Computer simulation of silicon-based materials as possible anode for lithium-ion batteries

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ABSTRACT

Silicon-based materials, such as amorphous Si, $SiO2$, and SiO, are promising anode materials for lithium-ion batteries due to their high energy capacity. However, significant volume changes during charge and discharge remains a critical challenge that hinders their commercialization. In this project, atomistic simulation using a reactive force field approach was employed to study the structural evolution as a function of lithium concentration in amorphous Si, $SiO2$, and SiO. The force field was first verified by comparing calculated structural characteristics with those obtained experimentally. The verified force field was then used to determine the structural changes at various states of lithiation, together with the corresponding lithium diffusivity. Atomistic insights obtained from our simulations help to design silicon-based materials that minimize their volume changes while maintaining sufficiently high lithium diffusivity.

INTRODUCTION

Silicon-based materials are a novel and effective way for storing more lithium due to their high energy capacity (up to 4200 mAh/g) compared to graphite materials (372 mAh/g). By alloying with lithium during the charging process, silicon can increase the energy density in these batteries. It offers promising improvements in performance, strength, and low discharge voltage. However, experimental studies show that silicon can expand by up to 300% during the alloying process resulting in mechanical stress that leads to a loss of capacity and battery life.

To address these challenges, it is important to utilize computer tools for simulations that provide accurate calculations and visualizations of chemical processes compared to experimental data. These simulations give developers a better understanding of what is needed to design better materials.

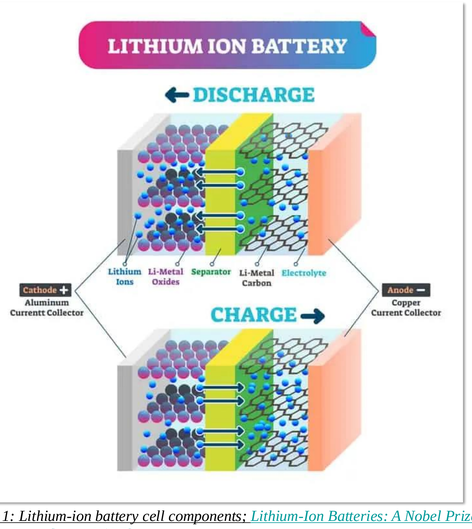

Figure 1: Lithium-ion battery cell components; Lithium-Ion Batteries: A Nobel Prize Win You Use Everyday - ANSI Blog

METHODS

The methods for obtaining atomistic insights into amorphous silicon-based materials involved several steps. Each potential anode material configuration was heated above its melting point (in Kelvin) using a force field with specific parameters to achieve a disordered structure.

MedeA Software: Used for simulating an analyzing material properties and behaviors in materials science.

LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator): Molecular Dynamics simulation software used to model the behavior of atoms and molecules in various materials.

ReaxFF(Reactive Force Field): Models chemical reactions and bond formation/breakage in complex systems.

After melting the structures at different temperatures above the melting point and choosing the best one that compared to experimental PDF, another simulation process takes place to cool the system at 10 ps (0.000000000011 s) from the chosen melted structure to 300 K (room temperature) and another 30 ps for equilibration at 300 K. This ensures structure stays amorphous.

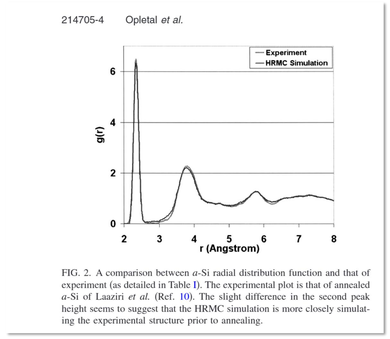

FIG. 2. A comparison between *a*-Si radial distribution function and that of experiment (as detailed in Table I). The experimental plot is that of annealed *a*-Si of Laaziri *et al.* (Ref. 10). The slight difference in the second peak height seems to suggest that the HRMC simulation is more closely simulating the experimental structure prior to annealing.

Figure 2: This figure illustrates the objective we aim to achieve for amorphous silicon (a-Si). It shows a comparison of the Si-Si pair correlation function between a simulation and an experiment conducted by other researchers. The same was done for a-SiO and a-SiO_2.

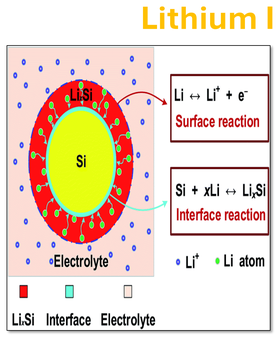

Figure 3: Lithium loses its electron easily due to weakly held, lone outer electron and low ionization energy. When a battery is charging, lithium ions migrate from the cathode to the anode where they combine with electrons to form neutral lithium atoms. Then the alloying process begins with Silicon, and we can see through simulations and experiments an expansion in volume.

