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Electrowinning of Silicon using SiO_2 – Overview and Industrial Perspectives

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Abstract – Decarbonization of the silicon production process can be done by electrowinning from SiO_2 at high temperatures using molten salts or oxides producing O_2 as the anode product. Thermodynamics combined with knowledge of state-of-the-art electrowinning processes can provide an understanding of the possibilities and limitations of the approach, to best compare with today's submerged arc furnace (SAF) process. Carbon, if used in carbothermic reduction or as a consumable anode in an electrowinning process, provides energy that is not available when the carbon is eliminated from the process. The result is that an optimized electrowinning process is likely going to require more energy than by SAF, and renewable energy must be used to eliminate the CO_2 from the process. This work further details the knowledge needs related to dissolution behaviour of the SiO_2, electrode materials, cell design and upscaling for both solid and liquid Si production.

1. INTRODUCTION

Electrolytic production of silicon is the most direct way to electrify and decarbonise the silicon production process, especially when renewable energy is readily available. Electrolysis by use of carbon anode, like for aluminium in the Hall-Héroult process, still produce CO_2, but use of oxygen evolving (inert) electrodes in such a process will eliminate all process-related CO_2 emissions. By using quartz as the silicon raw material, O_2 may be produced at the same time as the silicon.

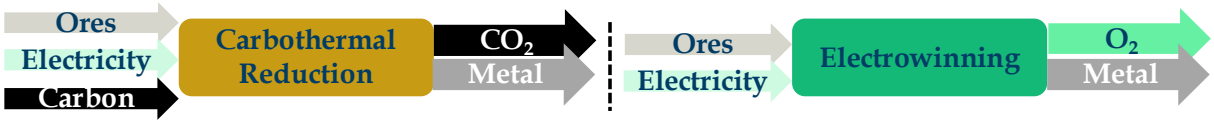
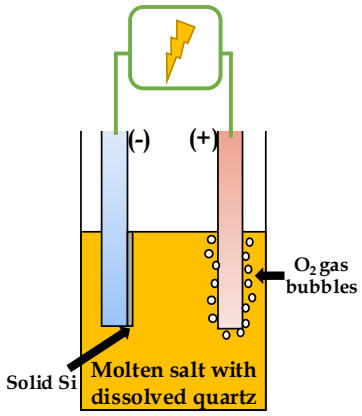


Figure 1: Comparison of today's process and a possible electrowinning process.

A lot of research has been done in relation to producing silicon by electrowinning and summarized in relevant reviews (Abramkin *et al.*, 2025; Tian *et al.*, 2023; Yasuda and Nohira, 2022). Historically, research focused on producing high purity Si to be used directly in photovoltaic (PV) production combined with a carbon anode. The production routes studied showed that although possible, they were not rendered cost effective enough to be industrially viable. However, the production of metallurgical grade silicon could be more promising as the impurity requirements are lower, especially when combined with O_2 evolving anode. As such, the product can be used as alloying elements in green steel and aluminium, making it possible to charge a premium.

In an electrolysis process for metal production there are two electrodes immersed in an electrolyte with dissolved metal cations and negative anions. The electrolyte should have high

mobility of the ions and high electrical conductivity. The positive metal cation is reduced at the negatively charged cathode where the metal is produced, and the negative anion is oxidised at the anode where another product, often a gas, is produced. For solid Si electrowinning producing O_2 at the anode, a typical lab setup and representative reactions (exact ions vary) are presented in Figure 2.



$Si^{4+} + 4e^- \rightarrow Si\ (s)$ $\quad 2O^{2-} \rightarrow O_2\ (g) + 4e^-$

Figure 2: Schematic Si electrowinning by dissolution of quartz and production of O_2.

Silicon cannot be produced by aqueous electrowinning, since the electrical reduction potential is much more negative than what is needed for electrochemically decomposition of water. Low temperature ionic liquids or organic solvents can allow for Si reduction, but the compounds are often expensive, the reduction rate very low, and quartz is not a suitable raw material. A high temperature electrowinning process with molten salts or molten oxides as electrolytes are the most promising to produce Si metal from quartz. Good overviews of the major electrolyte systems and electrochemical methods can be found in literature (Abramkin *et al.*, 2025; Yasuda and Nohira, 2022). More focus on general challenges can be found in another review (Tian *et al.*, 2023). Many excellent studies show the production of solid Si by use of K_2SiF_6 in combination with a CO_2-evolving anode, although recent studies (Padamata *et al.*, 2025) have demonstrated electrochemical production of Si through electrowinning using a SnO_2 oxygen evolving anode in molten salt with $CaCl_2$-NaCl-CaO-SiO_2.

Silicon is a semiconductor, resulting in low electrical conductivity of the metal and, when produced in solid form during an electrowinning process, will result in an electrode with low conductivity. This could potentially give rise to problems during an industrial electrowinning process.

Although there are good overviews of the different electrolyte options and many challenges have been identified, very few focus on some of the more practical aspects when using *quartz* as a raw material, and how this affects the possible industrialization. The goal of this paper is to show how the theoretical values that can be calculated by thermodynamics correlate to real electrochemical behaviour of an electrowinning cell for Si from quartz, and how limitations of different electrochemical systems will translate to business perspectives related to production rate, energy consumption, and cost.

