Project ID: ES095

# In Situ Electron Microscopy of Electrical Energy Storage Materials

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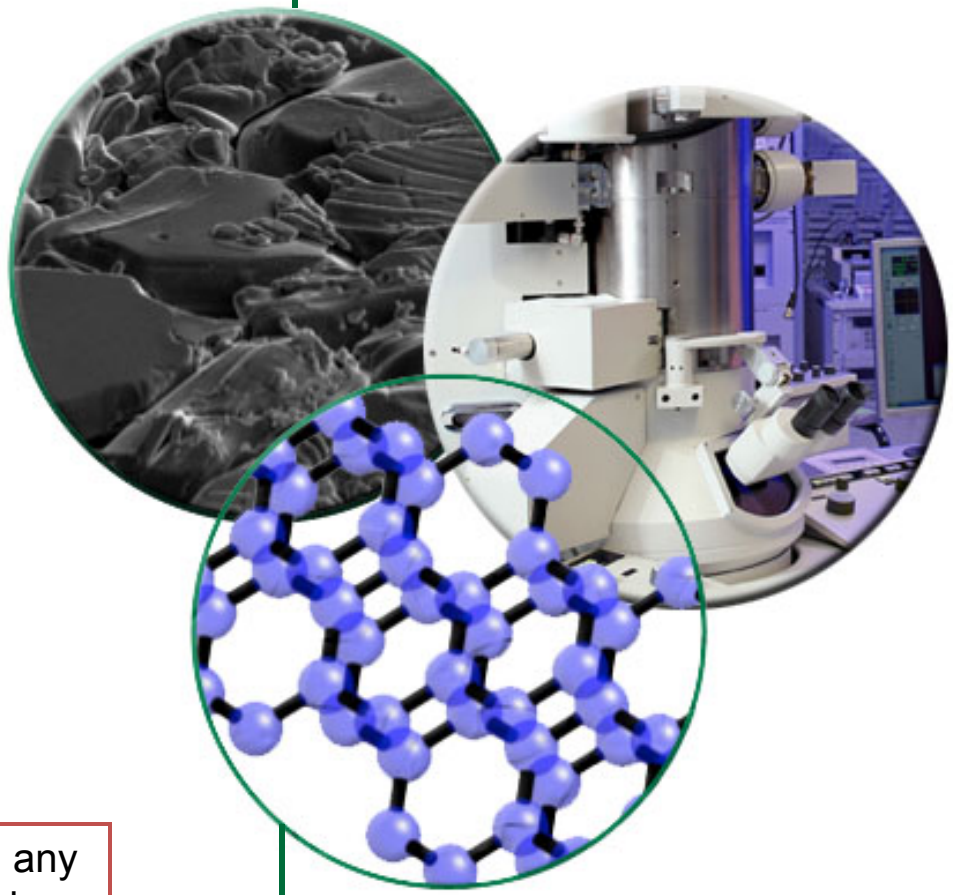

Annual Merit Review
DOE Vehicle Technologies Program
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U.S. DEPARTMENT OF ENERGY

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# Overview

## Timeline

- Project Start: January 2010
- Project End: Sept 2013
- Percent Complete: 90%

## Technical Barriers

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

## Budget

- Total Project Funding: 100% DOE
- Funding for FY10: $250k
- Funding for FY11: $250k
- Funding for FY12: $300k
- Funding for FY13: $300k

## Partners/Collaborators

- General Motors Global R&D
  - Drs Xincheng Xiao and Zhongyi Liu
- University of Texas Austin
  - Prof. A. Manthiram
- ORNL FIRST EFRC
  - Dr. David Wesolowski
- Argonne National Laboratory
  - Dr. Daniel Abraham
- ORNL BES ShaRE User Facility

# Objectives and Relevance

- **Objectives**
  - To understand nm-scaled microstructural and microchemical changes occurring within energy storage materials using in situ electron microscopy.
  - To develop, implement, and validate in situ electrochemical fluid cell microscopy, an **in situ transmission electron microscopy (TEM)-based characterization method,** to perform controlled and **quantitative** nanoscale electrochemistry experiments.


**Hitachi HF3300 S/TEM at ORNL for in situ TEM Characterization**

- **Relevance to Technical Barriers**
  - Understand fundamental issues related to performance, capacity loss, electrode degradation mechanisms and safety.
  - Specific technical barriers addressed in this program:
    - SEI Formation Mechanisms (Role of Electrolytes and Electrolyte Additives)
    - Electrode Degradation Mechanisms and Capacity Fading Mechanisms of Relevant High Voltage Cathodes
    - Electrolyte Stability (Reducing and Oxidizing Potentials)
    - Li Dendrite Formation

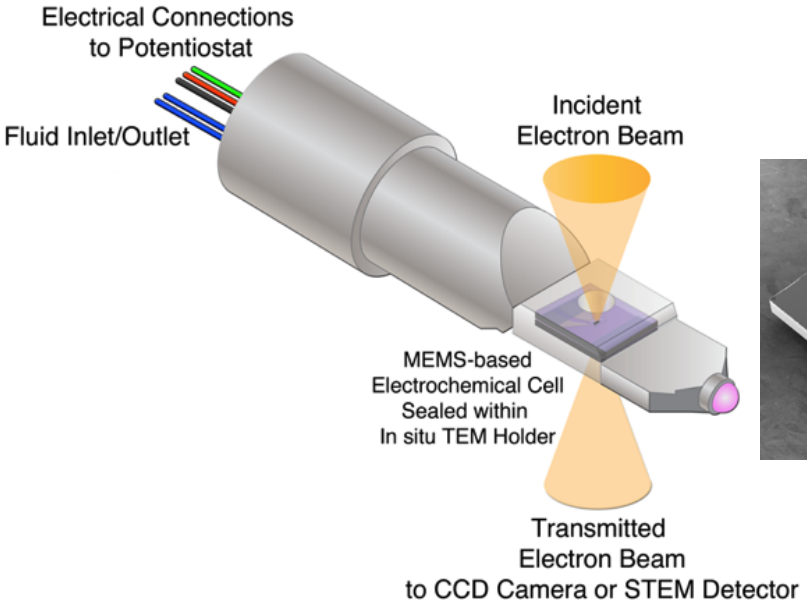
# Milestones FY13

| Description: | Target Deadline: | Status: |
|---|---|---|
| **Milestone 1:** Electrolyte decomposition mechanisms and kinetics of SEI on model graphite anodes | (May 2013) | **Completed** |
| **Milestone 2:** Electrolyte stability at high voltage cathodes with different electrolytes. | (May 2013) | **On Schedule** |
| **Milestone 3:** Investigate electrode degradation mechanisms in active electrodes. | (May 2013) | **On Schedule** |
| **Milestone 4:** Evaluate the usefulness of aberration-corrected STEM/EELS/EDS for combined in situ TEM characterization and chemical analysis. | (May 2013) | **Completed** |
| **Milestone 5:** Investigate dendrite formation mechanisms | (August 2013) | **On Schedule** |
| **Milestone 6:** Technique development: Design, develop and optimize 'on-chip' 2- and 3-electrode biasing microchips. | (August 2013) | **On Schedule** |

