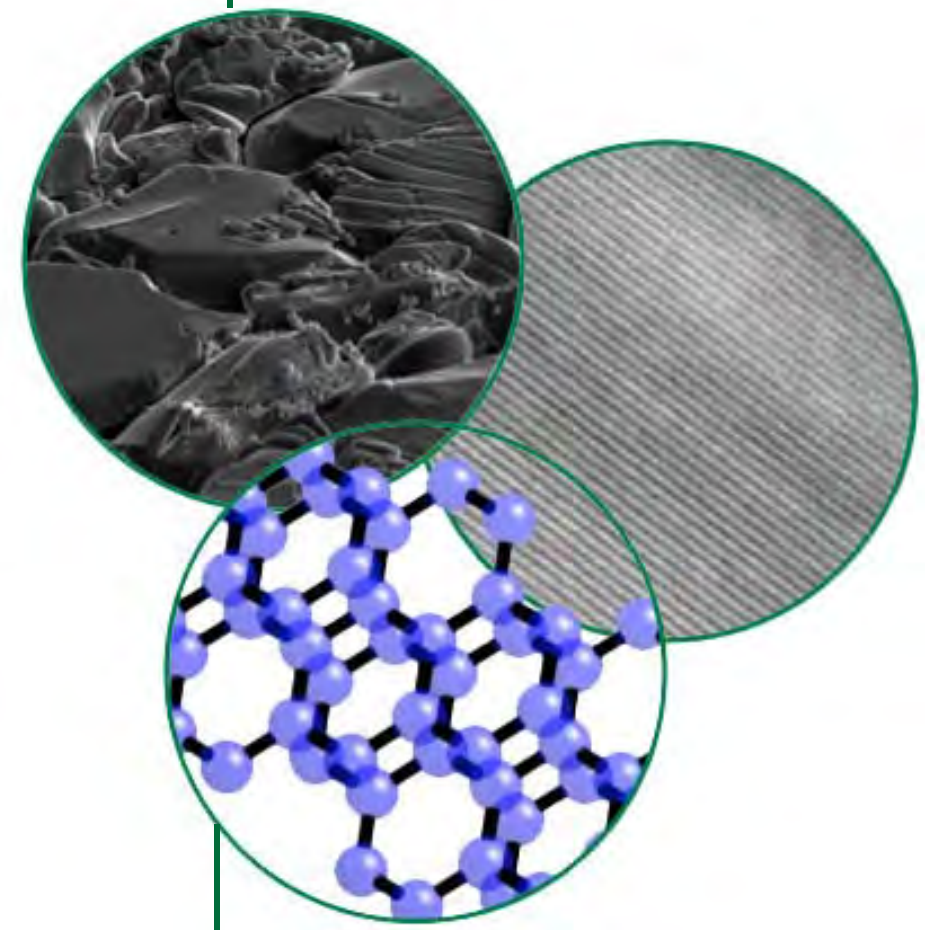
Project ID: ES095

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: TBD
- Percent Complete: N/A

Technical Barriers

- Limited Cycling Performance
- Limited Stability of Electrodes for High Voltage Batteries

Budget

- Total project funding
  - $250k/year
- Funding for FY10: $250k
- Funding for FY11: $250k

Partners/Collaborators

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

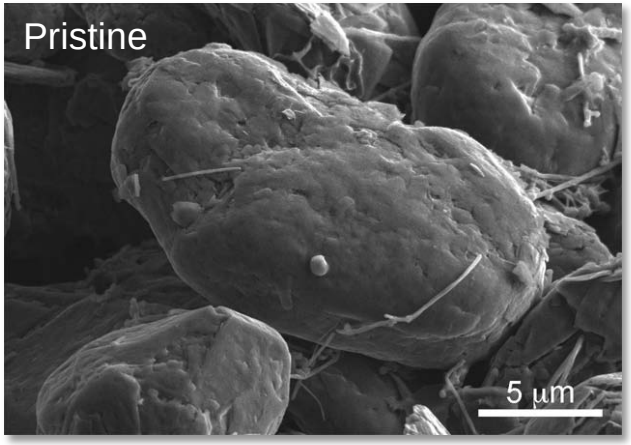
Scientific Relevance/Impact

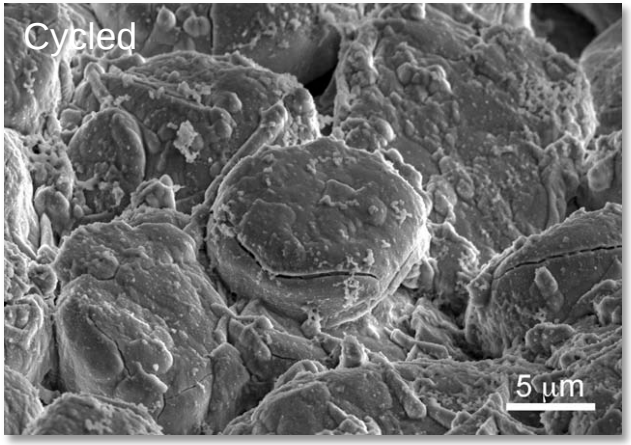
The accelerated development of materials for EES systems will depend on understanding the role of interfaces (electrode-electrolyte) on the physical and electrochemical energy conversion processes in energy storage systems.

