

## In-situ TEM Observation of Electrochemical Cycling of a Si/TiO<sub>2</sub> Composite NW

Sung Joo Kim<sup>1</sup>, Alireza Kargar<sup>2</sup>, Deli Wang<sup>2</sup>, Xiaoqing Pan<sup>1</sup>

<sup>1</sup> Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109

<sup>2</sup> Department of Electrical and Computer Engineering, University of California-San Diego, La Jolla, CA 92093

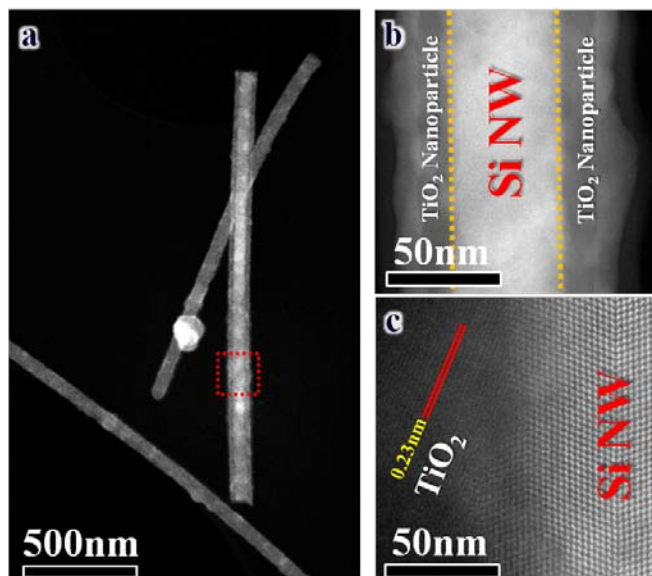
Graphite has been the most widely used Li-ion battery anode material due to its low lithiation potential and high capacity [1]. However, commercial use of graphite poses the potential problem of catastrophic battery failure due to short-circuiting via lithium electroplating. Hence, new state-of-the-art systems for anodes are under investigation, and silicon, in particular, has attracted great interest due to its high abundance in nature and extremely high specific capacity, 3340 mAh/g when fully lithiated to Li<sub>15</sub>Si<sub>4</sub>.

Nevertheless, silicon possesses a potential problem of its own, capacity retention, since the accommodation of Li causes large volumetric expansion, up to 300% [2], and irreversible phase formation. The formation of a solid-electrolyte-interface (SEI) layer is detrimental to chemical stability of a device. Furthermore, a silicon anode also suffers from extreme mechanical stress that often results in fracture and pulverization. To overcome this problem, numerous efforts have been made to modify the anode via nanoengineering, such as coating it with a material less reactive to electrolytes, thus improving mechanical stability of the device [3,4]. However, direct visualization of Li<sup>+</sup> diffusion and associated structural changes has not yet been reported in such anode systems. Here, for the first time, we examine the structural stability of a Si/TiO<sub>2</sub> core-shell nanowire (NW) anode using a transmission electron microscope (TEM) upon electrochemical Li<sup>+</sup> intercalation.

