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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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.

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.

![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.](image)
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 SnO₂ nanowire as the anode, ionic liquid as the electrolyte, and LiCoO₂ 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.

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.

**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**


**Contributed Presentations**


**Symposiums**


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.