In situ X-ray Reflectivity Study on the Atomic Scale Electrochemical Lithiation and Delithiation Process of Silicon

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Abstract:

Silicon is a promising anode material for lithium-ion batteries due to its excellent specific capacity (3579 mAh/g). However, the large capacity of Si is accompanied by a large volume expansion (~300%) which irreversibly destroys the Si crystallinity, resulting in loss of mechanical/electrical contact and capacity fading. In addition, capacity is lost due to the consumption of Li in the uncontrolled solid electrolyte interphase (SEI) growth. These issues render the main reasons limiting large scale commercialization of high capacity Si-based batteries.

Our study aims at a better understanding of the (de)lithiation mechanism of silicon (Si) electrodes and the concomitant SEI growth. Here, we used *in situ* synchrotron X-ray reflectivity (XRR) to investigate the first two (de)lithiation cycles of Si. Our model battery system consists of a native oxide terminated single crystalline Si (100) wafer as working electrode, Li metal as counter and reference electrode, and 1 M $LiPF_6$ in 1:1 EC:DMC electrolyte.

Our results show that the lithiation of c-Si is a layer-by-layer, reaction limited two-phase process;[1] the delithiation of Li_xSi (resulting in amorphous Si) and the lithiation of a-Si are reaction-limited single-phase processes.[2] Furthermore, the thickness-density product of the inorganic SEI layer is observed to increase during lithiation and decrease during delithiation, resembling a "breathing" behavior, and the inorganic SEI layer thickness is determined to vary between 40 and 70 Å. Additionally, a low-electron-density "Li-dip" layer is found between SEI and Li_xSi during the delithiation process, suggesting kinetically limited ion transport within the SEI during discharge, which we speculate to be one of the origins of battery's internal resistance.

Our findings provide a detailed mechanistic model of the first two lithiation processes, and sheds light on fundamental difference of Li ion reaction with crystalline and amorphous materials. The results on SEI also motivate further experimental and theoretical studies of the Li^+ diffusion properties in the SEI.

References:

1. C. Cao, H. G. Steinrück, B. Shyam, K. H. Stone, M. F. Toney, *In Situ Study of Silicon Electrode Lithiation with X-ray Reflectivity*. Nano Lett, 2016. **16**(12): p. 7394-7401.
2. C. Cao, H. G. Steinrück, B. Shyam, M. F. Toney, *The Atomic Scale Electrochemical Lithiation and Delithiation Process of Silicon.* Submitted to Advanced Materials Interfaces.