EMSL Research and Capability Development Proposals

In Situ Electron Microscopy and Spectroscopy Studies of Interfaces in Advanced Li-ion Batteries Under Dynamic Operation Conditions

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EMSL Lead Investigator:
Chongmin Wang, *Senior Research Scientist, EMSL Interfacial & Nanoscale Science Facility*

Co-Investigators: S. Thevuthasan (*EMSL, PNNL*), Gary Yang (*EED, PNNL*), Jun Liu (*FCSD, PNNL*), and Norman Salmon, *Hummingbird Scientific LLC* (8300 28th Ct NE, Unit 200, Lacey, Washington 98516)

Electrochemical energy storage devices (EES) such as Li-ion batteries are complex multi-component systems that incorporate widely dissimilar phases in physical and electrical contact as schematically shown in Figure 1. The operation of EES relies critically on electron and ionic transfer across solid–solid and solid–liquid interfaces and within each of the constituent phases. These interfaces may include a reaction front moving through a particle in a two-phase reaction or an interface between the conducting electrode and the electrolyte. The largest and most critical challenge facing the EES is the basic understanding of the structural evolution within the constituent materials across the interface/interphase during the cyclic operation of the cell and the consequence of such structural evolution on the cell's properties. For example, repeated charge and discharge of EES devices invariably leads to performance degradation due to irreversible changes in the structure, morphology, and composition of the materials. The BES Workshop on Basic Research Needs for EES concluded that breakthroughs required for tomorrow's energy storage needs will not be realized with incremental evolutionary improvements in existing technologies. Rather, they will be realized only with fundamental research to understand the underlying processes involved in EES. Obtaining insights on the fundamental mechanisms in the EES will enable the development of novel EES concepts that incorporate revolutionary new materials and chemical processes.

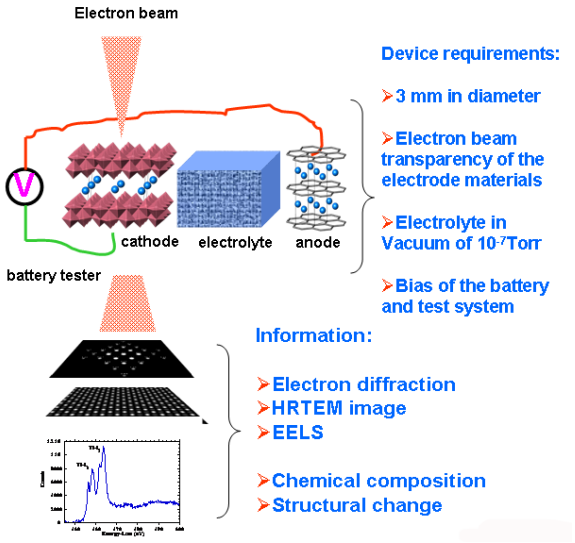

Figure 1. *Schematic drawing showing the components of a Li-ion battery cell and the information that can be collected in a TEM during the* in situ *experiment.*

Therefore, **one of the great challenges for battery development is to find ways to observe the microstructure evolution of the active materials during the operation of the battery.** The objective of this work is to develop *in situ* capabilities and to probe into the structural evolution during dynamic operation of the battery.

In this work, **we pioneered the concept of building a working battery using a single nanowire as an electrode,** which enables *in situ* transmission electron microscopy (TEM) imaging of the electrode during the battery's operation. Essentially, this is the smallest working battery in the world (Figure 2).

A prototype Li-ion battery was developed using a single SnO_2 nanowire as the anode, ionic liquid as the electrolyte, and $LiCoO_2$ as the cathode. This battery is integrated on a biasing holder for TEM. Related to the low vapor pressure of the ionic liquid, the battery can be directly loaded into the high vacuum column of the electron microscope for *in situ* observation during the charging and discharging of the battery. When associated to composition of the ionic liquid, the lithiation rate is dramatically decreased as compared to a standard electrolyte.

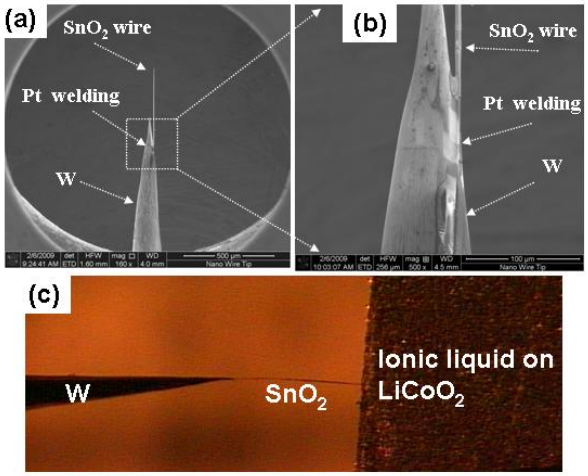

Figure 2. *FIB manipulation and welding of a single SnO_2 nanowire onto the W tip. (a) Low-magnification SEM image, (b) high-magnification SEM image showing the Pt welding, and (c) optical image showing the SnO_2 dipped into the ionic liquid.*

The capabilities that can be used for *in situ* testing of a prototype Li-ion battery include several key components:

1) Biasing holder designed and fabricated in collaboration with Hummingbird Scientific
2) Removable carrier allows integration of the prototype battery on the holder (Figure 3)
3) Setting up the battery testing system for *in situ* testing of the world's smallest working battery
4) Identifies the ionic liquid-based electrolyte that is compatible with high vacuum for *in situ* testing
5) Focused ion beam (FIB)/scanning electron microscope (SEM) manipulation of single nanowire for assembling the world's smallest battery.