2. SILICON ELECTROWINNING – ELECTROLYTE OPTIONS

Silicon can be produced as a solid or liquid product through the electrowinning process, depending on whether the process is carried out at a temperature higher or lower than the

melting point (1414 °C). Due to its high melting point, liquid Si production can only be carried out by molten oxide electrolysis (MOE), with stable oxides/slags used as the electrolyte. Molten salts, like chlorides and fluorides, can be used as electrolytes up to approximately 1000 °C producing a solid Si product.

Liquid production of metal is advantageous considering the potential of high throughput due to the kinetics allowing use of high current densities, no need to clean the product as it can be tapped directly, and the process can be done continuously through the feeding of raw materials. However, there are certain disadvantages to MOE, the major one being the typically low ohmic conductivity making the ohmic resistance (see section 3.2) high, influencing the real energy consumption (section 3.3). Due to the high temperature and corrosive nature of the oxides, materials challenges will occur. MOE is currently on a low technical readiness level (TRL) for silicon (Elwell and Rao, 1988; Mattei *et al.*, 1981) but is being carried out by Boston Metal for Fe at pilot scale (Boston Metal, 2025). Fe is easier to reduce than other typical metal oxides, but related to temperature the process on Fe must be carried out at even higher temperatures than for Si. However, Fe is denser than the oxide melt and the process can be similar as the Hall-Héroult process used for Al electrowinning, while Si is less dense and will end up floating on top. This requires a quite different design (section 6.2) than in the currently ongoing MOE process developement.

For production of solid Si product, the temperature could be done on significantly lower temperatures, enabling the use of molten salts which are typically thermally stable below 1000 °C. Besides the lower temperature, other advantages relate to the low viscosity (typically like water at the operating temperature) and high conductivity resulting in a low ohmic drop compared to the MOE system. The major drawbacks are that production of solid metal is very slow due to slow kinetics, as well as giving need of cleaning the electrolyte remains from the produced metal. Further advantages and disadvantages of chloride and fluoride melts are presented in Table I.

Electrodeoxidation, also known as the FFC Cambridge process (named after Fray, Farthing and Chen), is a different approach where the metal ion to be reduced is not dissolved in the melt. In Figure 3, the concept is shown compared to a more "conventional" electrowinning process. Si is reduced directly from a pellet of SiO_2 immersed in a molten $CaCl_2$ melt (850-900 °C) containing small amounts of CaO. As the reduction progresses, oxygen ions from the oxide are released into the melt and discharged at the anode as O_2 (when an inert anode is used). The reduction reaction takes place on the interface between the metal oxide pellet, molten electrolyte and cathode lead, and the Si phase propagates through the pellet until all the SiO_2 has been converted to Si. The FFC bypasses the problem of low SiO_2 solubility in chloride melts and was first suggested for the reduction of titanium from TiO_2 (Chen *et al.*, 2000). It has also been proven in laboratory scale for the reduction of other elements including silicon (Nohira *et al.*, 2003; Yasuda *et al.*, 2007). As suggested for TiO_2 by the OS method, the reduction mechanism is likely due to calciothermic reduction via Ca formation (Ono and Suzuki, 2002). Advantages and disadvantages are listed in Table I.

By use of a molten salt with both fluorides and chlorides, it may be possible to utilize the strengths of both systems. The better conductivity and oxide solubility of the fluorides can be combined with lower operating temperatures and easier cleaning of chlorides. From an industrial perspective, the KF-KCl melt is considered promising, and a lot of research has been conducted in this system.

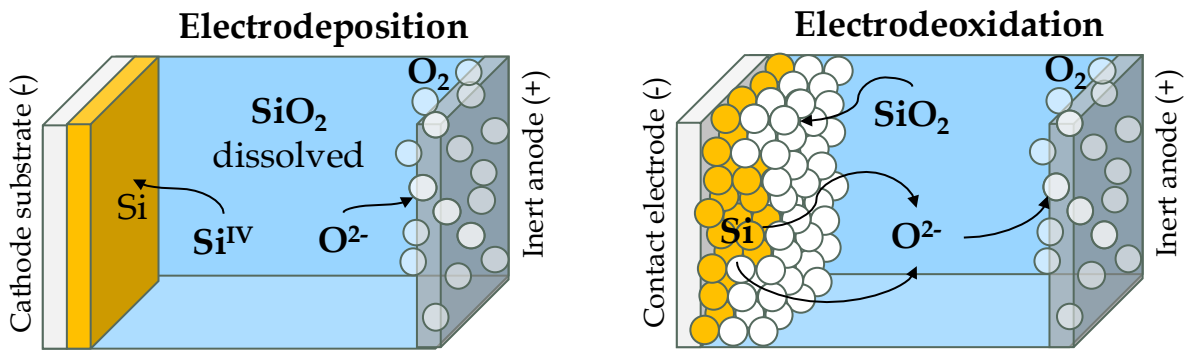


Figure 3: Electrodeposition of dissolved SiO_2 (left) and electrodeoxidation (FFC) of SiO_2 (right).