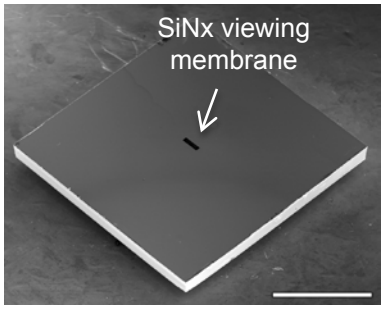
# Technical Approach and Strategy

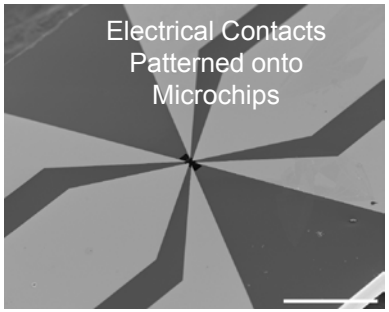
- Approach: In situ Electrochemical Liquid Cell Microscopy
  - MEM- based microchips are a platform for sealing electrodes and electrolyte between SiN membranes
  - Quantitative electrochemical measurements are performed
  - In situ characterization of electrochemical reactions

    **(via (S)TEM imaging/diffraction/spectroscopy)**
  - **No other method allows for the direct characterization of electrochemical process dynamics within native electrolyte environment under realistic testing conditions and while imaging at high spatial resolution with site-specific chemical analysis**



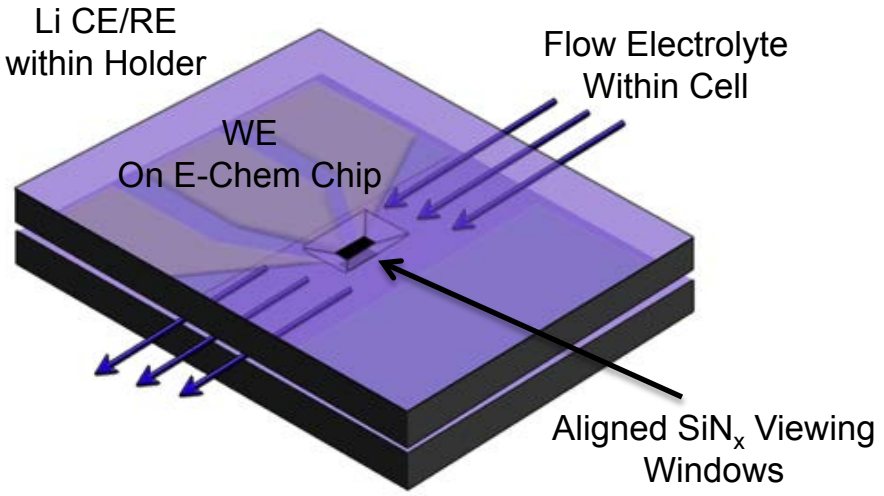

**M**icro**E**lectro**M**echanical**S**ystems (MEMS)
Microchip Platforms for In situ Electrochemistry

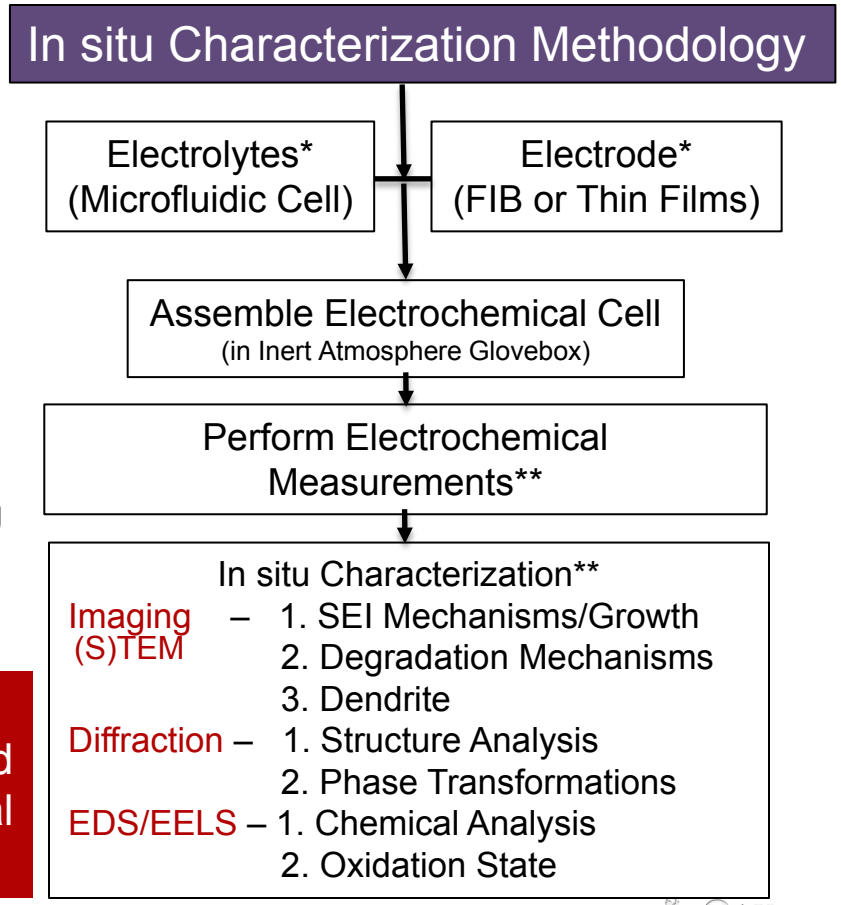



# Technical Approach and Strategy

- In situ Electrochemical Test Method: Energy Storage Materials
  - Electrochemical measurements in half-cell configurations, metallic Li as counter (CE) and reference (RE) electrode
  - Working electrode is electrode material (e.g. graphite, $LiMn_2O_4$, $LiMn_{1.5}Ni_{0.5}O_4$, Li-rich NMC, etc).



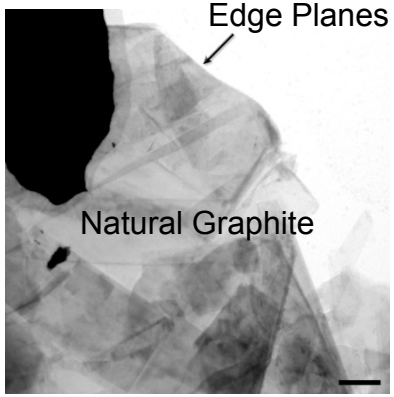

* Materials relevant to VT program
**Unique in situ characterization method developed in this program (FY10-FY12) to study fundamental issues limiting Li and Na ion batteries

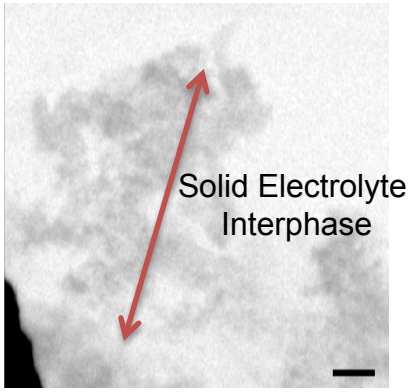
# Technical Accomplishments and Progress

- Executive Summary of Technical Accomplishments
  - Milestone 1: Solid Electrolyte Interphase (SEI)
    - Completed in depth study of in situ SEI formation mechanisms and growth kinetics
  - Milestone 2: Electrolyte Stability for High Voltage Cathodes
    - Developed method to deposit thin film electrodes on MEMS-based E-chips
  - Milestone 3: Electrode Degradation Mechanisms
    - Conducted In situ Investigation of intercalated induced fracture of silicon anodes
  - Milestone 4: Combining Analytical Electron Microscopy Methods
    - Demonstrated feasibility of EELS and EDS in for in situ chemical analysis
  - Milestone 5: Dendrite Formation
    - Conducted preliminary experiments of dendrite formation mechanisms and kinetics
  - Milestone 6: MEMS microchip development
    - Designed future MEMS based E-Chip platforms

