

Electrochemical Scanning Probe Microscopy Based Diagnostics for In Situ Monitoring of Charge Storage Processes in Oxide Nanoparticles  
 K.R. Zavadil, J. Huang, and P. Lu  
 Sandia National Laboratories  
 P.O. Box 5800, Albuquerque NM, 87185-0888

Advances in electrochemical energy storage science require the development of new or the refinement of existing *in situ* probes that can be used to establish structure – activity relationships for technologically relevant materials. The drive to develop reversible, high capacity electrodes from nanoscale building blocks creates an additional requirement for high spatial resolution probes to yield information of local structural, compositional, and electronic property changes as a function of the storage state of a material. In this paper, we describe a method for deconstructing a lithium ion battery positive electrode into its basic constituents of ion insertion host particles attached to a carbon current collector. This model system is then probed in an electrochemical environment using a combination of electrochemical atomic force microscopy and scanning tunneling spectroscopy to correlate local activity with morphological and electronic configurational changes.

Nanoparticle populations of a variety of stoichiometric oxides are grown through reactive deposition in vacuum onto graphite substrates, including  $\beta$ -MnO<sub>2</sub> (rutile) and cubic spinel Li<sub>1+x</sub>Mn<sub>2-x</sub>O<sub>4</sub>. Particles grown on the basal plane of graphite nucleate and grow at step-terrace boundaries. Control of deposition rate, temperature, and cumulative quantity of oxide are used to determine the size, shape and distribution of the particles. Populations ranging from individual particles up to two dimensional nanowires of oxide can be grown along step edges. The wires are produced by thermal ripening at temperatures of 400 to 600°C and these wires are comprised of fused, individual grains. The structure and composition of these structures are determined using transmission electron microscopy, single particle electron backscatter diffraction, and Auger microprobe analysis.

The response of these structures to Li ion insertion and de-insertion are studied using *in situ* atomic force and scanning tunneling imaging (AFM, STM) and spectroscopy in polar aprotic electrolytes, including lithium hexafluorophosphate in ethylene carbonate:diethylcarbonate. Structural changes induced by the process of ion insertion and removal from the host oxide are detected and measured. Figure 1 shows an example of the impact of Li insertion into a  $\beta$ -MnO<sub>2</sub> nanowire on graphite. Repetitively cycling the potential from its equilibrium (pre-lithiation) value of 3.4 V to a value of 2.3 V (vs. Li/Li<sup>+</sup>) results in a loss of individual grain definition along the nanowire length, presumed to result from in-plane strain with Li<sup>+</sup> ion insertion. This loss of grain definition is more clear when comparing an average linescan along the length of the wire for the 3.4 and 2.3V cases (inset to Fig.1). The average width of the wire is also observed to increase by 7% with cycling. Lastly, a protrusion forms at the site of a grain boundary at the upper end of the nanowire (indicated by arrow in Fig.1b), which appears to be the result of buckling of this structure resulting from cumulative strain along the length of the wire induced by ion insertion. Imaging of individual particles, as opposed to wires, show cyclic size changes with potential cycling consistent with some degree of reversible ion uptake and release. The results

suggest that a particle of sufficiently small size may not fully undergo the expected rutile to spinel phase transition argued for mircoscale  $\beta$ -MnO<sub>2</sub> (1).

Current work is focused on applying spectroscopic electrochemical STM (2) to determine the extent of ion insertion based on changes in the tunneling current as a function of tip-particle potential difference using ultrafast potential sweeps. Comparison of particle responses will be made with that of the cubic spinel Li<sub>1+x</sub>Mn<sub>2-x</sub>O<sub>4</sub>, which is also grown on graphite. This ability to measure a combination of *in situ* structural and electronic configuration changes in situ is being pursued as a general approach for establishing size-activity relationships for ion insertion materials. Other potential applications may include probing size-thermodynamic reversibility relationship in conversion compounds.

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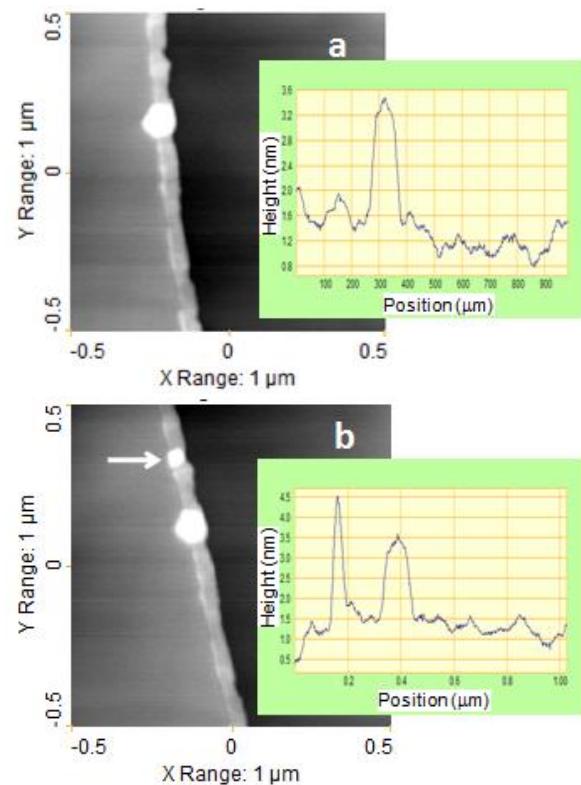


Figure 1.  $\beta$ -MnO<sub>2</sub> nanowire grown along a step edge on graphite and imaged under potential control in 1M LiPF<sub>6</sub> EC:DEC: a) at 3.4 V prior to Li insertion and b) at 2.3 V after cycling between 3.4 and 2.3 V several times.

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