Computational Studies of Amorphous SiO_x as Anode Materials for Lithium-Ion Batteries

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Introduction

With the rapid growth of electric vehicles and electronic devices, lithium-ion batteries (LIBs) remain a critical factor for high performance energy storage. LIBs have three components: cathode, electrolyte and anode (Fig. 1). The focus of this study is on material for the anode. Enhancing anode materials is essential to overcoming limitations in rechargeable power systems and improving both battery life and energy capacity.

Silicon (Si) has emerged as a promising anode due to its high theoretical capacity (~4200 mAh/g), which far exceeds traditional graphite. Additionally, Si is abundant, low-cost, and exhibits a low lithiation potential [2].

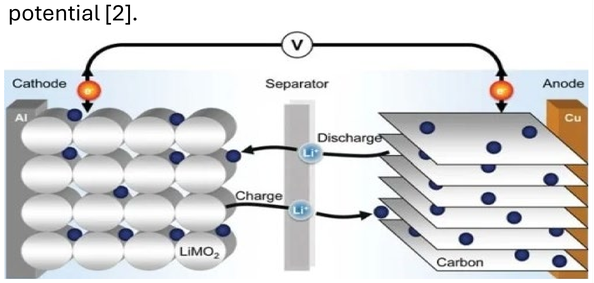


Figure 1. Lithium-ion battery cell diagram [1].

However, Si anodes have various limitations including up to 300% volume expansion during charge and discharge cycles, which can lead to mechanical failure, as shown below in Fig. 2 [2].

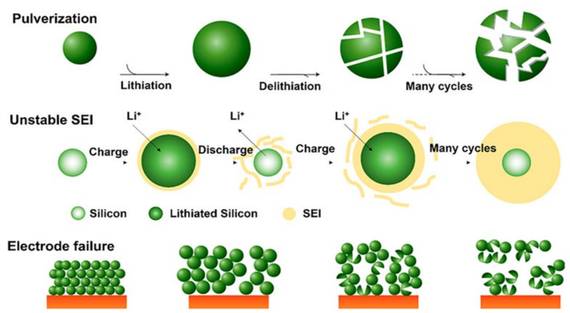


Figure 2. Effects of volume expansion in Si anodes [2].

To overcome these challenges, amorphous silicon oxides (SiO_x, $0 \le x \le 2$) can balance between capacity and structural stability. Figure 3 illustrates the structural differences between crystalline and amorphous SiO_x (a-SiO_x). However, experimental characterization of amorphous structure is very challenging, while computationally generated amorphous structures suffer from inconsistency due to varying simulation history. This work aims to develop a robust computational protocol to generate reliable amorphous SiO_x structure.

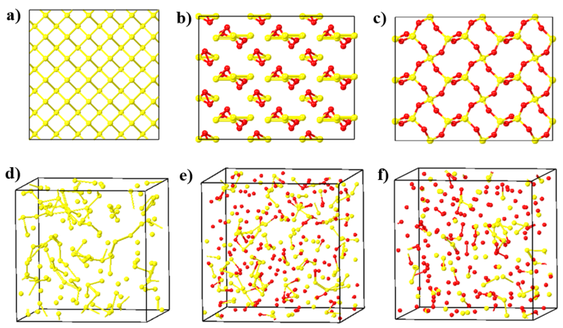
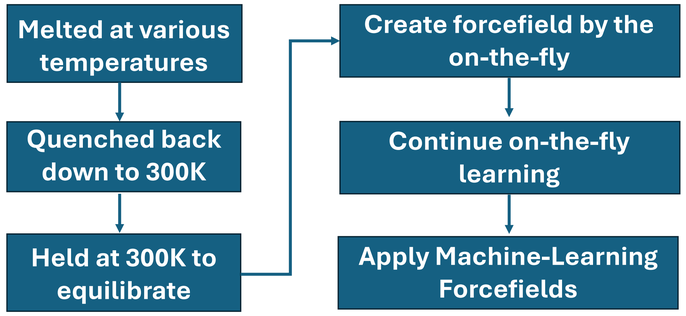


Figure 3. Atomistic structures of a) crystalline Si, b) crystalline SiO, c) crystalline SiO2, d) amorphous Si, e) amorphous SiO, and f) amorphous SiO2.

Methodology

Ab initio molecular dynamics (AIMD) simulations were conducted using the Vienna Ab initio Simulation Package (VASP) within the MedeA environment to generate amorphous SiO_x structures (Fig.3). Then, a melt, quench, and equilibration process was applied across varying temperatures, densities, and simulation times. A design of experiments (DOE) approach evaluated how these parameters, along with thermostat conditions, affect the resulting structures.

The optimal computational setup for producing reliable amorphous structures was then used as the basis for developing machine learning force fields (MLFFs), which enable studies of lithiation behavior and energy storage across Si-based anodes.



Scheme 1. Schematic respresentation of the experimental workflow for the melt, quench and equilbration process.

Results and Discussions

Amorphous SiO_2

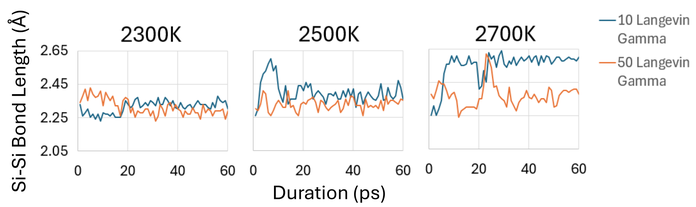


Figure 4. Evolution of Si-Si bond length during melting at different temperatures.

Table I. Comparison of Peak Positions of AIMD and MLFF with Experimental Data for a - SiO_2 [3].