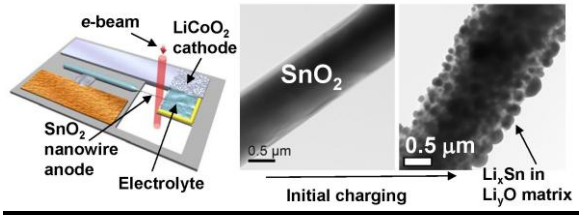

Figure 3. *Schematic drawing showing the concept of the smallest working battery based on a single nanowire (left). TEM image of the SnO_2 anode before charging (middle). TEM image of the SnO_2 anode following the initial charging (right). Note the microstructural evolution following the initial charging.*

Products and Output

New Capability for EMSL Users

The hardware for *in situ* TEM battery testing is now available for EMSL users through the user proposal system. The prototype battery concept conceived in this project has been widely adopted by others for *in situ* TEM study.

Peer-Reviewed Publications

Wang C.M., Z.G. Yang, S. Thevuthasan, J. Liu, D.R. Baer, D. Choi, D.H. Wang, J.G. Zhang, L. Saraf, and Z.M. Nie. 2009. "Crystal and electronic structure of lithiated nanosized rutile TiO_2 by electron

diffraction and electron energy-loss spectroscopy." *Applied Physics Letters* 94(23):233116. DOI: 10.1063/1.3152783.

Wang C.M., W. Xu, J. Liu, D.W. Choi, B. Arey, L.V. Saraf, J.G. Zhang, Z.G. Yang, S. Thevuthasan, D.R. Baer, and N. Salmon. 2010. "*In situ* transmission electron microscopy and spectroscopy studies of interfaces in Li-ion batteries: Challenges and opportunities." *Journal of Materials Research* 25(8):1541-1547. DOI: 10.1557/JMR.2010.0198.

Contributed Presentations

Wang C.M., et al. 2010. "*In Situ* TEM studies of Lithium Ion Battery." to be presented at *Microscopy and Microanalysis 2010*, August 1-5, 2010, Portland, Oregon.

Wang C.M., W. Xu, L. Saraf, B. Arey, J. Liu, D. Choi, Z.G. Yang, J. Zhang, S. Thevuthasan, D.R. Baer, and N. Salmon. 2010 "Direct observation of solid electrolyte interface layer formation in lithium ion battery using *in situ* TEM." presented at the *Materials Research Society (MRS) Spring Meeting*, April 5-9, 2010, San Francisco, California.

Wang C.M., W. Xu, L. Saraf, B. Arey, J. Liu, Z.G. Yang, J.G. Zhang, S. Thevuthasan, and D.R. Baer. 2009. "*In Situ* TEM Study of Interfacial Layer Formation in Li-Ion Battery." presented at the *Materials Research Society (MRS) Fall Meeting*, December 1-3, 2009, Boston, Massachusetts.

Wang D., D. Choi, J. Li, Z. Yang, Z. Nie, R. Kou, C. Wang, L. Saraf, J. Zhang, I. Aksay, and J. Liu. 2009. "Metal Oxide-Graphene Hybrid Materials for Li-Ion Battery." presented at the *Materials Research Society (MRS) Fall Meeting*, December 1-3, 2009, Boston, Massachusetts.

Zhang J., J. Xiao, D. Wang, J. Liu, D. Choi, C. Wang, Z. Yang, W. Xu, and G. Gordon. 2009. "Silicon Based High Capacity Anode for Li-Ion Battery Applications." presented at the *Materials Research Society (MRS) Fall Meeting*, December 1-3, 2009, Boston, Massachusetts.

Wang C.M., W. Xu, L. Saraf, B. Arey, J. Liu, Z. Yang, J.G. Zhang, S. Thevuthasan, and D.R. Baer. 2009. "Direct Observation of Interfacial Layer Formation in Li-Ion Battery Using *In Situ* TEM and EELS." presented at the *American Vacuum Society 56th International Symposium & Exhibition*, November 8-13, 2009, San Jose, California.

Wang C.M., et al. 2009. "*In Situ* and *Ex Situ* TEM Imaging and Spectroscopy Study of Li-Ion Battery." presented at *Microscopy and Microanalysis 2009*, July 26-30, 2009, Richmond, Virginia.

Wang C.M., et al. 2008. "*In situ* electron microscopy and spectroscopy studies of interfaces in advanced Li-ion batteries under dynamic operation conditions." presented at the *American Vacuum Society 55th International Symposium & Exhibition*, October 21-23, 2008, Boston, Massachusetts.

Symposiums

Wang C.M. 2010. "Fundamental Challenges and Opportunities for *in situ* TEM Studies of Energy Storage Materials." to be presented at *ORNL-PNNL-ANL-IBM 3rd Symposium on Scalable Energy Storage Beyond Li-Ion: Materials Perspectives*, October 7-8, 2010, Oak Ridge, Tennessee.

Invitation to organize symposium on *in situ* microscopy and spectroscopy for *Microscopy and Microanalysis 2010*, August 1-5, 2010, Portland, Oregon.

Invitation to organize symposium on *in situ* TEM and related techniques for *Materials Research Society (MRS) Spring Meeting*, April 5-9, 2010, San Francisco, California.