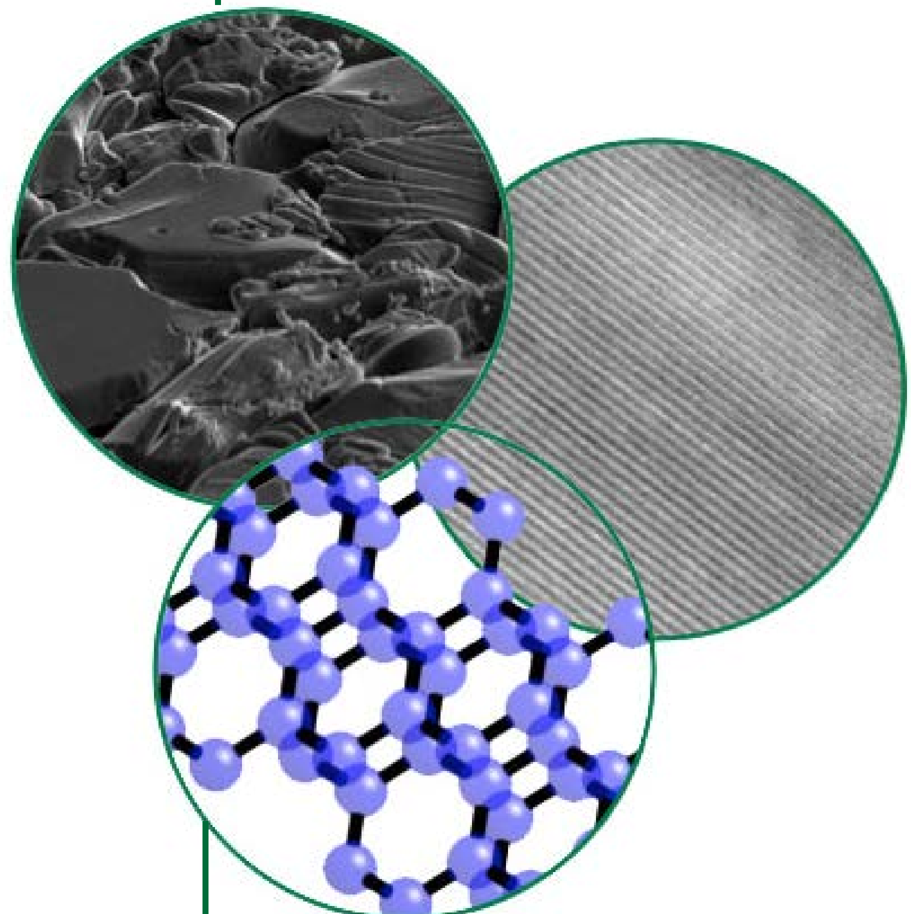
Project ID: ES095

In-Situ Electron Microscopy of Electrical Energy Storage Materials



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U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Overview

Timeline
- Project Start: January 2010
- Project End: Ongoing
- Percent Complete: N/A

Technical Barriers
C: Design Data and Modeling Tools
D: Performance

Budget
- Total project funding
  - Funding for FY10: $250k
  - Funding for FY11: $250k
  - Funding for FY12: $300k

Partners
- Hummingbird Scientific
- University of Texas Austin
- Drexel University
- ORNL FIRST Energy Frontier Research Center

Technical Relevance

- Present lack of *in situ* characterization methodologies that can be used to understand the role of interfacial electrochemistry or electrochemical reaction mechanisms limit insight into the dynamics of electrochemical processes that are crucial to device functionality in electrical energy storage and conversion devices.

- We have developed *in situ* electrochemical fluid cell microscopy to perform controlled nanoscale electrochemistry experiments. This method allows for the direct, real-time imaging of electrochemical processes within a liquid electrolyte at high spatial and temporal resolution.