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

- The dynamically evolving nature of this *nm*-scaled interface makes it difficult to elucidate fundamental mechanisms controlling SEI formation and growth as a function of electrochemical cycling.

In-situ transmission electron microscopy (TEM) provides a unique means for investigating structure-property relationships at the nm-scale and in real-time using specialized i*n-situ* TEM holders





Scientific Objectives

To develop and utilize advanced *in-situ* TEM/STEM to study electrochemical energy conversion processes in EES systems, such that nm-scaled microstructural and microchemical changes are characterized during electrochemical cycling at high temporal and spatial resolution for novel electrode materials and liquid electrolytes.

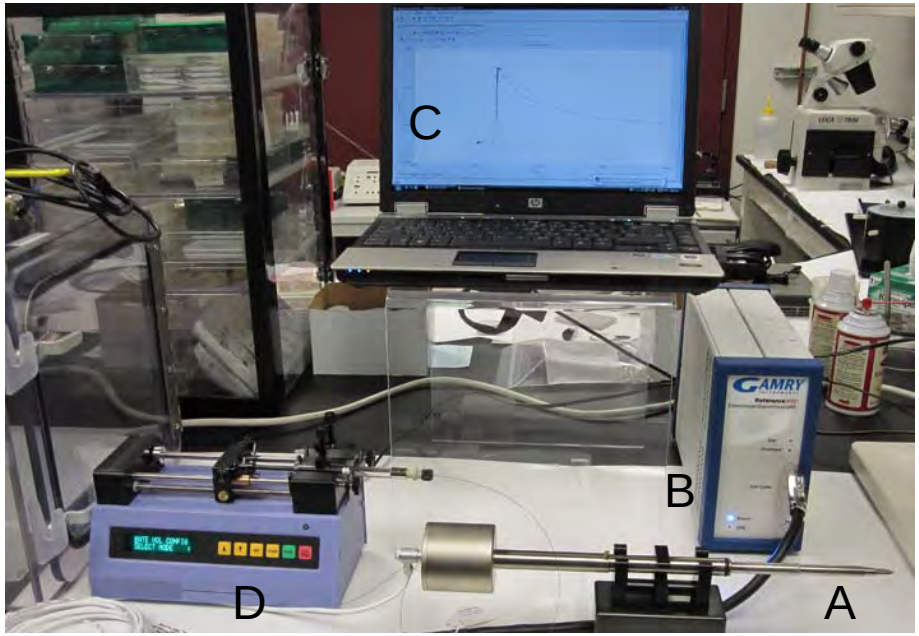
ORNL's Hitachi HF-3300 TEM/STEM

Immediate opportunities for EES research using the techniques developed in this program include:

- *In-situ* TEM characterization of structural and chemical changes in battery electrodes.
- Direct observation of SEI formation at electrode/electrolyte interfaces during electrochemical cycling.
- Influence of electrolyte/electrolyte additives on SEI formation and stability.
- Direct observations of Li^+ ion intercalation and elucidation of intercalation induced stresses.

Technical Approach

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



(A) In-situ TEM Holder, (B) Potentiostat, (C) Laptop (D) Microfluidic Syringe Pump

The *in-situ* holder consists of the following unique features:

1) Silicon Microchips
Si chips with electron transparent SiN viewing windows and imprinted electrode contact pads are used as a platform for attaching nm-μm sized electrodes.

2) Fluid Delivery System
Liquid electrolyte is introduced into the cell via a microfluidic syringe pump and microfluidic tubing.

3) Electrical Biasing Connections:
The microchips with battery electrodes attached are interfaced with an external potentiostat for electrochemical testing via biasing contacts and chemically inert conductive wire.

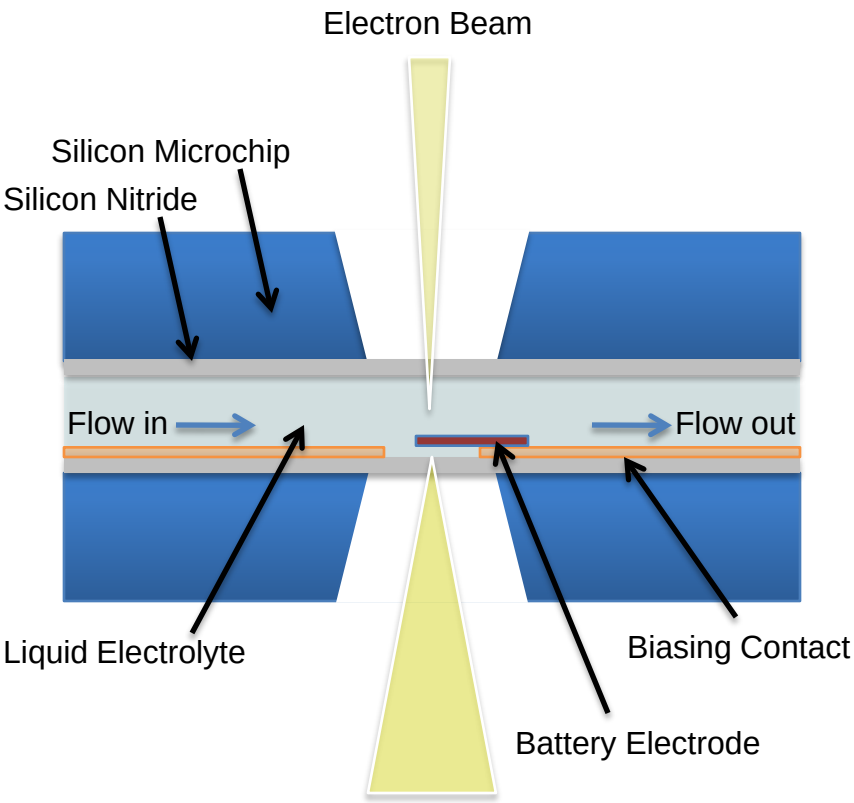
Technical Approach

- The electrochemical cell is created when two patterned silicon microchips are stacked upon one another and placed into the tip of the *in-situ* TEM holder.

