Investigations of Graphite Current Collectors (part 1) and Metallic Lithium Anodes (part 2)

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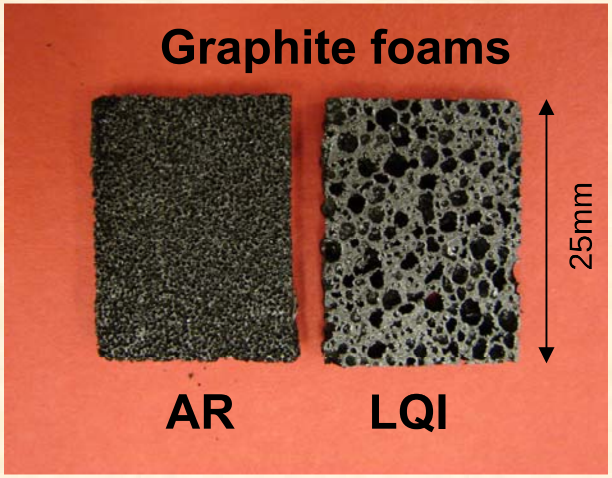
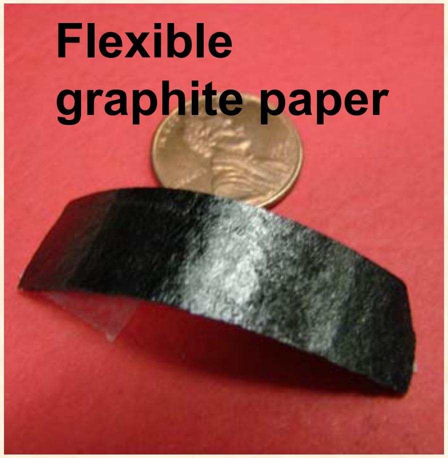
This presentation does not contain any proprietary or confidential information.

Purpose of work *(graphite)*

- **Evaluate graphite foam and fiber structures for battery (cathode) current collectors**
  - **Develop baseline data to project energy, power, and thermal performance for different structures**
  - **Evaluate bonds formed of active cathode particles to graphite and to each other**



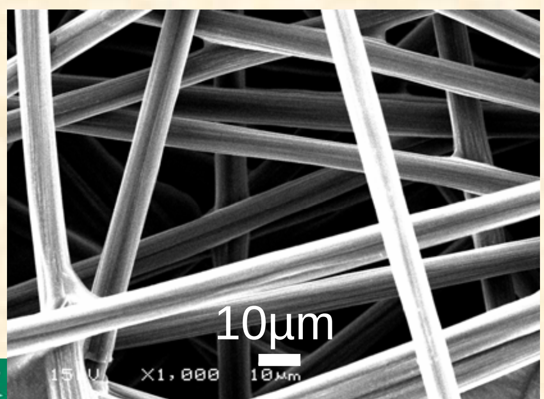
Carbon-bonded carbon fiber (CBCF)

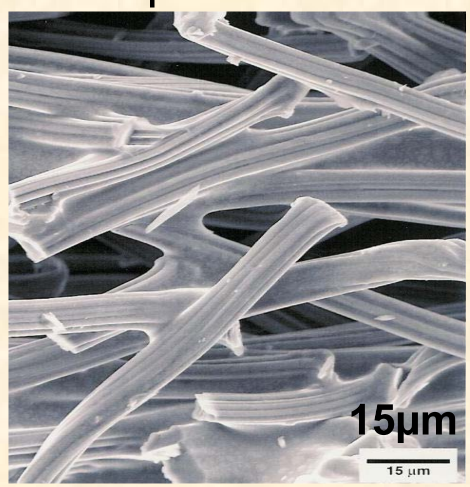


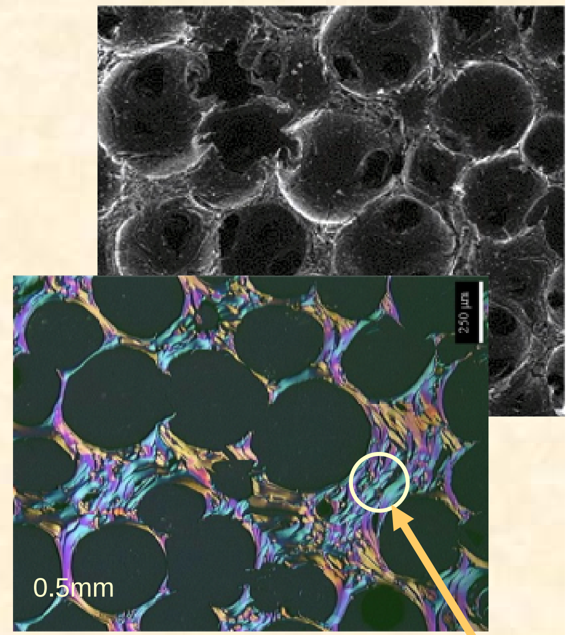
Al foil +binder +additive (traditional)

Technical barriers *(graphite)*

- **Safety and long cycle life are major challenges for HEV and PHEV batteries.**
  - Overcoming these barriers will reduce petroleum use.
- **Potential advantages of foam (or fiber) graphite current collectors:**
  - Thermal management (particularly foams)
  - Uniform conductivity and charge distribution
  - Robust sintered particle bonds within electrode, rather than bonds formed by compaction
    - No organic binders, no conductive additive
    - Less stress because not pressed
  - Corrosion resistance







