Conducting Quantitative Electrochemistry on a TEM to Study Rate Dependencies in the Reversible Lithiation of Silicon Nanowires

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Nanowires, rods, and struts are a common motif in nanoscale architectures proposed for high energy and power density electrodes. The structural and interfacial stability of these constitutive components is expected to impact the performance and long term viability of the storage device (e.g., battery) in which the electrode is used. Nanowire anode materials, such as Si, are of interest because of their potential ability to readily accommodate volume expansion upon lithium alloy formation while retaining electronic transport when compared to their meso- to macroscopic structural forms.[1,2] The rational design of Si nanowire heterostructures capable of facilitating reversible alloying over many cycles while maintaining a maximum storage capacity requires new strategies for characterizing both structural and compositional evolution *in situ* at the single nanowire level. Transmission electron microscopy has been previously applied to study Si nanowires *in situ* under potentiostatic conditions, but without knowledge of the rate at which charge is being driven.[3,4] In this paper, we demonstrate a next level of advancement in the electrochemical TEM approach whereby microelectroanalytical measurements are made on the TEM column through galvanostatic means for which the rate of charge injection and extraction are precisely controlled to study rate dependencies of structural and compositional changes.

Quantitative chronopotentiometry is demonstrated in Figure 1, where the response of a partially immersed[3], VLS grown Si nanowire (<112> axial orientation) is shown for a series of charge/discharge cycles. The wire was charged and then discharged galvanostatically at 1.8 pA for 1200 seconds per half cycle for five full cycles (first four displayed) in an ionic liquid electrolyte (ILE, 0.5M LiTFSI in 1-butyl-1-methylpyrrolidinium TFSI). A LiFePO$_4$ (LFP) composite cathode was used as a lithium source, consequently the Si anode potential is plotted with respect to that of the phosphate. A 9.5 μm length of the wire was found reacted during post-electrochemical TEM imaging providing an equivalent charging and discharging rate of 1.4C. The native nanowire equilibrium potential (first charge cycle, first 120 s) of -2.7 V is a reasonable value when comparing the potentials of Si and LFP vs. Li (1.2 and 3.5 V, respectively). When current is first applied the potential rapidly decreases, reaches a minimum of -3.8 V at 200 s, and then increases to a steady state value of -3.3 V at times beyond 1000 s. Note that subsequent charging cycles all show a rapid rise to a steady state charging potential of -3.3 V, indicating a reproducible charging potential. The discharge curves show the expected symmetric behavior where the initial equilibrium potential is -3.3 V, application of current produces a +100 mV polarization of the Si wire, followed by a gradual increase of potential, and finally a rapid rise in potential toward the LFP value (0 V) as de-alloying is completed. In this example, we show that it is possible to generate electroanalytical measurements, specifically the endpoint for de-alloying, in a single nanostructure. A bright field image of the nanowire, removed from the electrolyte, is shown in Figure 2 along with a selected area diffraction pattern. This image was acquired perpendicular to the <110> anisotropic expansion axis for these wires[5] and shows a remnant crystalline Si core 44 nm in diameter, surrounded by a 144 nm amorphous Si shell devoid of Li. The coulombic efficiency for each cycle based on the time necessary to reach this endpoint, is plotted in Figure 2 and exhibits values ranging from 77 to 89%. We note that a low value of efficiency is not observed during the first cycle, arguing that the potential minima observed is related to constraints other than electrolyte breakdown, such as an overpotential required to modify the Si surface oxide or for nucleation of the alloy phase. This data demonstrates that it is possible to conduct electroanalytical measurements on a TEM column to facilitate structural characterization for the constitutive components of 3-D electrode architectures.

This capability is currently being used to explore the evolution of structure within Si nanowires as a function of charge injection and extraction rates. Our goal is to develop an understanding of how changes in activity of constitutive components of a 3-D electrode architecture with cycling lead to performance change and degradation. The results from several different methods of nanowire immersion, including fully immersed configurations that allow the use of volatile electrolytes, will be discussed.

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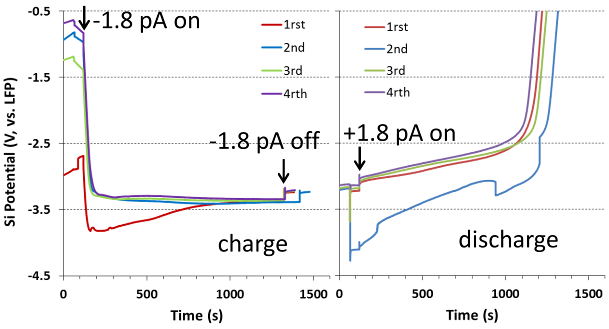

Figure 1. Charge and discharge curves for a 9.5 μm length of a 140 nm diameter Si nanowire cycled at a 1.4C rate

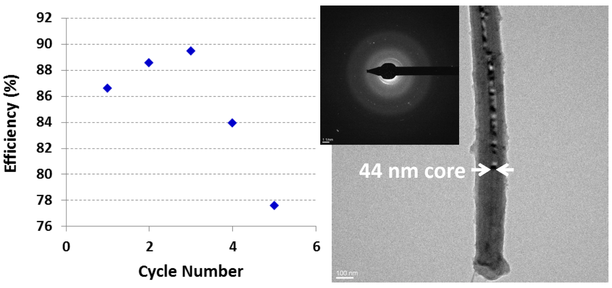

Figure 2. Coulombic efficiency as a function of cycle number calculated from the curves in Fig.1. An image of and diffraction pattern from the immersed portion of this Si nanowire cycled at 1.4C.