# First Direct Visualization of SEI Formation under realistic conditions

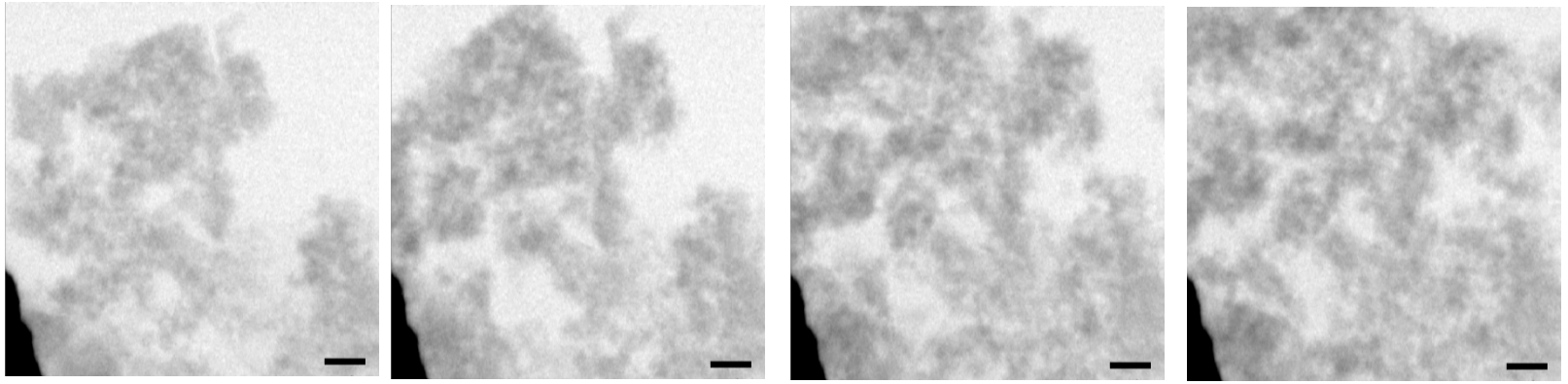
- System is Graphite vs Li/Li$^+$ and results reveal:
  - Direct observation of SEI growth on natural graphite anode during cell discharge
  - **1M $LiPF_6$ EC:DEC Electroyte**
  - Structure of SEI comprised of nanocrystalline species and has a porous morphology.
  - There is sufficient resolution to image SEI within the liquid electrolyte and measure growth rate.




First in situ TEM study of SEI growth mechanisms and kinetics using relevant electrode/electrolyte system and under realistic testing conditions.*

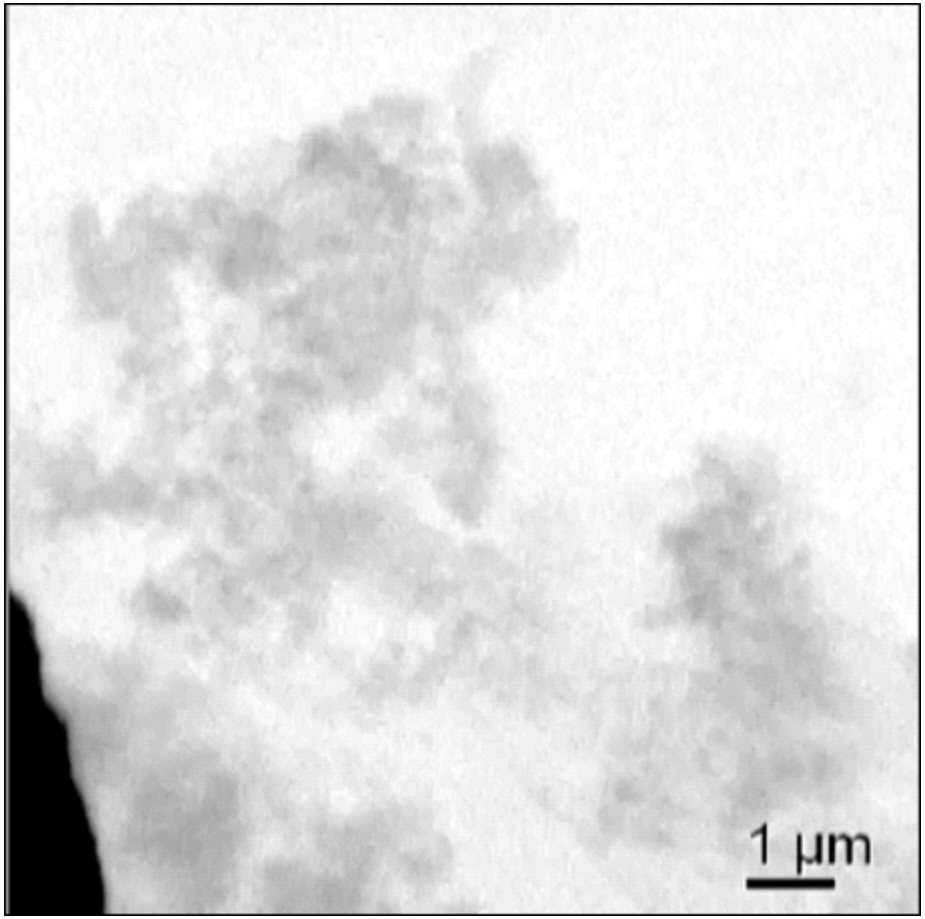
**Direct Imaging of Electrochemical Reactions in Li-ion Batteries.** R.R. Unocic et. al., submitted.



Time-lapsed TEM images of SEI Growth at Constant Cell Potential (1.25V)

*** In situ SEI studies is crucial for fundamentally understanding irreversible capacity loss, capacity fading, and electrode cyclability issues.**

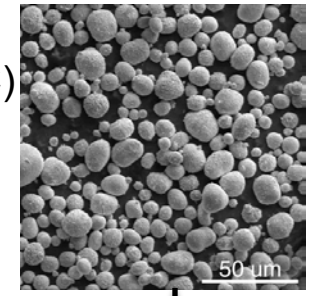
# In situ Video of SEI Growth in Relevant Systems

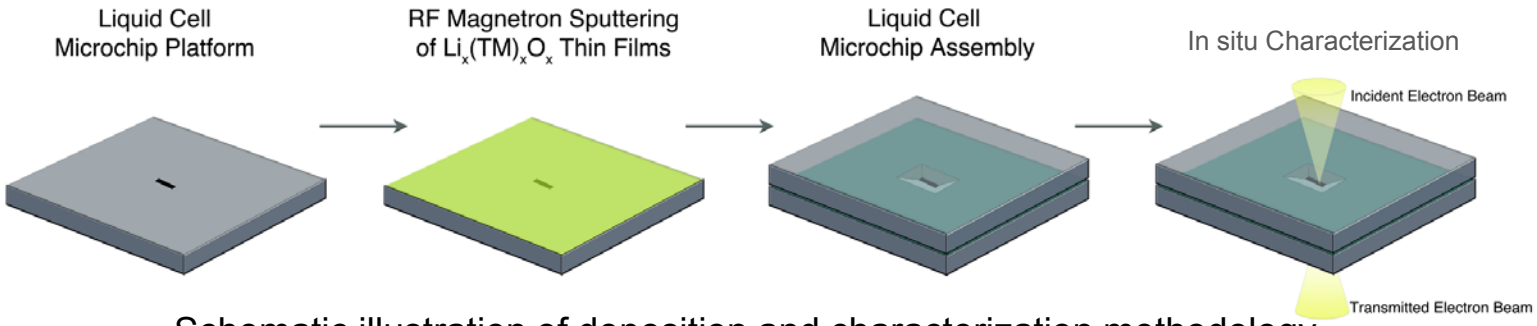



Experimental Details:
(Graphite vs $Li/Li^+$) within 1M $LiPF_6$ EC:DEC Electrolyte
Video sequence acquired during potential hold at 1.25V

