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Lithiation of silica through partial reduction

Chunmei Ban,1,a) Branden B. Kappes,2,a) Qiang Xu,1 Chaiwat Engtrakul,1 Cristian V. Ciobanu,2 Anne C. Dillon,1 and Yufeng Zhao1,b)
1National Renewable Energy Laboratory Golden, Colorado 80401, USA
2Department of Mechanical Engineering and Materials Science Program Colorado School of Mines, Golden, Colorado 80401, USA

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We demonstrate the reversible lithiation of SiO2 up to 2/3 Li per Si, and propose a mechanism for it based on molecular dynamics and density functional theory simulations. Our calculations show that neither interstitial Li (no reduction), nor the formation of Li2O clusters and Si–Si bonds (full reduction) are energetically favorable. Rather, two Li effectively break a Si–O bond and become stabilized by oxygen, thus partially reducing the SiO2 anode: this leads to increased anode capacity when the reduction occurs at the Si/SiO2 interface. The resulting Li$_x$SiO$_2$ ($x < 2/3$) compounds have band-gaps in the range of 2.0–3.4 eV.

Since the discovery of tin oxide as a potentially promising anode materials for Li-ion batteries,1 tremendous research effort has been devoted to the development and commercialization of anode materials based on the oxides of tin and silicon.2–12 Pure silicon especially has been pursued as a high-capacity anode material.13–15 However, widespread manufacturing and commercialization of these anode materials are still hindered by poor cyclability due to the drastic volume changes during charge-discharge processes. At the same time, the occasional observation of SiO2 as a potential anode material16–18 for reversible lithiation/delithiation is important and surprising as a fundamental scientific problem. It is well known that SiO2 is a wide band-gap material with a very high conduction band minimum (CBM),19–22 which means that SiO2 is an extremely poor electron acceptor. In addition, the rigid and strong Si–O bonds in SiO2 are consistent with its chemical inactiveness. On the other hand, the reducing nature of Li, with a much lower electronegativity than Si, thermodynamically favors the lithiation of SiO2 if the barrier to break the Si–O bonds can be overcome at reasonable temperatures.

In this study, we focus on identifying the low-energy Li defect structures and the lithiation mechanism in SiO/SiO2 powder mixtures. We demonstrate experimentally a surprising increase in Li-ion capacity of SiO1.83 that occurs over ~200 charge-discharge cycles. Using density functional theory (DFT) and molecular dynamics (MD) simulations, we have studied the Li defects in silica and will show that neither interstitial Li, nor the formation of Li2O clusters and Si–Si bonds (i.e., full reduction) are energetically favorable. Instead, two Li effectively break a Si–O bond and become stabilized by oxygen, thus only partially reducing the SiO2 anode. We also propose a mechanism of lithiation in which partial reduction at the Si/SiO2 interface enlarges the Si side of the interface; since the Li capacity of Si is significantly greater than that of SiO2, this mechanism provides an explanation for the increased anode capacity observed in our experiments.

SiO$_x$ was synthesized from tetraethoxysilane (TEOS) as the silicon source, polyvinylpyrrolidone (PVP) as a dispersant, and ethanol as a solvent. The precursor solution was solvothermally treated at 150 °C for 24 h, followed by a rinse in ethanol, and finally, dried in air. A binder-free fabrication method23 was used to make the electrode for a 2032 coin-type cell from the as-prepared SiO$_x$. A Bio-Logic VMP3 was used to cycle the cell between 0.005 and 3 V (vs. Li/Li$^+$) at 100 mA/g. Figure 1 shows an unexpected increase in the Li-ion capacity of the SiO1.83 anode material with the number of charge-discharge cycles. This contravenes conventional wisdom for two reasons. First, SiO2 is a well-known wide band-gap insulator, and therefore, a poor electron acceptor. Second, recent nuclear magnetic resonance (NMR)24 and x-ray photoelectron spectroscopy (XPS)17 experiments indicate that the reaction with Li transforms SiO2 irreversibly into Li2O and Li$_4$SiO$_4$. On the other hand, it is indeed promising to use SiO2 as an anode material because this material is stable, light-weight, cheap, and environmentally benign.

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a)C. Ban and B. B. Kappes contributed equally to this work.
b)Author to whom correspondence should be addressed. Electronic mail: Yufeng.Zhao@nrel.gov.

