

Electronic Supplementary Information (ESI)

Atomistics of the Lithiation of Oxidized Silicon (SiO_x) Nanowires in Reactive Molecular Dynamics Simulations

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(S1) Development of reactive force field for the Li-Si-O system

The reactive force field (ReaxFF) parameters of the Li-Si-O system were developed based on the Li-Si parameters^{S1} that we have previously developed. For the ternary Li-Si-O system, additional ReaxFF parameters with regard to Si-O and Li-O bonds, etc., are required. Here, the parameters concerning the Si-O bond were obtained from Ref. S2. In this work, we developed the Li-O parameters based on density functional theory (DFT) calculations of Li₂O and Li₂O₂ molecules. To calculate the bond dissociation energy of the Li-O bond, we used the hybrid B3LYP functional with the 6-311G** basis set in the Q-Chem^{S3} software.

Validation results for the developed Li-O ReaxFF parameters are shown in Figure S1. The developed ReaxFF reproduces the bond dissociation energy for the Li-O bond obtained from the DFT calculations. In addition, the ReaxFF reproduces the Mulliken charge of a Li atom as obtained from the DFT calculations for an optimized Li₂O molecule (DFT: +0.35e versus ReaxFF: +0.39e) and Li₂O₂ molecule (DFT: +0.50e versus ReaxFF: +0.50e).

Moreover, in the trainset for developing the ReaxFF, we considered a bond dissociation behavior of Li₄SiO₄ cluster and an equation of state of the Li₂O crystal. The results are shown in Figures S2 and S3.

In addition, using the developed ReaxFF, we calculated bulk moduli for c-Si and a-SiO₂, which is shown in Figure S4. The ReaxFF predicts the bulk modulus of 70.3 GPa for c-Si, which is comparable to experimental (97.6 GPa)^{S4} and DFT (88.7 GPa)^{S5} values. And, the ReaxFF predicts 47.9 GPa for *a*-SiO₂, which is also in the reasonable range between the previous experimental (36.7 GPa)^{S6} and theoretical (51.5 GPa)^{S7} values.

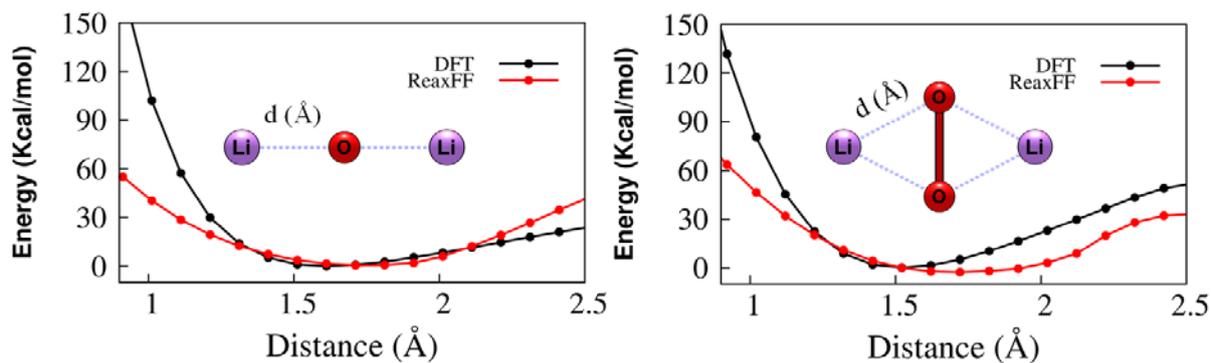


Figure S1. Comparison of DFT and ReaxFF through bond dissociation curves of Li-O bond in Li_2O (left) and Li_2O_2 (right) molecules.

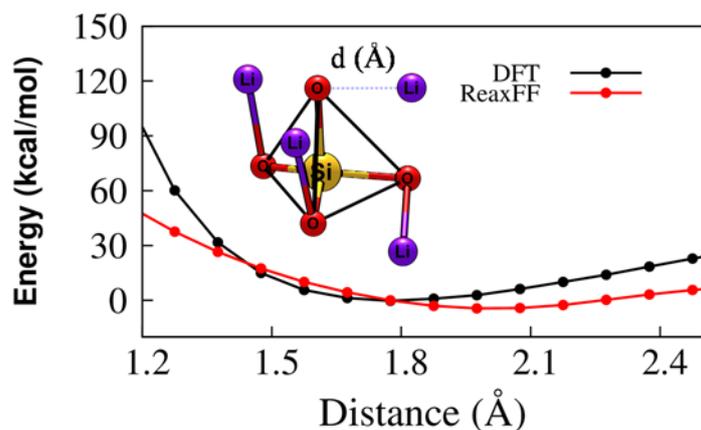


Figure S2. Comparison of DFT and ReaxFF through a dissociation curve of the Li-O bond in Li_4SiO_4 .