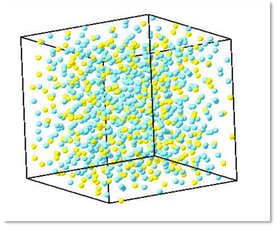

Figure 4: $(a\text{-}SiO_2)_{300}$ system used for MD simulation.

RESULTS

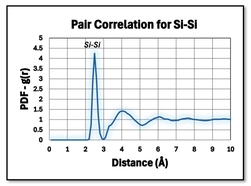

Figure 5: a-Si pair correlation function after melting at 2500 K and then cooling to room temperature (300 K) in 10 ps. Peaks in the PDF correspond to commom interatomic distances, indicating preferred bonding lenghts and structural features.

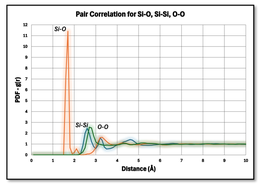

Figure 6: a-SiO pair correlation function after melting at 2500 K and then cooling to room temperature (300 K) in 10 ps. Peaks in the PDF correspond to common interatomic distances, indicating bonding lengths and structural features.

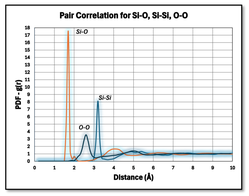

Figure 7: a-SiO_2 pair correlation function after melting at 3500 K and cooling to room temperature (300 K) in 10 ps. Peaks in the PDF correspond to common interatomic distances, indicating bonding lengths and structural features.

System	Si-O peak	Si-Si peak	O-O peak	Density	System Size
c-Si	----------	2.45(2.35*)	----------	2.40 (2.29*)	512
a-Si	----------	2.45(2.35*)	----------	2.42 (2.29*)	512
c-SiO	1.65(1.64*)	3.15(2.45*)	2.75(2.64*)	2.61 (2.13*)	600
a-SiO	1.65(1.64*)	3.15(2.45*)	2.75(2.64*)	2.20 (2.13*)	600
c-SiO_2	1.65(1.610*)	3.15(3.08*)	2.65(2.63*)	2.546 (2.33*)	300
a-SiO_2	1.65(1.610*)	3.15(3.08*)	2.65(2.63*)	2.293 (2.33*)	300

Table 1: Comparison of computational data including density and pair correlation bonds to experimental data (*). This ensures that our simulations accurately reflect real-world materials. By aligning our simulations with experimental measurements, we validate the reliability of our models and confirm that they correctly represent the material's structure and properties.

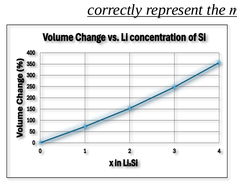

Figure 8: Representation of volumen expansion for: a-Si, a-Li_3Si, a-$Li_{12}Si_7$, a-$Li_{13}Si_4$, a-$Li_{15}Si_4$ as x represents concentration of lithium.

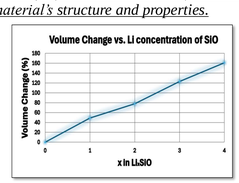

Figure 9: Representation of volumen expansion for: a-SiO_2, a-$LiSiO_2$, a-Li_2SiO_2, a-Li_3SiO_2, a-Li_4SiO_2 as x represents concentration of lithium.

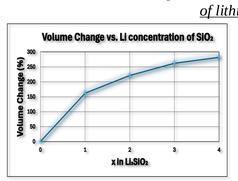

Figure 10: Representation of volumen expansion for: a-SiO_2, a-$LiSiO_2$, a-Li_2SiO_2, a-Li_3SiO_2, a-Li_4SiO_2 as x represents concentration of lithium.

CONCLUSIONS

In conclusion, utilizing experimental data for comparison with our computer simulations was essential for accurately selecting the most suitable silicon structure for further analysis. This approach ensures the relevance and reliability of the simulated models. Both crystalline and amorphous were then simulated by melting and quenching the best structure, and further tested for lithium diffusion calculations. The study focused on evaluating the volume expansion of these silicon forms upon lithium alloying. The results revealed significant differences in volume expansion in the insertion of lithium for the different structures at different ratios. This can tell us a lot about material selection and how to proceed with better improvements for lithium-ion batteries. As mentioned, volume expansion hinders commercialization. Further research will continue to explore diffusivity as high diffusivity is crucial for lithium-ion movement without damaging the silicon-based anode.

Figure 11: Silicon visual with its metallic luster and grayish color appear as one of the most abundant elements in the Earth's Crust. Its use plays a critical role in driving technological advacements like renewable energy and electronics given its inert nature.

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