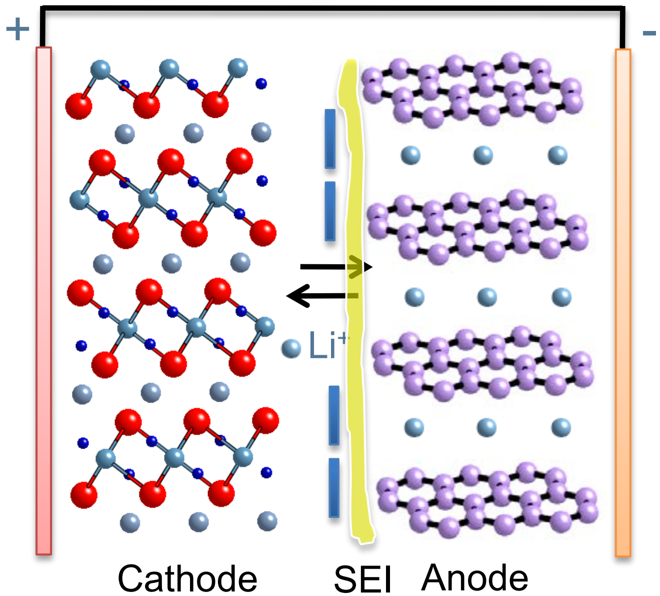
    - Develop a fundamental understanding of SEI formation mechanisms as a function of electrochemical cycling.

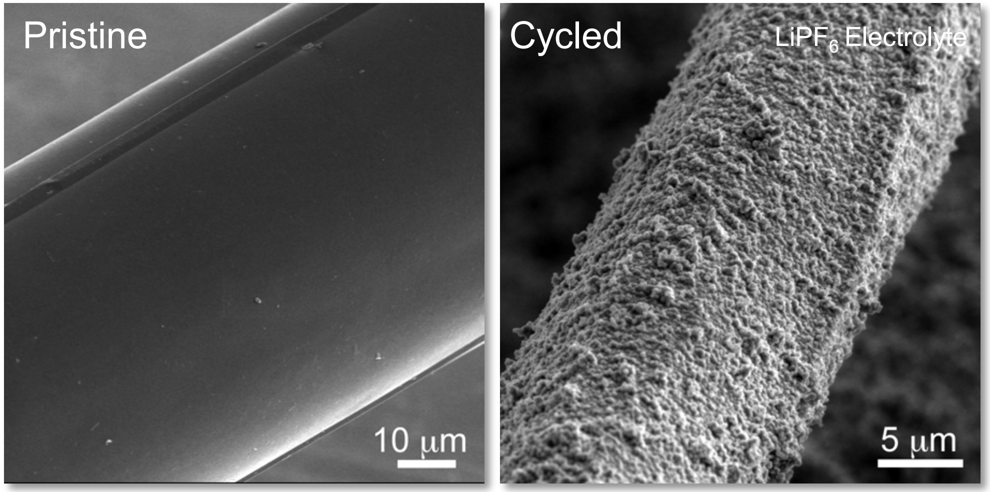
    - Characterize nm-scaled microstructural and microchemical changes during electrochemical cycling.

    - Experimentally validate computational models with observations to elucidate the physics of charge/mass transfer mechanisms in energy storage devices.

Technical Relevance

The accelerated development of materials for EES systems will depend on understanding the role of interfaces (electrode-electrolyte) on the electrochemical energy conversion processes in energy storage systems.





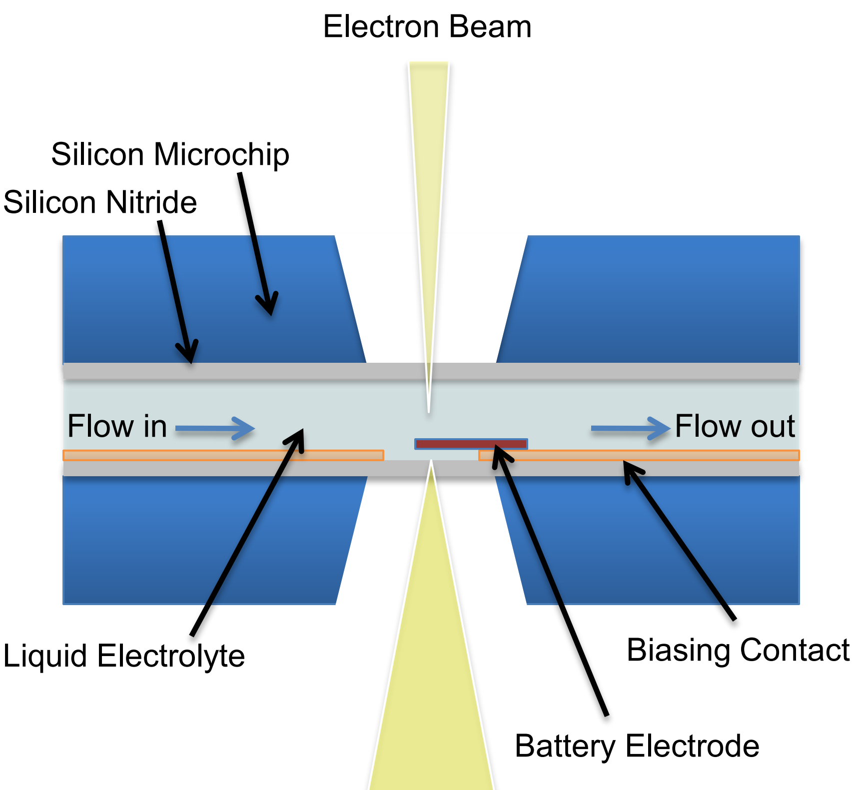
- The solid electrolyte interphase (SEI) is nm-scaled passive interfacial layer that forms as a result of electrolyte decomposition, which is comprised of inorganic and organic products.