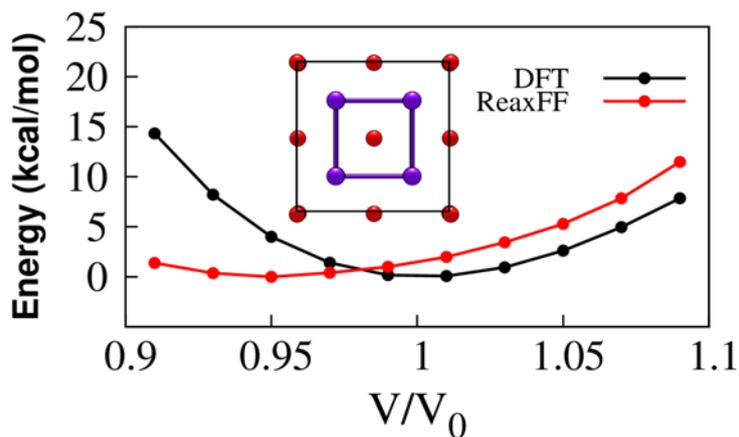


Figure S3. Comparison of DFT and ReaxFF through an equation of state of the Li_2O crystal.

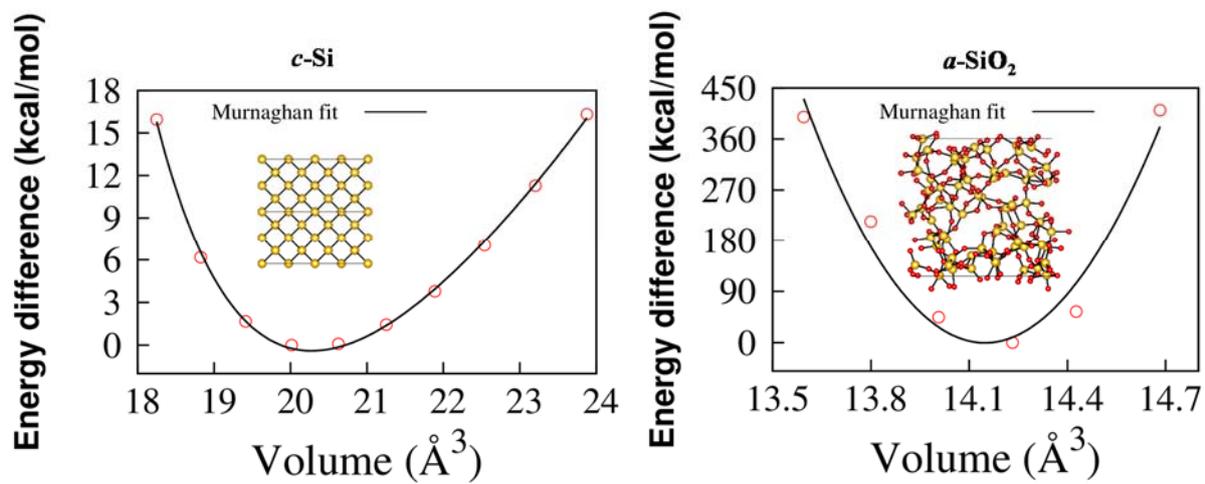


Figure S4. Bulk moduli of *c*-Si (left) and *a*-SiO₂ (right) calculated by the developed ReaxFF. Here, in calculating the bulk moduli from the ReaxFF results, the Murnaghan equation is used.

(S2) Force Field Optimization

For the force field optimization, we used a successive one-parameter search method which was developed by van Duin et al.^{S8,S9} The method is used to minimize the sum-of-square error function given as

$$\mathbf{error} = \sum_i \left[\frac{(\omega_{i,QM} - \omega_{i,ReaxFF})}{\sigma_i} \right]^2$$

where, $\omega_{i,QM}$ and $\omega_{i,ReaxFF}$ are DFT and ReaxFF computed values, respectively. And σ_i is the assigned weight in the *i*th data point.