- Allows for direct imaging of battery electrodes through a liquid electrolyte wholly contained between two electron-transparent SiN membranes supported on silicon microchips.

- Integrated biasing connections enable electrochemistry experiments to be performed while electrode surfaces are imaged and analyzed simultaneously using the TEM.

In-situ observations of dynamic electrochemical events are captured using a finely focused probe in BF or HAADF STEM modes or with conventional TEM imaging using parallel beam illumination in mode.



Schematic of in-situ electrochemical cell using silicon microchips with electron transparent silicon nitride membranes.

Milestones

Month/Year	Milestone Description	Status
June 2010	Develop Si/SiN microchips and design TEM holder with robust electrical connections for *in-situ* TEM electrochemical cycling experiments	Completed
Sept 2010	Initiate *in-situ* electrochemistry experiments using *in-situ* TEM holder	Completed
April 2011	Optimize liquid electrochemical cell holder and biasing chip design for versatile testing capabilities	On Schedule
April 2011	Validate *in-situ* TEM characterization methodologies against controlled base-line laboratory testing of select battery materials	On Schedule
August 2011	Establish standardized *in-situ* electrochemical experiment protocols and report results.	On Schedule

Summary of Technical Accomplishments

- Development of *in-situ* electrochemical cell/TEM holder

  Description: A liquid cell design has been modified to include robust electrical connections for interfacing with potentiostat for *in-situ* TEM electrochemistry experiments.

  Status: Prototype has been designed and fabricated in collaboration with Hummingbird Scientific

- Microchip Development

  Description: Si microchips with SiN viewing windows will be the platform for creating micro-batteries that will be integrated within a liquid flow cell *in-situ* TEM holder.

  Status: Prototype Si microchips have been fabricated with integrated biasing contacts.

- *In-situ* TEM specimen preparation laboratory

  Description: Specialized lab equipment and work stations have been assembled to assist in specimen preparation for *in-situ* electron microscopy experiments.

  Status: Completed

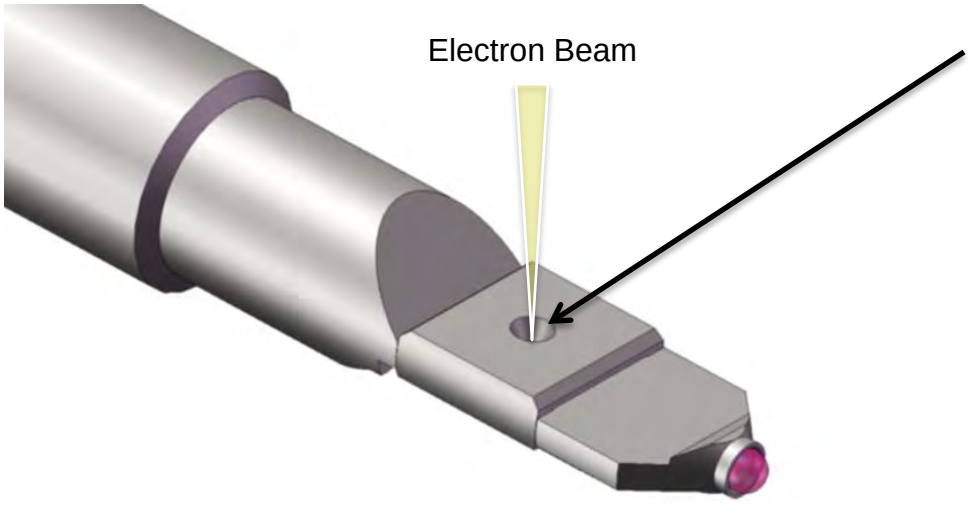
- Electrochemical evaluation of micro-battery

  Description: μm-sized battery electrodes have been joined to the biasing contacts on the Si microchips.

  Status: Preliminary electrochemistry testing has demonstrated the feasibility of *in-situ* electrochemical studies using the microchip platform within a TEM.

Technical Accomplishments-Holder Development

- An *in-situ* TEM holder capable of flowing and containing liquid electrolytes between silicon microchips with silicon nitride membranes has been developed.
- This holder allows for the direct TEM imaging of electrodes within a liquid electrolyte. Strategically placed seals ensures liquid does not escape from the holder and into the microscope.
- Biasing contacts patterned on the microchips are interfaced with an external potentiostat for electrochemical testing.



Schematic illustration of the in-situ electrochemical cell TEM holder developed in collaboration with Hummingbird Scientific for the Hitachi HF-3300 S/TEM at ORNL.