1200-1700 W m^{-1} °K^{-1}
3800-6400 S/cm
(5X to 10X values for Al)

Approach FY08 *(graphite)*

- **Electrode fabrication** - *a few examples, not trying to optimize*

Graphite structures (ORNL materials-commercial - collaborate with inventors)

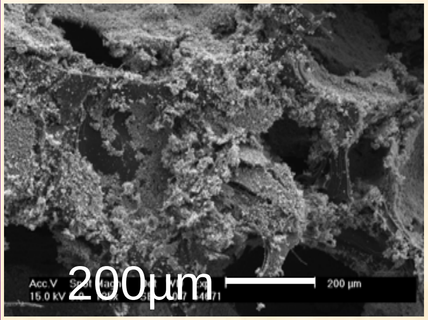
Graphite foams –two types AR and LQI (aromatic resin & low quinoline insoluble)
Can tailor: •pore & window sizes, •surface areas, • densities, • conductivities

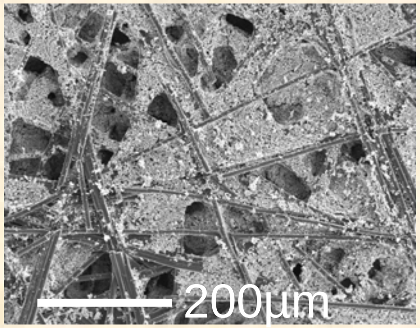
Carbon bonded carbon fibers (CBCF)
lower density, 3D-connected 10μm fibers

Commercial carbon fiber paper (Toray)
thinner flexible sheets

Cathode coatings
$LiFePO_4$+ 2% C-coating (as example)
Slurry infiltrated graphite.
Bonded by heating at 700°C, no pressure & no added organic binder

Adjust: •loading (by slurry conc.), •carbon source, •particle size,





- **Questions**
  - **When is structure too thick? Too dense? Too clogged?**
  - **When is loading too high? Coating too thick? Too resistive?**
  - **Does $LiFePO_4$ become inactive? Poorly connected?**

Approach FY08 *(graphite)*

- **Evaluation**

Battery tests → Energy-power
→ Cycle tolerant bonding

Electron microscopy → bonds before/after cycling
→ advanced in-situ or in-electrolyte (wet)

Thermal conductivity analysis

High Temperature Materials Laboratory, EERE funded national user center

Projections of energy and power comparison with 18650 cells

Modeling -- to optimize structures (graphite & coating & voids)

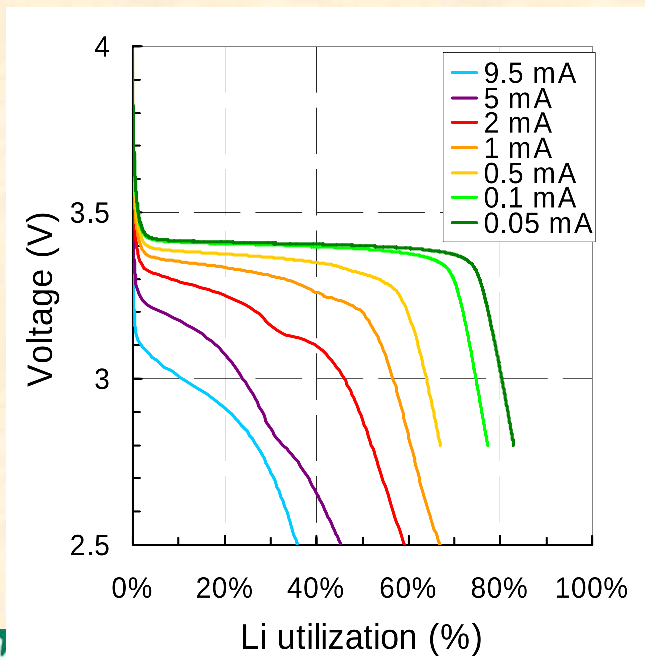
Ann Marie Sastry, Univ. of Michigan; ORNL finite element for foams

