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Low Temperature Molten Salt Production of Silicon Nanowires by Electrochemical Reduction of $CaSiO_3$

Yifan Dong[1,2], Tyler Slade[1], Matthew J. Stolt[1], Linsen Li[1], Steven N. Girard[1, 3], Liqiang Mai[2*] & Song Jin[1*]

Abstract: Silicon is an extremely important technological material, but the current industrial production of silicon by carbothermic reduction of SiO_2 is energy intensive and generates CO_2 emission. Here we developed a new and more sustainable method to produce silicon nanowires in bulk quantities via direct electrochemical reduction of $CaSiO_3$, an abundant and inexpensive silicon source soluble in molten salts, at a low temperature of 650 °C by using low melting point ternary molten salts $CaCl_2$-$MgCl_2$-NaCl, which still retains high $CaSiO_3$ solubility, and a supporting electrolyte of CaO, which facilitates the transport of O^{2-} anions, drastically improves the reaction kinetics and enables the electrolysis at low temperatures. The Si nanowire product can be used as high-capacity Li-ion battery anode materials with excellent cycling performance. This environmentally friendly strategy for the practical production of silicon at lower temperatures can be applied to other molten salt systems and also promising for waste glass and coal ash recycling.

Silicon is not only the foundational material for microelectronics, but also a key material in many renewable energy technology and chemical and metallurgical applications.[1] The demand for silicon is increasing rapidly. For solar energy industry alone, demand is estimated to increase 30% each year.[2] As the second most abundant element in the earth's crust, silicon is naturally found in silica (SiO_2) and metal silicates, which are the primary components of rocks and sand.[3] Currently, silicon is industrially produced by the carbothermic reduction of SiO_2 by coke (elemental carbon or charcoal), which requires high operating temperatures (1700 °C or higher) in an electric furnace. The net reaction is:

$$SiO_2\,(s) + C\,(s) \rightarrow Si\,(l) + CO_2\,(g) \qquad (1)$$

While this approach is scalable, it has high energy consumption (>20 kWh kg^{-1}), poor energy efficiency (<30%),[4] and produces significant carbon emissions both from the CO_2 product and the generation of electricity required to power high temperature furnaces[5]. Additionally, purification steps based on hydrochlorosilane via the Siemens process are needed to make high-purity silicon for applications.[6] Therefore, the primary reason that Si is expensive is the high cost and large energy consumption associated with its production. Thermal reduction with reactive metals such as Mg can also reduce silica to silicon,[7] but Mg comes from electrolysis as well. These factors make developing a more sustainable and energy efficient method for producing Si in one step at low temperatures highly desirable.

Electrochemical reduction methods using inorganic molten salts as electrolytes have achieved great success in industrial production of aluminum (Hall–Héroult process), as well as extraction of other active metals.[8] Electrolytic silicon extraction via direct electrochemical reduction of solid silica in molten salts has also been studied. In this process, a working electrode supplies electrons to reduce the SiO_2 solid wrapped by the electrode and submerged in molten $CaCl_2$ at 850 °C via following reaction:[9]

$$SiO_2 + 4e^- \rightarrow Si + 2O^{2-} \qquad (2)$$

This approach has two major advantages over carbothermic reduction:[10] the use of molten salts significantly reduces the reaction temperature (850 *vs* ~1700 °C) and Si is produced in a single step.[11] Furthermore, CO_2 emission is reduced by virtue of lower energy consumption. However, since the electrolysis occurs at the three-phase interface between the working electrode, insulating silica solid, and molten salt, it is difficult to achieve complete reduction of the silica and the yield of Si is very low, as only silica in contact with metal electrode is readily reduced.[12] Another significant issue is that the operating temperature is still too high for practical production using available compatible materials.[13] If the reaction yield can be improved and the operating temperature can be reduced further by just a few hundred degree Celsius, the residual heat of many industrial processes can be used as the heat sources to enable practical and large scale production of Si.[14]

Herein, we overcome these significant limitations and develop a novel process more similar to the Hall–Héroult process to realize the low temperature electrochemical production of silicon in bulk quantity via the reduction of soluble $CaSiO_3$ precursor using a carefully designed low-temperature ternary eutectic melt that lowers the operating temperature yet retaining the solubility of $CaSiO_3$, and CaO as a supporting electrolyte that provides higher concentration of O^{2-} ions to facilitate the reaction kinetics. The synergistic effect of these advances enabled the high yield electrolytic synthesis of Si nanowires at a low reaction temperature of 650 °C.