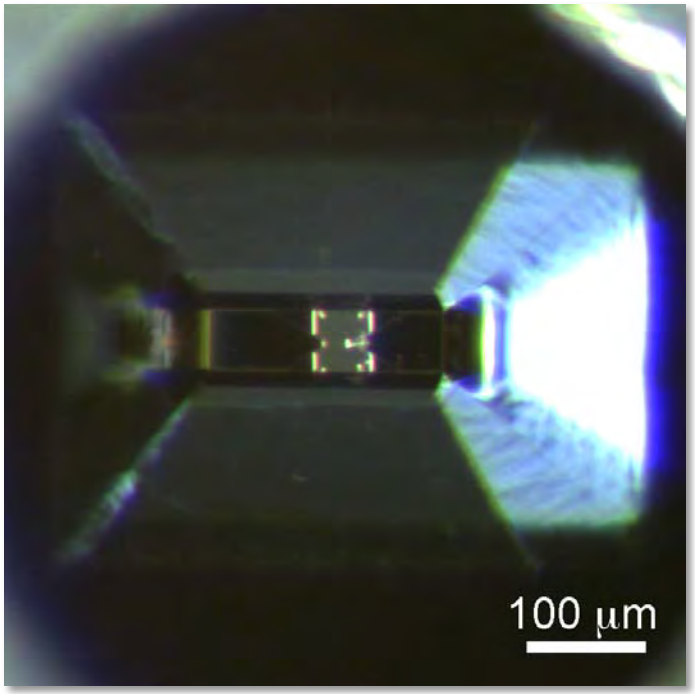
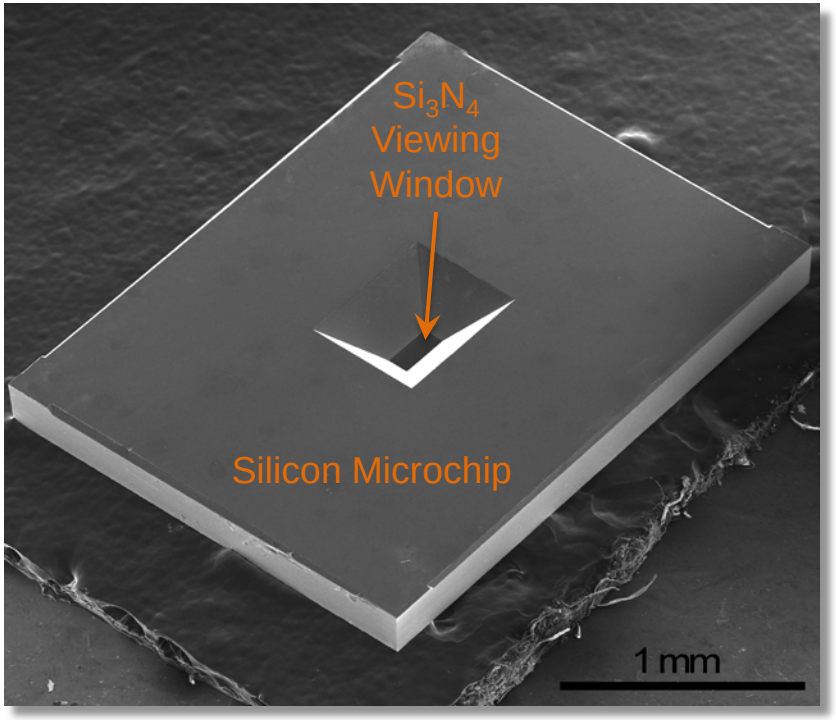


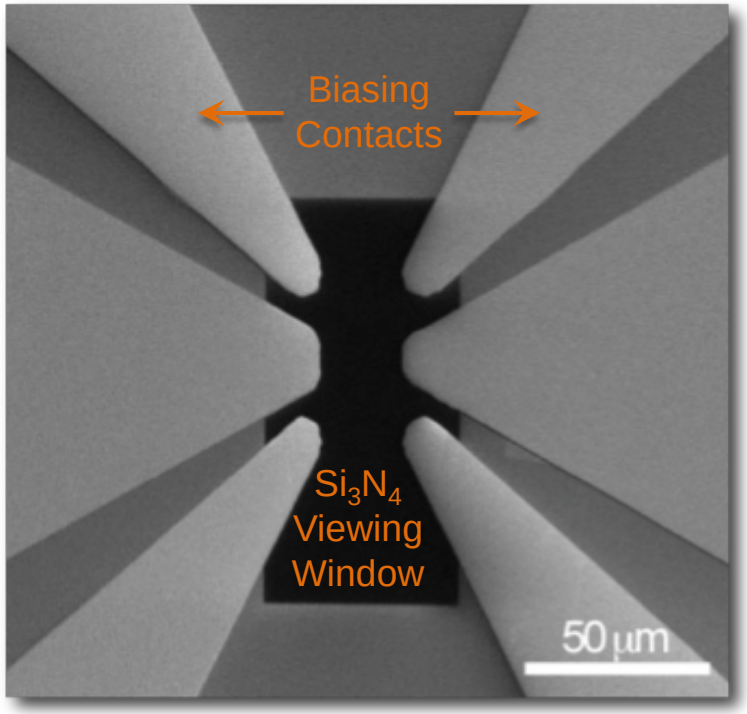
Image of the silicon microchips through the viewing windows within the in-situ TEM holder.

