

## Progress toward Understanding Lithiation Mechanisms of TiO<sub>2</sub> Via In-situ TEM

X.Q. Pan<sup>1</sup>, S.J. Kim<sup>2</sup>, K. Zhang<sup>2</sup>, J. R. Jokisaari<sup>2</sup>, A. Kargar<sup>3</sup>, D. Wang<sup>3</sup>, G. W. Graham<sup>2</sup>

<sup>1</sup>Dept. of Materials Science, University of California - Irvine, Irvine, CA 92697 USA

<sup>2</sup>Dept. of Materials Science and Eng., University of Michigan, Ann Arbor, MI 48109 USA

<sup>3</sup>Dept. of Electrical & Computer Eng., University of California-San Diego, La Jolla, CA 92093 USA

Owing to eventual depletion of fossil fuels and increasing demand for renewable energy resources, lithium ion batteries (LIBs) have attracted great interest for green energy storage application in hybrid-electric vehicles (HEVs) and portable electronics. TiO<sub>2</sub> has been considered for LIB anodes due to its chemical stability, non-toxicity, and abundance. The two widely studied TiO<sub>2</sub> polymorphs are rutile and bronze, known for good capacity and cyclability, especially in nanostructured forms [1]. Despite their optimized performances, understanding of lithiation mechanisms in these polymorphs is still controversial, since most studies have been performed using bulk characterization techniques like X-ray diffraction and X-ray absorption near edge structure, which do not show local morphology. Here, we employ in-situ transmission electron microscopy (TEM) and aberration-corrected scanning TEM (STEM) to perform nano-scale structural studies of TiO<sub>2</sub> upon cycling.

We first study the lithiation mechanism of rutile TiO<sub>2</sub> in the form of a nanowire (NW), especially focusing on its structural transformation [2]. Rutile TiO<sub>2</sub> NWs were grown on Ti foil via a hydrothermal method before scraping a single NW onto a Cu rod for in-situ TEM. Our nano-scale electrochemical cells were assembled inside the TEM by connecting a TiO<sub>2</sub> electrode to a tungsten tip scraped in Li metal that serves as the counter-electrode. Li<sub>2</sub>O naturally formed on the Li metal due to air exposure acts as a solid electrolyte. After a couple of electrochemical cycles, the NW underwent irreversible phase transformation from rutile to a monoclinic phase, accompanied by a large anisotropic volumetric expansion of approximately 120% (Fig. 1a and b). At this stage, no further morphological change was found to occur, even after 20 cycles, indicating remarkable structural stability of the NW. More injection of Li ions into the NW, accomplished by sustained bias at a constant lithiation potential of xx V, however, induced bubble-like dilation and further phase transformation to another phase, with rock-salt structure (Fig. 1c), thus completing a two-step lithiation process (Fig. 1d).

Bronze TiO<sub>2</sub> (TiO<sub>2</sub>-B), known to have the highest charge capacity among all TiO<sub>2</sub> polymorphs, was synthesized as a thin film oriented along [001] by pulsed laser deposition [3]. To better explore the atomic-scale phenomena induced by Li ion insertion, both in-situ TEM and ex-situ high-resolution STEM were employed. Upon applying a bias through the *c*-plane of the film, Li ions immediately wetted the film surface before they found the most favorable spots for insertion into the TiO<sub>2</sub>-B lattice (Fig. 2a and b). During this *c*-axis lithiation, Li ions first diffuse into energetically favorable interstitial sites of the top TiO<sub>2</sub>-B layer before inducing a low-energy shear that allows continued lithiation deeper into the lattice (Fig. 2c). Interestingly, a high concentration of Li ions at the top surface also interacts with nearby TiO<sub>2</sub>-B layers to form another crystalline phase.

In conclusion, we have directly probed the lithiation mechanism of two well-known TiO<sub>2</sub> polymorphs, rutile and bronze. We expect our findings to contribute to the further understanding of Li ion insertion chemistry of these promising anode materials.

**References:**

- [1] Arico, A. S. *et al.*, *Nature* **4** (2005) 366-377; Deng, D. *et al.*, *Energy Environ. Sci.* **2** (2009) 818-837  
 [2] Kim, S. J. *et al.*, *Chem. Commun.* **50** (2014) 9932  
 [3] Zhang, K. *et al.*, *Adv. Mater.* **26** (2014) 7365-7370  
 [4] This work was supported by the Center for Solar and Thermal Energy Conversion, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0000957.

