First-principles Molecular Dynamics Study of Molten Salt

Yifan Zhang[a], Adam Powell[a], Yu Zhong[a], Uday Pal[b], Michael Gao[c]
[A] Worcester Polytechnic Institute, [b] Boston University, [c] National Energy Technology Lab

Backgrounds

Silicon is the dominant solar material because of its abundance, low cost, and high solar efficiency. But manufacturing high-purity silicon required for solar energy is very complex, hard to scale, and unsafe since it involves dealing with toxic flammable gases. Therefore, a new solar silicon production technology based on molten salt electrolysis has been proposed as shown in Figure 1.

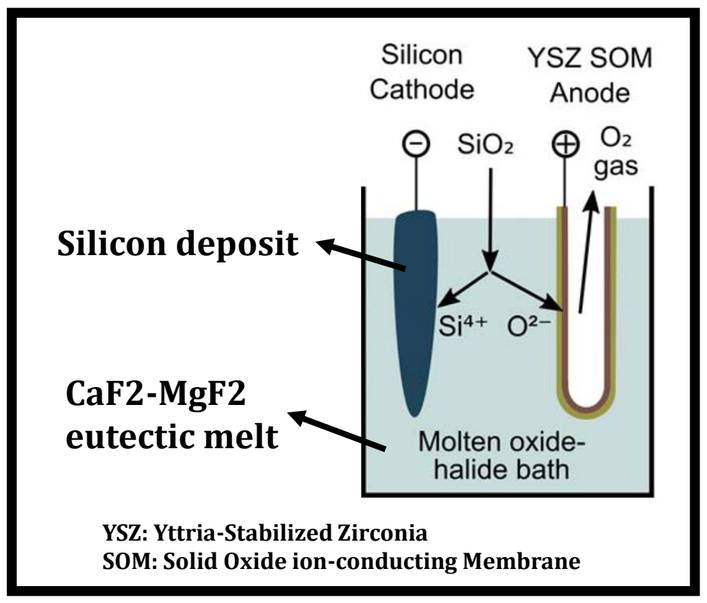

Figure 1. Silicon molten salt electrolysis

Silicon will deposit on a silicon cathode via epitaxial electrodeposition from dissolved SiO2, with closed-end yttria-stabilized zirconia (YSZ) solid oxide ion-conducting membrane (SOM) tube containing anodes. Molten salt electrolysis is widely used for electrometallurgy, such as electrolytic reduction of metallic compounds to metals and purification of impure metals to purer metals. However, due to severe working condition of molten salt, the measurements of properties that people interested are usually very difficult. Therefore, compared to trials and errors method, computational simulations not only save time and cost, but also can efficiently carry out high-throughput calculations with various conditions. For example, CALPHAD, DFT, and molecular dynamics.

Methods

The primary tool for understanding molten salts is the phase diagram. A large number of binary and ternary phase diagrams have been measured for chloride and fluoride salt systems. For our specific system, calcium fluoride, magnesium fluoride and silicon oxide. The addition of yttrium fluoride is to improve stability of YSZ, to prevent leaching of yttrium ion into the bath. As we can see from the Figure 2 and Figure 3, the solubility of silicon ions will increase with adding silicon oxide, but system will also produce harmful substances such as silicon fluoride.

