



## Energy Focus

SnO<sub>2</sub> nanowire lithiation in a TEM viewed in real time

A year ago at Sandia National Laboratories, a nanowire wriggled and twisted like a snake hatching from an egg. Researchers watched in real time as a SnO<sub>2</sub> nanowire electrode charged with lithium inside a tiny electrochemical device. In the December 10, 2010 issue of *Science* (DOI: 10.1126/science; p. 1515), J.Y. Huang, L. Zhong, C.M. Wang, and colleagues across five institutions have reported on the design of the device inside a high-resolution transmission electron microscope and have analyzed the phase and morphological changes that occurred in the electrode. Nanowire electrodes recently have shown the potential for longer life and improved performance over other material structures for electrochemical energy storage.

In a cell with ionic liquid electrolyte, the researchers applied a negative potential to a SnO<sub>2</sub> nanowire with respect to a LiCoO<sub>2</sub> counter electrode. This spurred lithium ions to react with the tin oxide nanowire, producing a reaction front that propagated longitudinally through the single crystal. In the front's wake, an amorphous-reacted phase actively started to bend and coil while lengthening and swelling. After fully charging, the nanowire was composed of amorphous Li<sub>2</sub>O and nanoparticles of Li<sub>x</sub>Sn and Sn, as determined by electron diffraction and electron energy-loss spectroscopy, and had a total volume change of over 200%.

SnO<sub>2</sub> has promising electrochemical storage capacity, but in bulk, the material is brittle. The researchers reported, however, that the tested nanowires showed high plasticity during phase transformation and no signs of fracture after lithiation. During charging, they witnessed

a high density of dislocations continuously nucleate at the amorphous-crystalline interface and subsequently consumed by the advancing reaction front (see figure). The researchers said that the very high stresses resulting from the differ-

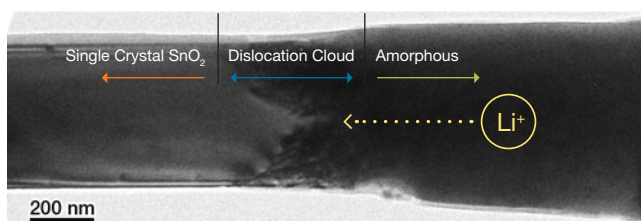
ence in wire diameter at opposite sides of the interface nucleated the dislocations in the crystalline phase. An electrochemically-driven solid-state amorphization of the nanowire took place, possibly caused by the dislocations driving the crystal far away from equilibrium but at a temperature too low for it to become liquid. Plasticity on both the crystalline and amorphous sides of the wire prevented fracture during the phase transformation.

The investigators also studied why the nanowire morphology showed a greater increase in length compared to diameter during charging. Using density functional theory calculations of three-dimensional bulk material, the researchers said that lithium insertion in the material contributed to volume expansion, but the elastic boundary conditions of the nanowire and the low Li ion flux from the ionic liquid at the nanowire surface resulted in preferential wire elongation.

Further experiments investigated the discharge of the nanowires, and the researchers said, "The methodology described [in this report] should stimulate real-time studies of microscopic processes in batteries and lead to a more complete understanding of the mechanisms governing battery performance and reliability[.]"

A video of the nanowire charging can be accessed at <http://www.efrc.umd.edu/highlights/list.php?id=18>.

**Ashley Predith**



A dislocation cloud forms at the reaction front where the single crystal SnO<sub>2</sub> nanowire charges with lithium ions. The reaction front propagates to the left, leaving behind a plastically-deformed, amorphous phase of Li<sub>2</sub>O with nanoparticles of Li<sub>x</sub>Sn and Sn. Reproduced with permission from *Science* **330** (2010) DOI: 10.1126/science; p. 1515. © 2010 AAAS.

## Nano Focus

## Individual quantum dots immobilized and positioned at the nanoscale

Techniques for precisely arranging nanoscopic objects are essential to fully realizing their potential in emerging technologies. Controlled placement of quantum dots (QDs) on a surface could be key to engineering photonic or plasmonic structures on the nanoscale. C. Ropp and a multidisciplinary team from the University of Maryland have recently devel-

oped a microfluidic technique for moving quantum dots with nanometer precision before individually immobilizing them within a polymer shell.

Published in the November 10, 2010 issue of *Nano Letters* (DOI: 10.1021/nl1029557; p. 4673), their work makes use of the electroosmotic control of CdSe/ZnS QDs in microfluidic channels. These particles are suspended in a unique water-based photoresist, which fills two channels formed between molded poly(dimethylsiloxane) and a glass slide. The X-shaped channels connect

two pairs of electrodes which allow two-dimensional control of the electric field in the 100 μm square intersecting region. The flow direction of the fluid in this region, along with the suspended QDs can be precisely controlled using the electroosmotic effect of the applied field (see figure).

The real strength of this technique, however, is a continuous feedback loop between the electrodes controlling the movement and a camera imaging the position of the QD, which emit light when illuminated with a green laser. Using a