Table I: Advantages and disadvantages of electrolytic production of Si in different molten salt systems.

	Advantages	**Disadvantages**
Fluoride electrodeposition	• High electrical conductivity • High SiO_2 solubility • Demonstrated in pilot scale • Capitalize on Al electrolysis/Hall-Heroult • C anode possible (CO_2)	• Volatility: F emissions • Salt removal needs strong acids and/or high temperature • Very corrosive and might need frozen side ledge →Heat loss
Chloride electrodeposition	• Less corrosive electrolyte than fluorides • Salt removal possible with *water* • Does not require frozen side ledge → less heat loss and energy consumption	• Hygroscopic salt • Lower electrical conductivity than fluorides • Low SiO_2 solubility → Require need of additional oxide to enhance dissolution, and risk formation of Cl_2 • C anode not feasible (CO_3 formation → carbon reduction)
Chloride FFC	• Simple • Commercialised by Metalysis for Ta, Ti and high-entropy alloys • Many studies	• Very slow process and low current efficiency • Needs to inhibit SiO_2 dissolution → Cl_2 produced more easily than O_2 • Si is a semiconductor, difficulties with electrical conductivity of negative electrode

3. THERMODYNAMICS, ENERGY REQUIRERMENTS AND CO_2 FOOTPRINT

The energy use for today's production of silicon is typically in the 11-13 kWh/kg_{Si}, and direct carbon emissions from the process are ca. 5 $kgCO_2/\ kg_{Si}$ (Hoover *et al.*, 2024). Si and CO is produced in the reaction according to equation 1, via formation of SiC and SiO gas, with CO finally ending up as CO_2 after being oxidized by air.

$$SiO_2 + 2C \rightarrow Si + 2CO \quad [1]$$

By use of electrowinning processes to produce Si, equation 2 is the resulting electrochemical reaction when using a carbon anode. The electrochemical reaction on the anode can be assumed to result in CO_2, as for aluminium electrowinning, and not CO as in the carbothermal reduction process. When producing oxygen with an inert anode, the main driving force behind choosing this new technology, equation 3 represents the total electrochemical reaction.

$$SiO_2 + C \rightarrow Si + CO_2 \quad [2]$$
$$SiO_2 \rightarrow Si + O_2 \quad [3]$$

3.1 Standard potential

The fundamental thermodynamic relationship between the change in Gibbs free energy ($\Delta G°$) and the standard cell potential ($E°$) for an electrochemical reaction can be expressed with equation 4, where n is the number of electrons (4 in the case on Si), and F is Faraday's constant (96485 C/mol) representing the total electric charge carried by one mole of electrons. As can be deduced, using a negative sign in the equation ensures that for non-spontaneous reactions at standard states, $\Delta G°>0$, a negative cell potential is calculated since the electric cell requires an external power source to drive the reactions (Newman and Balsara, 2021).

$$E^o = -\frac{\Delta G^o}{nF} \quad [4]$$

In Figure 4 the traditional Ellingham diagram is shown together with the corresponding standard cell potential for an electrochemical reaction for a number of metal oxides per mol O_2. It can be observed that Fe and Mn will be produced electrochemically simultaneously with Si, since the $E°$ for these reactions are less negative than for Si. This means that if these more noble metal oxides have been introduced as an impurity in the quartz, co-reduction and production of a metal alloy or impure silicon product will be the resulting metal. It is not possible to eliminate these reactions if these oxides are present in the raw material, and therefore they should not be present as part of the electrolyte for molten oxide electrolytes for liquid Si production. The graph in Figure 4b also demonstrates that the MOE-process is most easily applicable to Fe, as other metals are not co-reduced, while for Mn, the presence of Fe in the oxide ore can prove problematic.

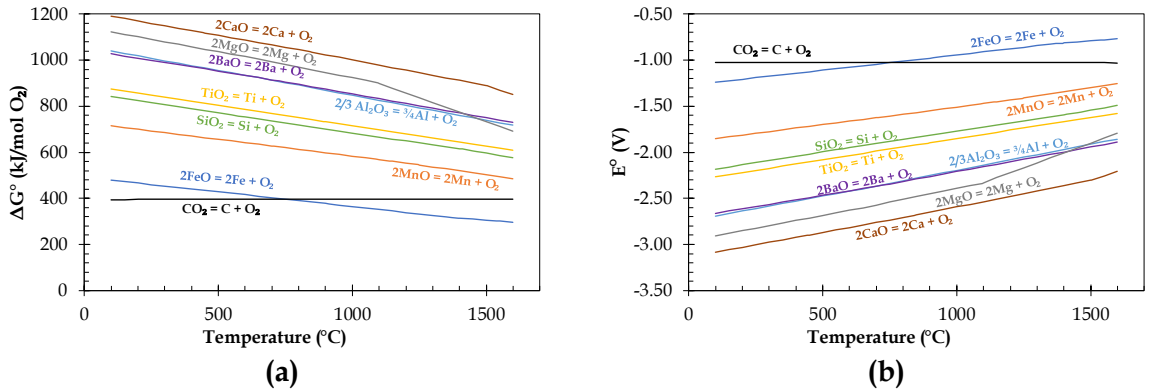


Figure 4: The (a) Ellingham diagram and (b) correlating standard cell potentials of a comparable electrowinning process of metal oxides, as found by FactSage 8.4 (Bale *et al.*, 2016).

