Lithium-assisted plastic deformation of silicon electrodes in lithium-ion batteries

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Energy storage is a crucial aspect of integrating renewable energy sources into power grids, making the development of efficient high-energy-density batteries an important technological challenge.[1] For the applications sensitive to weight and size, such as portable electronics and electrical cars, lithium-ion batteries are the industry standard.[2] Battery-powered cars, plugged into an increasingly green grid, would secure energy independence while maintaining individual mobility. A system of distributed batteries and a smart electric grid can accommodate the unpredictable nature of renewable energy sources, allowing energy to be stored during times of low demand, and be drawn back to meet peak demand.[3] Worldwide companies are racing to develop next generation lithium-ion batteries for electric cars.

At the heart of a lithium-ion battery is a process coupling mechanics and chemistry. Each electrode consists of host atoms and guest atoms (lithium atoms). The host atoms form a framework, into which lithium atoms are inserted. For instance, during discharge, lithium atoms are dissociated into lithium ions and electrons at the interface between the anode and electrolyte. Lithium ions pass through the electrolyte, electrons pass through the external wire. Upon reaching the cathode, lithium ions and electrons recombine to form neutral lithium atoms. Lithium atoms diffuse into the cathode, and react with the cathode. The diffusion and reaction cause mechanical deformation in the electrodes. The deformation is often constrained by various conditions, such as crystalline grains of different orientations, a transient distribution of lithium, mismatch between active and inactive materials, etc. Under such constraints, insertion/extraction of lithium induces in an electrode a field of stress. In practice, the stress causes the electrodes to fracture or to change its morphology. Loss of structural integrity typically reduces the electric conductance, leading to a steady fading of capacity during charge-discharge cycles.[4]

Mechanical stability has become one of the key criteria for the selection of materials for commercial batteries. The electrodes have to maintain its mechanical integrity and chemical properties over a long cycle lifetime. Lithiation-induced fracture not only limits the lifetime of existing commercial batteries, but also acts as a bottleneck for developing high-capacity lithium-ion batteries. For example, the extremely high capacity of silicon, which can host up to 4.4 lithium atoms per silicon atom, has motivated intense research, but the large amount of absorbed lithium results in volume swelling of ~400%, which pulverizes the electrodes. The mechanical failure largely prevents silicon serving as a viable electrode for commercial batteries.

One way to circumvent the mechanical damage is the use of plasticity of lithiated silicon. Lithiation-induced large deformation of silicon electrodes can be accommodated by plastic flow. This feature makes it possible to maintain good capacity over many cycles for silicon anodes with small size, such as thin film, nanowires, and porous structures. The coupled lithiation reaction and elastic-plastic deformation have stimulated intensive studies by using experimental measurements, continuum theories, and atomistic simulations.

In this paper, we employ first-principles computational methods to explore the atomic-scale mechanisms of lithiation and the relation to mechanical behaviour. Here we present first-principles studies of the atomistic mechanism of large plastic deformation in lithiated crystalline (c-Si) and amorphous silicon (a-Si). We find that the local atomic structure in a silicon network is altered by lithium insertion, with Si atoms breaking a bond and reforming a new bond with different neighbors. In this process, the lithiation-induced weakening of bonds between Si atoms and the high mobility of Li in the network play key roles. The continuous breaking and reforming of Si-Si bonds accommodates the large plastic deformation of lithiated silicon.