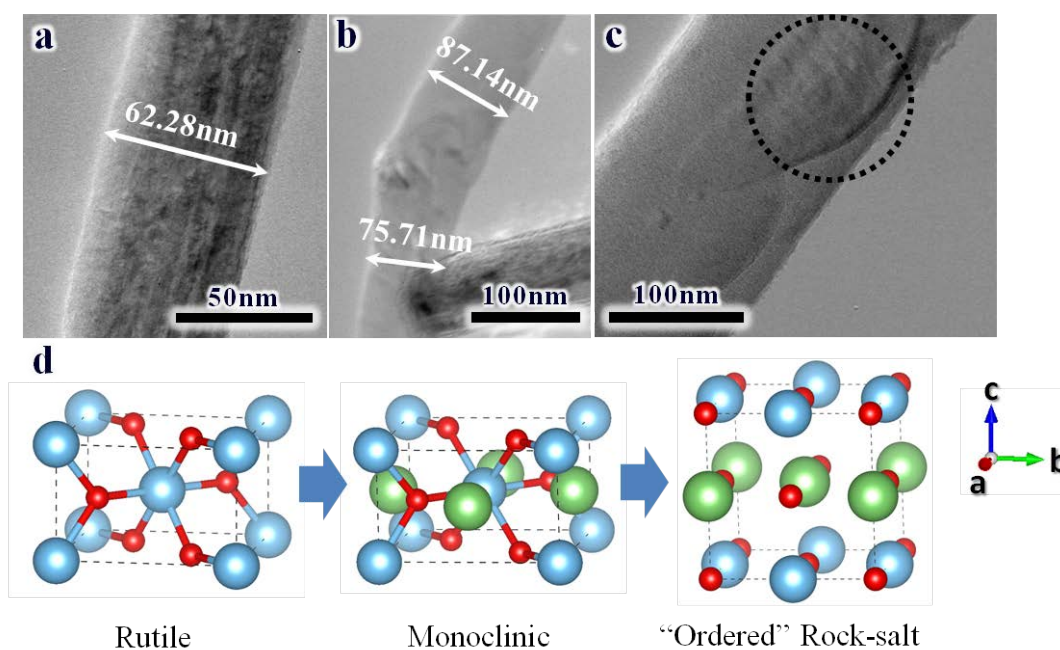


Fig. 1. (a, b, c) Sequential TEM images showing the two-step structural transformation of a rutile TiO<sub>2</sub> NW at different stages of lithiation and (d) schematics illustrating phase transformation corresponding to these stages.

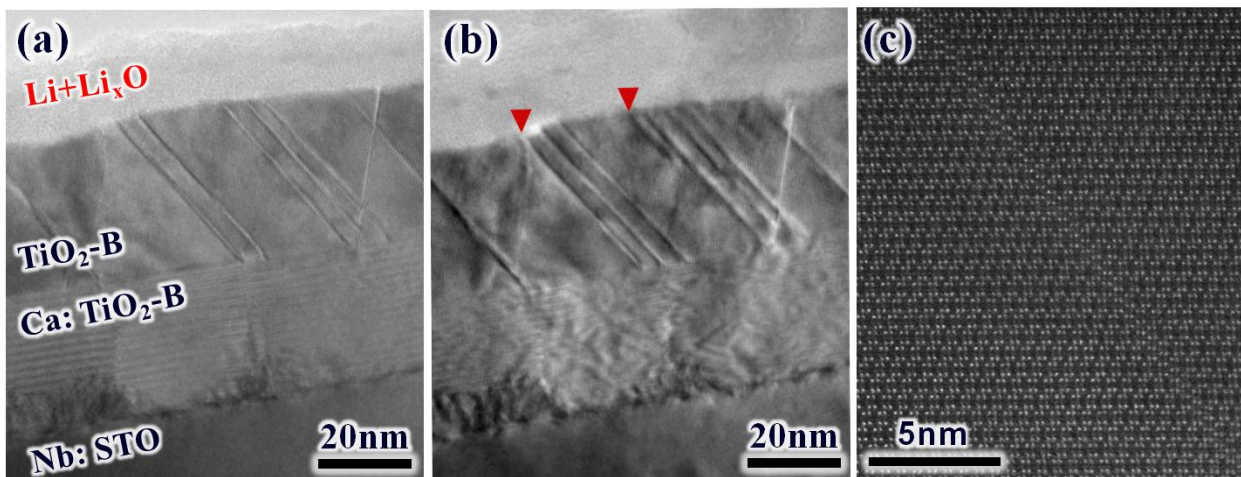


Fig. 2. TEM micrographs of a TiO<sub>2</sub>-B thin film at (a) the earlier and (b) the later stage of lithiation. (c) High-resolution STEM showing a half unit-cell shear induced by Li ion insertion.