- The formation and stability of the SEI is crucial to the performance, durability, and safety of lithium ion batteries.

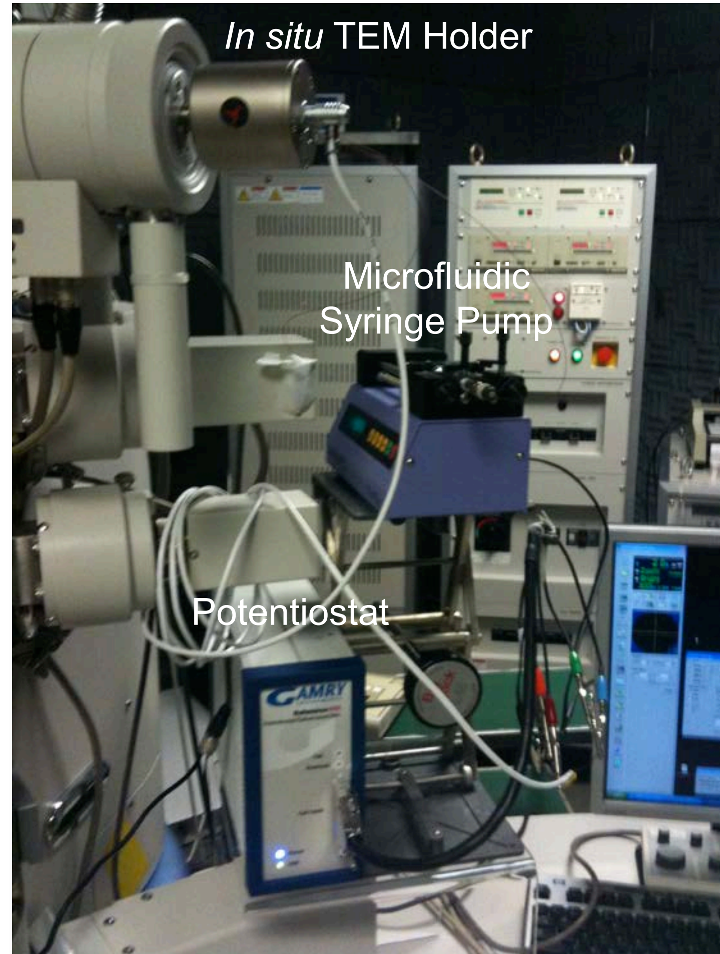
- Goal: Investigate SEI formation mechanisms with *in situ* electrochemical fluid cell microscopy

Technical Approach

- An *in-situ* electrochemical cell TEM holder has been developed in collaboration with Hummingbird Scientific.



Schematic illustration of *in situ* electrochemical cell using silicon microchips with electron transparent silicon nitride membranes as a platform for controlled nanoscale electrochemistry experiments.



Experimental setup in the Hitachi HF-3300 S/TEM at ORNL's ShaRE User Facility

Milestones

Month/Year	Description	Status
June 2012	Fundamental studies of electrolyte decomposition mechanisms on graphite anodes (SEI formation mechanisms)	Completed
June 2012	Coupling *in situ* Electron Microscopy with Electron Energy Loss Spectroscopy for chemical analysis	Completed
August 2012	*In situ* characterization of reaction mechanisms for nanocomposite conversion electrode systems and metal-air batteries	Planned
August 2012	*In situ* characterization of electrode degradation mechanisms	Planned

Summary of Technical Accomplishments

- Core Technology: *in situ* electrochemical fluid cell/TEM holder

  Description: A liquid cell design has been developed with electrical connections for interfacing battery electrodes to a potentiostat for *in-situ* TEM electrochemistry experiments within a thin fluid electrolyte layer

  Status: *in situ* TEM holder has been designed and fabricated in collaboration with Hummingbird Scientific.