Quartz, or the naturally occurring quartzite, typically has above 99 % of SiO_2. Typical impurities are Al, Fe, and Ti. Of these, Fe will always end up in the produced metal, while Al

and Ti should theoretically remain in the bath since they have a more negative cell voltage. However, metal reduction can also occur by forming alloys, which results in activities less than zero and the reduction happening at less negative potentials. This means that Al and Ti may potentially end up in the metal due to alloying with the produced Si, especially if it accumulates to high concentrations in the electrolyte. This accumulation may potentially require bleeding of the electrolyte, i.e. periodic removal of electrolyte, to ensure a pure product is produced at high efficiencies.

3.2 Cell voltage

The reversible, equilibrium cell voltage (E_{rev}), depends on temperature T (in Kelvin), and the reaction quotient Q (depending on activities of Si and SiO_2 and partial pressure of O_2 for the proposed reaction in equation 3). This is expressed by Nernst equation (equation 5).

$$E_{rev} = E^o - \frac{RT}{nF}\ln(Q) \quad [5]$$

The cell voltage (E_{cell}) needed for a reaction is always higher than E_{rev} (Newman and Balsara, 2021). The actual driving force for the reaction depends on kinetics and transport limitations, and these contributions are commonly denoted as overpotentials at each electrode. There is an activation energy barrier as reactions on a surface does not occur instantaneously, resulting in an activation overpotential (η_{act}). There is also a concentration overpotential (η_{con}) near each electrode in the case of limitation by mass transport, generating a concentration gradient of the electroactive species near the electrode. The sum of these on each cathode and anode is typically denoted η_c and η_a respectively.

Finally, an ohmic contribution to the cell voltage depends on the resistance (R) between the cathode and anode, and the current (I) through the system. This ohmic resistance depends on bath conductivity and anode-cathode distance. The ohmic contribution is as such strongly dependent on the geometry of cell, the chosen electrolyte and temperature, the total amperage and production rate of the system. In total, the cell voltage during the electrolysis can be expressed by equation 6. Small scale lab experiments typically have very low total current, and in some cases also very low current density, which can give a much lower IR contribution to the cell voltage than in an industrial cell.

$$E_{cell} = E_{rev} + \eta_a + |\eta_c| + I \cdot R \quad [6]$$

In practice, it is not possible to accomplish electrolysis at a reasonable rate without having considerable overvoltages and ohmic losses, and it is the total cell voltage which is important when evaluating the energy consumption of a proposed process, not the theoretically calculated values.

3.3 Energy consumption

The minimum energy needed is defined by the conditions in a hypothetical cell without loss in current efficiency, no side reactions, and without heat loss to the surroundings (i.e., adiabatic and isothermal conditions), and the energy needed to heat the raw material to the chosen reaction temperature (SiO_2). The isothermal cell voltage (E^{iso}) is the cell voltage needed to maintain electrolysis at these isothermal and adiabatic conditions, and it can be calculated by exchanging $\Delta G°$ with the change in enthalpy ($\Delta H°$) in equation 4. The theoretical energy related to the electrochemical reactions ($EC_{\text{theory,rx}}$) can then be calculated at a given temperature using the change in enthalpy ($\Delta H°$) and the molar mass (M) of the produced metal, by equation 7 (Helbæk and Kjelstrup, 2006).

$$EC_{theory,rx} = \frac{E^{iso} \cdot nF}{M \cdot 3600} = \frac{\Delta H^o}{M \cdot 3600} \quad (\frac{kWh}{kg}) \qquad [7]$$

Assuming an electrowinning process for silicon at 1000 °C, the energy of heating SiO_2 from 25 °C to 1000 °C is 0.62 kWh/kg_{Si}. For Si produced at 1000 °C using a carbon anode according to equation 2, the theoretical energy consumption for the electrochemical reaction is calculated to be 5.01 kWh/kg_{Si}, while using an inert anode as in equation 3 it requires more energy, 8.93 kWh/kg_{Si}. This correlates to a 1 V difference in standard potential of the relevant reactions. Summarizing, the resulting total theoretical energy consumption, assuming 100 % current efficiency, no heat losses, no overvoltages and no ohmic voltage drop, is 5.63 and 9.55 kWh/kg_{Si} for carbon anode and inert anode, respectively. The large difference between the two processes relates to the chemical energy in carbon, which needs to be replaced by electrical energy in the case of inert anodes.

