Nano-Micro Conference

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Investigating structure and stress evolution in Si anode using in situ high pressure technique and Raman microscopy

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Received: 22 May 2017, Accepted: 18 June 2017, Published Online: 15 October 2017

Citation Information: Zhidan Zeng, Nano-Micro Conference, 2017, 1, 01028 doi: 10.11605/cp.nmc2017.01028

Abstract

Silicon is widely regarded as one of the most promising anode materials for next-generation lithium-ion batteries, making Li-Si an important energy storage system. During Li insertion into Si, stress of gigapascal level is introduced accompanied by a volume expansion up to 280%, alters properties of materials, and leads to mechanical failure of Si anodes.

$Li_{15}Si_4$ (alpha- $Li_{15}Si_4$, space group: I-43d), the only crystalline phase that forms during lithiation of the Si anode in lithium-ion batteries, was found to undergo a structural transition to a new phase (beta- $Li_{15}Si_4$) at approximately 7 GPa (see Figure 1). Ab initio evolutionary metadynamics calculations suggest beta-$Li_{15}Si_4$ has an orthorhombic structure with an Fdd2 space group. This new beta- $Li_{15}Si_4$ has substantially larger elastic moduli compared with alpha- $Li_{15}Si_4$, and has good electrical conductivity. As a result, beta- $Li_{15}Si_4$ has superior resistance to deformation and fracture under stress. The theoretical volume expansion of Si would decrease 25% if it transformed to beta-$Li_{15}Si_4$, instead of alpha- $Li_{15}Si_4$, during lithiation. In addition, the fact that beta- $Li_{15}Si_4$ can be recovered back to ambient pressure, provides opportunities to further investigate its properties and potential applications [1].

Nanostructured Si are important materials to address mechanical stress issues in batteries although their stress were only calculated and no experimental data are available. Using in situ Raman microscopy to monitor the shift of the first-order Raman peak of Si, we were able to measure for the first time the lithiation-induced stress in Si nanoparticles. The shift of Raman peak of Si under hydrostatic stress was calibrated via an in situ high pressure Raman experiment. We observed a transition in the stress in Si core of nanoparticles during lithiation, from tensile to compressive (see Figure 2). At the beginning of lithiation, the reduction of the native oxide surface layer of the Si particle results in a tensile stress of approximately 0.2 GPa in Si. During the formation of amorphous Li_xSi in the outer layer of the nanoparticles, an increasing compressive stress up to 0.3 GPa is introduced to the Si core. This evolving stress explains the cracks that developed in the amorphous Li_xSi layer during lithiation of the Si nanoparticles, and is also consistent with modeling results. These results improve our understanding of lithiation-induced stress in nanostructured Si anodes, and provide valuable information for their theoretical study and future design [2].

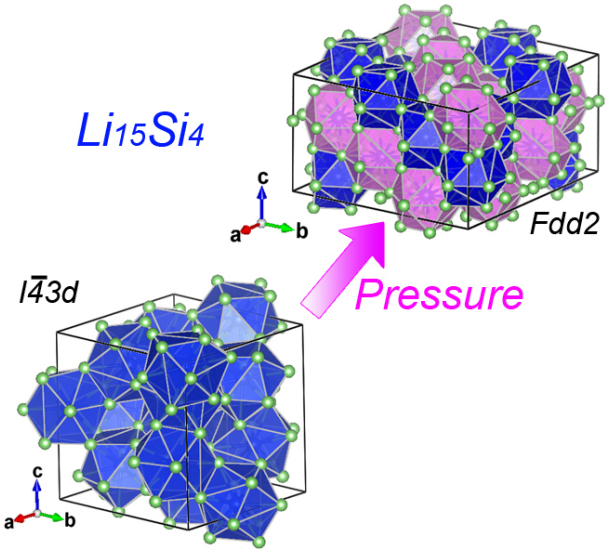

***Figure 1**. The atomic structure of alpha-$Li_{15}Si_4$ (lower left) and beta-$Li_{15}Si_4$ (upper right). Each silicon atom is surrounded by lithium atoms (green spheres) with the coordination number of 12 (shown in blue polyhedra) or 13 (shown in pink polyhedra).*

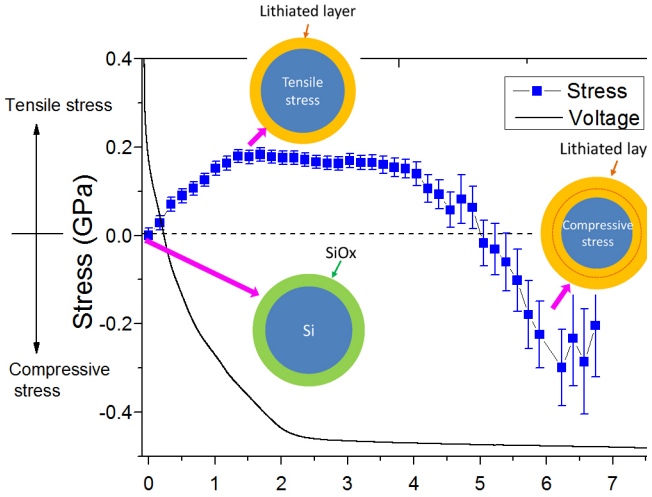

***Figure 2**. The stress in Si nanoparticles (left y-axis) and the potential of the half cell versus Li^+/Li (right y-axis) as a function of lithiation duration.*

doi: 10.11605/cp.nmc2017.01028

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