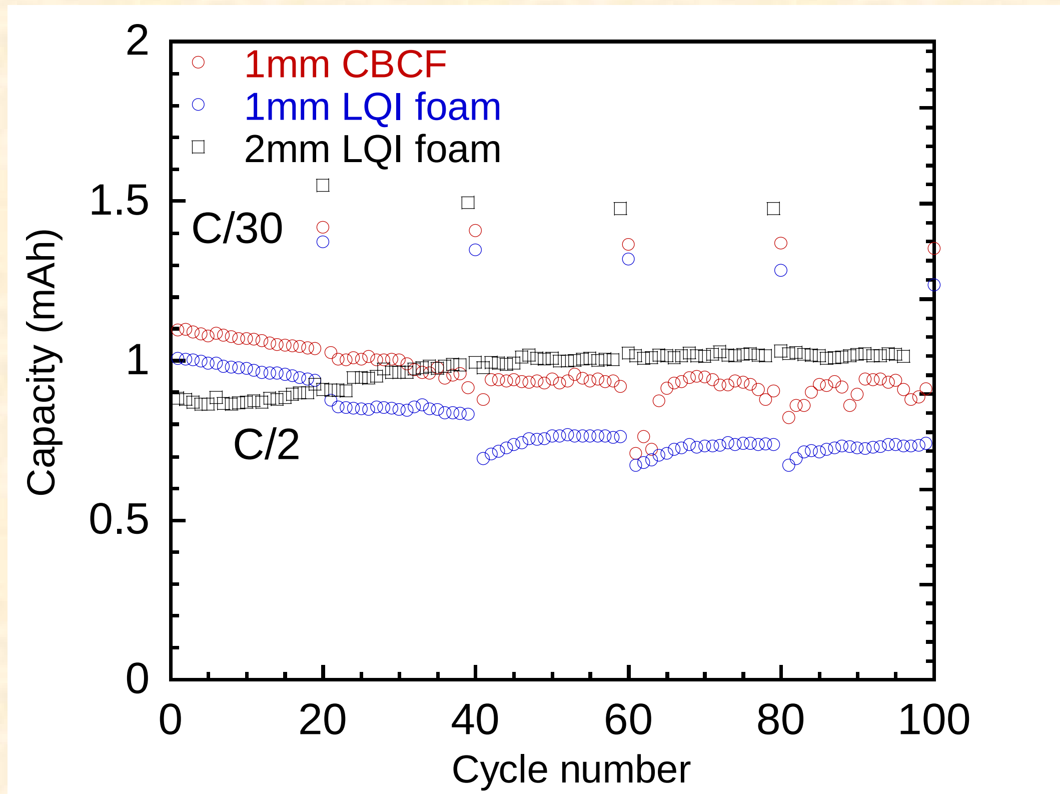
Modified fabrication

Accomplishments *(graphite)*

- **Good cycling, so thermal bonds of $LiFePO_4$ on graphite are robust.**
  - **Little loss of active material with >100 cycles.**
  - **Small increase of cell resistance. Lithium degradation also contributes.**
  - **Early results published, ECS Transactions 3, (27) 23 (2007).**

Cell: (1cm dia. disks)
Anode- Li metal (Ni)
$LiPF_6$(EC+EMC) or (EC+DMC)
Cathode- $LiFePO_4$-C (Al wire)