Bond Type	Calculated Peak Position (Å) - AIMD	Calculated Peak Position (Å) - MLFF	Experimental Peak Position (Å)
Si-Si	2.97 (1.65%)	2.97 (1.65%)	3.02
Si-O	1.65 (3.13%)	1.65 (3.13%)	1.6
O-O	2.61 (3.16%)	2.61(3.16%)	2.53

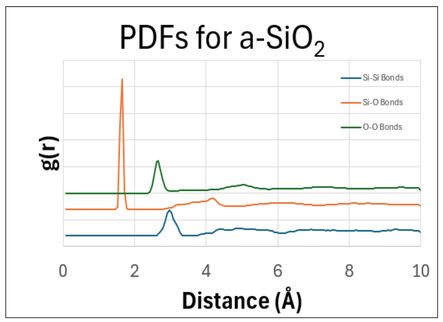


Figure 4. Pair correlation functions (PDF) for Si-Si, Si-O and O-O bonds in amorphous SiO_2. First peak positions from the MLFF and MD simulations closely matched experimental values with low error.

Amorphous SiO

Table II. Comparison of Peak Positions of AIMD with Experimental Data [4].

Calculated Peak Position (Å) - AIMD	Experimental Peak Position (Å)	Error Percentage (%)
1.65	1.65	0
2.37	2.35	0.85
2.67	2.65	0.75

Density Change After Melts and Equilibration

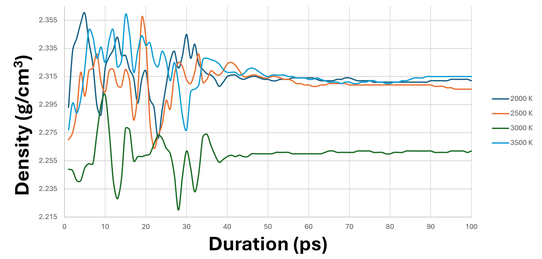


Figure 6. Densities after quenching SiO with a density of 2.25 g/cm³ at different temperatures while quenching and holding at constant rates.

PDFs for a-SiO

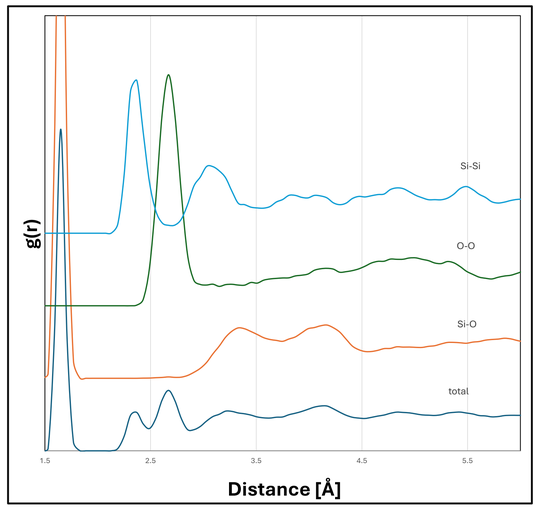


Figure 7. Pair correlation function of SiO with a density of 2.3 g/cm³ after melting at 2500K for 100 ps, cooling to 300K for 5 ps, and holding at 300K for 100 ps.

Amorphous Si

Table III. Comparison of Peak Positions of AIMD with Experimental Data.

Calculated Peak Position (Å) - AIMD	Experimental Peak Position (Å)	Error Percentage (%)
2.37	2.35 [5]	0.84%
3.93	3.86 [5]	1.78%
5.67	5.74 [6]	1.23%

Density Change After Melt and Equilibriation at Various Temperatures.

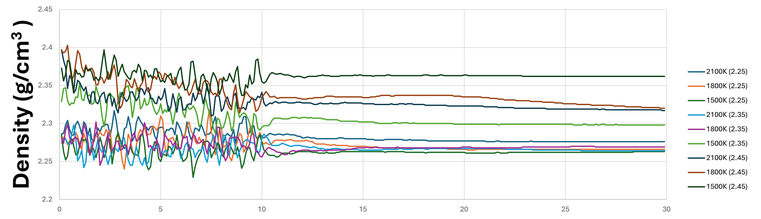


Figure 8. Densities quenching a-Si with a thermostat setting of Langevin 10 Gamma at different temperatures after quenching and holding at 300K.

PDF for a-Si Melted at 2100K Before Equilibration

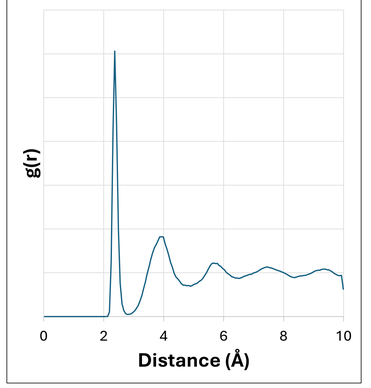


Figure 9. Pair correlation function of a-Si with a density of 2.35 g/cm³ [7] after melting at 2100K for 100 ps, cooling to 300K for 5 ps, and holding at 300K for 30 ps.

Conclusions

- It is important to monitor the Si-Si bond length during the melting step in SiO_2. Consistent a-SiO_2 structures can be obtained if the Si-Si bond length transitions to be around 2.6 Å.
- A transition in Si-Si bond length was not observed in SiO or Si structures. Consistent a-SiO and a-Si structures can be obtained by monitoring resulting densities of the system.
- Optimal computational settings to generate reliable a-SiO_x structures have been determined and can be applied in the study of other amorphous materials.
- MLFFs can be used in the future to enhance data collection and validation to accelerate future research.

References

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