Technical Accomplishments-Biasing Microchip Fabrication

- Silicon microchips with electron-transparent SiN membranes and biasing contacts have been fabricated using standard lithographic patterning, metal deposition, and wet-etching procedures.



SEM image from the backside of a silicon microchip showing the etched region to the silicon nitride membrane

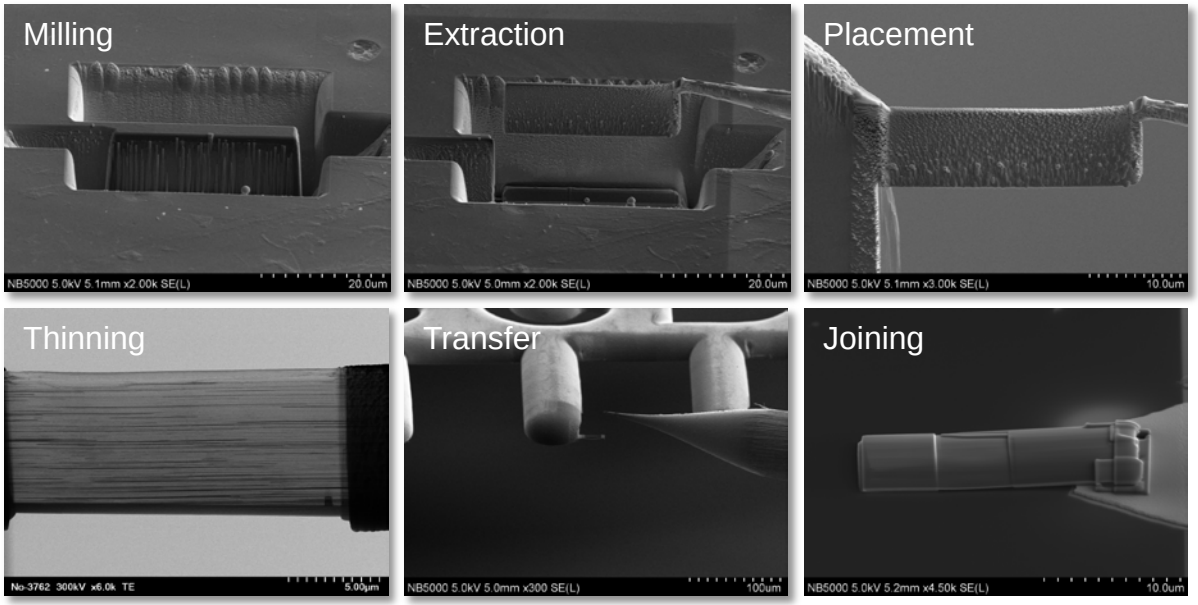


SEM image from the membrane side of the silicon microchip showing deposited metal biasing contacts used to attach battery electrodes for in-situ electrochemical testing within a TEM.

Technical Accomplishments-Microbattery Fabrication

- Procedure to create a working “Micro-Battery” on the Si microchips:
  - A focused ion beam (FIB) instrument was used for site-specific milling of battery electrodes from bulk HOPG (Anode) and sintered $LiCoO_2$ (Cathode) particles → μm-scaled electrodes.
  - Electrodes were then placed on the biasing contacts using a micromanipulator and joined by ion beam deposition with carbon → electrochemical cell.