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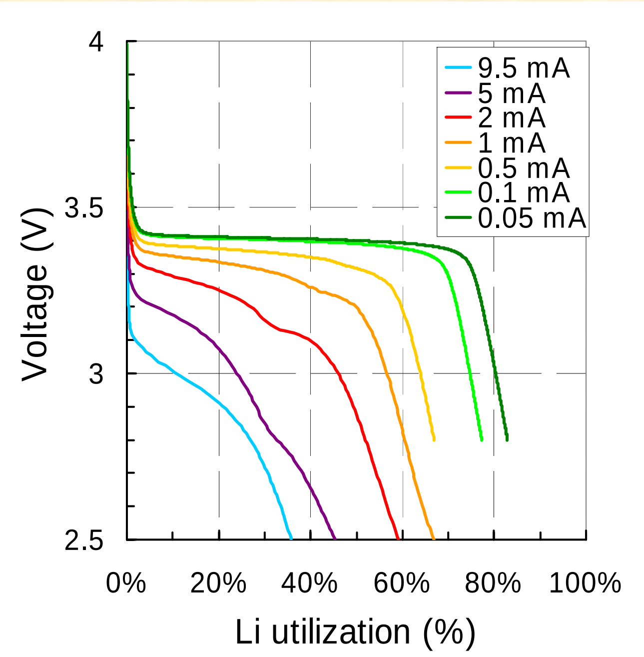
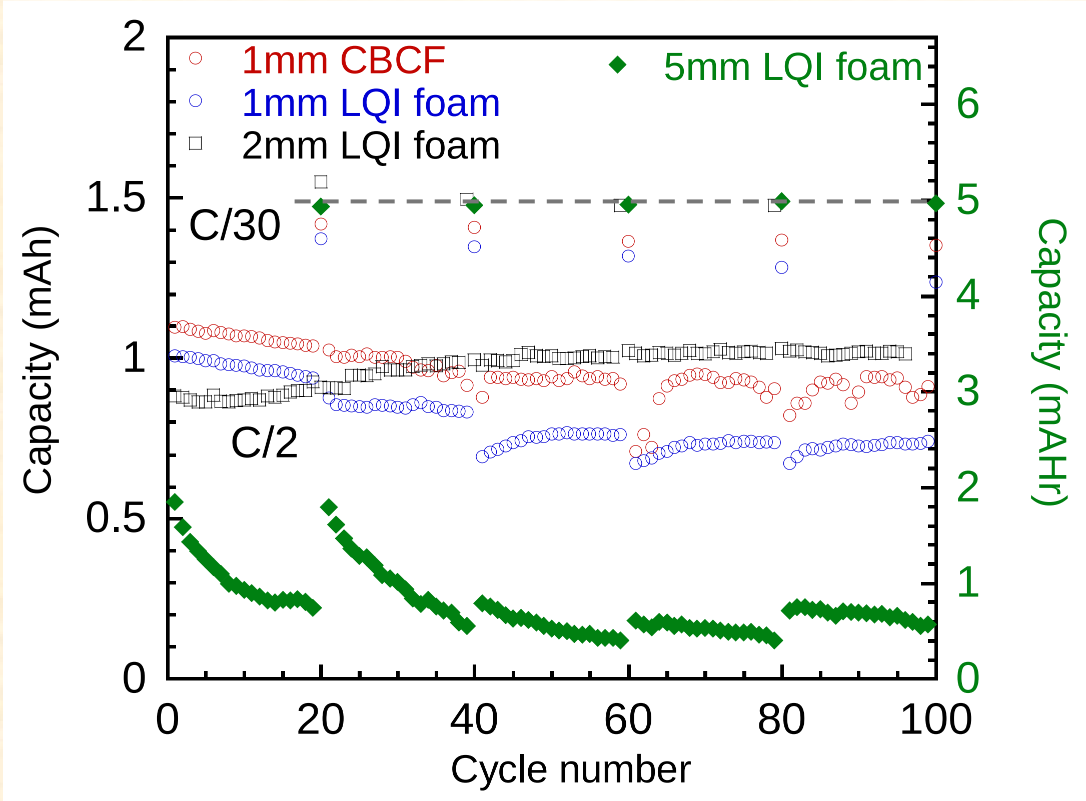
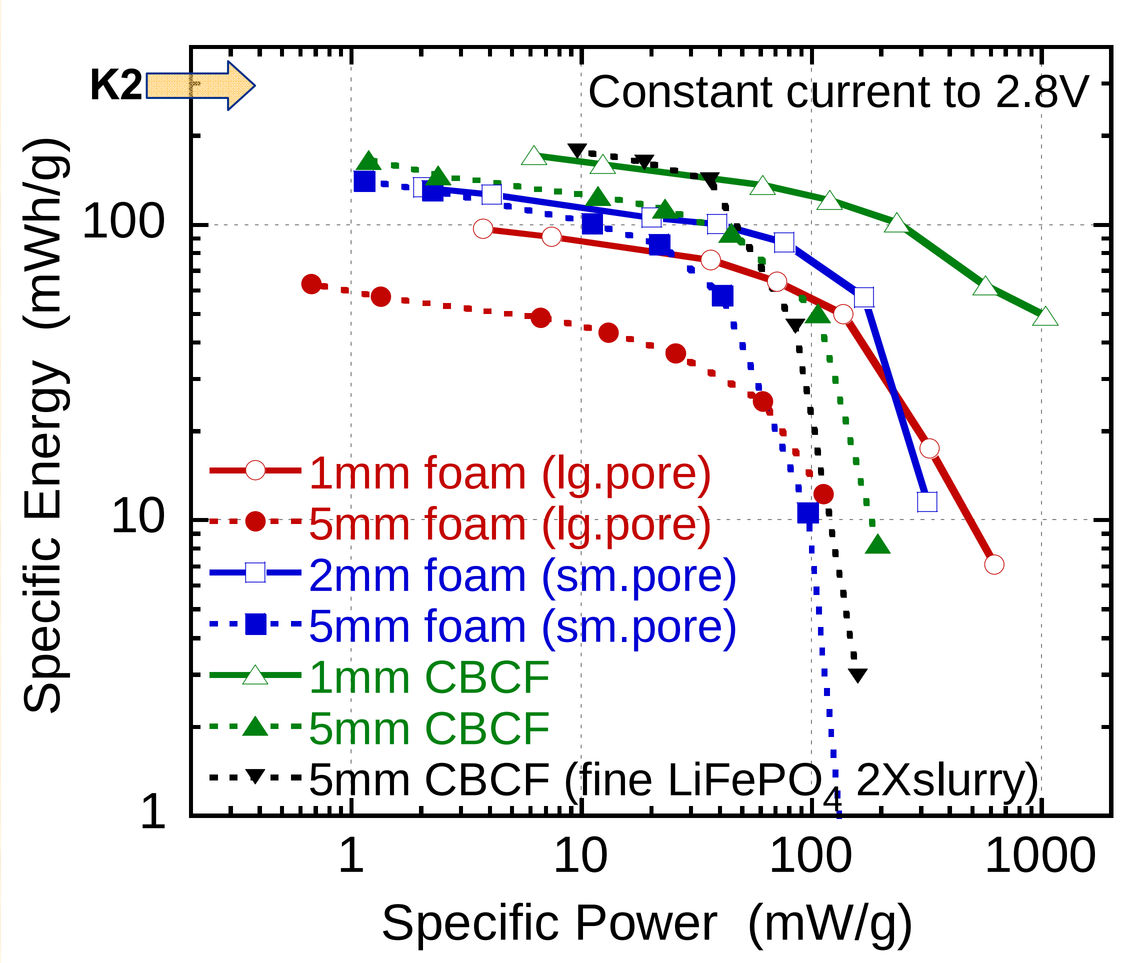




Accomplishments *(graphite)*

- **Energy and power normalized by $LiFePO_4$+C support**
- **Power is best for:**
  - **thin samples (1mm)**
  - **carbon fibers**
- **Energy is higher with:**
  - **Higher loading on fibers and small pores**
  - **Concentrated slurries**
- **$LiFePO_4$ utilization (120-140 mAh/g)**
- **K2 Energy Solutions, Inc. used as benchmark. 18650 cell ~300mWh/g cathode**

Selected samples – illustrate trends for different supports and plate thickness



Accomplishments *(graphite)*

- **Compare cathodes with commercial technology**

For cathode + the current collector only ★	**K2 Energy Solutions18650**	**Projected AR foam**	**Projected LQI foam**
$LiFePO_4$ wt. (g)	**12**	**12**	**12**
$LiFePO_4$ / C wt.ratio		**3X current**	**4X current**
Current collector wt. (g)	**1.5–2.6** Al foil**	**4.8 foam**	**9.4 foam**
Binder+additive (g)	**(1-3, est.)**	**0**	**0**
Energy (mWh/g) ★	**250 – 310**	**270**	**210**
$LiFePO_4$ coating (µm-thick)		**50***	**140***
Heat transport (W/°K)	**0.035 – 0.062**	**0.19**	**0.75**
Foam pore diameter (µm)		**500**	**1500**
Foam surface area (cm²/g)		**260**	**50**
Thermal cond. (W/m/°K)	**235**	**50**	**180**