We carried out the electrochemical reduction reactions in a symmetrical two electrode setup (Figure 1) using individual graphite rods as the cathode and anode. We tried to electrochemically reduce SiO_2 powder in a $CaCl_2$ melt to produce Si at 850 °C following reaction 2 at a constant voltage of -1.6 V following earlier reports.[4] The reaction produced a small quantity (~25 mg) of micrometer silicon particles after electrolysis for 3 h (Figure S1).

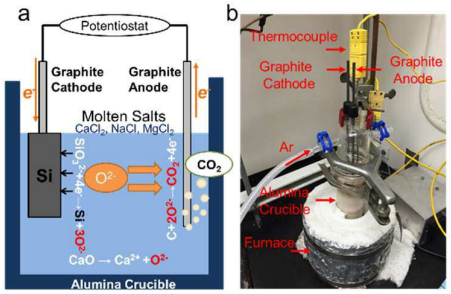

Figure 1. a) Schematic illustration of a molten salt electrochemical cell and the various species and reactions involved. b) Photograph of the working cell.

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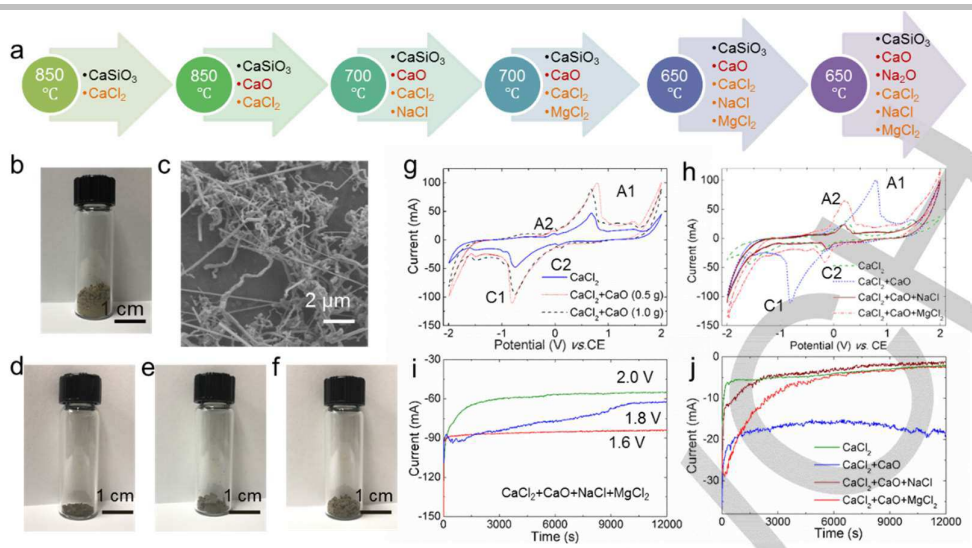

Figure 2. a) The progression of reaction designs that led to the final efficient low temperature electrochemical reduction of $CaSiO_3$ precursor. b) Photograph of the product and c) SEM image of the product dispersed on a Si wafer from electrolysis of $CaSiO_3$ in $CaCl_2$ melt with CaO as supporting electrolyte. d-f) photographs of the products formed from electrolysis in $CaCl_2$-NaCl, $CaCl_2$-$MgCl_2$, and $CaCl_2$-NaCl-$MgCl_2$ melts, respectively. CV curves before the electrochemical reduction process g) with different amounts of CaO added to molten $CaCl_2$ and h) in $CaCl_2$, $CaCl_2$-NaCl, and $CaCl_2$-$MgCl_2$ melts. i) Current-time curves of electrolysis in th optimized $CaCl_2$-NaCl-$MgCl_2$ melts (2:4:1) at constant voltages of -1.6, -1.8 and -2.0 V, j) Current-time curves of electrolysis in $CaCl_2$-NaCl, $CaCl_2$-$MgCl_2$, and $CaCl_2$-NaCl-$MgCl_2$ melts, respectively, at a constant voltage of -1.6 V.