Fig. 1. Measured specific capacity as a function of the number of charge/discharge cycles for SiO1.83.
To uncover the mechanism behind this experimental result, we have performed four types of calculations: (a) bulk structures of Li metal, diamond Si, and α-quartz (SiO$_2$) as reference calculations; (b) point defects that form in α-quartz after incorporating Li atoms at a 1/8 Li-to-Si ratio to probe the initial stages of Li reaction with SiO$_2$; (c) crystal structures of partially reduced SiO$_2$ at higher Li-to-Si ratio, ranging from 1/4 to 2/3, which are representative of the charging process; and (d) structural optimizations of lithium ion insertion using molecular dynamics simulations.

For the first three types of calculations, we have used the DFT method as implemented in the VASP package; for the fourth type of simulations, we have used MD as implemented in the LAMMPS package. The DFT calculations have been carried out in the local density approximation (LDA), with projector-augmented wave pseudopotentials and the Ceperley-Adler exchange-correlation functional. Super-cells of 2 x 2 x 2 conventional α-quartz units were used, with a total of 72 atoms; to these, we have added up to 16 Li atoms spanning a range of the Li-to-Si ratios from 0 to 2/3. The plane-wave cutoff was 400 eV, the Brillouin zone was sampled with a 3 x 3 x 3 Monkhorst-Pack grid, and the structures were relaxed until the residual force on any atom became smaller than 0.01 eV/A. To explore a wider range of low-energy configurations, we have also performed MD simulations using the reactive force field (ReaxFF) parameterized for Li–Al silicates. A low-temperature annealing schedule was carried out, in which the system was equilibrated at 50 K for 150 ps, and then cooled to 0.01 K over 100 ps.

We have performed DFT modeling of three types of point defects by incorporating two Li atoms in the 2 x 2 x 2 supercell of α-quartz, corresponding to a 1/8 Li-to-Si ratio. The first type of defect is the direct intercalation of Li atoms into the interstitial sites in the bulk SiO$_2$. With a formation energy of 0.87 eV/Li (computed with respect to the Li metal and the perfect SiO$_2$ crystal), the intercalation of free Li interstitials in α-quartz is energetically unfavorable. In the second type of defect that we considered, two Li atoms attack the oxygen atom shared by two SiO$_4$ tetrahedra [refer to Fig. 2(a)] and form a local Li$_2$O cluster and a Si–Si bond [Fig. 2(b)]. This represents the full reduction of silica by two Li atoms, but also has a high (positive) formation energy, 0.28 eV/Li. The third type of defect shows the attack of a Si–O bond by two Li atoms [Fig. 3(a)], resulting in the displacement of the Si atom outside of its original SiO$_4$ tetrahedron. Both atoms from the attacked Si–O bond become 3-fold coordinated, Si(III) and O(III) [Fig. 3(a)]. As shown in Fig. 3(b), the dangling bond of the Si(III) atom is saturated through electronic charge transfer from a Li atom to the Si(III) atom. This defect represents the partial reduction of silica, and turns out to be thermodynamically favorable, i.e., it has a negative formation energy, ~0.25 eV/Li.

Next, we focus on analyzing the electronic structure of a few hypothetical Li$_x$SiO$_{2-x}$ crystal structures that are derived through the partial reduction of SiO$_2$, with 1/4 ≤ x ≤ 2/3. For these structures, the band-gaps decrease significantly with respect to the pure α-quartz value, ranging between 2.0 and 3.4 eV, depending on the structure. The structure with the lowest formation energy that we have found [−0.68 eV/Li, refer to Fig. 4(a)] corresponds to x = 2/3 and has a band-gap of 2.4 eV. In this structure, 1/3 of all Si atoms are partially reduced through the mechanism shown in Fig. 3(a). The dangling bonds of Si(III) atoms are saturated by lone-electron pairs from the Li atoms, as suggested by the partial electronic charge density near the Fermi level [Fig. 4(b)]. The site-projected density of states [Fig. 4(c)] shows significant overlap between the states associated with the two Li atoms and those of the Si(III) and O(III) atoms, both below and above the band-gap; this is consistent with the partial charge densities showing saturation of Si(III) dangling bonds [Fig. 4(b)].

