

Dynamic Rate Mechanism of V₂O₅ Coated SnO₂ Nanowires for Lithium Ion Batteries Studied by *in situ* TEM

Lifen Wang^{1,2}, Zhi Xu¹, Xuedong Bai¹, Jianguo Wen², and Dean J. Miller²

¹ Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

² Electron Microscopy Center - Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439

Coating strategies are commonly employed to avoid lithiation-induced fracture and improve electrochemical performance of lithium storage materials with higher capacity and longer cycle life [1, 2]. Correlation of structure with electrochemical performance of such materials is needed to guide further design. This work mainly focuses on realizing a working lithium battery inside the transmission electron microscope (TEM) to measure and understand electrochemical mechanisms of vanadium pentoxide loaded tin dioxide (V₂O₅/SnO₂) nanowire. We achieve this by using a nanomanipulator to assemble an open electrochemical cell inside a TEM that consists of target materials, a Li-containing counter electrode (Li or Li cobalt oxide), and a solid-state electrolyte (Li₂O) [3]. To directly capture the dynamic structural changes of electrode materials during the lithiation process, open lithium cells were characterized via real-time *in situ* high resolution transmission electron microscopy (HRTEM) imaging, electron diffraction (ED) and electron energy-loss spectroscopy (EELS).

The cells were set up with a single V₂O₅/SnO₂ nanowire as the cathode material and cycled in galvanostatic mode. TEM images of the lithiation process at a lower rate (300 pA) are shown in Figure 1. The bright-field images in Fig. a, b-d show the effect of lithiation on overall nanowire morphology, revealing lithium intercalation into the interlayer spaces of V₂O₅ with only a subtle volume expansion while in the core, lithium alloys with Sn, giving rise to ~200% volume change. As seen in Fig. 1, cracks in the lateral direction due to the volume expansion mismatch are observed, and these cracks appear to be the main cause for the capacity loss at low rate. A rather different lithiation process is observed at a higher rate (3 nA) as shown in Figure 2. At this higher rate, we observe Sn nanoparticles growing along the nanowire and the alloy reaction is retarded in the first lithiation process. Layered material V₂O₅ in the shell with inactive Li₂O in the core forms a more stable structure and active Sn nanoparticles aggregate along the stable nanowire, giving rise to a new nanostructure and better cycle life.

A comparison of the lithiation mechanisms revealed by this *in situ* TEM approach reveals new insight into the dependence of lithiation and delithiation on charging rate for these V₂O₅/SnO₂ nanowires. At low charge rates, lithium intercalates into the interlayer space of V₂O₅ in the shell and alloys with Sn in the core. Mismatch in volumetric expansion between the lithium intercalation-V₂O₅ compound and the lithium alloy-SnO₂ causes mechanical fracture in the core/shell nanowire. The volume expansion of crystalline SnO₂ is confined in the lateral direction by the V₂O₅ surface coating. This results in crack formation along the coating surface, which leads to capacity fade. In contrast, at higher rates, the alloy reaction of Sn with Li to form Li-Sn is retarded, and Sn particles that are the active host for Li aggregate on the surface of the host nanowire, minimizing deleterious effects of volume expansion and providing much better cycle performance.

References:

- [1] Jian Yan , Afriyanti Sumboja , Eugene Khoo , Pooi See Lee, *Advanced Materials* **23**, (2011), p. 746.
 [2] LF Cui, R Ruffo, CK Chan, H Peng, Y Cui, *Nano Letters* **9** (2008), p. 491.
 [3] JY Huang, L Zhong, CM Wang, JP Sullivan, W Xu, LQ Zhang, SX Mao, *Science* **330** (2010), p. 1515.
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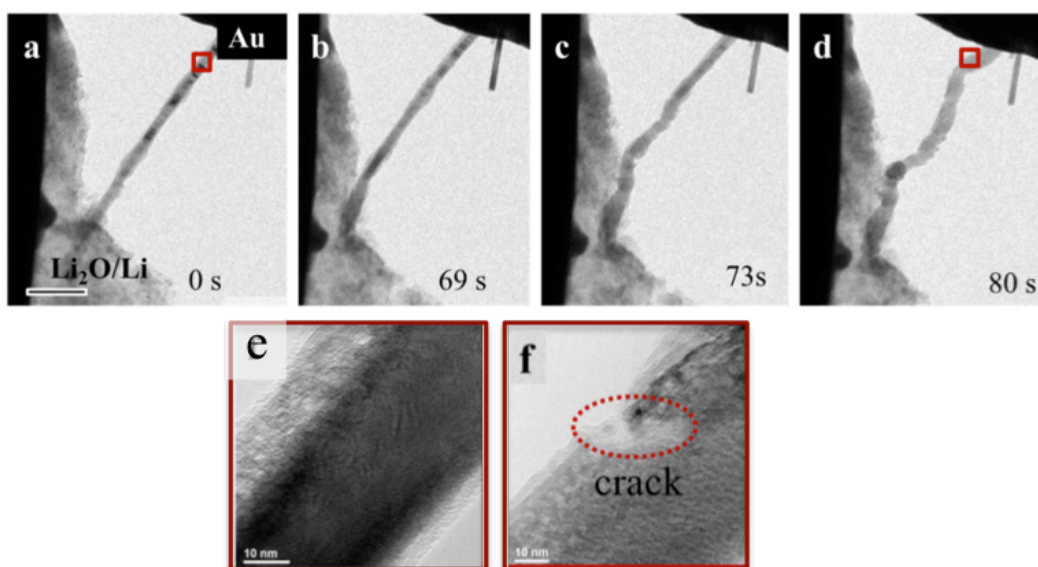


Figure 1. (a-d) Snapshots of SnO₂ nanowire during the first lithiation process at lithiation current of 300 pA. Cracks that form along the coating shell are visible in (d). (e, f) Bright field images of the same area before and after the first lithiation process as marked by the boxed area in (a) and (f) showing cracks forming in the shell of the nanowire.

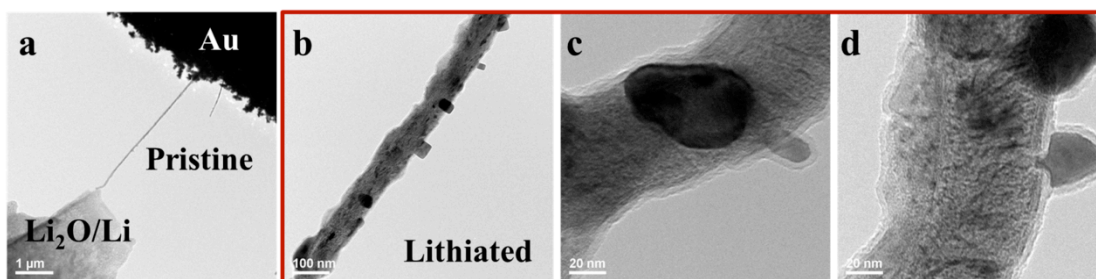


Figure 2. (a) Bright field image of a pristine V₂O₅/SnO₂ nanowire. (b-d) Images of the nanowire after the first lithiation process under 3 nA lithiation current showing Sn nanoparticles aggregating along the surface of the nanowire.