- *In situ* TEM specimen preparation laboratory

  Description: Specialized lab equipment and work stations have been assembled for specimen prep

  Status: Addition of Air Protection/Transfer system for TEM/FIB Characterization of Air Sensitive Materials.

- Microreference and counter electrode design

  Description: Development of two and three electrode electrochemical cell for for controlled nanoscale electrochemistry experiments

  Status: Prototype design developed and experimentally validated

- Coupling analytical electron microscopy with in situ experiments

  Description: Utilization of electron energy loss spectroscopy for chemical analysis in liquid cells

  Status: Feasibility of liquid EELS demonstrated with high voltage $LiMn_{1.5}Ni_{0.5}O_4$ cathodes.

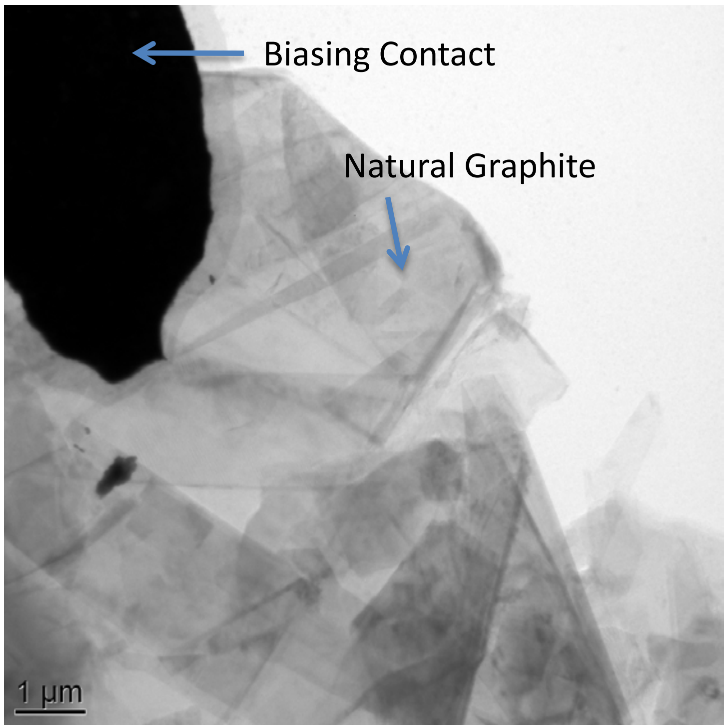
- In situ electrochemistry of energy storage materials

  Description: Performed *in situ* electrochemical testing of to study electrolyte decomposition mechanisms

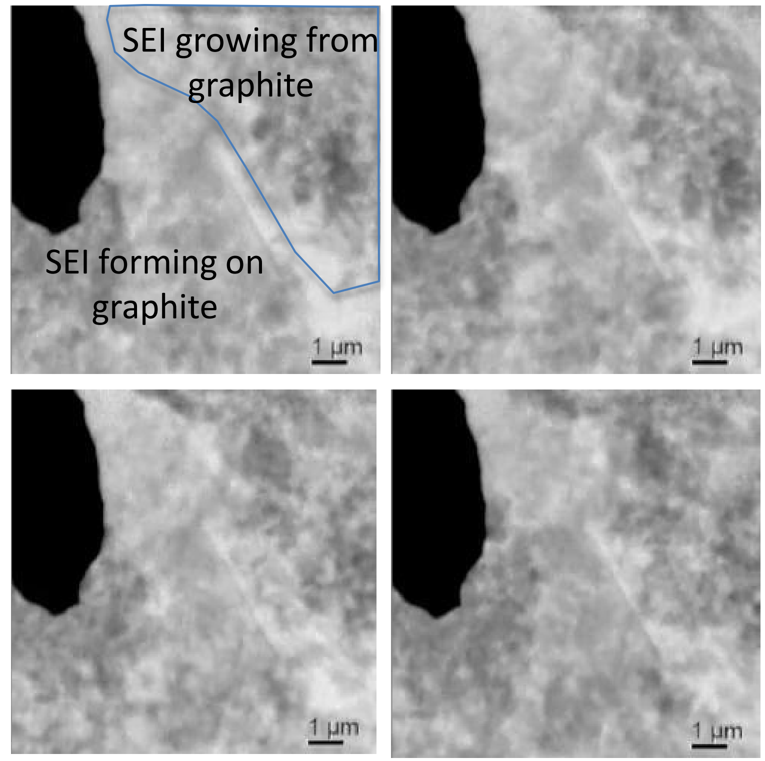
  Status: Primary focus on SEI formation mechanisms on negative anode