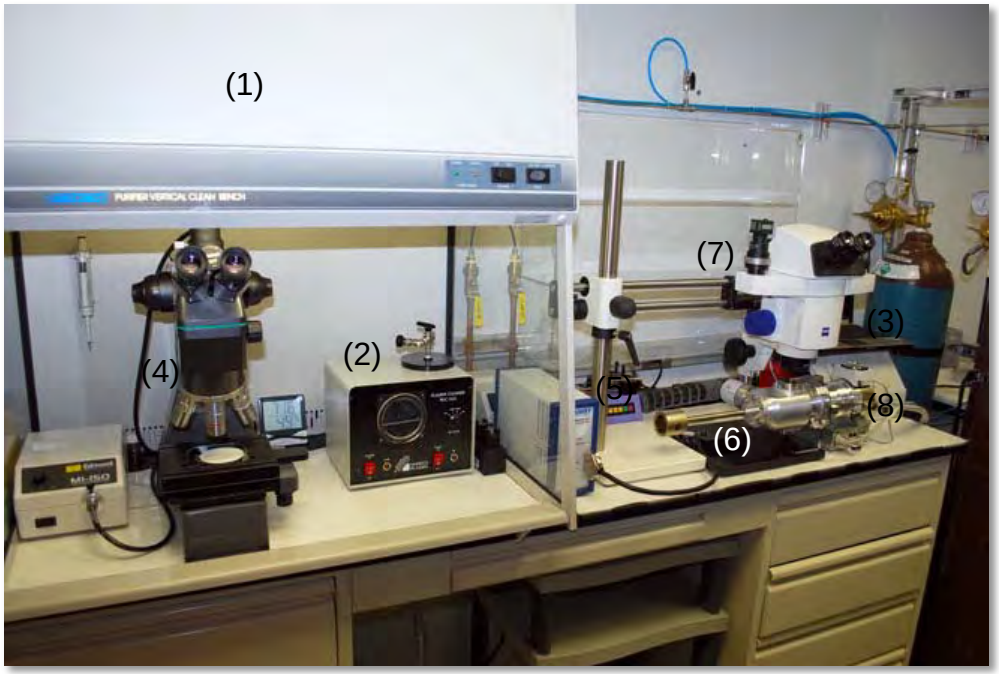
ORNL’s Hitachi NB5000 FIB-SEM



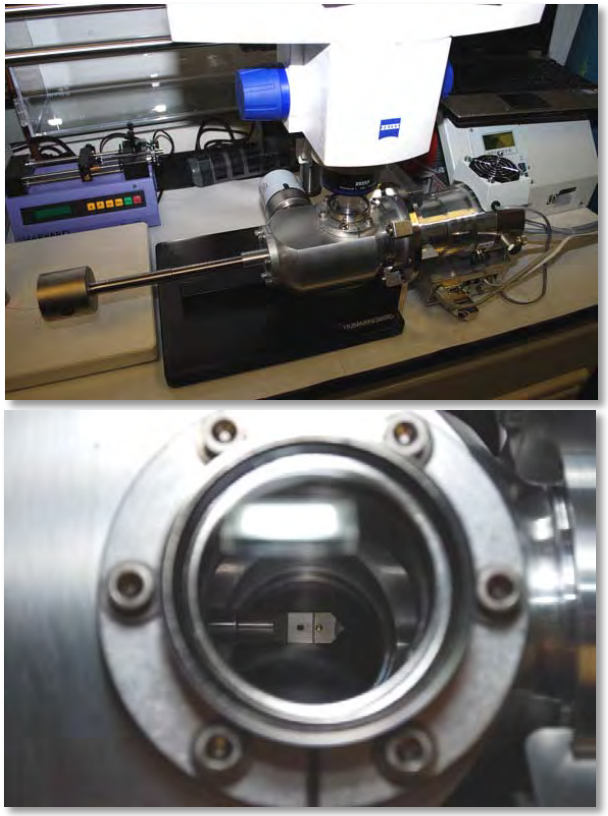
Series of SEM micrographs showing the steps used to extract battery electrodes from bulk specimens, thinning, and transfer to biasing contacts on Si microchips using the FIB instrument

Lab Equipment and Experimental Setup

- An *in-situ* TEM specimen preparation lab has been assembled which uses specialized equipment for cleaning, inspecting, handling, and assembling the components necessary for the *in-situ* TEM research activities



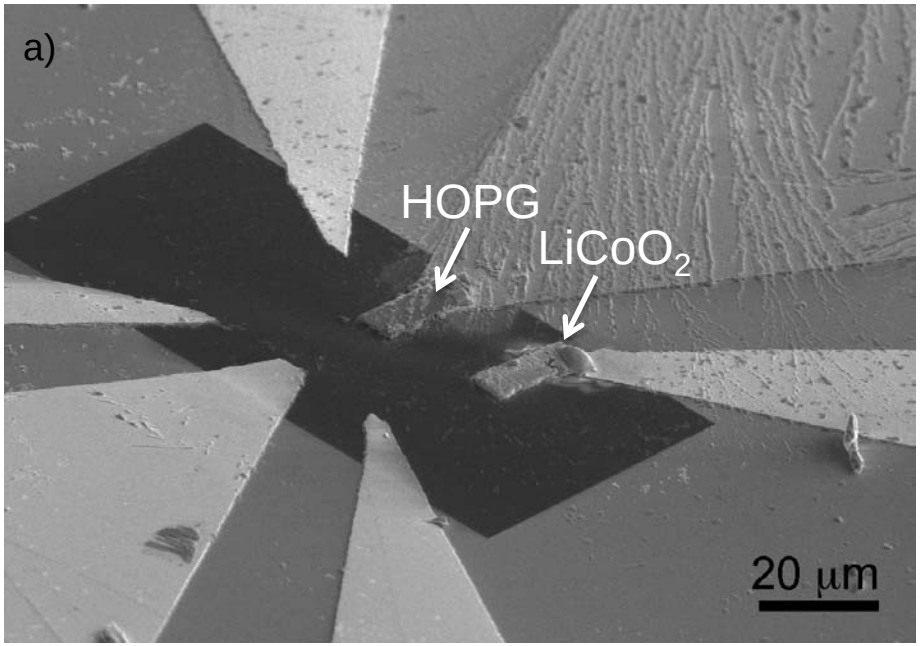
Specimen preparation equipment/workstation:

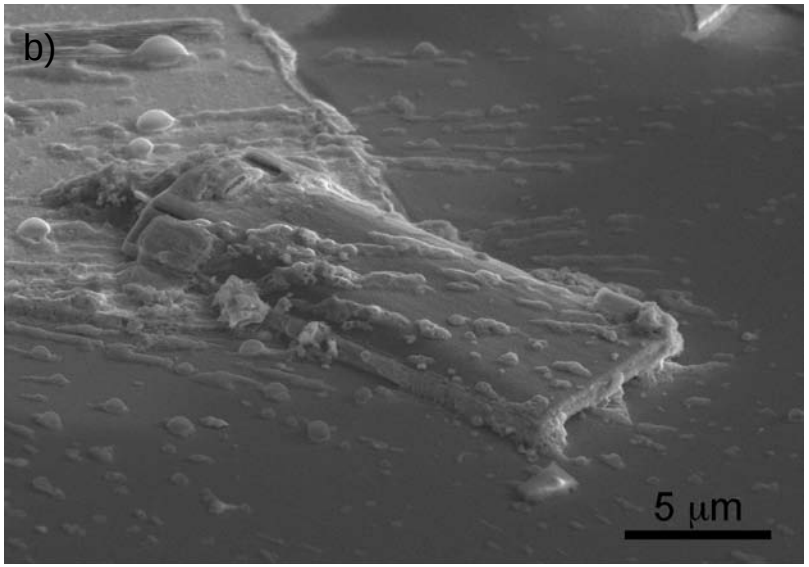


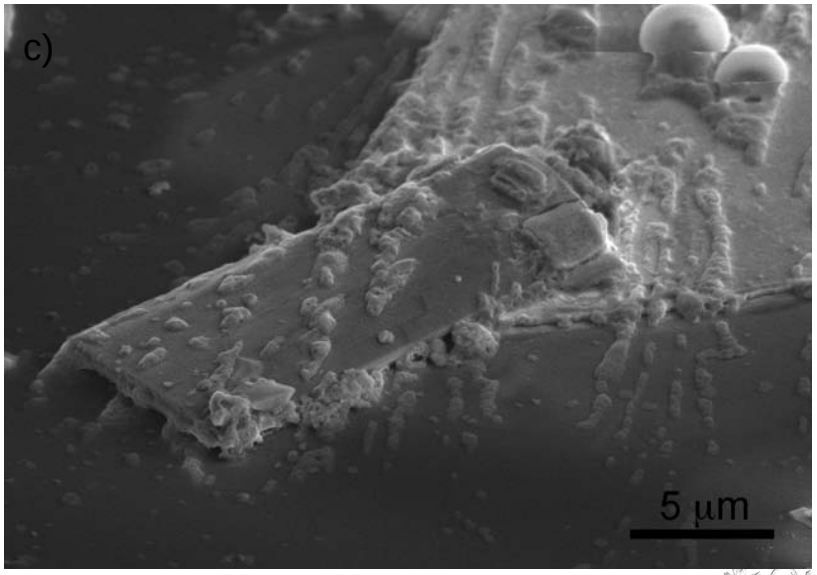
In-situ TEM holder within dry pumping station which is used to check for electrolyte leakage under vacuum before inserting into the electron microscope.

SEI Formation on Graphite Electrode

- To experimentally validate the use of *in-situ* electrochemical cell TEM holder, chronoamperometry (2-4V in 0.25V steps) was used to charge a micro-battery
  - HOPG anode
  - $LiCoO_2$ cathode
  - $LiClO_4$ in EC:DEC electrolyte