(S3) Production of SiO_x NWs from ReaxFF-MD simulations

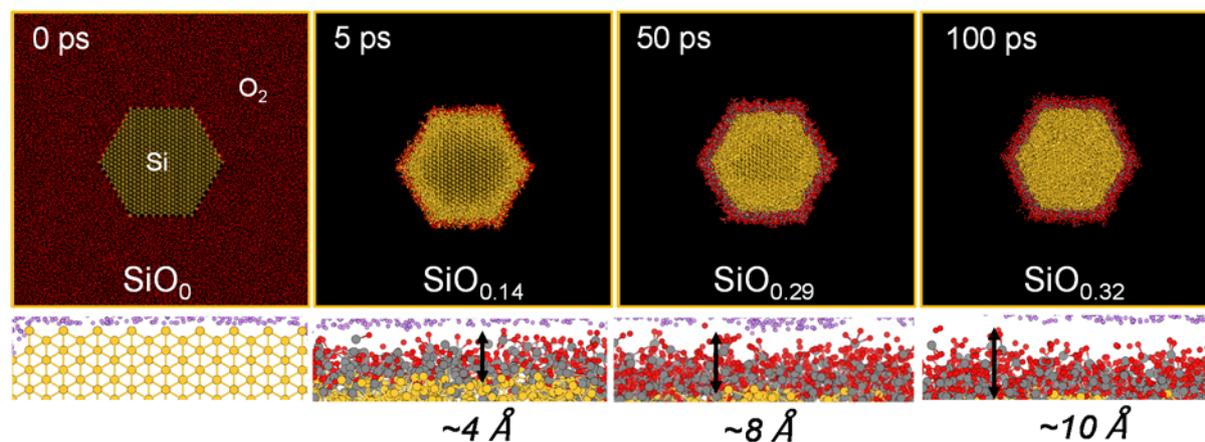


Figure S5. The process of preparing SiO_x NWs by ReaxFF-MD simulations.

Figure S5 shows the process of preparing SiO_x NWs by means of chemical reactions between pristine Si NWs (~ 5 nm in diameter and ~ 10 nm in length) and O_2 molecules. A pristine Si NW was immersed in a simulation cell filled with O_2 molecules with periodic boundary conditions in all directions; the dimensions of the simulation cell were $105.2 \text{ \AA} \times 105.2 \text{ \AA} \times 97.8 \text{ \AA}$. ReaxFF-MD simulations at 500 K were then performed to predict the chemical reactions between the Si NW and the O_2 molecules, for which an MD time step of 0.5 femto seconds (fs) was used. At 500K, O_2 molecules were easily dissociated on the surface of the Si NW, leading to the formation of silicon oxides. The oxide thickness depended on the oxidation time, with a longer oxidation time leading to a thicker oxide layer. We considered three oxidation times: 5, 50, and 100 ps, resulting in the $\text{SiO}_{0.14}$, $\text{SiO}_{0.29}$, and $\text{SiO}_{0.32}$ NWs, respectively.