Technical Accomplishments: SEI Formation Mechanisms

- Method for performing controlled nanoscale electrochemistry experiments in a 2 and 3 electrode cell configuration has been designed and incorporated for use with *in situ* electrochemical fluid cell approach.
- Li Half-cell used to study SEI formation on natural graphite with electrolyte consisting of 1M $LiPF_6$ in EC:DMC



BF TEM image of natural graphite attached to biasing contact in electrochemical fluid cell

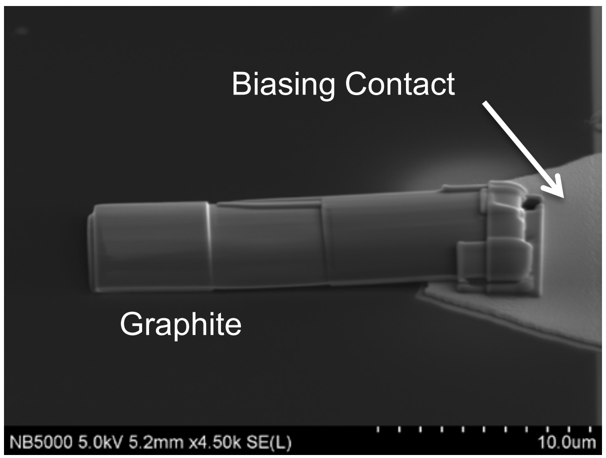


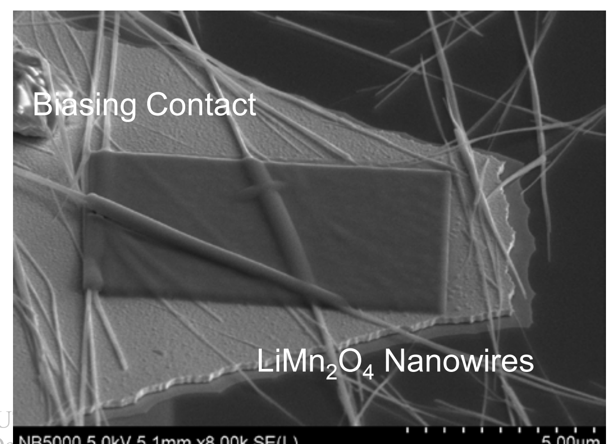
Time-lapsed frameshots from *in situ* experiment of SEI formation on graphite anode

Technical Accomplishments:
Methods for On-chip Battery Electrode Fabrication

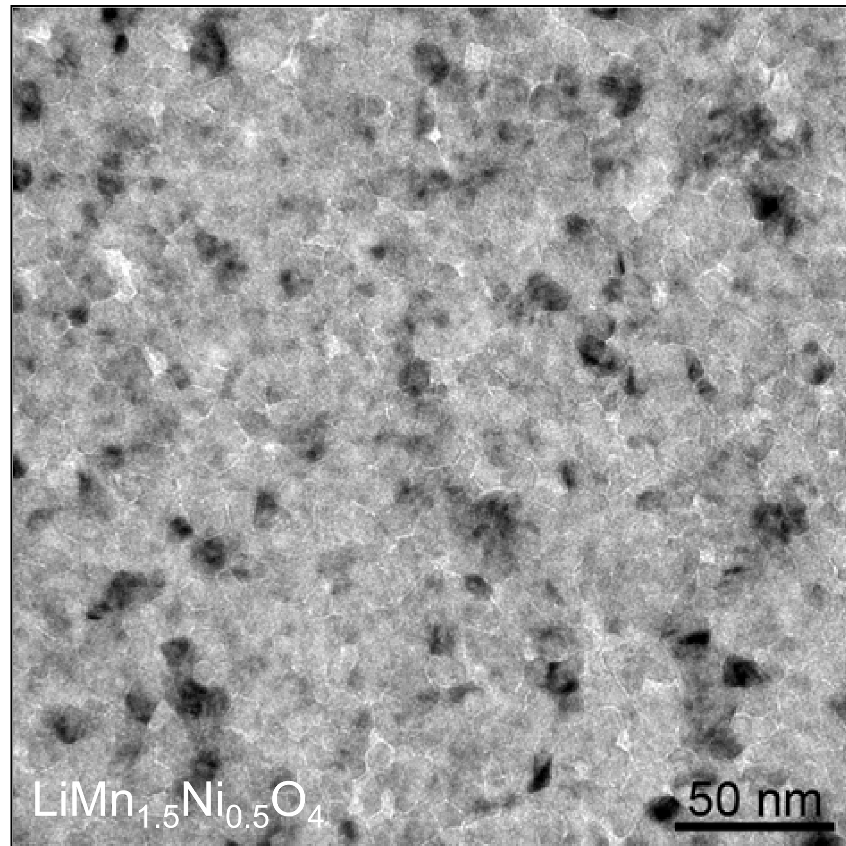
- Developing improve methods of specimen preparation for in situ experiments
- Variety of specimen preparation techniques evaluated for joining electrodes to electrical contacts on biasing microchip