Although the theoretical energy consumption is useful to evaluate the difference between a carbon and inert anode, the specific energy consumption of the reaction ($EC_{specific}$) is highly dependent on the cell voltage as described in equation 6, and not the isothermal cell voltage, in addition to the current efficiency. The formula for energy consumption for a given electrowinning process is given in equation 8, where the current efficiency (ε) is presented as the fraction (0-1) rather than the often-reported percentage. High cell voltage due to overvoltages and ohmic contribution can increase the specific energy consumption significantly compared to the theoretical values. Low current efficiency has the same effect, since this factor is reduced below 1 for not-ideal electrolysis (Newman and Balsara, 2021).

$$EC_{specific} = \frac{E_{cell} \cdot nF}{M \cdot \varepsilon \cdot 3600} \quad (\frac{kWh}{kg}) \qquad [8]$$

The current efficiency describes how much of the total current applied contributes to the wanted reaction (e.g. Si production). Deviations from 100 % current efficiency are typically resulting from re-oxidation of the metal (back-reaction), dissolution of the metal into the electrolyte (avoided by polarization of electrodes, which protects the metal), and parasitic reactions. The parasitic reactions can be due to co-deposition of other metals, which is strongly dependent on the quality of the raw material, but can also be loss of electrons used for reducing higher valency metals without producing the metal. The current efficiency of a metal *x* is given by Faraday's law for production rate ($\dot{m}$) in equation 9 (Newman and Balsara, 2021).

$$\dot{m}_x = \frac{I \cdot \varepsilon \cdot M_x}{nF} \quad (\frac{kg}{s}) \qquad [9]$$

Electrowinning of Al in a cryolite (fluoride) molten salt with a consumable carbon anode typically occurs around 4 V, significantly higher than the reversible voltage of 1.22 V. Much of this increase is due to the ohmic resistance in the bath. Si has a lower reversible voltage than aluminium, so assuming a cell voltage of 3 V (2 V is reported by use of carbon anode (Zou *et al.*, 2011), and 80 % current efficiency, the specific energy consumption would be ca. 14 kWh/kg_{Si}. Work with a fluoride system with SiO_2 and O_2-evolving anode gave 3.4-4.2 V cell voltage, and the energy consumption could also be a bit higher (Moudgal *et al.*, 2021). By comparison, MOE has a very high resistivity in the bath, typically resulting in much higher cell voltages than with molten salts. Previous work on Si MOE (Mattei *et al.*, 1981) gave 16 V cell voltage using 2 A (1 A/cm^2), and a very low current efficiency of 15-22 %, which results in an extremely high energy consumption above 300 kWh/kg_{Si}.

When evaluating values found in literature, it is important to confirm which anode reaction is occurring together with the Si production on the cathode, and relate this to the measured cell voltage in each specific experiment. Producing Si by electrowinning with carbon has in some cases been presented to give comparable, or even favourable improvements when comparing energy requirements to today's SAF-process. However, if the goal is to eliminate the CO_2 it is no longer comparable, since the theoretical energy consumption is higher with almost 4 kWh/kg_{Si}. Many experiments have not had any oxygen source in the experiment at all, using K_2SiF_6 as the raw material, and in these cases neither O_2 nor CO_2 is produced on the anode; typically, chlorine or fluorine/perfluorocarbon gases are the likely product depending on the melt and the resulting cell voltage depends on this reaction. Certain anodes may also react anodically at lower voltages than oxygen production potentials, giving a cell voltage significantly lower than when producing oxygen.

The theoretical values and what experience can be transferred from other electrowinning processes, like Al-production, shows that the energy consumption in a new electrowinning process for silicon is likely to have higher energy consumption than today's process with SAF.

3.4 CO_2 footprint

By use of an inert anode, the CO_2 produced in today's process, or in an alternative electrowinning process with consumable carbon anodes, can be eliminated completely as a process product. With the higher energy consumption compared to the SAF, this indicates that the energy mix used for the electrowinning will be detrimental to the associated CO_2-emissions per kg Si produced.

Calculations related to the change from carbon to inert anodes for aluminium production can be useful for the case of silicon. For aluminium, it is documented (Solheim, 2018) that the change from carbon anode to inert anode increases the minimum specific energy consumption from 6.24 to 9.16 kWh/kg_{Al}. By including the energy lost in the form of heat, the state-of-the-art Al electrowinning process ends up at 12.0 kWh/kg_{Al}, and the process with inert anodes at 14.9 kWh/kg_{Al}. Using a coal-fired powerplant operating at a 40 % efficiency, the total amount of CO_2/kg_{Al} is reported as 14.91 for the carbon anodes, and 16.10 for the inert anodes. This demonstrates that when using fossil energy sources, the positive result of producing O_2 instead of CO_2 is cancelled out, and electrowinning processes with oxygen evolving anode, due to its high energy requirement, must be done by use of renewable energy sources.

For silicon, the cell voltage for SiO_2 decomposition to Si and O_2 is less negative than for Al_2O_3 to Al and O_2 (Figure 4b), but due to the difference in electrons partaking in the reactions, the theoretical energy consumption ends up in the same range as for aluminium. Including heat losses the energy consumption, the total energy consumption is likely going to be higher than the 11-13 kWh/kg_{Si} today, and the CO_2 emissions are fully dependent on the energy source.

4. QUARTZ SOLUBILITY

In an MOE process the metal oxides are part of the electrolyte, and for Si the quartz would likely be present together with Al_2O_3, CaO and MgO (or other less noble metals). The basic oxides, CaO and MgO, dissociate easily into ionic forms, while the acidic oxides, SiO_2 and Al_2O_3, form networks and does not generally dissociate into their respective cat- and anions (Rosenqvist, 2004). For Si, this means that the three-dimensional polymerised network should be broken apart by basic oxides, enhancing the mobility of the electroactive species (SiO_x^{y-}), making them, as well as the oxygen species, available for the electrochemical reactions.