(S4) Coordination number

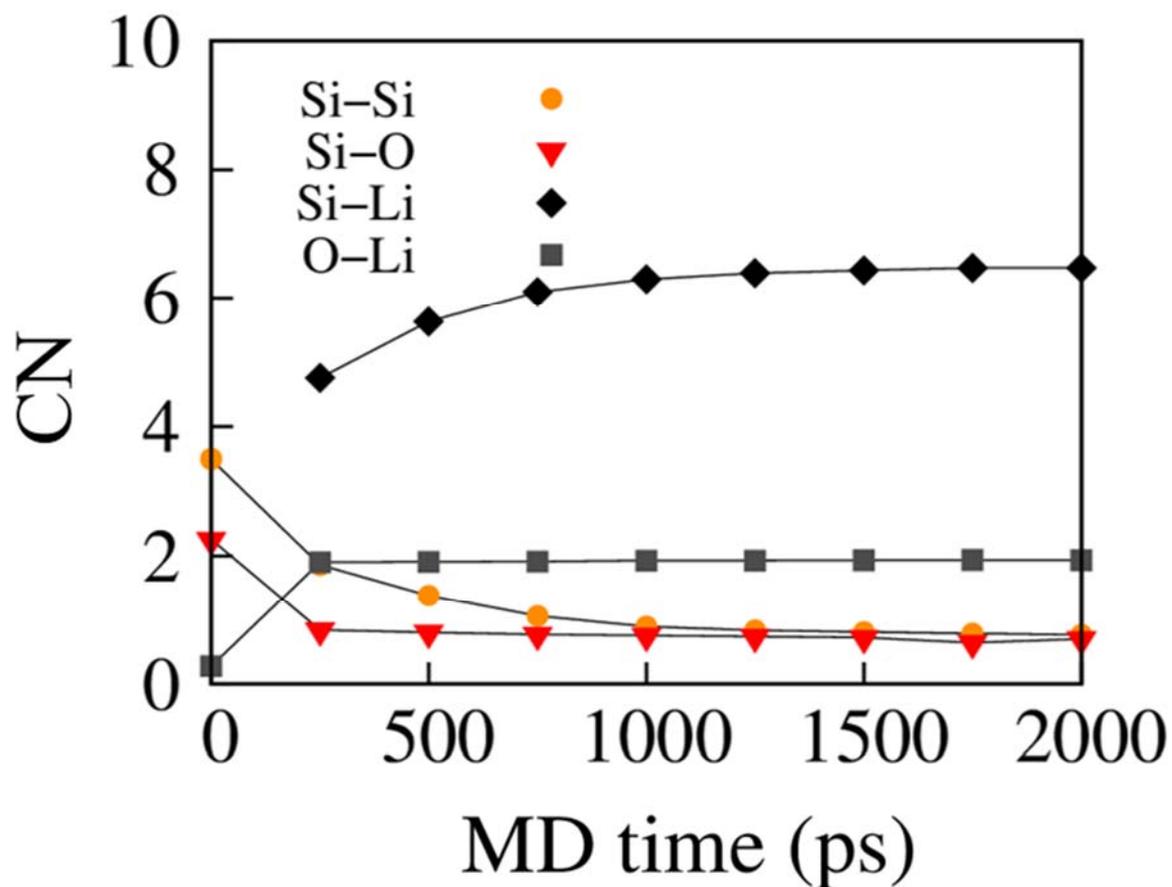


Figure S6. Calculated average coordination numbers (CNs) for Si, O, and Li atoms in the $\text{SiO}_{0.32}$ NW with a MD time. The cutoff radii for $\text{CN}_{\text{Si-Si}}$, $\text{CN}_{\text{Si-O}}$, $\text{CN}_{\text{Si-Li}}$, and $\text{CN}_{\text{O-Li}}$ are 2.40, 1.85, 2.90, and 2.55 Å, respectively.

(S5) Interface mobility

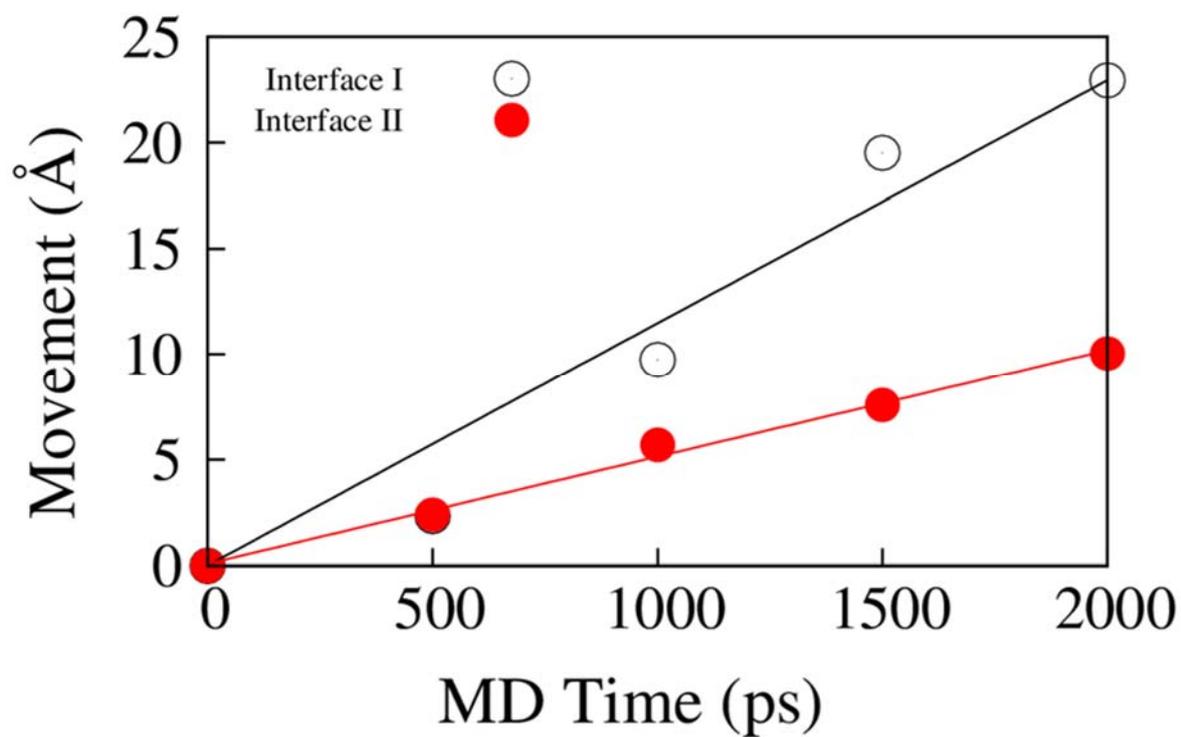


Figure S7. The mobility of the interfaces I and II with a MD time.