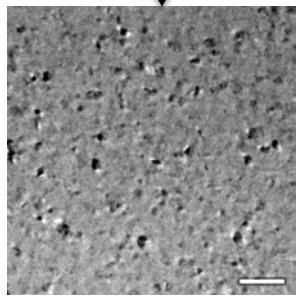
# Electrode Thin Films as a Model System

- Thin film electrodes are model systems for in situ TEM experiments
  - Major Advantages:
    - Sputtering target directly from electrode material of interest (e.g. Li-rich NMC)
    - Chemical composition can be controlled
    - Electrode thin films directly deposited on E-Chem Chips




Schematic illustration of deposition and characterization methodology

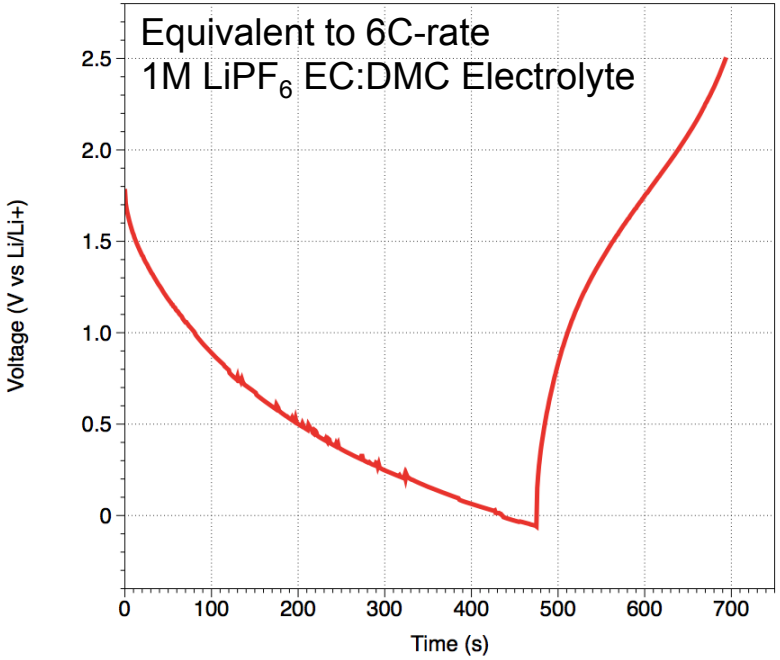


Nanocrystalline Grains

Current Inventory of Thin Film Electrode Materials Successfully Deposited on E-Chem Chips:
Cathodes: **Li-Rich NMC, $LiMn_{1.5}Ni_{0.5}O_4$, $LiMn_2O_4$**
Anodes: **$Li_4Ti_5O_{12}$, Cu-Sb, Cu-Sn**
Note: Coordinating within VT Program for relevant systems to investigate (ORNL, ANL, UT Austin)

# Charge-Discharge Behavior of Cu-Sb Anodes within In Situ Holder

- **Key Question:** **Can the thin film electrodes deposited on the E-Chem Chips be cycled?**
- Results show that we can conduct constant current charge-discharge experiments (and vary C-rate)




The use of thin film electrodes opens a new pathway to investigate a wide range of materials systems of interest within the VT Program

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Results demonstrate feasibility to conduct controlled electrochemical charge-discharge cycling experiments

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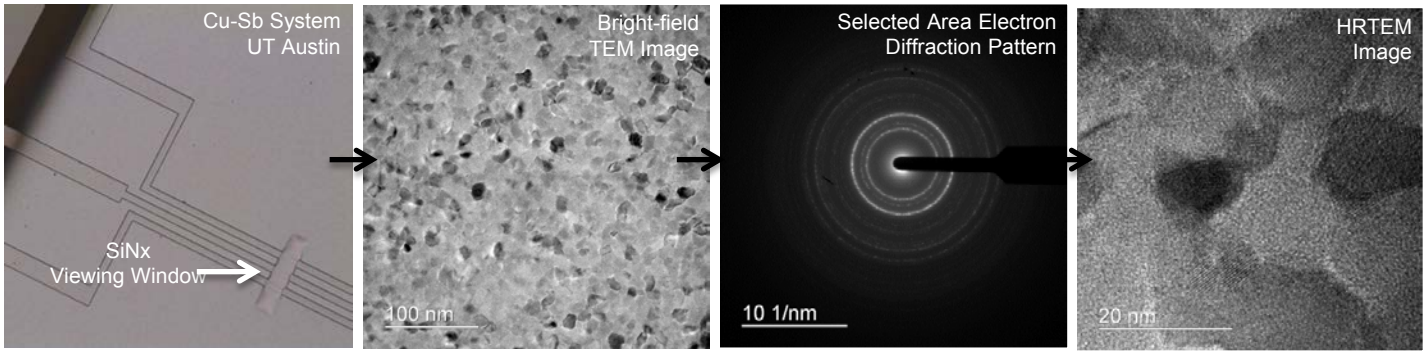
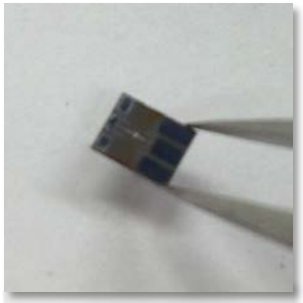
Rate performance and cycle-life can be assessed while structural and chemical changes can be simultaneously characterized



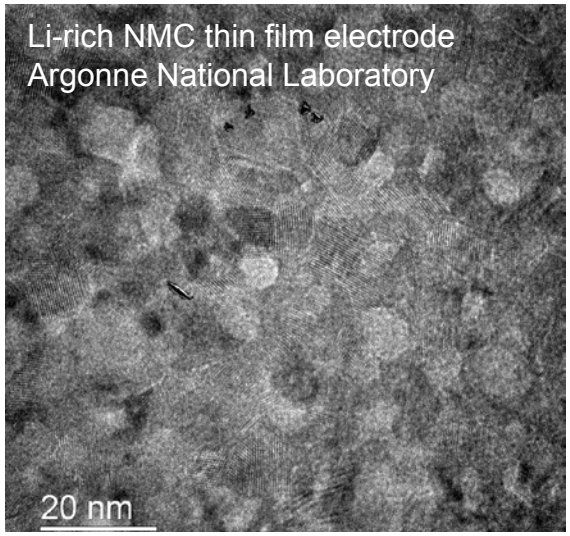

Promising means for in situ characterization on varying length scales

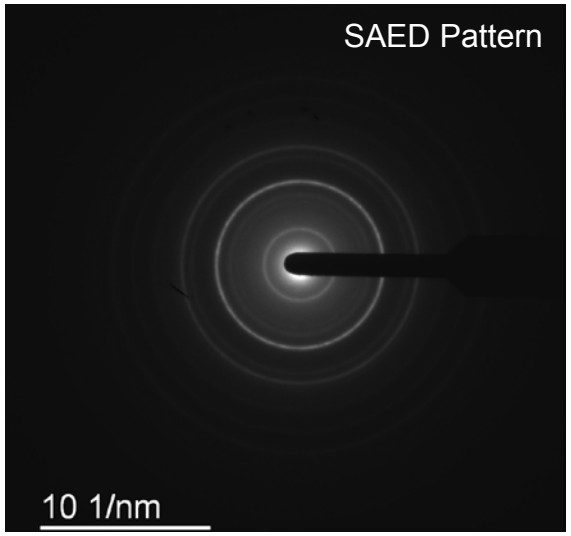
# New Insight into Degradation Mechanisms in High Voltage Cathodes