In order to increase the product yield, we used soluble $CaSiO_3$ instead of the sparingly soluble SiO_2 as the Si source. It was hypothesized that the higher solubility of $CaSiO_3$ in molten $CaCl_2$ could facilitate the reduction of SiO_2,[12] therefore we just directly used $CaSiO_3$ as the precursor, which is an abundant and inexpensive silicate mineral.[3] The reaction preparation process and the process flow to separate the product formed on the graphite cathode from molten salts is described in detail in Methods and Figure S2. After an identical electrolysis reaction at 850 °C for 3 h at -1.6 V, the total mass of the deposited Si product from $CaSiO_3$ on the graphite rod was doubled to 55 mg (Figure S3). Unlike previous reports on solid-solid electrochemical reduction of SiO_2,[9, 15] in the melt, $CaSiO_3$ would dissolve to generate Ca^{2+} and SiO_3^{2-} ions:

$$CaSiO_3(s) \rightarrow Ca^{2+} + SiO_3^{2-} \quad (3)$$

Then, on the surface of cathode, SiO_3^{2-} (including SiO_4^{4-} and $Si_xO_yCl_z^{n-}$ or other complexes. Here we used SiO_3^{2-} as a representative example.) is reduced to Si under constant influx of electrons and generates O^{2-} ions through the following reactions (Figure 1a):

$$SiO_3^{2-} + 4e^- \rightarrow Si(s) + 3O^{2-} \text{ (cathode)} \quad (4)$$

$$C(s) + O^{2-} \rightarrow CO_2 + 4e^- \text{ (anode)} \quad (5)$$

Overall, O^{2-} anions are the limiting charge carriers in the cell and drive the electrochemical reaction from cathode to anode. Therefore, the diffusion of O^{2-} ions and the solubility of $CaSiO_3$ would be two crucial factors that govern the electrolysis rate. In order to enhance the reaction kinetics limited by the diffusion of O^{2-} ions, we sought to increase the concentration of the dissolved O^2 by adding CaO as a supporting electrolyte (Figure 2a). CaO will dissociate into Ca^{2+} and O^{2-} in the molten salt. Even though CaO is not directly involved in the electroreduction of SiO_3^{2-}, a higher concentration of CaO could increase the ionic flux of the O^{2-} ions in the melt, and thus improve the reaction kinetics. Additionally, the deposition potential of calcium is too low to be considered. Initially, 0.5 g of CaO was added to the $CaCl_2$ melt (40 g) (1.25 wt%). This electrolyte system yielded significantly more Si product from 55 to 135 mg (Figure 2b) after 3 h electrolysis at 850 °C. The impact of CaO is also apparent in the cyclic voltammetric (CV) curves in various $CaCl_2$ melts with or without CaO (Figure 2g). For the $CaCl_2$ melt without CaO, two pairs of pronounced CV peaks are observed at around -1.56/1.48 V (denoted as A1/C1) and -0.35/0.25 V (donated as A2/C2). As the reaction is configured as a symmetrical two-electrode system, the anodic and cathodic peaks in each pair of CV peaks are based on the same redox reactions. The initial peaks, A1 and C1, are attributed to the reduction of the dissolved silicates to form Si (reaction 4). The second pair, A2 and C2, are attributed to the formation and dissolution of Ca.[16] The addition of CaO clearly significantly increased the A1/C1 peak area while the potential difference between two peaks slightly decreased. This indicates CaO also makes the electroreduction of silicate slightly more energetically favorable. However, when the amount of CaO was increased to 1.0 g (2.50 wt%), the product yield barely increased (137 mg). The CV curve was nearly identical to that with 1.25% CaO with only a small increase in A2/C2 peak area. This suggests that the O^{2-} anions were likely saturated in molten $CaCl_2$. This value is lower than the reported solubility of CaO in molten $CaCl_2$ (13 wt%) at 850 °C,[17] as the dissolved $CaSiO_3$ decreases the solubility of CaO in the same solution. Therefore, any additional CaO would result in little change in the reaction rate. This is also confirmed by the current-time curves at constant voltage of -1.6 V (Figure S4). When 1.25% and 2.5% CaO were added, the current remained saturated at around -20 mA, while the reaction without CaO stabilized at a current of around -10 mA.

