KF molten salts using K₂SiF₆ as solute [17]. This value is too low, which may inhibit its production application.

2.8 Reduction Mechanism

There are mainly two different aspects considering the mechanism of the electrodeposition of silicon from a solution of K₂SiF₆ in molten fluoride electrolytes. Rao and Elwell et al. [16, 17, 21, 22] proposed that the reduction process is a quasi-reversible reduction of silicon (IV) to silicon (0), and that the rate-determining step is the charge-transfer process for the deposition process. Moreover, the deposition kinetics appeared to be influenced by a chemical reaction preceding the charge-transfer, which is probably related to the dissociation of Si_nF_{2n+2} polynuclear complexe. Li et al. [32, 33, 37] also concluded from studies by cyclic voltammetry and chronopotentiometry that the electrochemical process is controlled by diffusion of Si (IV) with a quasi-reversible electron transfer step. Bieber et al. [38] suggested that silicon electrodeposition process in NaF-KF molten salts involved an instantaneous nucleation with diffusion-controlled nuclei growth.

However, Boen and Bouteillon [26, 27] suggested a two-step reduction mechanism for electrodeposition of silicon from a solution of Na₂SiF₆ in KF-NaF-LiF molten salts. The proposed reduction reaction is as follows,

3 Silica as Silicon Precursor

SiO₂ is probably the ideal source material of silicon since it is extremely plentiful and available in high purity natu-

ral deposits. In 1970s, much work on the SiO_2 electrolysis in cryolite melts were carried out by Grjotheim and Welch et al. [40–43]. Their aim was direct codeposition of an aluminum-silicon alloy in the Hall-Heroult cell, which is used for aluminium production. The work on the production of SoG-Si using SiO_2 as a material source by normal electrolysis method has mainly been done since 1980.

Elwell et al. attempted electrowinning of molten silicon from different kind of electrolyte [44,45]. It was reported that silicon was deposited in a 63.2 mol% SiO_2 , 22.2 mol% BaCO_3 , 14.6 mol% BaF_2 melt, using graphite electrodes at 1465°C without pre-electrolysis [44]. The purity of the deposited silicon was 99.97 wt%. This level of impurities is too high for solar cell applications, but the authors pointed out that the purity could be enhanced by pre-electrolysis using a sacrificial cathode. However, in this electrolyte system, the density of the silicon was very similar to that of the melt, which made it difficult to remove the silicon efficiently from the melt. The authors suggested that a prolonged electrolysis time could improve the separation of the silicon from the melt since the deposited silicon coagulated.

NaF or KF and BaF_2 , CaF_2 and MgF_2 were also tested for the silicon electrodeposition using SiO_2 as a solute [45]. Among the tested electrolyte systems, NaF/CaF_2 eutectic turned out to be the best electrolyte in terms of silicon electrodeposition. One problem was that the deposit was in the form of small particles typically 30–50 μm in diameter dispersed in the solidified solvent rather than a continuous mass. This is mainly associated with a form of instability in which the grains which nucleate first grow preferentially, and therefore prevent nucleation on the substrate in their immediate vicinity by depleting the solution of solute ions. The authors concluded that NaF/CaF_2 and KF/CaF_2 eutectics appeared less attractive for silicon deposition than cryolite or the $\text{LiF}/\text{NaF}/\text{KF}$ eutectic. The authors suggested avoiding the use of LiF as a solvent due to its low solubility in water and acids, which makes it difficult to eliminate the excess of salt adhered to the electrodeposited silicon.

In recent years, one of the authors (G. M. Haarberg) studies the possibility to deposit silicon from the CaCl_2 - NaCl - CaO - SiO_2 melt at 850°C under argon atmosphere, and some of the results have been published as seen in reference [46,47]. Analysis results indicated that the contents of boron and phosphorus in the refined silicon obtained by potentiostatic electrolysis were reduced from 36 ppmw and 25 ppmw to 0.27 ppmw and 0.89 ppmw respectively [47].

Recently, Cai et al. [48] investigated the electrochemical behavior of silicon in the NaCl - KCl - NaF (1 : 1 : 2 in molar ratio) system which saturated with SiO_2 at 800°C using cyclic voltammetry and chronoamperometry techniques. A molybdenum wire with 1 mm diameter was used as the working electrode. The electrochemical reduction of Si was a single-step charge-transfer process and the cathode process was irreversible. Chronoamperometry studies indicated that electrocrystallization of Si was controlled by pro-

gressive nucleation with a three-dimensional growth mechanism. The diffusion coefficient of the Si^{4+} ions was calculated to be $1.32 \cdot 10^{-3} \text{ cm}^2/\text{s}$ by cyclic voltammetry.