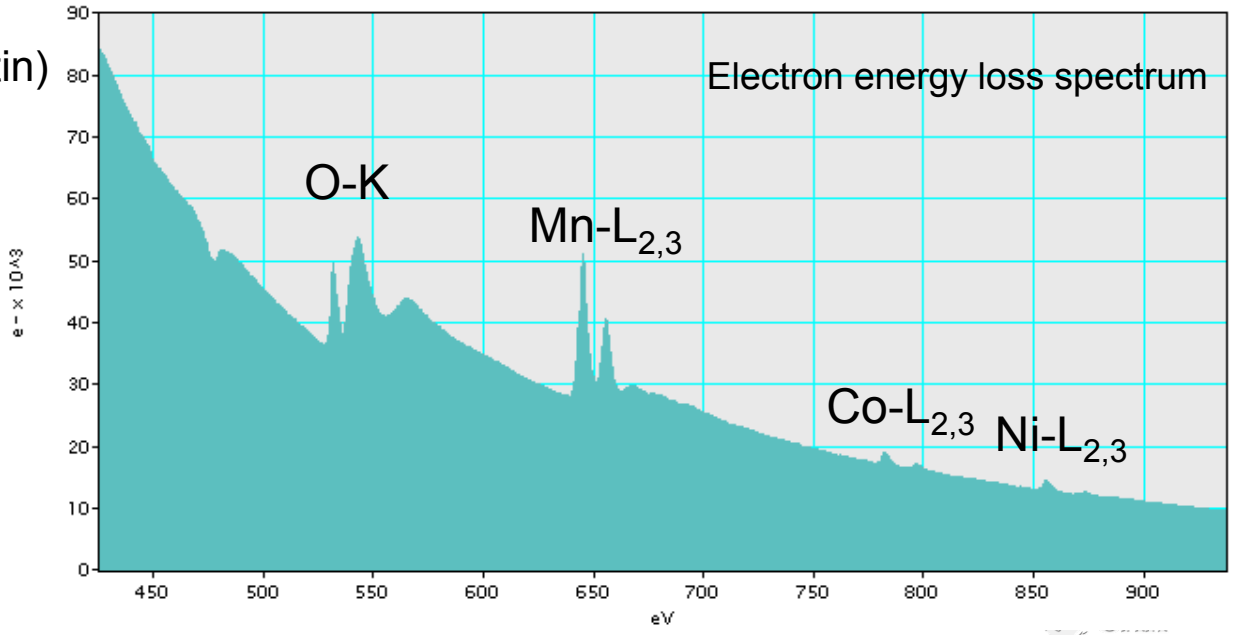
- **High Voltage Cathodes:**
  - Can we study phase transformations? Layered/Spinel
  - Can we image electrolyte stability at High Voltage (5V) in oxidizing conditions?
- **Results:**
  - Materials
    - Li-rich NMC (ANL)
    - $LiMn_{1.5}Ni_{0.5}O_4$ (UT Austin)



Electrode thin films of High Voltage Cathode Materials successfully deposited on MEMS E-Chem Chips.
*In situ characterization is in progress.*

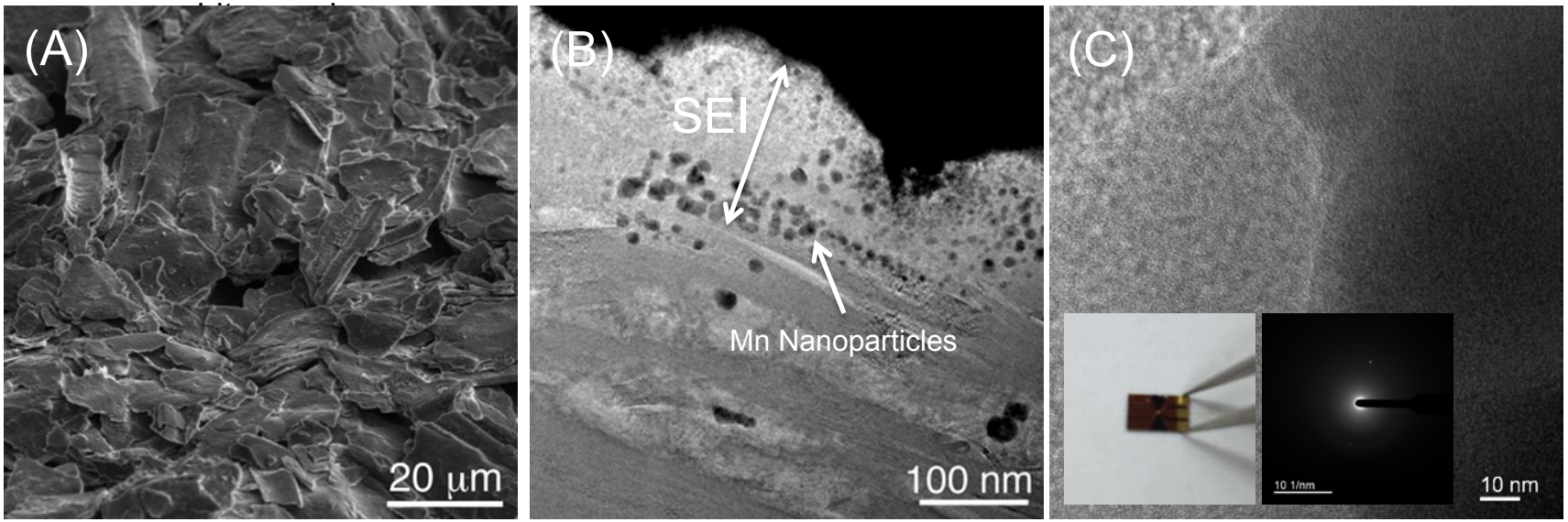


# Understanding Capacity Fading Issues in High Voltage Cathodes

- Mn dissolution linked to capacity fade mechanism in High Voltage Cathodes
  - Collaboration with General Motors Global R&D:
    - Cycled graphite anode and LMO cathode.
    - Post-mortem SEM/FIB and STEM/HRTEM analysis shows Mn nanoparticles within SEI on