**For energy & power cells. *For 50% dense.

Accomplishments (graphite)

- **Improved slurry and coating processes**
  - **Slurry concentration increased 7-fold, still very fluid**
    - **Future samples will have higher energy density with single coat**
  - **$LiFePO_4$ particle size reduced to 0.3-0.8µm by Spex milling with 0.3mm media.**
    - **Anticipate further reduction with 2-stage milling**
  - **Carbon precursors yielding graphitic carbon perform better than those giving glassy carbon**
    - **Anticipate improvement with > 2 wt.% carbon**

Future work and Tech Transfer *(graphite)*

- **Characterize sintered bonds with active material ★**
  - **Use electron microscopy and dual beam FIB+SEM**
  - **Extend electrical cycling beyond 100 cycles (need to match with high cycle anode)**
- **Project energy and power densities ★**
  - **Compare to existing technology**
  - **Demonstrate performance with higher $LiFePO_4$ loading**
- **Advanced modeling**
  - **Identify directions where large improvement possible**
- **Technology transfer opportunities**
  - **ORNL has IP position in graphite structures, motivation to develop battery application**

★ **Milestones for FY08**

Investigations of Graphite Current Collectors (part 1) and Metallic Lithium Anodes **(part 2)**

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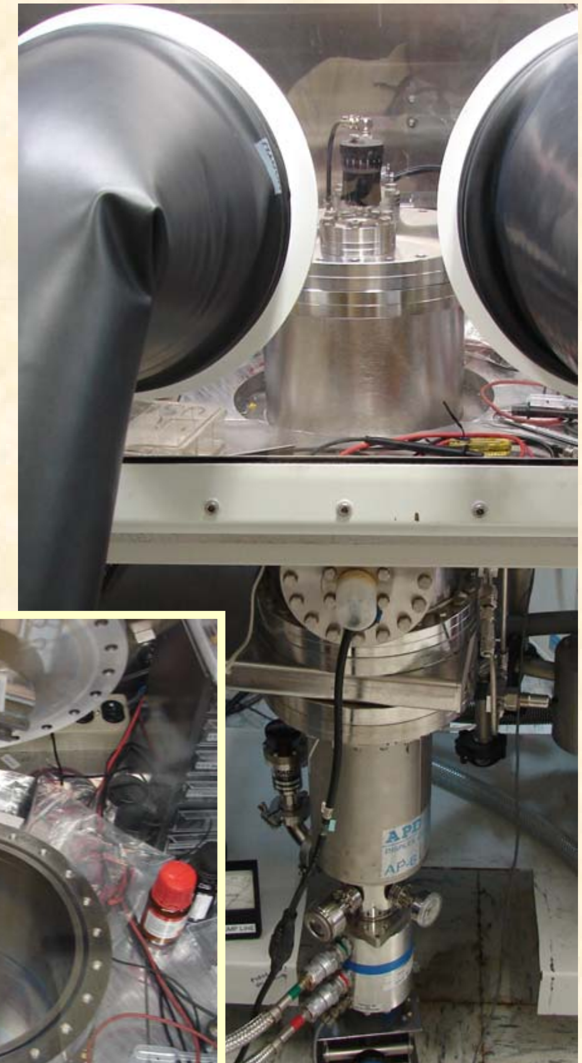
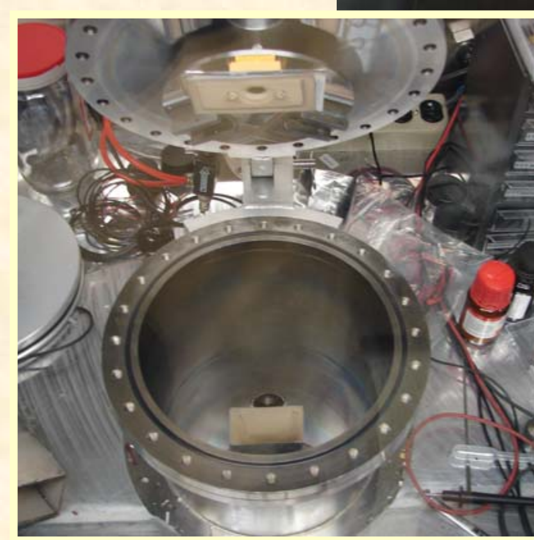
Purpose of work *(lithium anode)*

- **Understand interface instabilities at the lithium metal anode when cycled with a liquid or polymer electrolyte.**
  - **Current models for lithium dendrite initiation are inadequate.**
  - **Investigate roughening with pristine lithium surface formed by vacuum evaporation.**