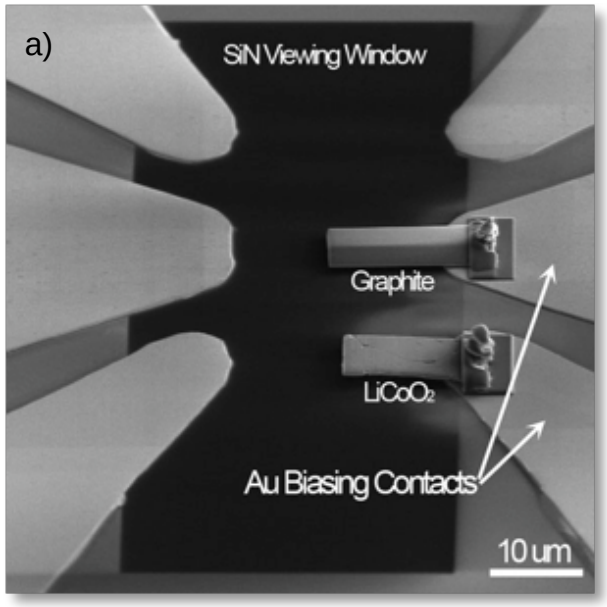


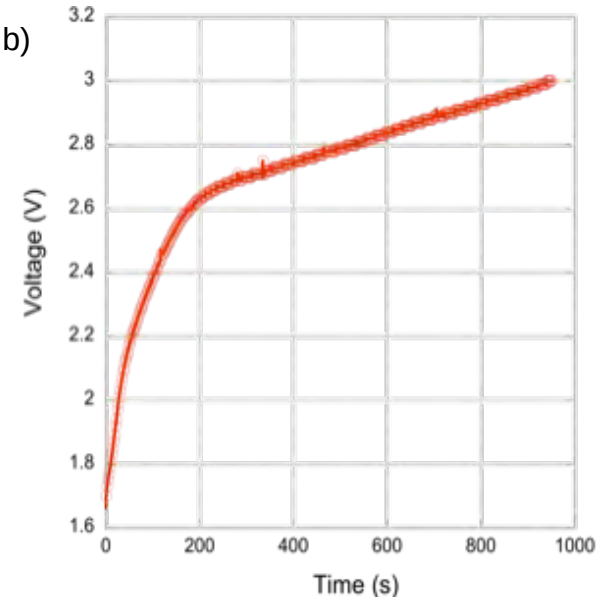


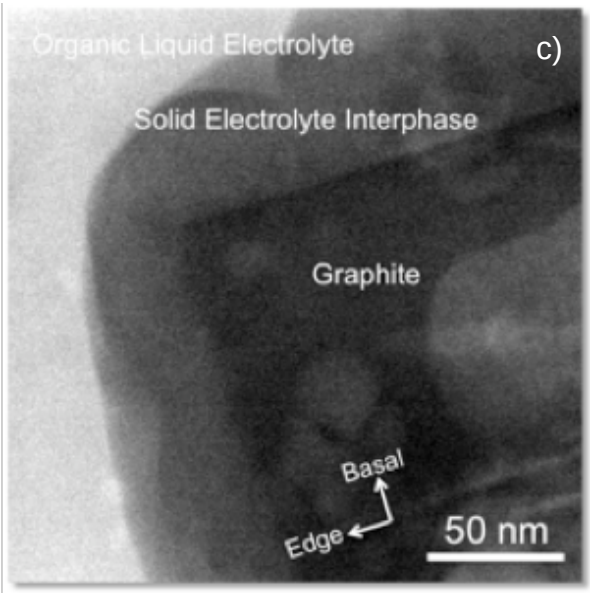
SEM images of a) biasing microchip following testing and b,c) SEI formation on the surface of the HOPG.

In-situ TEM of SEI Formation on Graphite Electrode

- Similar experiments have been performed *within* the Hitachi HF-3300 S/TEM to show the formation of the SEI *in-situ.*







a) FIB-prepared "on-chip" micro-battery with HOPG anode and $LiCoO_2$ cathode
b) charging curve of the micro-battery in an organic electrolyte (1M $LiClO_4$ in EC:DEC) during in-situ TEM electrochemistry
c) individual frame acquired during in-situ electrochemistry TEM showing SEI formed on graphite anode

Future Research

Holder Development and Validation

- Validate small scale electrochemical testing methods developed within this program to lab standard methods and results.
- Optimize FIB specimen preparation techniques and explore alternative methods of joining battery electrodes to biasing contacts on microchips.

Collaborations

- *In-situ* TEM studies on SEI growth mechanisms using graphite anodes and layered metal oxide cathodes. (FIRST EFRC)
- Compare *in-situ* observations of SEI formation with atomistic simulations of electrolyte decomposition mechanisms. (FIRST EFRC)
- Perform *in-situ* TEM studies on electrode intercalation and degradation mechanisms
- Explore the use of combining electron energy loss spectroscopy with *in-situ* experiments for analytical analysis of SEI chemistry. (ORNL)
- Extend *in-situ* studies for next generation high voltage electrode materials, electrolytes, and electrolyte additives to elucidate their role on SEI formation and stability. (UT Austin)
- Perform *in-situ* electron microscopy characterization in support of basic and applied electrode/electrolyte development programs. (ORNL)

Collaboration/Coordination with Other Institutions

- A cross-disciplinary team of researchers at ORNL have been utilizing this technology to synergistically accelerate the development of more durable and efficient Li-ion batteries through materials research and computational materials modeling efforts within the Energy Frontier Research Center (EFRC) FIRST (Fluid Interface Reactions, Structures, and Transport) Center at ORNL

- The research and development activities summarized here will be available for wide-spread collaborative use with access to both staff expertise and this unique instrumentation, by university, national laboratory, and industrial partners for the characterization of current, state-of-the-art battery electrode materials during FY11 and FY12 via the SHaRE program at ORNL, which is sponsored by the Office of Basic Energy Sciences, US Department of Energy.

Publications/Presentations

- RR Unocic, LA Adamczyk, NJ Dudney, DH Alsem, NJ Salmon, KL More, *"In-situ TEM Characterization of the SEI in Li-ion Batteries,"* Fall Electrochemical Society Meeting, Las Vegas, NV, Oct 10-15, 2010. (Poster Presentation)

- RR Unocic, LA Adamczyk, NJ Dudney, DH Alsem, NJ Salmon, KL More, *"Use of In-situ TEM Characterization to Probe Electrochemical Processes in Li-ion Batteries,"* MRS, San Francisco, CA, April 25-29, 2011. (Oral Presentation)

- RR Unocic, LA Adamczyk, NJ Dudney, DH Alsem, NJ Salmon, KL More, *"In-situ TEM Characterization of Electrochemical Processes in Energy Storage Systems,"* Microscopy and Microanalysis Annual Meeting, Nashville, TN, Aug 7-11. (Conference Paper Submitted/Oral Presentation)

Summary

- An advanced *in-situ* electrochemical cell TEM holder has been developed to probe electrochemical processes in electrical energy storage systems.

- Silicon microchips with electron transparent SiN windows have been fabricated and have served as a platform for performing electrochemistry experiments within a high-resolution TEM.

- Micro-batteries have been constructed on the silicon microchip platform using a FIB-SEM, where battery electrodes are extracted from bulk specimens and placed on the biasing chip contact pads.

- Initial research has demonstrated the feasibility of conducting *in-situ* electrochemistry experiments using this device, where the formation of the SEI on graphite electrodes has been studied *in-situ*.

- Collaborations with other research institution and industrial partners are currently being established, which will accelerate the versatility of this technology and aide in research development of next generation electrodes and electrolytes for the EES community.

Acknowledgements

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