- Focus ion beam joining methods



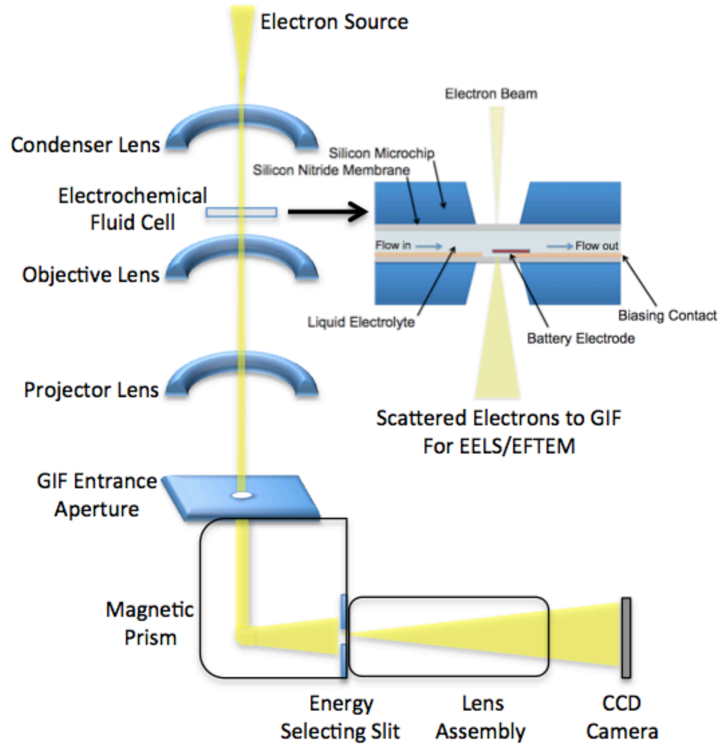


- Thin Film Deposition Methods

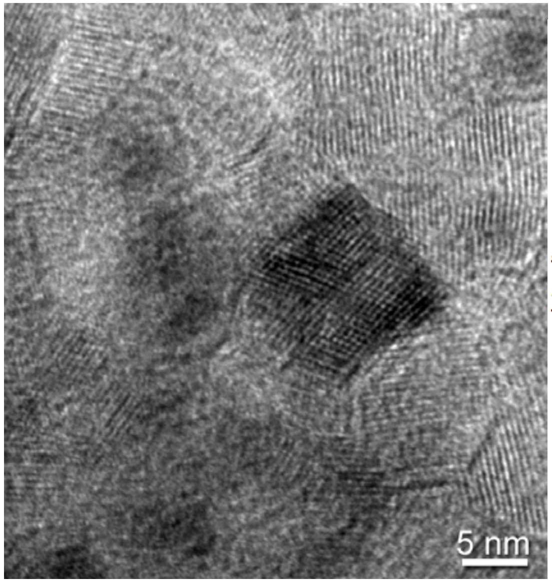


Technical Accomplishments-Analytical Electron Microscopy

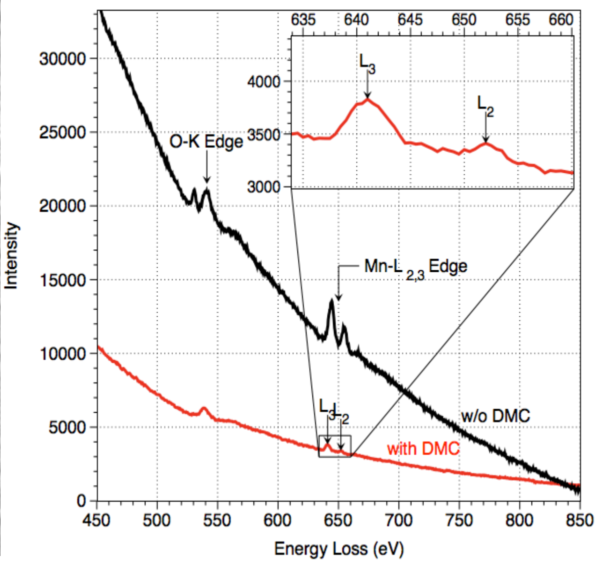
- Electron energy loss spectroscopy used to determine oxide state changes of transition metals in high voltage cathodes within environmental fluid cell.
- EEL spectra collected from $LiMn_{1.5}Ni_{0.5}O_4$ with and without dimethyl carbonate
- This research demonstrates the capability of extracting chemical information in situ within a thin layer of electrolyte.