After we understood the importance of CaO, we tried to lower the electrolysis temperature by finding suitable eutectic molten salts with lower melting points than pure $CaCl_2$ (782 °C) while fixing the supporting electrolyte CaO at 0.5 g. Using the $CaCl_2$-NaCl eutectic system with the lowest melting point of 601 °C, the reaction temperature could be lowered to 700 °C (Table

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S1). However, after a 3 h electrolysis at -1.6 V, the best product yield was significantly lower at merely 15 mg (Figure 2j and S5). We then turned to $MgCl_2$, which can also decrease the overall eutectic temperature, and has similar properties to $CaCl_2$.[17] In the $CaCl_2$-$MgCl_2$ melts, the product yield reached 60 mg at the same reaction temperature of 700 °C (Figure 2j). We hypothesized that the product yield is correlated with the solubility of $CaSiO_3$ in the molten salts. Thus, we carried out solubility tests in $CaCl_2$-NaCl and $CaCl_2$-$MgCl_2$. The solubility of $CaSiO_3$ reaches up to 0.8 wt% at 700 °C in $CaCl_2$-$MgCl_2$ mixture, however, it remains marginal (below 0.2 wt%) in $CaCl_2$-NaCl (Figure S6). We concluded that even though NaCl can lower the melting point the solubility of $CaSiO_3$ in $CaCl_2$-NaCl is too low to realize low-temperature electrolysis.

In order to achieve both low melting point and high $CaSiO_3$ solubility to realize low-temperature electrolysis in high yield, we further investigated the ternary eutectic melts of $CaCl_2$-$MgCl_2$-NaCl. Previous report[18] has shown that different salt ratios vary the chemical potentials, thus creating a molten salt eutectic and lowering the melting point and the viscosity of the mixtures. The electrolyte with a mass ratio of NaCl: $CaCl_2$: $MgCl_2$ at 2:4:1 is decreased to 424 °C according to the phase diagram in Figure S7. The solubility of $CaSiO_3$ in this melt (Figure S6) increases with temperature between 450 to 750 °C, but the solubility remains small (less than 0.2 wt%) below 550 °C. However the solubility increases sharply between 550 to 650 °C, at which point the solubility is about 1.0 wt% and then further rises to 1.2 wt% at 750 °C. Therefore, we chose a reaction temperature of 650 °C, which is lower than that of the binary melts yet maintains sufficient $CaSiO_3$ solubility, to allow for a fast electrolysis rate and a good yield. As summarized in Table S1, the electrolysis in the most optimized $CaCl_2$-NaCl-$MgCl_2$ ternary melt (with mass ratios of 4:2:1) at 650 °C leads to the Si yield of 75 mg (Figure 2f), the highest yield among those low-temperature electrolysis reactions. The Coulombic efficiency of electrolysis (electrolytic reaction yield) is generally about 70% for optimized reaction conditions (see details of calculations in the SI). We further investigated the reaction mechanisms using the different melts under different reaction time and voltages using electrochemical characterization. As shown in Figure 2h-j and discussed in the Supporting Information, the optimized applied voltage of -1.6 V in the optimized $CaCl_2$-NaCl-$MgCl_2$ melts with the CaO supporting electrolyte at 650 °C indeed show favourable kinetics and stable electrodeposition of Si.

The Si produced on the graphite cathode was then separated from the solidified molten salts, cleaned, and characterized. The PXRD patterns of the samples produced under different voltages of -1.6, -1.8, and -2.0 V (Figure 3a) were almost identical and could be indexed to silicon (JCPDS: 00-027-1402). The sharp diffraction peaks indicated the high crystallinity of the products and their high purity (99.52%) was confirmed by EDS (Figure S9) and ICP-AES (Figure S10). The products from other reactions in different electrolytes were also well-crystallized Si (Figure S11). SEM images revealed nanowire (NW) morphology for the products made under optimized conditions (Figure 3b) and other conditions (Figure S12). The NW diameter can be from about 80 to 300 nm and the length is from several micrometers up to hundred micrometers. EDS analysis (Figure S13) confirmed that the NWs consisted mainly of silicon. The oxygen was likely from the formation of a thin native oxide layer. HRTEM image (Figure 3d) highlights the single crystalline nature of the Si NWs. The cubic Si structure was confirmed by indexing the FFT (Figure 3d). The observed plane spacings of 0.190 and 0.111 nm correspond well to the $(02\bar{2})$ and (422) lattice planes of Si, respectively. All of the indexed reciprocal lattices show that the NW axes are parallel to the (011) crystal directions. The curved NWs seen in the SEM consist of multiple domains assembled together with rough surfaces (Figure S14). It is interesting that the reduced silicon products are mostly of the NW morphology. This is not fully understood at present, but suspected to be due to metal impurities that could act as catalytic sites essential for the continuous anisotropic growth of silicon.[15B]