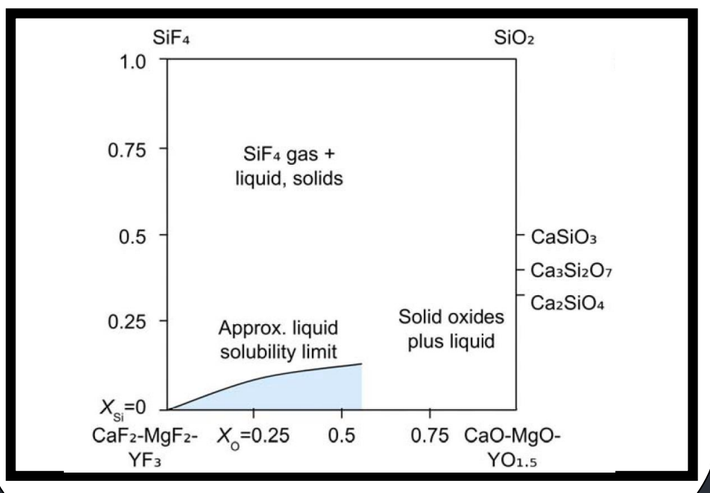

Figure 2. Partial phase diagram I

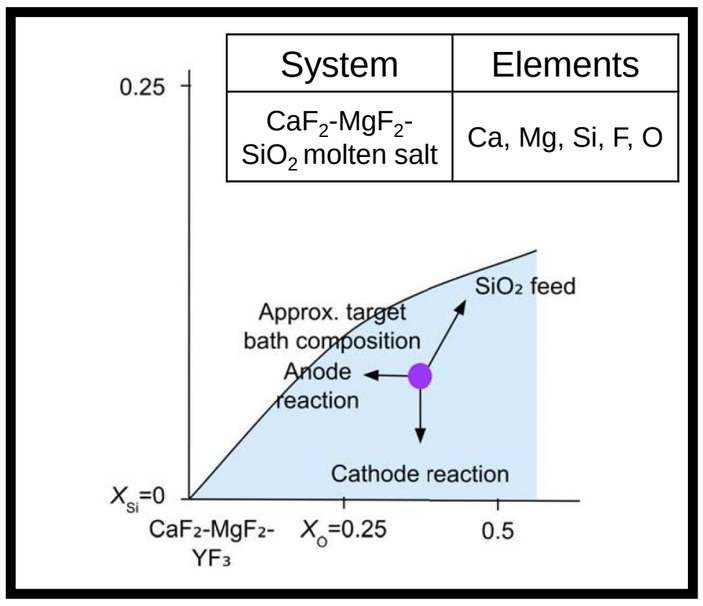

Figure 3. Partial phase diagram II

Besides the phase diagram, molecular dynamics (MD) is another effective way to study molten salt. It is important to be able to accurately predict and understand liquid structure and dynamics both in the bulk and at salt/material or salt/vapor interfaces. MD simulation can help explain transport properties, including viscosity and the origin of different length-scale features in the x-ray structure function, as well as real-space radial distribution functions. It can also be particularly useful in understanding the effects of structural voids and defects formed under radiolytic conditions, as well as determining their effects on material transport and thermal conductivity. this is particularly important for understanding possible structural heterogeneities in the molten salt system. Figure 4 shows 64 atoms of CaF_2 crystal structure before melting.

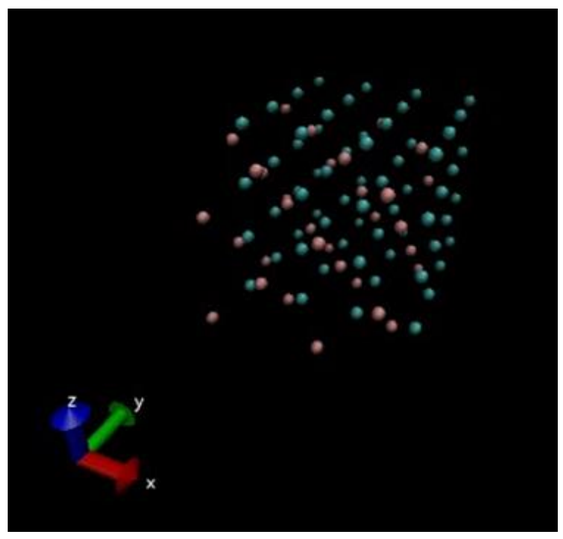

Figure 4. 64 atoms of CaF2 crystal structure

The basic idea of MD is to solve the Newton's equation of motions. and based on the difference in describing potential, MD is divided into two types, classical MD and first-principles MD. Classical MD use the empirical potentials, works well for simple system, and simulation is pretty fast for large particle numbers. The FPMD will have higher accuracy but also higher computing effort, and the limitation of supercell size and simulation time.

Strategy

For this project, we plan to use the combination of IPMD and FPMD, because both of them have advantages and shortcoming. Through the combination, we could foster strengths and circumvent weakness of them. And the python will also be used as a convenient tool to link them and analyze the raw data from MD output. Figure 5 outlines the strategy used for this work.