Oxygen can exist in different species depending on its basicity, but O^{2-} is probably the species being discharged at the anode (Park and Rhee, 2001).

In molten salts the electrolyte constituent helps to dissolve and make available the ions. As mentioned previously, a lot of Si electrowinning research in molten salts has focused on using K_2SiF_6 as the silicon source. This raw material may have its own challenges related to solubility and stability (SiF_4 can form as a gas), especially in chloride melts without any other fluorides present to stabilize dissolved ions, but if the raw material is going to be quartz, a good understanding of the dissolution of this oxide and formation of stable cations and anions needed for the electrochemical reaction is needed.

Looking again at the state-of-the-art aluminium electrowinning process in cryolite, alumina is added from the top of the cell into the bath. Well-dispersed alumina dissolves within just a few seconds, but because of the alumina is added cold and hits a very hot melt, the temperature difference can cause the electrolyte to freeze around the particles and forming hard to dissolve agglomerates. The natural stirring that occurs due to the CO_2 bubbles and electromagnetic forces helps to keep the powder dispersed and avoids agglomerated "sludge" forming at the bottom of the cell. In addition, the type and concentration of alumina are important for the dissolution process.

Very little work has been done on dissolving quartz in molten salts, and it is one of the major research questions that needs to be answered before approaching future electrowinning processes. As can be seen in Table I, chlorides have low solubility of SiO_2 and typically require a helping oxide, e.g. $CaCl_2$ with 10 wt% CaO can dissolve at least 6 wt% SiO_2 (Olsen, 2002). The recent demonstration from Icelandic researchers (Padamata *et al.*, 2025) demonstrated electrowinning of Si with 90 mol% $CaCl_2$-10 mol% NaCl, adding 2 wt% CaO and 2.2 wt% SiO_2 (1:1 molar ratio CaO:SiO_2), showing that oxygen was possible to produce on the anode with only a few wt% of total oxide in the melt (avoiding chlorine). For the FFC-process, it is important that the SiO_2 electrode does not dissolve, and the electrolyte should only transport the O^{2-} discharged to the anode to produce O_2 (Figure 3). As this is always done in a chloride melt, one should avoid the dissolution-enabling oxide as it increases SiO_2 solubility, but given the slow process and very low concentrations of O^{2-} there is a high chance of producing Cl_2 instead of O_2 at the anode. Fluorides can dissolve SiO_2 without any other oxides present; the F^- have an important role in breaking the Si-O-Si bridges, replacing the oxygen ion in the silicate tetrahedron with a fluoride anion (Zaykov *et al.*, 2014).

Pure chloride or fluoride melts have their advantages and disadvantages (Table I), which is why the focus typically has been on mixed systems. A study including quartz looking into dissolution was done in Russia in the years 2013-2017. The system studied was molten KF-KCl, mainly also with 10 mol% K_2SiF_6, changing the KF:KCl ratio and temperature (Zaikov *et al.*, 2013). The results showed a linear increase in SiO_2 solubility with increasing KF:KCl ratio, demonstrating the role of F^- in breaking Si-O-Si bridges and that, on a given melt, the liquidus increases with greater SiO_2 dissolved. The SiO_2 solubility was also dependent on the presence of K_2SiF_6, with a 2:1 KF:KCl ratio the solubility of SiO_2 increased from 6.6 to 7.4 wt% when going from 0 to 10 mol% K_2SiF_6. Too high concentration of K_2SiF_6 reduced the SiO_2 solubility. This work shows that it might be fully possible to dissolve SiO_2 to suitable concentrations without K_2SiF_6, but further research must be conducted. Electrowinning trials always had K_2SiF_6 present together with the SiO_2, changing the solid coatings of Si when only K_2SiF_6 was present to nanowires when including quartz (Zaykov *et al.*, 2013), and no research on electrowinning has been reported in literature in this system with only SiO_2 in the melt. Finally, the same group also showed that the dissolution rate of SiO_2 was very slow and

electrochemical signals related to the Si-reaction increased over time (several hours) after SiO_2 addition to the melt (Zhuk *et al.*, 2017).

For an industrial process, a good understanding of quartz solubility in suitable systems is needed. This includes dissolution limits and rates, effect of stirring (bubbles), quartz quality and particle size, and effect on resulting Si produced.

5. ELECTRODE MATERIALS

5.1 Oxygen evolving anode

The material development for the oxygen evolving anode, often called an inert anode, is crucial for the proposed electrowinning process. Such an anode must be mechanically stable at elevated temperatures, and it must be electrically conductive with reliable electrical connections to the external circuit. The anode is not likely to be fully inert, but it needs to have slow enough corrosion rate/anodic dissolution so that regular anode changes become obsolete (i.e. several months between each anode change). The limiting factor is the required purity of the metal; the anode must have slow enough dissolution rate to avoid significant contamination of the metal. The anode must withstand oxidizing conditions on the surface, the O_2 (and possibly Cl_2) gas produced and a high electrical potential. The anodes should be easily fabricated by non-polluting methods (manufacture and disposal included), and economically attractive. Different electrolyte chemistries are likely to require different anode materials.

