

Ultrafast Lithiation of Si Nanowires Revealed with In-Situ Transmission Electron Microscopy

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Silicon is one of the most promising candidates for high-energy anodes in a lithium ion battery (LIB), but its rate performance is far below satisfaction due to the poor conductivity. In this talk, I will present our in-situ observation of the record-high charging rate, ~ 37600 A/g, or 10500 C with $1C = 3579$ mA/g, of the Si nanowire doped with phosphorus and coated with carbon [1]. An open nano-LIB consisting of an individual Si nanowire as the anode, bulk LiCoO_2 as the cathode, and an ionic liquid (LiTFSI) electrolyte was mounted onto a transmission electron microscopy – scanning probe microscopy (TEM-SPM) platform to enable real-time recording the microstructure evolution during operation [2]. First, we compared the effects of doping and carbon coating on the Si lithiation rates with respect to the intrinsic Si nanowires (Fig. 1). The carbon coating and phosphorus doping each resulted in a two to three orders of magnitude increase in electrical conductivity of the nanowires that, in turn, resulted in a one order of magnitude increase in charging rate. Ultrafast lithiation of Si nanowires was only achieved by combining both phosphorus doping and carbon coating, i.e., charging a Si nanowire in one second in a flooded electrolyte. This demonstrated an effective way to enhance the rate performance of Si-based anodes. Second, electrochemical solid-state amorphization (ESA) and inverse ESA were directly observed and characterized as a two-step phase transformation process during lithiation (Fig. 2): crystalline silicon (Si) transforming to amorphous lithium-silicon (Li_xSi) which transforms to crystalline $\text{Li}_{15}\text{Si}_4$ (capacity 3579 mAh/g). This confirms some earlier reports of $\text{Li}_{15}\text{Si}_4$ as the fully lithiated state in a LIB operated at room temperature [3], not the widely believed $\text{Li}_{22}\text{Si}_5$. Third, the integrated shape of the Si nanowires was maintained even at the highest charging rate, without pulverization at the largest volume expansion in the first charging process. This fundamental study shows great promise in engineering Si as the high-energy and high-power anode for advanced LIBs used in electric vehicles and high power tools.

References:

1. X. H. Liu *et al.*, submitted (2011).
2. J. Y. Huang *et al.*, *Science* 330 (2010) 1515.
3. M. N. Obrovac *et al.*, *Electrochemical and Solid State Letters* 7 (2004) A93.

This work was performed, in part, at the Center for Integrated Nanotechnologies, a U.S. Department of Energy, Office of Basic Energy Sciences user facility. Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the U. S. Department of Energy under Contract No. DE-AC04-94AL85000.