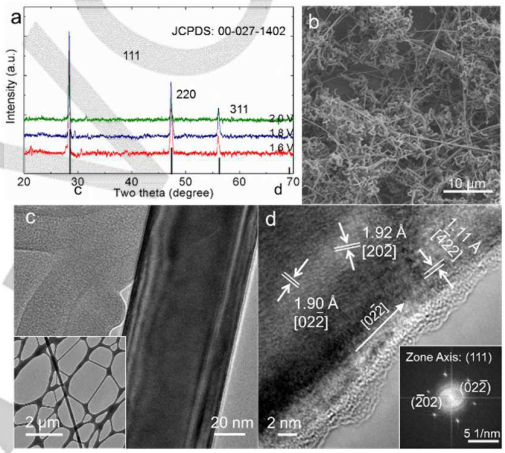

Figure 3. a) XRD patterns of the Si NWs synthesized by using the optimized melts at different voltages in comparison with the standard pattern (JCPDS 00-027-1402). b) SEM image, and c) TEM image and d) HRTEM image and the corresponding FFT of the Si NWs produced by using the optimized conditions.

One does not have to use pure $CaSiO_3$ as the only soluble Si precursor. For example, common glass is primarily composed of SiO_2, CaO, and Na_2O, and therefore, recycled glass waste can be a potential source for replacing $CaSiO_3$ in this reaction. Therefore, we carried out electrolysis reactions with the addition of Na_2O under the same reaction temperature of 650 °C to explore this possibility (the compositions of different salts and the reaction conditions are summarized in Table S1). As shown in Figure S15, the morphology of the product was Si NWs and PXRD confirmed that the phase was also mainly Si although some impurities were present. In fact, soluble Na_2O could also provide O^{2-} ions in the molten salts just as CaO does, therefore, replacing up to about 40 wt% of CaO with Na_2O in the melt mixture did not seem to affect the reactions. The highest product yield was 80 mg when an optimal combination of 0.40 g CaO and 0.11 g Na_2O was used, which is even slightly higher than the yield from the optimized molten salt mixtures using just CaO. These results, even though not fully optimized, suggest the feasibility for recycling glass waste, or even coal ash (whose major components are also SiO_2 and CaO[19]), to produce value-added silicon nanomaterials.

These results showed that the low temperature electrochemical production of Si in high yield is enabled by three key advances: i) the use of the soluble $CaSiO_3$ as the silicon precursor to enable the production of silicon in bulk quantity, ii) the enhanced diffusion of O^{2-} ions due to the introduction of the CaO (or Na_2O) supporting electrolyte, and iii), the design of the

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low melting point ternary $CaCl_2$-NaCl-$MgCl_2$ eutectic molten salts that retain sufficiently high solubility of $CaSiO_3$ precursor. Actually if a steady state concentration of CaO in the molten salts is maintained as the reaction proceeds, SiO_2 can also be dissolved into the melts through the formation of $CaSiO_3$ and thus be used directly as a precursor. This successful electrolysis synthesis of silicon from the abundant and inexpensive $CaSiO_3$ precursor at a much lower temperature of 650 °C is more sustainable and practically significant for several reasons. First, the low reaction temperature enable the recycling of residual medium-grade waste heat energy in various industrial and energy technologies and thus improve the overall cycle and power plant efficiencies.[14] Second, metal halide molten salts in the temperature range of 600-700 °C have been successfully utilized in the molten salt nuclear reactors and concentrated solar thermal energy conversion technologies as heat exchange