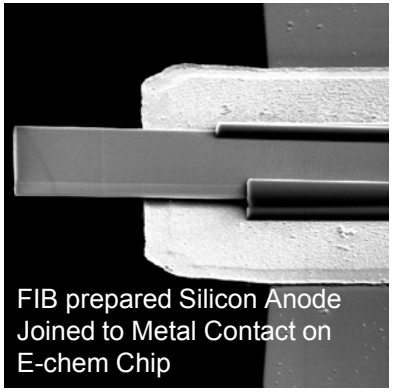


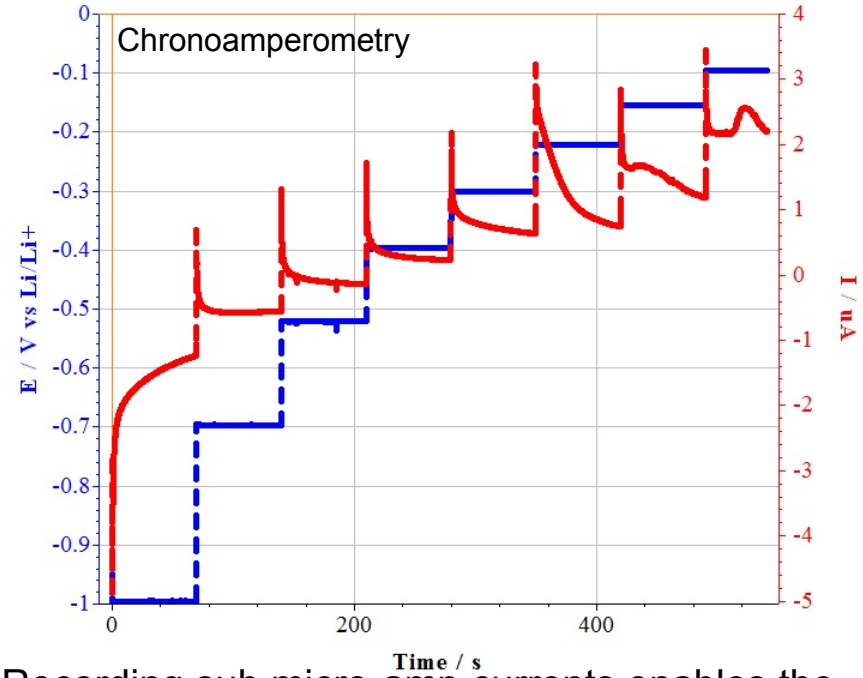

(A) SEM image of graphite anode material extracted from a cycle cell revealing SEI on the electrode surface and (B) TEM Image from FIB X-section showing Mn nanoparticles with SEI segregating locally at the SEI/graphite interface. (C) GM developed method to deposit graphite thin film electrodes on MEMS-based E-Chem Chips. Used as a model substrate for in situ Mn dissolution study.

SEI Characterization Study: Facilitated by Hitachi Vacuum Transfer/Air-Tight Argon Glovebox➔FIB/SEM➔(S)TEM Transfer System (Available at ORNL)

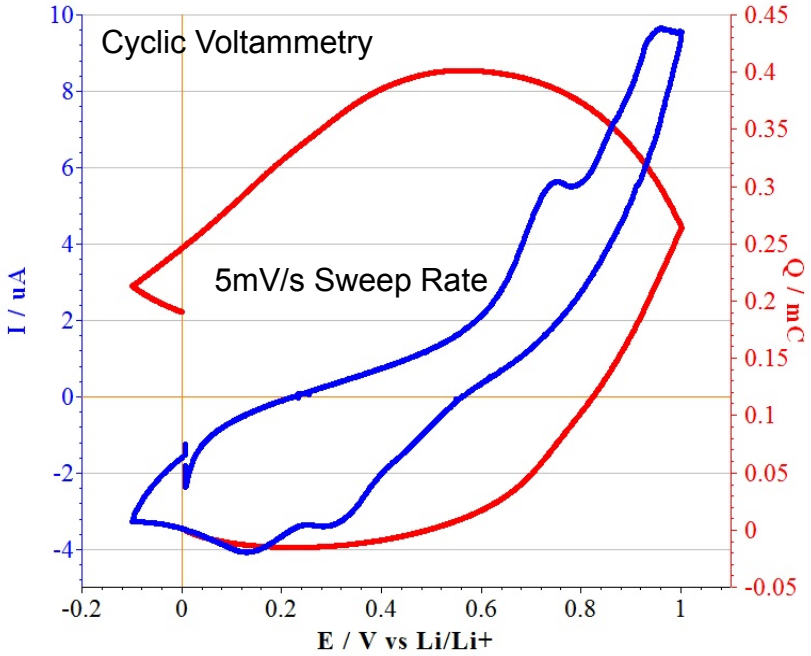
# Continued Development is Providing Quantitative Electrochemical Measurement Results

- **Evaluating In situ System for Quantitative Electrochemistry**
  - Working Electrode: FIB prepared Micron Sized Silicon Anode
  - Li Counter/Reference integrated into tip of TEM holder
  - Results demonstrate feasibility for in situ nanoscale electrochemical measurements



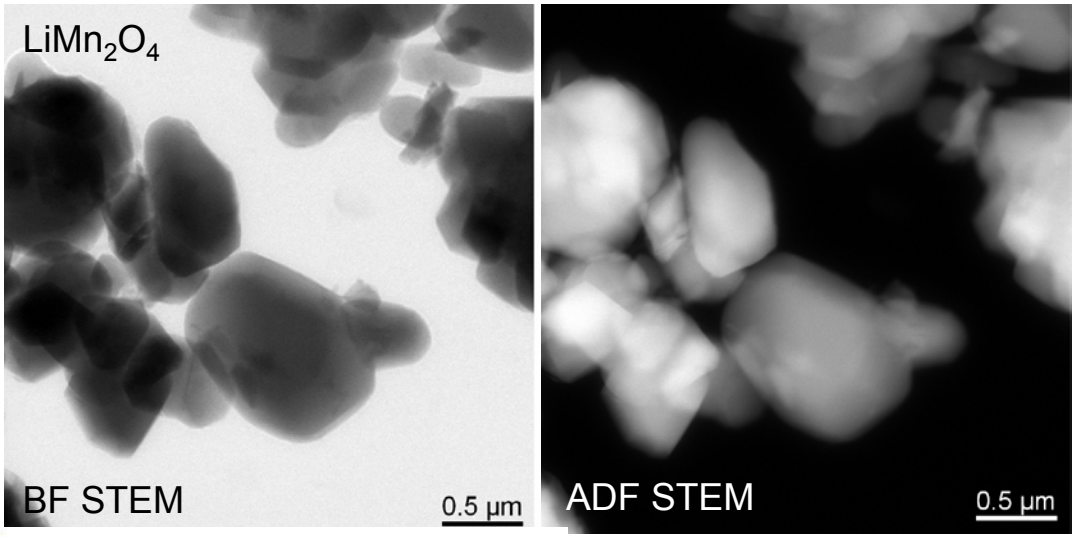

Recording sub micro-amp currents enables the counting of Li atoms into the Si anode along side TEM images of anode swelling and SEI formation