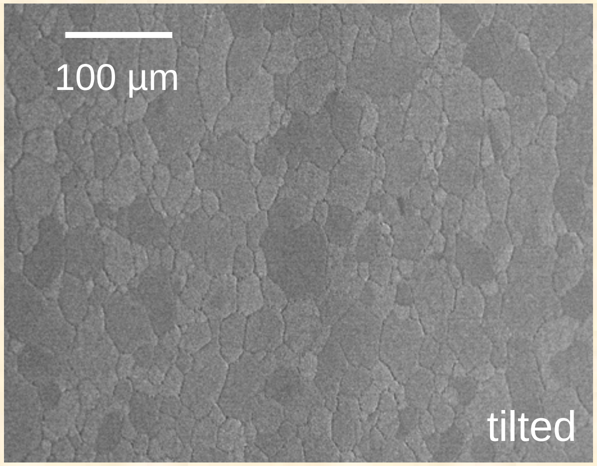




Technical barriers *(lithium anode)*

- **PHEV and HEV applications requires batteries with higher energy densities**
  - **Lithium metal 3.8Ah/g, carbons 0.37Ah/g**
  - **Lithium metal anodes give maximum cell voltage**
- **Technical Barrier – lithium roughening leads to rapid degradation, impacting safety and cycle life performance**
  - **Loss of active material, decrease capacity, increase of cell resistance**
  - **Possible shorting if lithium dendrites form and propagate through polymer or liquid electrolyte**
  - **Finely divided lithium (mossy lithium) is chemically reactive, but electrochemically inactive**
- **Solutions will enable petroleum savings for transportation**

Approach FY08 *(lithium anode)*

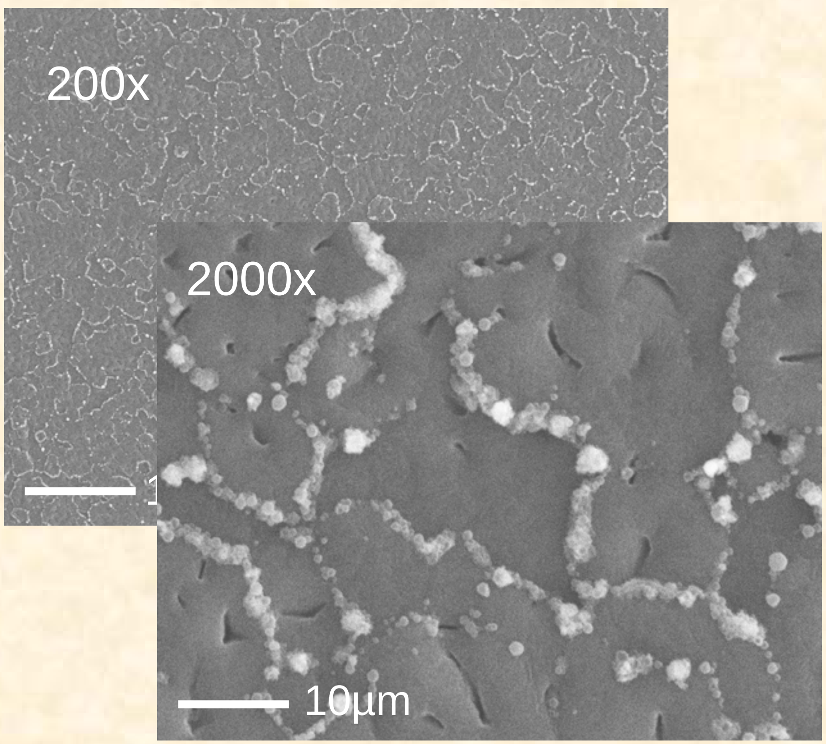


- **Approach has changed.**
- **First approach**
  - **Study dendrite initiation on very smooth and clean Li**
    - **Current density, time, surface features**
- **New approach – recognize effect of SEI**
  - **Study growth and 'breakdown' of SEI and/or reaction layer at Li – electrolyte interface**
    - **Use very smooth surfaces; replace when roughened**
    - **Incorporate surface coatings and barrier layers**
    - **Use electrochemical & quartz crystal microbalance tests**
    - **Observe by SEM the surface and fracture edge after aging**
- **Complements Alan West's program**
- **Collaboration with High Temperature Materials Laboratory for developing in-situ SEM and STEM techniques**

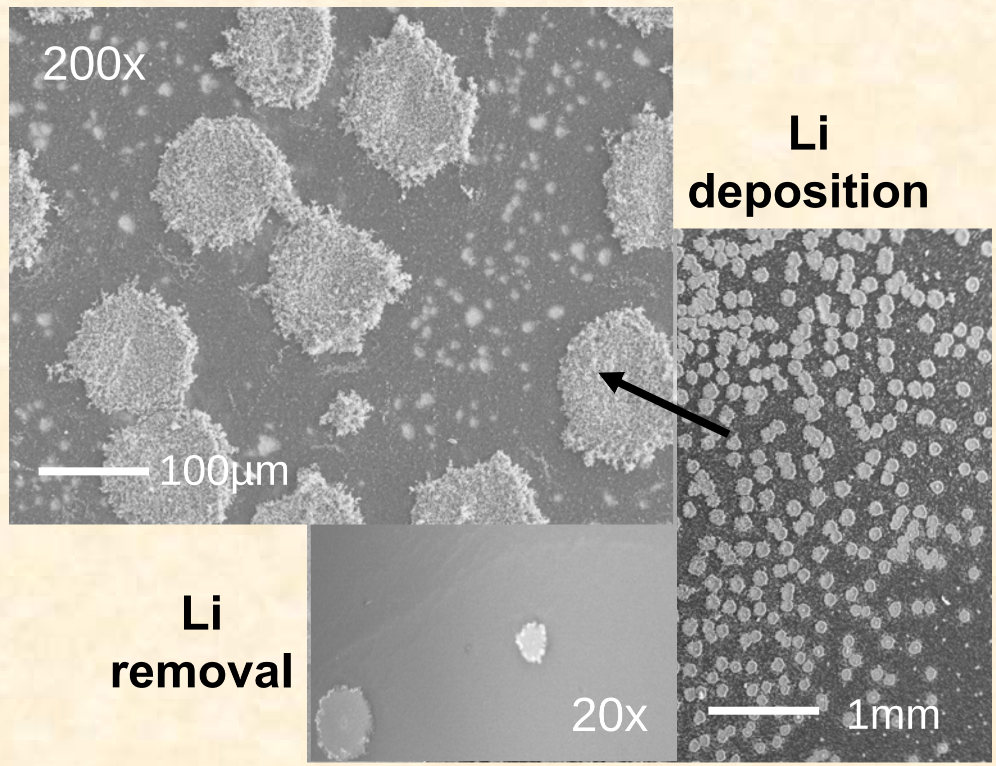
Cell details: WE=Li film on Ni, CE=Li ribbon or film; RE=Li on Ni wire
$LiPF_6$(EC+EMC) or (EC+DMC); no separator - 0.5mm gap; Teflon