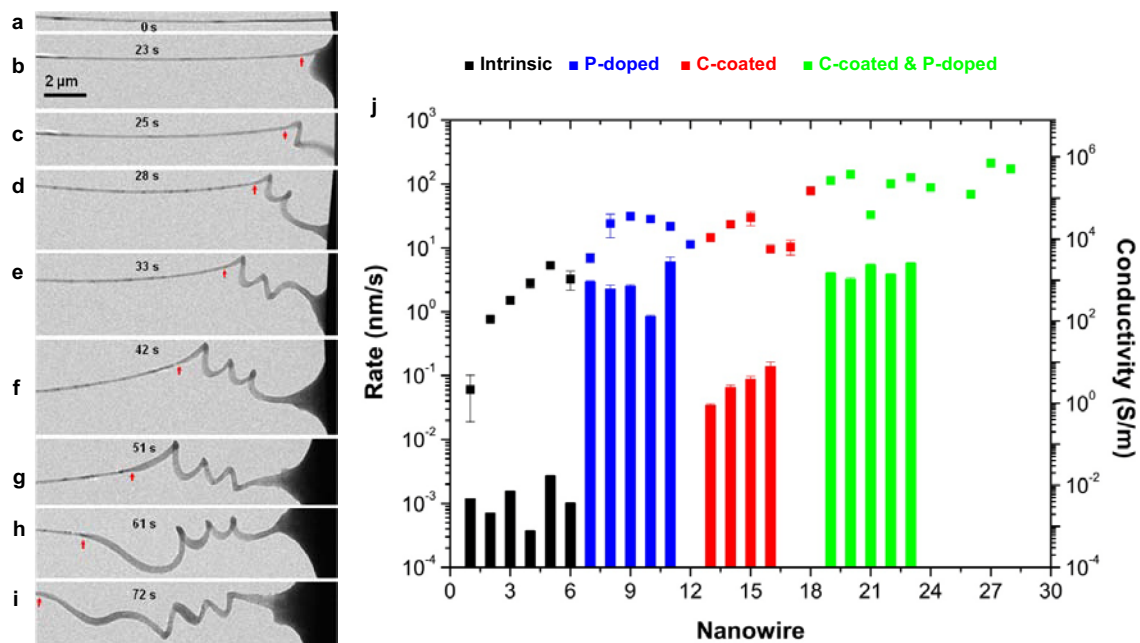


Fig. 1 Ultrafast lithiation of Si nanowires by carbon coating and phosphorus doping. (a-i) Time-elapse image series showing the microstructure evolution of a carbon-coated and phosphorus-doped Si nanowire. (j) Comparison of the charging rates (solid squares) and the electronic conductivities (columns) of four types of Si nanowires that are intrinsic (black), phosphorus doped (blue), carbon coated (red), and carbon-coated plus phosphorus-doped (green).

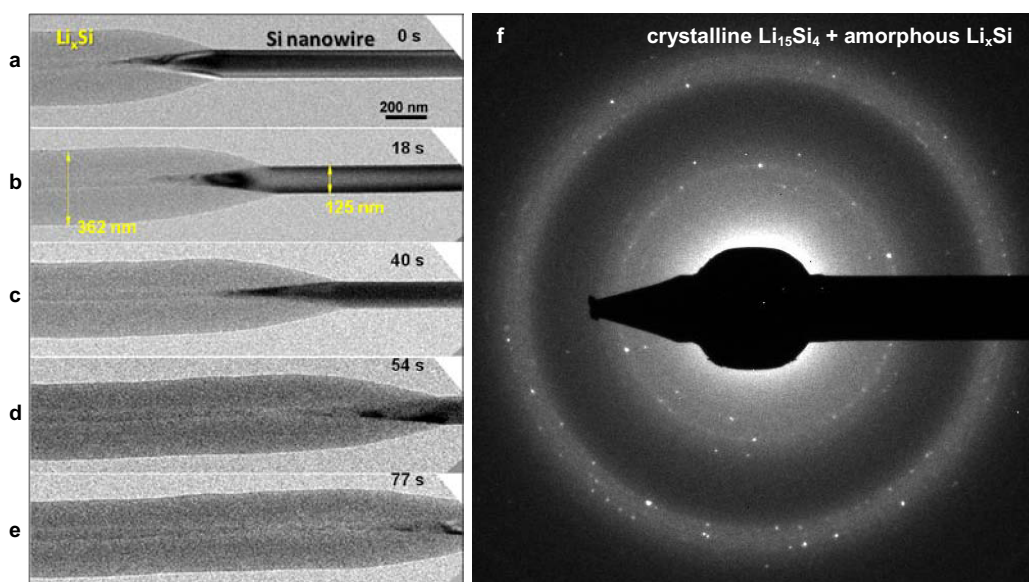


Fig. 2 Electrochemical solid-state amorphization (ESA) process during lithiation of a Si nanowire. (a-e) Closer view of the amorphization process and volume expansion during charging the Si nanowire. (f) Electron diffraction pattern showing coexistence of the crystalline Li₁₅Si₄ and the amorphous Li_xSi phases, indicating the former crystallizing out of the latter.