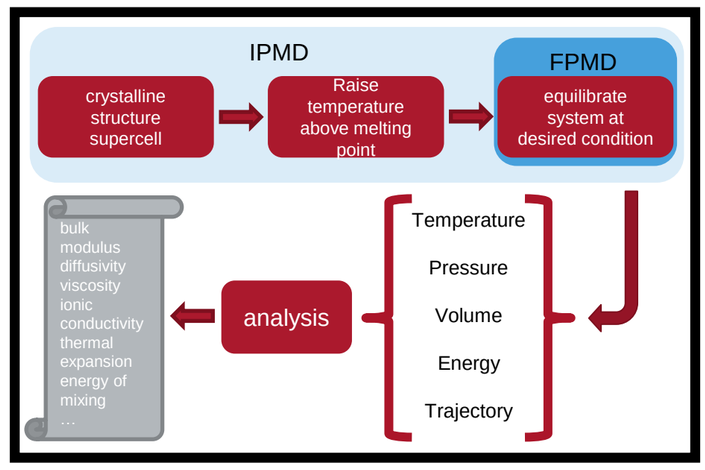

Figure 5. Flow chart of overall strategy

Preliminary results

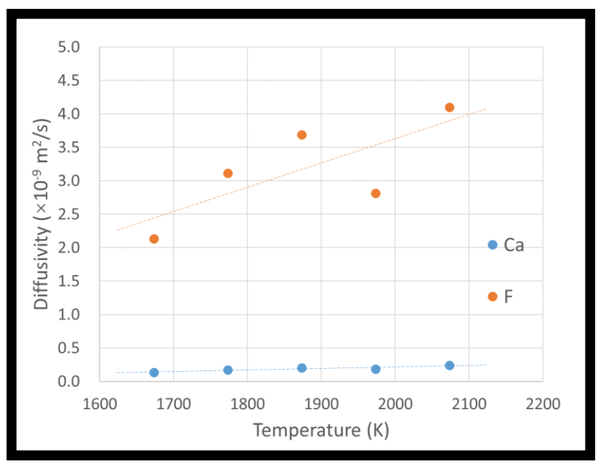

Figure 6. Self-diffusion coefficient of CaF_2 salt at multiple temperatures

The self-diffusion coefficients are analyzed from the mean square displacement of ions as a function of time using the Einstein relation shown below. Figure 6 shows the self-diffusion coefficient of CaF_2 salt at multiple temperatures. It's easy to see that the trend of the diffusion coefficient of ions is proportional to the temperature.

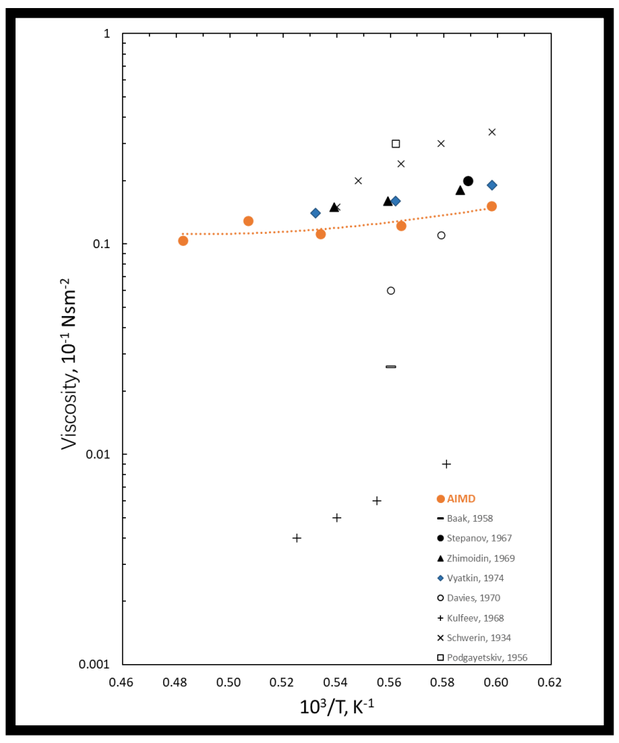

Figure 7. Calculated viscosity of CaF_2 salt at multiple temperatures

Base on the diffusivities we have, viscosity can be evaluated through the Stoke Einstein equation. As we can see from the Figure 7, compared with existed experimental viscosity data. Our results are within the acceptable range.

Conclusions

Molecular dynamics is a very important tool because of the difficulty of the experiment, and it can help explain transport properties and provide the predictive value. First-principles MD has much higher accuracy than classical MD, but much higher computing resource consumption and more limitations. Therefore, the combination of IPMD and FPMD is the best choice.