(S6) Delithiation process simulation

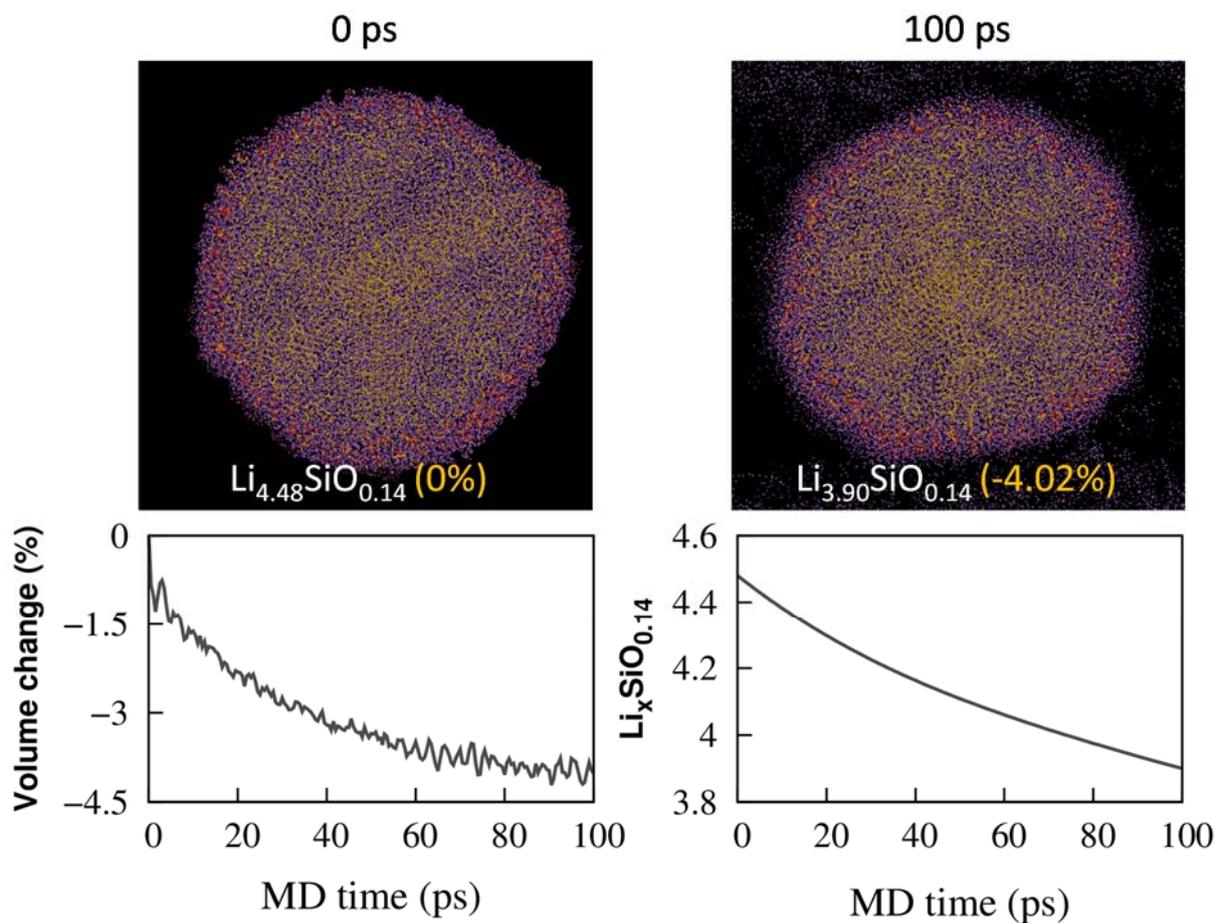


Figure S8. MD simulations on the delithiation process of the $\text{SiO}_{0.14}$ NW, where an external force $F = qE$ to each charged atom is applied. Here, the color codes are as follows: orange = Si, red = O, and pink = Li.

References

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