

# Macroscopic Modeling and Phase Field Modeling of Solar Grade Silicon by Molten Salt Electrolysis



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## Introduction

The sixth Intergovernmental Panel on Climate Change report (IPCC) recently released predicts a deep reduction in emissions to meet global goals of 1.5 °C reduction in temperature. It states that concentrations of CO<sub>2</sub> have continuously increased in the atmosphere reaching averages of 410 ppm in 2019 [1]. Therefore, it becomes imperative to reduce CO<sub>2</sub> in any way possible. Silicon, which is an important material for renewable energy, electronics, and metallurgy, is primarily produced by the carbothermic reduction of quartz. This metallurgical grade silicon is then refined by the Siemens Process to solar grade silicon using hydrogen chloride. The by-product of trichlorosilane from this process is highly volatile and unstable [2].

This work aims to achieve the above process of reduction in a single step using electrochemistry. This would eliminate multiple steps and save energy and cost and reduce emissions if a suitable inert anode is used in production. Understanding electrochemical cell characteristics therefore is needed to prove and scale this technology.

Macroscopic models help engineers to design, develop, and improve the efficiency of electrochemical cells. They solve conservation equations of mass, momentum, and energy and help determine electrode current distribution, fluid flow, heat distribution, and stability of the cell [3]. They also help in correlating experimental work and understanding measurements in cells from a lab scale to a plant scale. However, they do not predict the microstructure and plating of material on the cathode. This can be calculated using phase field models. These phase field models predict interface stability and deposition morphology in the cell. In this work, we present these models in addition to proof-of-concept experiments.

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## Materials and Methods

### *Cell Design*

The cell design followed here for the macroscopic models is described in Moudgal et al. [4]. The lab scale experimental apparatus complements the model except a carbon anode with a Ytria Stabilised Zirconia solid oxide membrane tube [5] with silver is used in the place of an inert anode. The carbon anode is currently being used as it provides higher conductivity. A new oxygen evolving porous lanthanum nickelate ( $\text{LaNiO}_3$ ) electrode with comparable conductivity is currently under development. The molten salt electrolyte used is a fluoride-based salt with a  $\text{CaF}_2$ – $\text{MgF}_2$  eutectic with  $\text{CaO}$ ,  $\text{YO}_{1.5}$ , and  $\text{SiO}_2$ . This salt was developed by Uday Pal et al. [6]. It has been shown that silicon can be reduced using a liquid tin cathode using this salt [7].

### *Macro Models*

The goal of the macro models is to solve conservation equations of mass, momentum, and energy to gain a better understanding of the cell. The model uses COMSOL version 5.6, and the modules used are the electrochemistry module, electrodeposition module, and the fluid flow and heat transfer modules.

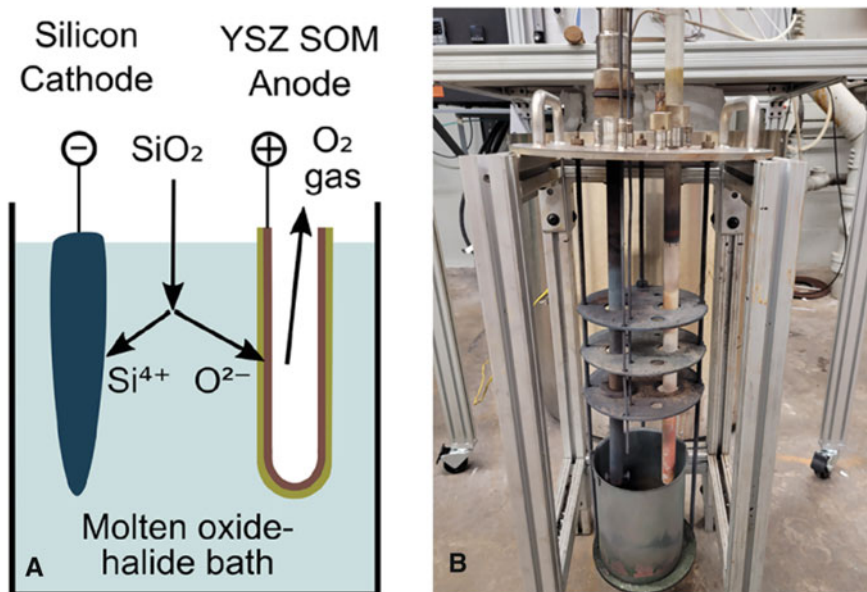
### *Phase Field Model*

The phase field model solves the Cahn–Hilliard equations for cathode growth with electric field concentration and cathode growth as described by Pongsaksawad et al. [8]. It uses one or more field variables of  $C$  to describe the composition and differentiate between the Si deposit and electrolyte in accordance with Eqs. (1) and (2) below.

$$F = \int \left[ H(C) + K |\nabla C|^2 + \frac{zF\rho}{M} (1 - C)\phi \right] \quad (1)$$

$$\frac{DC}{Dt} = \nabla \cdot \left( \kappa \nabla \left( \frac{\partial H}{\partial C} - K \nabla^2 C \right) + \kappa \frac{zF\rho}{RTM} \frac{1 - C}{1 + C} \nabla \phi \right) \quad (2)$$

where  $H(C)$  is homogeneous free energy,  $K$  is gradient penalty coefficient, and  $\kappa$  is mobility.



**Fig. 1** **a** Diagram of the proposed process. **b** Experimental setup of electrochemical cell at lab scale consisting of **a** stainless steel crucible

## Experimental

Experiments are conducted in a standard two-electrode high-temperature electrochemistry setup as shown in Fig. 1. Electrodes are completely immersed in the salt composition mentioned above, i.e.,  $\text{CaF}_2\text{--MgF}_2\text{--CaO--YO}_{1.5}\text{--SiO}_2$ . The base eutectic with the calcium oxide and yttrium oxide in composition by weight 45.5%  $\text{CaF}_2$ , 36.4%  $\text{MgF}_2$ , 9%  $\text{CaO}$ , and 3.6%  $\text{YO}_{1.5}$  are mixed first and dried in an inert environment of argon gas at 350 °C before being fused together at 1100 °C and crushed. 5 wt.%  $\text{SiO}_2$  is added, and the salt is dried again in argon before being electrolysed at 1100 °C. There is a low potential pre-electrolysis step carried out before successive electrolysis is carried out in multiple intervals. Characterization was done using scanning electron microscopy and energy-dispersive x-ray spectroscopy.

## Summary and Conclusions

In this work, the main goal is the decarbonization of silicon production to produce high-purity solar grade silicon at low costs. We have shown and described methods

that can be used to achieve this primary production in a single step. Further development and analysis of the anode and flux is currently underway. We anticipate that the methods described can be applied to a scaled-up electrochemical cell in the future.

**Conflict of Interest** The authors declare that they have no conflict of interest.

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