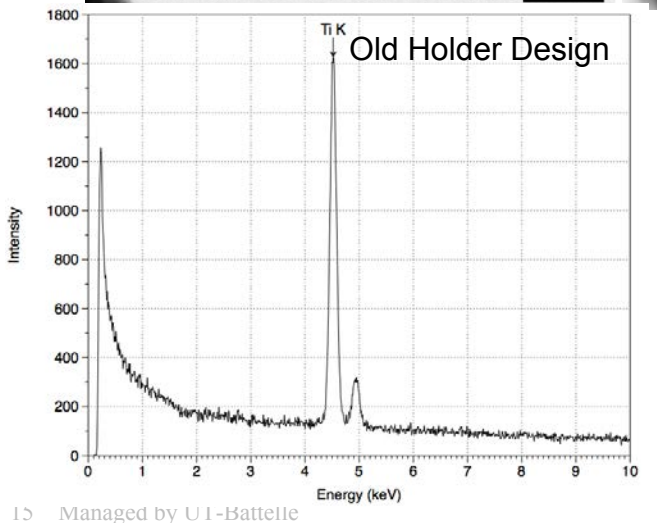


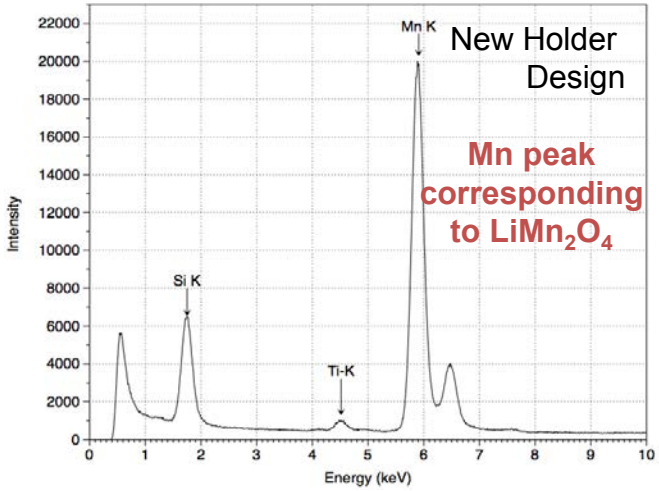

Holder integrated counter/reference minimizes IR loss for better cell control – mimics bench-top cell

# New Holder Design Enables EDS Chemical Analysis w/in Liquid Electrolyte

- **Energy Dispersive X-ray Spectroscopy (EDS) and Electron Energy Loss Spectroscopy (EELS):**
  - Analytical methods used for compositional analysis in combination with (S)TEM imaging
  - Relevant for investigating chemical changes during in situ electrochemical cycling experiments



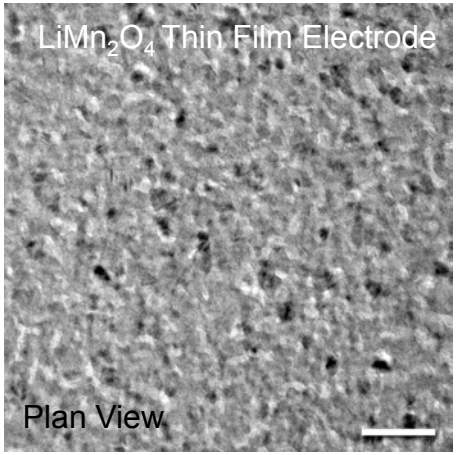



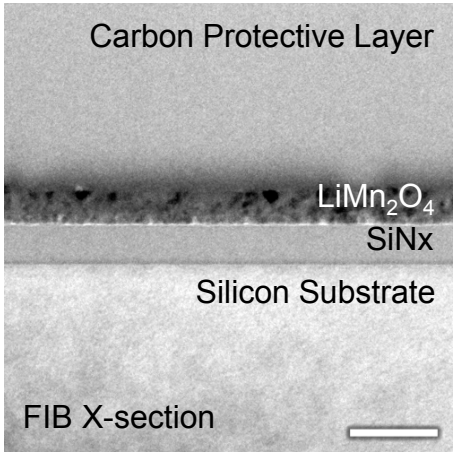

Old Design: X-rays generated within the specimen are effectively blocked by holder components

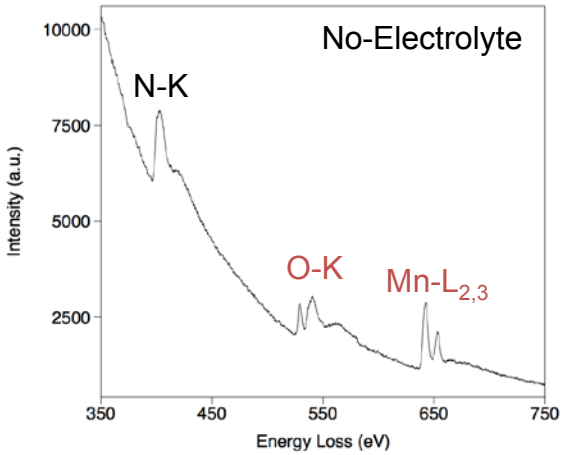
New Design: Improved holder design allows X-rays to escape specimen and reach EDS detector for chemical analysis

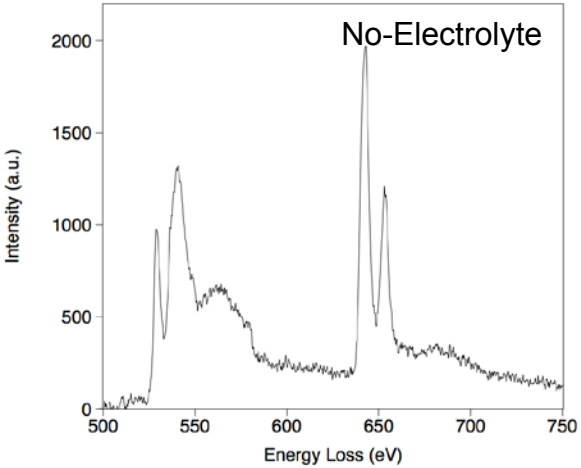
# EELS Chemical Analysis and Oxidation State Determination

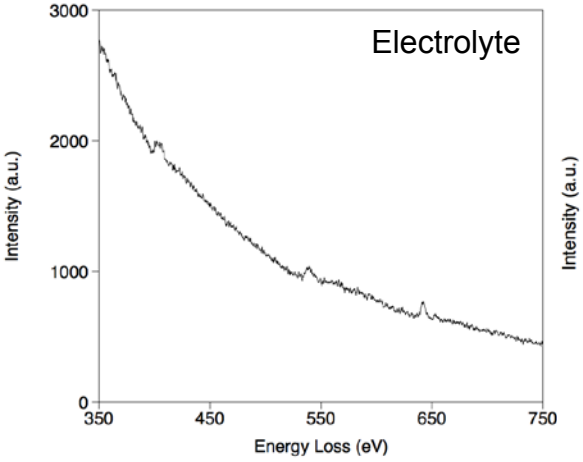
- **Electron Energy Loss Spectroscopy (EELS):**
  - Method used for chemical composition analysis and to directly determine oxidation state.
  - Oxidation state determined through core-loss spectra and transition metal "white-line ratio" method.
  - Relevant for in situ investigations of re-dox changes during electrochemical cycling.