Accomplishments *(lithium anode)*

- **Early investigation focused on initiation and growth of dendrites**
  - **Inconclusive results of current density, time to initiation, surface feature investigation**
  - **Form and location of dendrites varied**
  - **Deposition and also Li removal initiated at spots on surface**

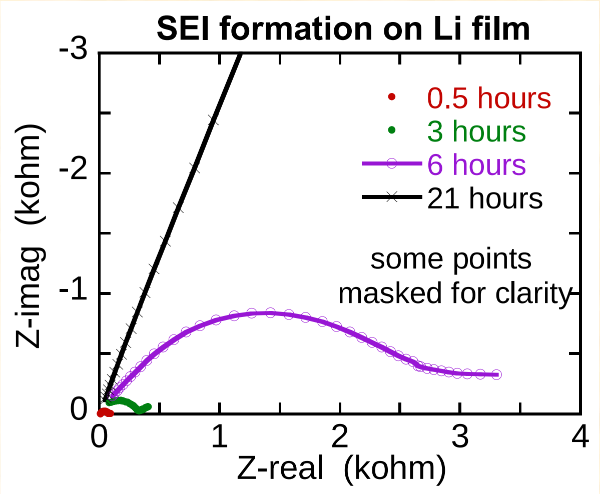


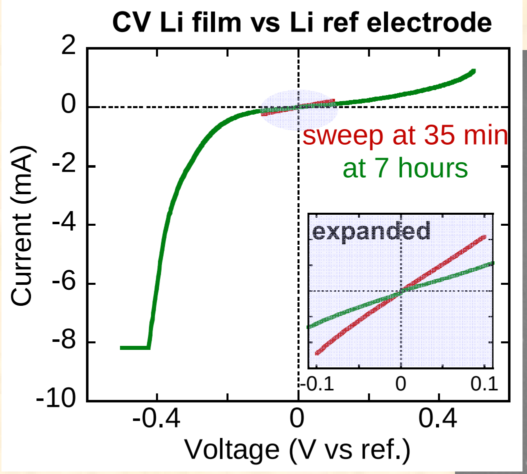
Li deposition at grain boundaries

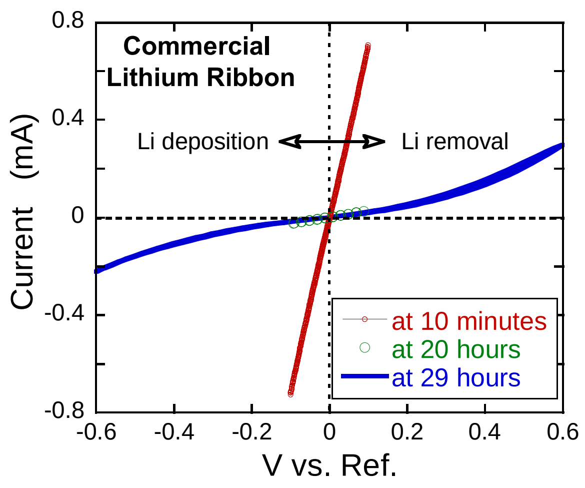


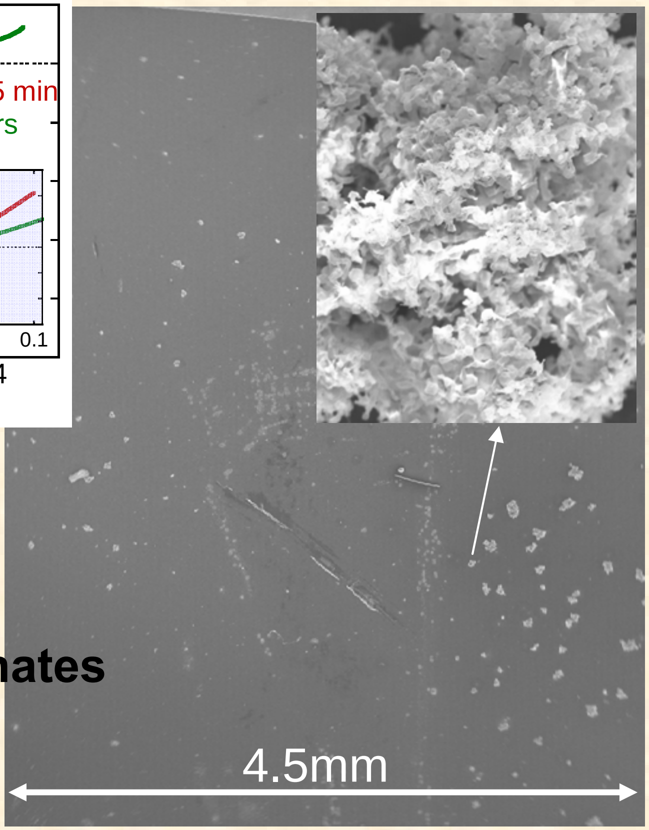
Accomplishments *(lithium anode)*

- **Progress characterizing SEI: its formation, breakdown, recovery**
  - **Resistance continues to increase, becomes non-ohmic.**
  - **'Breakdown' associated with dendrites. Samples retired.**