4 Direct Electro-Reduction Process

Apart from the above normal electrolysis process, direct electro-reduction process (FFC Cambridge Process) was developed for Si reduction from SiO_2 by some research groups after it was first reported for Ti production from TiO_2 in molten salts [49]. Nohira and Yasuda et al. may be the first one who reported the direct electro-reduction of solid SiO_2 to silicon in a molten CaCl_2 electrolyte, and they have published many research papers [50–56]. A quartz plate contacted by a molybdenum wire was used as a cathode in their research. When the electrode potential of the molybdenum wire is more negative than the reduction potential of SiO_2 , the corresponding oxygen fugacity at the electrode becomes low enough to deoxidize SiO_2 . Then, the oxygen in the SiO_2 near the three-phase interface moves to the interface due to a difference in oxygen chemical potential. The electron transfer was suggested to occur at the molybdenum/ SiO_2 interface.

The total reaction can be written as

When the oxygen is removed from SiO_2 large space is formed between silicon atoms because of the large decrease in molar volume upon reducing SiO_2 to Si. It is immediately filled with molten salt, and the reduction process continuously spreads to both the surface and the interior of the SiO_2 sample. The produced silicon serves as a new electron conducting medium. When SiO_2 is reduced, the 2O^{2-} ions move into the neighbouring electrolyte in the reduction-generated porous silicon layer, and are then transported to the bulk electrolyte and finally discharged at the anode. The rate-determining step of the reduction may be O^{2-} diffusion in molten CaCl_2 in the vacant space formed by the volume decrease caused by the deduction of SiO_2 to Si.

The shape of the deposited Si was columnar with a diameter of 5–10 μm , and there were many vacant spaces between the columns. Each Si column had a hexagonal prismatic and stacking structure, and the Si columns lay was perpendicular to the reduction interface between Si and SiO_2 layers. Yasuda et al. [52] explained that amorphous Si was first formed by electrochemical reduction and was immediately transformed to crystalline Si at high temperature via the bond-breaking process. However, the morphology

of the Si produced changed from columnar to plate-like by combining the sides of Si columns with the addition of Si to SiO₂ because the added Si particles played a role in combining the sides of neighboring Si columns at the reaction interface [53].

The reduction product was usually a mixture of columnar silicon and unreduced SiO₂. To prevent metal contamination from the conducting material, a silicon plate was used as cathode contacting material [55]. After separating Si from SiO₂ by melting the samples under vacuum at 1500°C followed by solidification, the purity of the silicon ingot was 99.80 at% due to contamination by carbon, oxygen, calcium, iron and manganese. The contamination by boron and phosphorus was very low in the ingot. The oxygen concentration in the silicon portion decreased to 0.6 at%. The contaminated oxygen is due to the surface oxidation during the washing treatment of the product, while the metal contaminations come from the metal container which is used as the cathode contacting materials. Recently, it was reported that the metal impurities could be decreased by Ca metal addition [56].

It was mentioned that the reduction rate was higher in the beginning but decreased afterwards because the reaction proceeded only in the inner direction after the whole surface was reduced to Si. The reduction rate was approximately 100–200 μm for 1 h at 1.00 V (vs. Ca²⁺/Ca) using a dense quartz plate [50]. The reduction rate of dense SiO₂ plate was found to be faster than that of a porous SiO₂ pellet, and suggested that the reduction rate could be accelerated by mixing Si into the SiO₂ as a conductive additive [53, 56], and powdery or porous SiO₂ were contacted with a fine wire mesh [51].

Similar works were done by other groups. G. Z. Chen et al. reported an electrolytic reduction of the pellet prepared from SiO₂ powder in CaCl₂ molten salts [57–62]. They suggested that this kind of porous SiO₂ cathode could be progress faster to completion by electrolysis than quarts, which is opposite to the point of Yasuda et al. [53, 56] and Ergül et al. [63, 64]. They pointed out that the electroreduction of the insulating SiO₂ might be limited to a certain distance in the depth direction, which is less dependent on the time of the applied potential. This depth limit may be mainly attributed to the limit of mass transfer through the porous silicon layer formed on the surface [57]. The powder particle size of SiO₂ should be limited to a certain size to gain a complete reduction within a practically tolerable time. They noticed that the 3 phase region propagation along the surface is much faster than that in the depth direction of the solid SiO₂. When the reduction occurs on the surface of solid SiO₂, the influence of diffusion of the O²⁻ ions is negligible and the reduction rate is mainly determined by charge transfer. However, in the depth direction, the reduction could be affected by O²⁻ ion diffusion and also ohmic polarization, both electronic and ionic, in the reduction-generated porous silicon layer. They obtained grey sili-