Several configurations of Li in SiO$_2$ have been predicted heuristically and their structures optimized using DFT; of these, the structure of Fig. 3(a) was found to be the most stable (lowest energy). To verify this, we turn to the cooperative use of molecular statics (MS), MD, and DFT. MS calculations based on the ReaxFF formalism and DFT show remarkable agreement (≤ 3 meV/atom) between the relative energies of the unstable interstitial lithium and the partially reduced Li$_{1/3}$SiO$_2$ of Fig. 3(a), validating the cooperative use of the DFT and ReaxFF formalisms. A lithium ion placed at a site known from DFT to be at a local energy minimum, but far from a lowest-energy configuration, is used as the starting point in a more deterministic approach to finding the final, low-energy structure. With a Li-ion placed at an interstitial site, a low temperature, MD anneal and subsequent DFT relaxation recovers the same structure as that seen in

![FIG. 2. Local reduction of an O atom (red) by two Li atoms (green). (a) The two Li atoms react with a nearby O to form a local Li$_2$O cluster. The two Si atoms (yellow), originally bound to the O atom, now form a Si–Si bond. (b) Partial charge density near the Fermi level shows the electronic charge of a Si–Si bond.](image-url)
Fig. 3. This methodology reveals the benefit of exploring the configurational space accessible through atomic-level simulations coupled with the accuracy of DFT calculations. As a bond order potential, the reactive force field follows empirically established “bonding rules” throughout the MD simulations. Using a low temperature MD annealing schedule, this potential correctly predicts the formation of both stable (Li₄SiO₄) and transitional (Li₂O) type of defects, and gives insight into the pathway of their formation. These pathways reveal that the partial reduction of Si forms a Li–O bond and a three-fold coordinated Si displaced outside of the original (unreacted) SiO₄ tetrahedron [refer to Fig. 3(a)]. Using DFT, we have found that the removal of the Li (e.g., during discharge) leaves a zero-barrier path for the Si(III) atom to form the previously-broken Si–O bond and recover the ideal α-quartz structure.

So far, we have discussed lithiation in ideal α-quartz. Below, we propose a mechanism for lithium insertion and removal in random mixtures of Si and SiO₂ that form SiOₓ, where y < 2. The recombination of the first Li ion and an electron (first Li⁺/e⁻ pair) in the anode leads to the partial reduction of an SiO₂ bond and the formation of a three-fold coordinated silicon atom with a single unpaired electron [Fig. 3(a)]. The Si(III) atom is highly reactive and will readily accept another electron upon recombination with the second Li⁺/e⁻ pair, leaving the Li⁺ stabilized by hydrogen bonding to the four oxygen atoms neighboring the interstitial site. The resulting structure is very similar to Li₄SiO₄, which is consistent with recent NMR measurements.

Subsequent removal of lithium from LiₓSiO₂ fully recovers the bulk quartz structure (as discussed above, there is zero barrier for the Si(III) to reform the Si–O bond upon delithiation), except at the Si/SiO₂ interfaces (Fig. 5). As show in Fig. 5, rather than becoming three-fold coordinated, as it would in quartz, the Si atom that is displaced outside its original SiO₄ tetrahedron enlarges the adjacent Si particle, since the Si side of the Si/SiO₂ interface gains that displaced silicon atom. Insertion of the second Li creates a Li₄SiO₄-like environment (see Fig. 5), which acts as a lithium trap and reduces the reversibility of lithium insertion. The
observed increase in global capacity upon further cycling [Fig. 1] is explained by the growth of the Si phase: the Si volume gained, capable of holding ~4 Li per Si, has a substantially larger capacity than the SiO2 volume lost. While this process is naturally limited by the constraint that the Si:O ratio remains constant, we have not considered structures that may form when this limitation prevents further Li4SiO4-mediated Si growth.

In conclusion, we have shown that the Li storage capacity of a SiO1.83 anode increases (after some initial parasitic losses) over 200 charge/discharge cycles. Combined DFT and MD simulations reveal that partial reduction of SiO leads to the formation of Li-containing defects and an ~4 eV decrease in the band-gap. While earlier interpretations attribute the Li2SiO4 that persists through charge/discharge cycling to the irreversible reduction of Si in SiO2, we find that the insertion of Li forms Li4SiO4-like defects that are reversible within bulk SiO2, but irreversible at Si/SiO2 interfaces. When formed at an interface, these structures increase the volume fractions of Si and Li4SiO4, and increase the lithium storage capacity, which explains both our observed cycling behavior and the Li–Si–O phases identified both here and elsewhere.17,24

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