Inert anodes for aluminium electrolysis are typically divided into three (He *et al.*, 2021).

- Ceramic anodes. Especially SnO_2 anodes have been investigated on lab and bench scale, with Sb_2O_3 and CuO to improve properties. They typically have high corrosion resistance and stability.
- Metal anodes, often Cu-Ni-Fe based. They form a protective layer of oxides during electrolysis but also dissolve. They have high electric conductivity, strength and toughness.
- Cermet anodes. A mixture of ceramic and metal, also with a protective oxide layer but less dissolution, resulting in a long service life with small consumption.

For silicon electrowinning with fluoride melts, the same strategies as for aluminium would likely be suitable, however, the temperature could potentially be a bit lower than for aluminium electrolysis giving more options. However, most developers do not specify what type of inert anode they are targeting in their development of a CO_2-free aluminium process. For Si produced in chlorides, some work have been done using ceramic SnO_2, but there might be issues with formation of insulating $CaSnO_3$ over time (Lomax *et al.*, 2020) as well as dissolution and contaminating the product (Padamata *et al.*, 2025). Other oxides anodes for silicon electrowinning have been done with very expensive materials including ruthenium (Hu *et al.*, 2015). Use of titanium-based anodes have also been demonstrated (McGregor *et al.*, 2006). The long-term behaviour has not been investigated for Si electrowinning. In MOE, research have been done on metallic anodes, e.g. CrFe-anodes (Allanore, 2013).

If both O^{2-} and Cl^- are present, as when using a chloride melt, the oxygen and chlorine evolution reactions compete on the anode. This makes it important to ensure that the anode chosen results in a low overvoltage for the oxygen reaction compared to the chlorine reaction. This is especially important if the O^{2-} concentration is low compared to the Cl^-.

5.2 Metal producing cathode

The choice of metal producing cathode is also difficult and depends on the targeted silicon morphology. In lab scale, Si product typically varies from coherent films, dendritic films, grains, powders, particles, alloys with other metals, or porous sponges and nanowires. The result depends on a variation of electrochemical parameters (e.g. temperature and current efficiency), including the cathode where the metal is produced. When producing solid silicon in molten salts, research typically focus on use of metals like Ag, Fe, Al, W and Mo, carbon materials like glassy carbon and graphite, single- or polycrystalline Si, or even metallurgical grade Si (Yasuda and Nohira, 2022). After the initial Si deposition, the produced Si continues to act like the cathode. After electrolysis, the produced Si must be separated from the cathode material and the bath remains; in the case of films these can often adhere very well to the substrate making them difficult to extract.

In MOE systems, little is typically specified on the cathode material; for electrowinning processes where the metal is produced at the bottom, a starting pool of the metal to be produced is typical. For Si, due to the density vs the slag electrolyte, this could be done only if it is alloyed with another metal, resulting in the alloy staying at the bottom. A vertical approach using inert cathodes could be applied, e.g. by use of TiB_2, which should have good wetting behaviour towards liquid slag and metal.

6. UPSCALING

Solid Si electrowinning has been demonstrated in pilot scale using cryolite (as for aluminium) in the 60s (summarized by Elwell and Rao, 1988), SiO_2 raw materials and carbon anodes at 0.8 A/cm^2, but the process was not commercial at the time due to the slow deposition rates (despite 0.8 A/cm^2 being quite high for solid deposition rates). Alloying with Al has also been demonstrated at 0.027-0.053 A/cm^2 (Stubergh, 2002). Solid Si-nanowires have been produced at pilot scale via the FFC-method in chlorides (Yu *et al.*, 2020), running for 14 months at 2.7 V. Pilot scale production of Si with MOE has been demonstrated up to 1 A/cm^2, but at these values the cell voltage was very high and current efficiency very low, resulting in very high energy consumption (as mentioned in section 3.3).

6. 1 Dimensions and capacity

The size of an electrowinning plant is fully dependent on the current density; by finding the optimal current density, the production rate of the process is scalable since it depends on the total current (equation 9). More total current results in more produced metal and simply needs more area, resulting in a final area footprint for the production. Liquid aluminium is produced at 1 A/cm^2, resulting in 3 kg/h/m^2 electrode area while liquid rare earth metals alloys can be produced at 5 A/cm^2 and 63 kg/h/m^2.

For carbothermal reduction of Si, one furnace with approximately 7 m in diameter, area 38 m^2 and a power of 20 MW can produce 40-60 tonne Si/day. For Al electrowinning, one cell, e.g. at Hydro Sunndalsøra, has size around 48 m^2, run on 1.2 MW and produce ca. 2.2 tonne Al/day. As such, the production is scaled by increasing the area footprint; Sunndalsøra have 340 cells (area for cells: 16320 m^2) running a total of 420 MW and produces around 1000 tons Al/day. The area needed for an Si electrowinning plant will have to be much higher than for today's process, despite not targeting the same amount of metal produced as in aluminium.