con product [57] while Ergül et al. [63, 64] and Pistorius et al. [65] got brick-red silicon product. Pistorius et al. suggested that the brick-red color may result from an interference effect of the very fine-scale mixture of silicon and calcium silicate [65], while Ergül et al. indicated that this kind of color dues to nanometer scale crystallite size [62, 63]. Juzeliūnas et al. also reported that nano-micro-scale crystallite silicon was obtained by electro-deoxidation of silica in CaCl₂ molten salts [66].

Wang et al. [67] studied the direct electro-reduction reaction of silicon dioxide in the equimolar molten mixture of CaCl₂ and NaCl using the AC impedance spectrum method. The AC impedance spectra showed that the direct electro-reduction reaction of silicon dioxide was a two-step reaction. They concluded that charge transfer was the rate control step of the electro-deoxidation of SiO₂. The intermediates SiO, CaSiO₃ and Ca₂SiO₄ were found in the reaction system.

Apart from the CaCl₂ salt used as the electrolyte for direct reduction of Si from SiO₂, some other types of electrolyte have also reported. Yasuda et al. [68] used LiCl-KCl-CaCl₂ eutectic electrolyte for the direct electro-reduction of solid SiO₂ to silicon at 500°C. The reduced layer is a spongelike structure with a particle size smaller than 50 nm, and the thickness is about 50 μm for 2 h electrolysis time. The composition is 61.7 at% Si and 38.3 at.% O. The authors suggested that most of the oxygen was caused by the surface oxidation of the produced Si. Lee et al. [69] studied on the electrochemical reduction of SiO₂ in LiCl-Li₂O molten salt at 650°C. In their work, SiO₂ powder which was contained in a porous magnesia basket was used as the cathode, and Pt rods were used as an anode. They found out that the deposits rinsed with distilled water and methanol in sequence did not contain silicon since Li₂SiO₃ was formed during the water washing, as shown in the following reactions:

They suggested that the electrochemical reduction proceeds via electrolysis of Li₂O and then a chemical reaction between Li and SiO₂ resulting in the formation of Li⁺ and O²⁻. The O²⁻ ion was transported to the anode, oxidized and eventually evolved as O₂ gas. The resultant Li⁺ can be re-reduced and used for a further reduction of SiO₂. Li metal production via electrolysis of Li₂O and reduction of SiO₂ took place simultaneously inside the cathode basket of an electrolysis cell.

5 Summary and Conclusions

The typical achievements about electrodeposition of silicon in high temperature molten salts are presented in Table 2.

Electrolyte	Si species	Cathode	Anode	Temperature	Current density or potential	Cathode Current efficiency	crystal size	Si Purity	Reference
LiF-KF	K ₂ SiF ₆ (8–14 mol%)	graphite or Ag	graphite	750°C	10–100 mA/cm ²	30–50%	250 μm	>99.99%	[16–18, 23]
BaO-BaF ₂	SiO ₂ (63.2 mol%)	graphite	graphite	1465°C	60–1000 mA/cm ²	15–22%		99.97%	[44]
CaCl ₂	SiO ₂	SiO ₂ pellet	graphite	850°C	1 V (vs. Ca ²⁺ /Ca)	>90%	5–10 μm	>99.37%	[50, 51]

Table 2. Typical electrolysis parameters and results for electrodeposition of silicon contained in the paper.

Compared with using SiO₂ as solute, the purity of silicon product is higher when using K₂SiF₆ as solute in LiF-KF and LiF-NaF-KF molten salts. However, the current efficiency is only about 50% for silicon electrodeposition process using K₂SiF₆ as solute in fluorid molten salts, while it is about 90% for direct electro-reduction SiO₂ to Si. However, the silicon product purity needs to be improved for direct electro-reduction method.

Although the purity of the deposits does not satisfy the SoG-Si quality yet, the laboratory scale experiments are promising for the prospect of developing a process for direct fabrication of solar cells. The highest purity reported is 10 ppm of total impurities, which can probably be tolerated in silicon solar cells. However, there are also some problems; such as low deposition rate, entrapment of electrolyte, and surface oxidation. More suitable electrolytes need to be developed, and electrodeposition mechanism need to be further studied since it is still controversial in the reports.

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