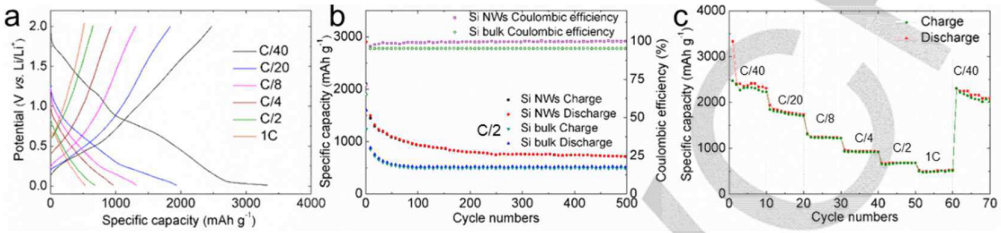

Figure 4. The electrochemical performance of the electrochemically synthesized Si NWs as lithium-ion battery anode material. a) Charge–discharge curves of the Li/Si battery in the potential range of 0.01–2.0 V vs. Li/Li^+. b) The cycling performance and the columbic efficiency at a current density C/2. c) The rate performance at the different current density of C/40, C/20, C/8, C/4, C/2, and 1C.

medium.[13, 20] the material compatibility and other practical issues have already been addressed at the industrial scale. Furthermore, this also suggests a sustainable pathway to recycle glass waste or coal ash to produce value-added silicon nanomaterials.

The electrolytically produced silicon NWs are useful materials for high-capacity (~4200 mAh g^{-1}) lithium battery anodes. Nanostructured silicon materials, such as Si NWs, can better accommodate the volume expansion involved in the Li battery cycling than bulk silicon.[27,28] Here we also used bulk silicon as a comparison. The charge–discharge profiles of Si NWs at current densities from C/40 to 1C over a potential window of 0.01 to 2.0 V for the first cycle are presented in Figure 4a. The specific discharge capacity at C/40 was 3333 mAh g^{-1}, indicates the final structure contains between 2.93 and 3.48 Li atoms per Si atom. The discharge curve exhibited an obvious voltage plateau consistent with previous studies corresponding to Si alloying with Li.[21] There was an obvious drop in the capacity during the 2nd cycle to 2468 mAh g^{-1}, which is mainly attributed to the formation of solid electrolyte interface (SEI) and other side reactions. For the cycling performance under C/2 rate (Figure 4b), the initial discharge capacity was 2865 mAh g^{-1}. After 500 cycles, the discharge capacity still reached 714 mAh g^{-1}. At 1C, the capacity still reached 521 mAh g^{-1}(Figure 4c). When the current density returned to C/40, no obvious capacity decay is observed. These results demonstrated the good performance and the promise of these electrochemically synthesized Si NWs as high-capacity Li-ion battery anode materials. Their performance can be further improved by further accommodating the volume change and stabilizing the SEI layer.[22]

In conclusion, we have developed a novel molten salt electrolysis method to produce Si NWs from inexpensive soluble $CaSiO_3$ precursor at a low temperature of 650 °C by designing a ternary molten salt system to decrease reaction temperature and introducing CaO to facilitate transport of the oxygen ions. These advances enable the electrochemical reduction at 650 °C for effective Si production in high yield. This work opens up a new route for more practical and sustainable direct production of Si at an industrial scale that is compatible with existing industrial processes and can be integrated with medium waste heat recycling. It also provides general new insights to molten salt electrolysis reactions that could help to improve other important electrolytic metal extraction processes,[8] and further points to the possibility of recycling glass waste and coal ash to produce value-added materials in an environmentally friendly way.

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Keywords: silicon nanowire • molten salt • electrolysis • supporting electrolyte • Li-ion battery

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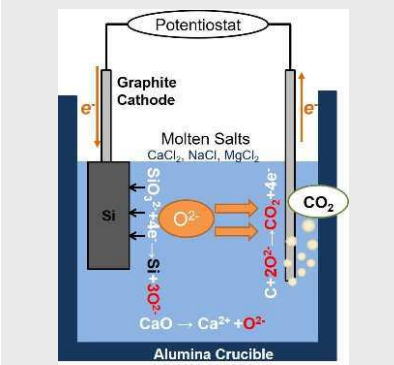

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