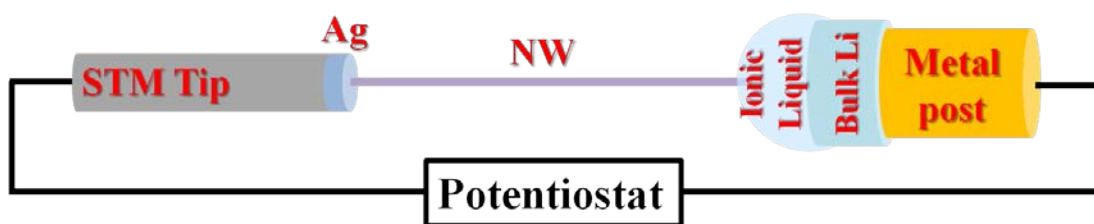
Si NWs were grown on a silicon substrate via chemical vapor deposition (CVD), followed by atomic layer deposition (ALD) of a 10 nm rutile TiO<sub>2</sub> layer, and then imaged using scanning TEM (STEM) (Fig. 1). A specimen for in-situ TEM was prepared by mechanically detaching and loading the NWs onto a tungsten STM tip. A NW-loaded tip was then assembled in a half-cell with metallic Li as a counter electrode inside the TEM (Fig. 2). An ionic liquid-based electrolyte (ILE) was used for in-situ TEM due to its low vapor pressure and stability in high vacuum conditions. During electrochemical lithiation of the NW anode at -4V, Li ions begin to migrate into the NW along the [001] direction, inducing both radial dilation and vertical elongation of the NW. However, the lithiation front usually accompanying amorphization of Si and conversion to Li<sub>x</sub>Si was not observed due to the presence of the TiO<sub>2</sub> shell, which remained relatively intact during lithiation. A rutile TiO<sub>2</sub> shell has only a single Li<sup>+</sup> diffusion channel that is oriented differently from that of Si, thus limiting the degree of Li<sup>+</sup> intercalation into the shell. The radial dilation of the Si NW was thus limited to ~150% in electro-chemical lithiation, successfully suppressing the dilation by 50%. Also, after the 2<sup>nd</sup> delithiation at 4V, successful extraction of Li ions produces 24% radial contraction and induces almost no visible damage to either Si core or TiO<sub>2</sub> shell (Fig. 3). The first two electrochemical cycles suggest that the TiO<sub>2</sub>/Si core-shell NWs are mechanically robust.

In summary, we have directly observed lithium intercalation into Si/TiO<sub>2</sub> core-shell NWs and have confirmed the mechanical stability of this composite nanostructure. This finding contributes insight to structural optimization of one of the promising Li-ion battery anodes for a high-performance battery.

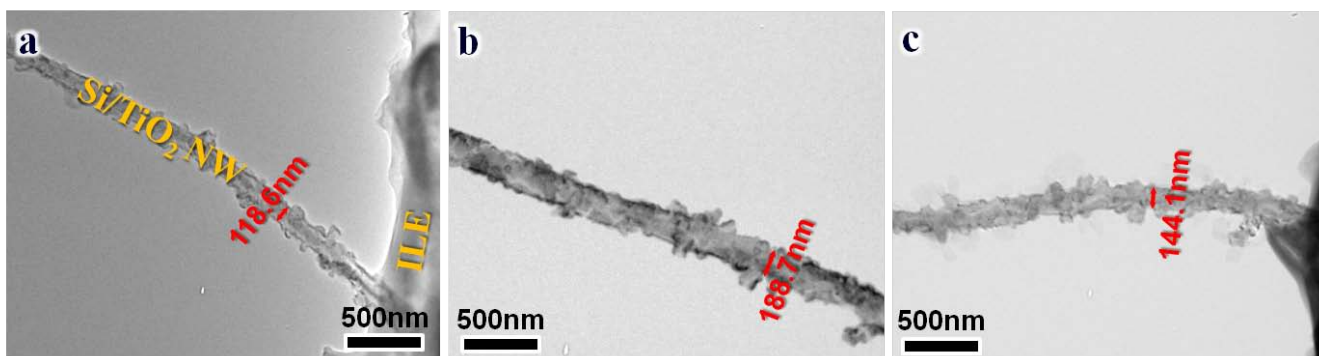
- [1] V. Etacheri *et al*, *Energy Environ. Sci.*, 4 (2011) 3243-3262.  
 [2] B. Key *et al*, *J. Am. Chem. Soc.*, 131 (2009) 9239-9249.  
 [3] Z. Y. Zeng *et al*, *Electrochem. Solid-State Lett.*, 11 (2008) A105-A107  
 [4] E. M. Lotfabad *et al*, *Phys. Chem. Chem. Phys.*, 15 (2013) 13646-13657



**Fig 1.** STEM images of a Si/TiO<sub>2</sub> core-shell NW under (a and b) low and (c) high magnification.



**Fig 2.** Schematic of in-situ set-up of Li-ion electrochemical cell inside the TEM.



**Fig 3.** Sequence of TEM images of a Si/TiO<sub>2</sub> core-shell NW at a Si-electrolyte interface during 1st and 2nd electrochemical cycles.