Schematic of electrochemical fluid cell microscopy within a TEM coupled with a post-column energy filter for EELS and EFTEM imaging.



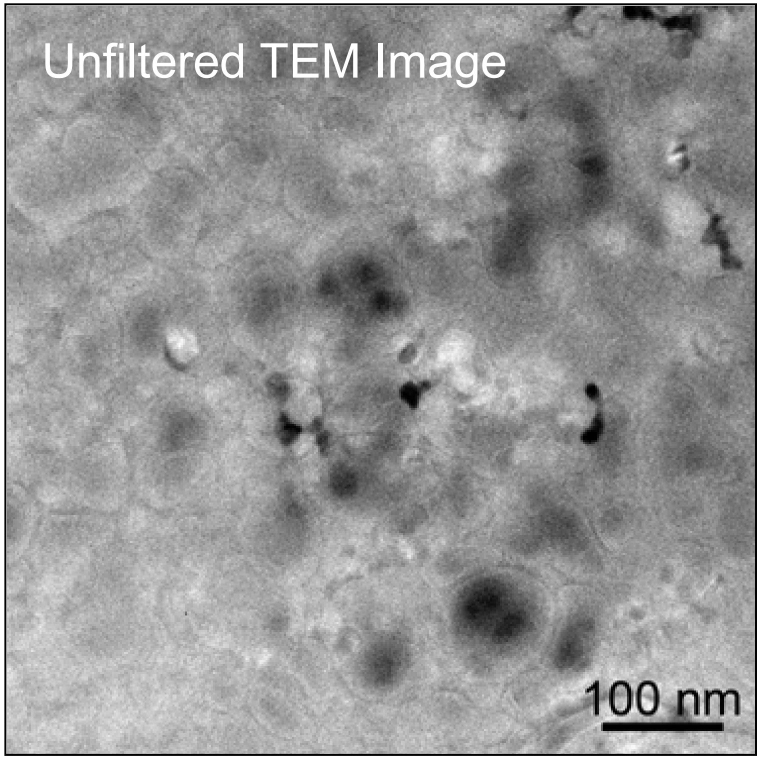
HRTEM image of $LiMn_{1.5}Ni_{0.5}O_4$ on SiN membranes

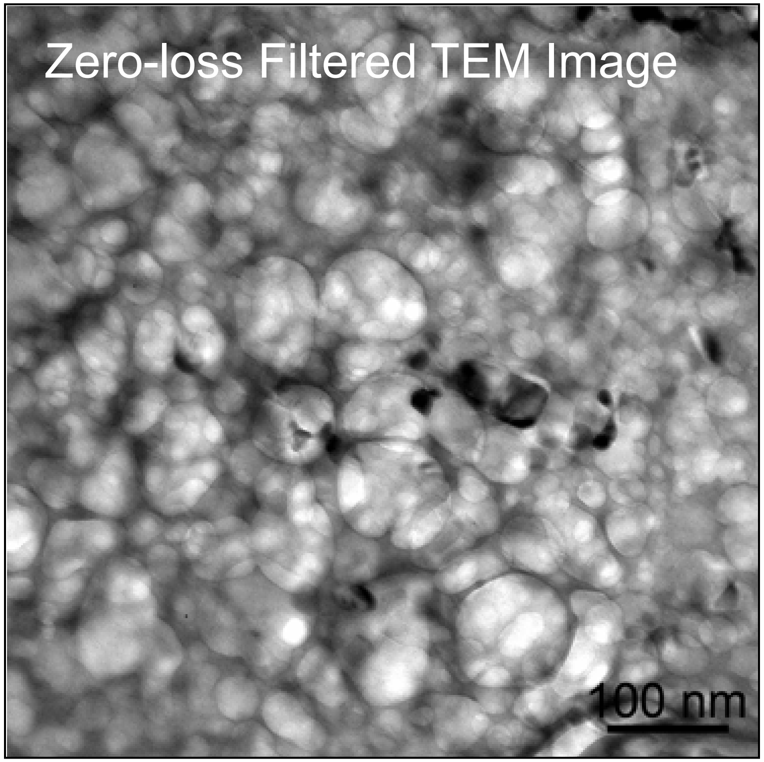


Corresponding EEL spectra with and without Dimethyl carbonate

Technical Accomplishments-Analytical Electron Microscopy

- Utilize energy filtered TEM to increase spatial resolution in liquid environments
- Zero-loss filtered TEM image has been shown to dramatically enhance image resolution.