6.2 Materials and cell design

Outside of choosing suitable anode and cathode material, everything else for use in the cell must withstand the high temperatures and conditions of the electrowinning process. The cell

typically consists of refractories and insulation material as lining, covers and shells, and current collector bars. A lot of materials from the aluminium electrolysis process are likely also suitable for Si electrowinning, especially for fluoride molten salts and possibly also molten oxides, despite the large difference in temperature. Chamotte, a silica/alumina ceramic, is typically used as a refractory material in aluminium electrolysis. Also, steel is typically part of electronic connections for the electrodes, but these are important to protect due to the corrosive environment. This can be done with a frozen side ledge (frozen electrolyte), and protective coatings can be helpful.

For solid state Si electrowinning, a setup with vertical electrodes alternating anode and cathode will be the most effective cell design with respect to area footprint. The gas produced must be collected with a ventilation system, and the gas needs a scrubbing system to remove fluoride traces (for fluoride melts), and/or should scrub any unwanted chlorine gas.

For MOE, the liquid Si is less dense than the electrolyte and will float on the top. This requires a very different design than for aluminium electrowinning, or MOE producing Fe or Mn, as the metal cannot short circuit the cell by touching both cathode and anode. Modifying known design for electrowinning of magnesium or sodium (the Down's cell) could be a suitable approach, with anodes coming vertically from the bottom and cathodes either from the sides or vertically from the top. The electrodes should ideally be separated with a diaphragm, to limit the back reaction. To protect the silicon floating on top of the cell from oxidizing before collection, an inert atmosphere is required. The inert gas is going to be costly but may be recycled if separated from the other gases, including the produced O_2. Another option is a type of double cell with two compartments, alloying Si with a heavier metal like Cu (having the metal production on the bottom again). The other compartment will have a refining process (Johansen *et al.*, 2007).

6.3 Cost

The economic viability of a process depends on factors such as the number of process steps, specific energy consumption and production footprint (Humbert *et al.*, 2024).

The operational costs (OPEX) correlate with the costs of labour, energy, and raw materials. Compared to carbothermic processes, there will be no need for coke, and the sole raw material is SiO_2. The high purity of quartz is a large advantage for the operational costs of an electrolysis cell, as it requires little front-end processing, and allows feeding the raw material continuously with a speed matching the metal production rate. If the raw material contains other elements that does not co-deposit with Si it will alter the electrolyte chemistry with time. This will eventually causing operational problems and need for adjustment of electrolyte amounts and composition, increasing complexity and labour demand. The cell voltage and thus the energy consumption unavoidably increases with increasing current density, so a trade-off between production rate and energy costs must be made. Likewise, as high current efficiency as possible is essential to keep down the energy costs per unit metal produced. Another cost driving factor is the complexity of the harvesting and post processing of the metal. If Si is deposited in solid state, it can require acid leaching or vacuum distillation to separate the product from the electrolyte. This is avoided if Si is produced in its molten state.

Predicting the capital costs (CAPEX) for a new electrowinning process can be quite challenging and requires a different methodology than the chemical engineering procedures for upscaling and industrialization of conventional chemical processes. Stinn and Allanore developed a new, electrochemical engineering scaling law to predict the capital cost of electrochemical facilities (Stinn and Allanore, 2020). According to their work, an important main CAPEX driver

for an electrolyzer is the temperature (material cost), however this is compensated by the fact that the current density will be higher (higher production rate per area footprint).

The work of Stinn has been used to carry out techno-economic modelling of a 160 000 tonne/year solar silicon molten salt electrolysis process with inert anode (Moudgal *et al.*, 2021). The system studied was a CaF_2-MgF_2-CaO electrolyte with quartz as raw material, and vertical electrode set up with 0.2-0.3 A/cm^2 cathodic current density, giving a slightly lower area footprint than Hall-Heroult aluminium smelting. The Si is produced in solid state in the temperature region 980-1100 °C. The energy balance indicated that a self-heating cell at 1100 °C would require 14.3 kWh/kg Si produced, giving OPEX 1.74 \$/kg_{Si} and CAPEX: \$10 500 /tonne/year.

7. CONCLUSIONS AND OUTLOOK

When evaluating technologies to eliminate CO_2 from today's carbothermic reduction process for Si production, electrowinning from the use of SiO_2 is a very strong contender. It is important to be aware of the higher energy consumption compared to today's SAF process related to removing the carbon from the reactions. The low productivity rates related to the low current density of solid silicon production will result in high area footprint for an electrowinning plant, while the high resistivity in molten oxide melts might result in high cell voltages and high energy consumption when producing liquid Si at higher production rates. The choice of melt is not trivial, especially related to the processes that may affect cost, the complexity of gas atmosphere, gas cleaning and post processing.

High purity Si has previously been demonstrated at pilot scale using carbon anodes, but the TRL level related to the oxygen evolving reaction is low. Choosing a suitable anode material is important, as it needs to facilitate the oxygen evolving reaction in the specific system. It will not be fully inert, and the slow corrosion will influence the silicon purity. This is one of the most important knowledge needs related to an industrial process, together with the need for a better understanding of solubility of quartz in suitable systems.

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