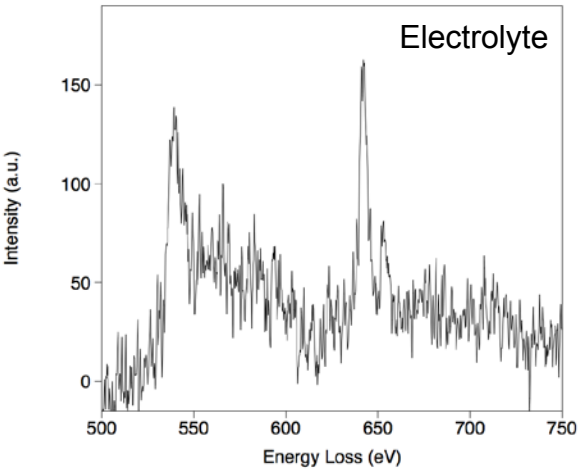


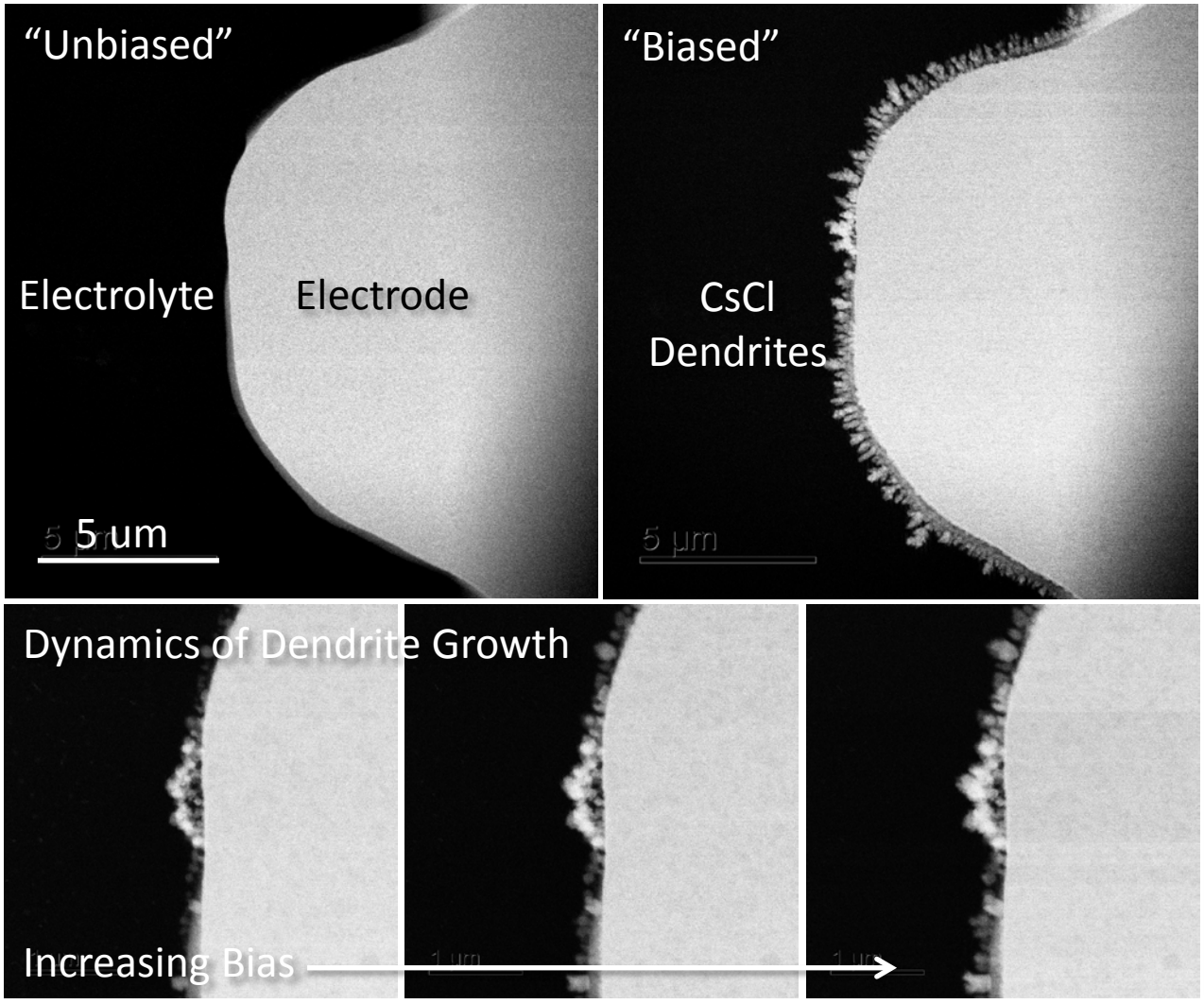




Fourier-Log Deconvolution and Background Subtraction

Improved Signal-to-Noise with thinner membranes and/or thinner electrolyte layer

# In Situ Characterization of Dendrites - Safety

- Real time characterization of dendrite formation mechanisms:




The In situ method developed in this program can directly be used to investigate dendrite nucleation and growth mechanisms in Li-ion batteries

- Relevance:
  - Safety Concern: Internal short circuiting, overheating, electrolyte flammability
  - Better understanding of dendrite formation can lead to new discoveries that will minimize or mitigate dendrite formation during cell operation.
  - Li dendrites at graphite, alloy anodes and/or current collector.

# Collaborations and Coordination

- **UT Austin**
  - Cu-Sb Material (Anodes)
    - Supplied Cu-Sb powder➔sputtering target➔deposited thin film electrodes on MEMS E-Chip
- **Argonne National Laboratory**
  - Li-Rich NMC Material (Cathodes)
    - Supplied Li-Rich NMC ➔sputtering target➔deposited thin film electrodes on MEMS E-Chip
- **General Motors Global R&D**
  - Model thin film graphite electrode, Mn dissolution mechanisms
    - GM developed method to fabricate graphite thin film electrodes on MEMS E-Chip
    - Mn dissolution mechanisms from High V cathodes
- **ORNL FIRST EFRC**
  - SEI Studies, Si Anode Degradation Mechanisms
    - In situ SEI formation mechanisms and growth kinetics on graphite and Si
    - Si electrode fracture mechanisms

# Future Work – FY 13

- **Capacity Fading Issues (High Voltage Cathodes)**
  - Investigate structural changes in situ with electron diffraction and EEL spectroscopy
  - Investigate Mn dissolution mechanisms.
- **Electrode Degradation Mechanisms (Si Anodes)**
  - Continue investigation of Li intercalation mechanisms and electrode degradation and fracture mechanisms
- **Solid Electrolyte Interphase**
  - Conduct further in situ SEI studies on graphite anode with different organic electrolytes
    - $LiPF_6$ in EC:DMC and $LiPF_6$ in PC
    - Other electrolyte and electrolyte additives relevant to VT program
- **Dendrite Formation in Li Metal Anodes**
  - Investigate Li metal dendrites
  - Determine dendrite nucleation mechanisms and quantify growth rates

# Summary

- **Relevance**
  - Advanced in situ characterization microscopy methods play a vital role in understanding the basic electrochemical processes that currently limit battery performance
- **Approach**
  - In situ Electrochemical Liquid Cell Microscopy method developed
  - Apply in situ characterization method to investigate fundamental issues related to performance, capacity loss, electrode degradation mechanisms and safety.
- **Technical Accomplishments and Progress**
  - Investigated SEI formation mechanisms and growth kinetics
  - Demonstrated the quantitative electrochemistry capabilities of system
  - Developed method to deposit thin film electrodes on MEMS-based E-Chem Chips and evaluated the cycling behavior
  - Demonstrated feasibility to conduct in situ chemical analysis with EDS/EELS
- **Future Work**
  - Continue SEI studies with different electrolytes/electrolyte additives
  - Continue work on capacity fading issues related to High Voltage Cathodes
  - Continue studies of Li dendrite growth mechanisms

# Acknowledgements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- General Motors Global Research
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