Benefit of EFTEM imaging:
- Removal of inelastic scattered electrons
- Reduce effect of chromatic aberration
- Improved image contrast for *in situ* studies of SEI formation

Proposed Future Research

Technique Development

- Develop novel methods of performing nanoscale electrochemistry experiments using this *in situ* platform.
- Increase spatial resolution using thinner viewing membranes and spacers
- Couple analytical electron microscopy methods for chemical characterization of materials in a fluid environment

Collaborative Research

- *In situ* TEM studies on SEI growth mechanisms on model electrode system with different electrolyte and electrolyte solvents
- Combine EELS with *in situ* experiments to study redox reactions in high voltage cathode materials
- Understand electrode degradation mechanisms in active electrode materials
- Extend *in situ* studies for next generation high voltage electrode materials, electrolytes, and electrolyte additives to elucidate their role on CEI formation and stability. (UT Austin)
- Perform *in situ* electron microscopy characterization in support of basic and applied electrode/electrolyte development programs. (ORNL)
- Experimentally validate multi-length scale simulations of SEI with ORNL FIRST Energy Frontier Research Center

Collaboration/Coordination with Other Institutions

- Program with ORNL/UT Austin to investigate electrolyte stability for high voltage cathode materials. (CEI formation mechanisms)

- Collaborative use with access to both staff expertise and unique instrumentation, by university, national laboratory, and industrial partners for the *in situ* electrochemical characterization of energy storage systems via the ShaRE program at ORNL, which is sponsored by the Office of Basic Energy Sciences, US Department of Energy.

- ORNL Energy Frontier Research Center (EFRC) FIRST (Fluid Interface Reactions, Structures, and Transport) investigating SEI formation mechanisms through multi-scale modeling approaches. In situ microscopy is providing experimental validation for modeling activities

Publications/Presentations FY 12

- Unocic RR, Sun X, Adamczyk LA, Dudney NJ, Alsem DH, Salmon NJ, More KL, "Development of *in-situ* TEM Electrochemical Fluid Cells for Electrical Energy Storage Research," Frontiers in Electron Microscopy in Materials Science, Sonoma, CA, September 2011. *(Poster Presentation)*

- Unocic RR, Alsem DH, Salmon NJ, Chi M, Veith GM, Adamczyk LA, Dudney NJ, More KL, "The Versatility of *In-situ* Environmental Fluid Cells for Materials Science Research," MS&T 2011, Columbus, OH, October 2011. (*Oral Presentation-Invited)*

- Unocic RR, Baggetto L, Unocic KA, Veith GM, Dudney NJ, More KL, "Coupling EELS/EFTEM Imaging with Environmental Fluid Cell Microscopy," Microscopy and Microanalysis Annual Meeting, Phoenix, AZ, August 2012. (*Conference Paper /Oral Presentation-Invited*)

Summary

In situ Electrochemical Fluid Cell Development

- An *in situ* electrochemical fluid cell has been developed for controlled nanoscale electrochemistry experiments with the capability of simultaneously characterizing structural and chemical changes of batteries through S/TEM imaging, spectroscopy, or diffraction all within a liquid electrolyte and at high spatial resolution.

Experimental Method Development

- Half-Cell and Full-Cell approaches have been developed for *in situ* TEM battery testing
- New insight into electrolyte decomposition mechanisms have elucidated (SEI)
- Developed new strategies for specimen and device fabrication

Coupling Analytical Electron Microscopy Methods in Fluid Cell Microscopy

- Utilized post-column energy filter for EELS and EFTEM of materials in liquid env.
- Demonstrated that energy filtered zero-loss imaging improves resolution when imaging through thick fluid layers within the electrochemical fluid cell
- Coupled TEM imaging and EEL spectroscopy to determine structure and chemistry of high voltage cathode materials within an electrolyte solvent.

Collaborations

- Continually developing collaborations with other research institutions and industrial partners where in situ microscopy can provide insight into the fundamental mechanisms of electrochemical processes in energy storage materials.

Acknowledgements

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