We first investigate the mechanisms through which the presence of Li atoms in the crystalline silicon lattice can lead to the breaking of Si-Si bonds. We begin this investigation by determining the stable positions of a single lithium atom in c-Si. A single Li atom was placed into the supercell at different nonequivalent sites, including the tetrahedral site (Td), the hexagonal site (Hx), the center of a Si-Si bond (Bc), the center of the distance between next nearest silicon neighbors (Cn), and a substitutional site. We find that lithium insertion into the tetrahedral (Td) or hexagonal (Hx) positions results in an energetically favorable structure. We note that substitution of Si by Li is energetically costly, and that the bond center is an unstable position for a Li atom, in contrast to the case of hydrogen atoms in a silicon lattice, for which the most stable configuration is the bond-center site. The binding energy of a single Li at a Td position is lower in magnitude than the energy of a Si-Si covalent bond of 2.72 eV, which indicates a relatively weak interaction between the Li and Si atoms. The energy difference of 0.55 eV for a lithium atom at the Td and Hx sites is close to the diffusion energy barrier, given the known Td–Hx–Td diffusion pathway for Li in the c-Si lattice. In order to elucidate the bond breaking mechanism induced by lithiation, we plot in Fig. 1 the total valence electron charge density distribution on a (110) plane for the stable configuration with 4 Li atoms. Close inspection of this charge density plot shows that the bond between Si atoms A and B is indeed broken, and a weaker bond of mixed covalent-ionic character is formed between the Si atom at position B and the Li atom at position 1. This is consistent with the expectation mentioned above that the Li atoms can saturate the dangling bonds of the Si atoms upon bond

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breaking; the Si-Li bond is expected to be asymmetric and polar, due to the large difference in electronegativity between the two elements (0.98 for Li vs. 1.90 for Si).

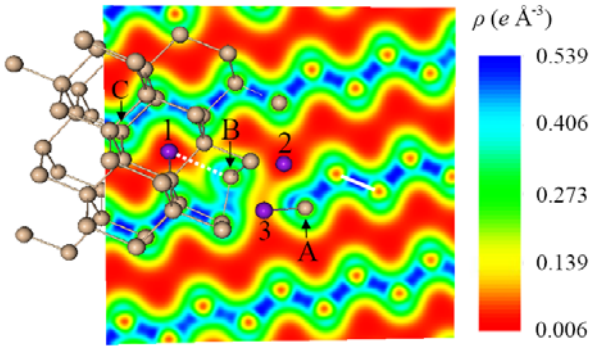

Fig. 1. Valence electron charge density distribution on a (110) plane in the lowest-energy configuration of c-Si with 4 Li atoms.

In an attempt to capture the essential atomistic aspects of the plastic deformation mechanisms we further performed a set of simulations that model a uniaxial tension experiment on lithiated silicon at various Li concentrations. In the simulation, we prescribe a given stress level along the x-direction of the structure, and measure the nominal strain after full relaxation. The results indicate that a brittle-to-ductile transition occurs as the lithium concentration increases, with very different behavior for $f = 0$ and $f = 0.125$ vs. $f = 0.25$ and $f = 0.50$, where f represents the concentration of lithium. The corresponding strength decreases as well with increasing Li concentration. In the pure silicon structure, loading leads to nonlinear elastic behavior and the unloading path follows the loading path exactly; there is no permanent deformation after unloading. In the case of lithium concentration $f = 0.125$, a small permanent strain is observed after unloading. As the lithium concentration increases to $f = 0.25$ and $f = 0.50$, the stress-strain curves show substantial plastic deformation. The network can be stretched by 33.5% and 40.5%, respectively, without fracture. After unloading, large permanent deformation remains in both cases.

In conclusion, we have studied the effects of Li in both crystalline and amorphous Si, using first-principles calculations based on Density Functional Theory. Our main findings are: first, Td interstitial positions are the lowest-energy sites for Li insertion into c-Si, and that when four Li atoms surround a single Si-Si bond the covalent bond readily breaks and the two Si dangling bonds are essentially saturated by the formation of weak bonds of mixed ionic-covalent character with the nearby Li atoms. Also, in a-Si with sufficiently high Li concentration (roughly $f = 0.125$ or higher) the structure undergoes a brittle-to-ductile transition with significantly lower Young's modulus, and plastic deformation becomes relatively easy. The essence of these results is that the chemical interactions of lithiation give rise to pronounced effects on the mechanical behavior of silicon structures. In particular, as the stresses induced by lithiation are limited by the yield strength, the fracture failure of the silicon electrode can be largely remediated by taking advantage of the plasticity of lithiated silicon. At the microscopic scale, we have identified and described by specific examples the atomistic mechanism responsible for plastic deformation, which consists of continuous Si-Si bond breaking and reformation in the presence of Li; we suggest that this process may also be responsible for the steady flow at the macroscopic scale.

References

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