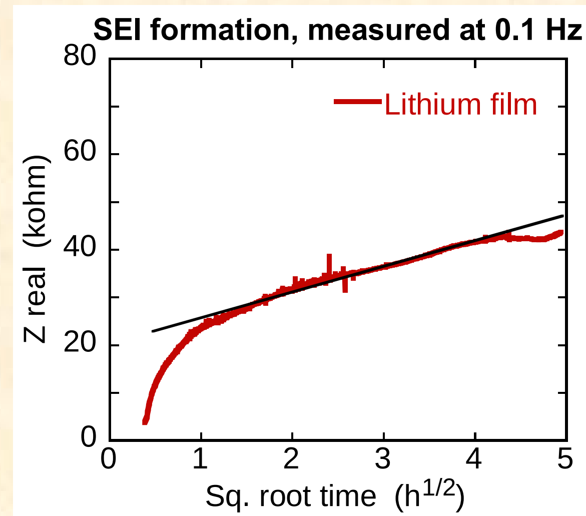


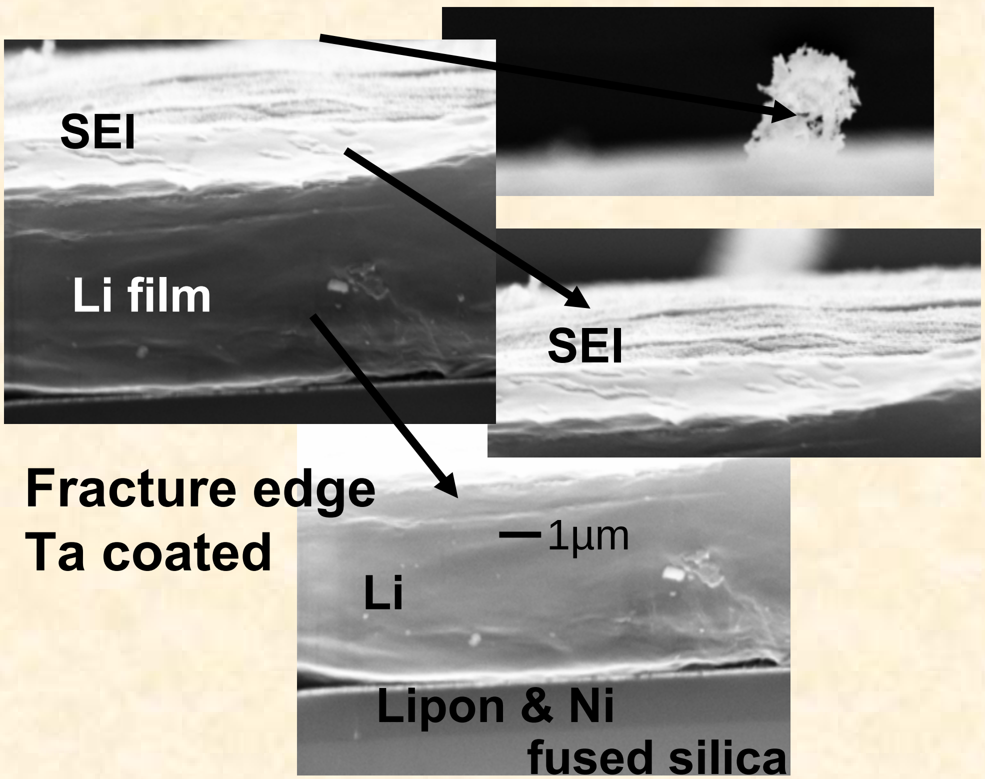


Li alkylcarbonates
σ ~1 nS/cm
P. Ross

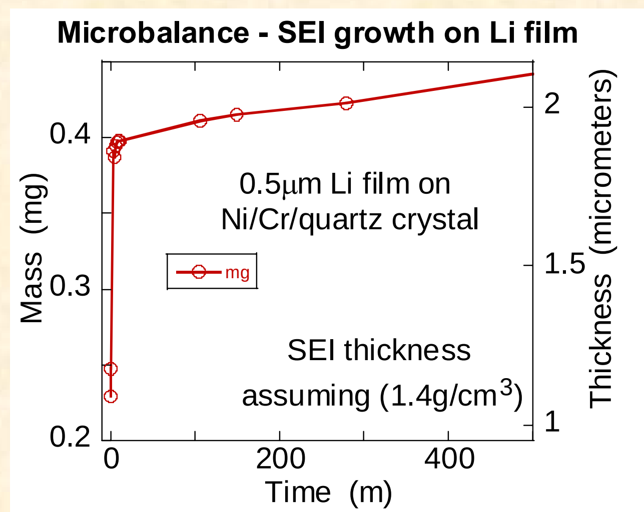
Accomplishments *(lithium anode)*

- **Quartz crystal microbalance and direct observation to evaluate SEI layer formation kinetics**
  - **Resistance may increase due to density, composition, or thickness**



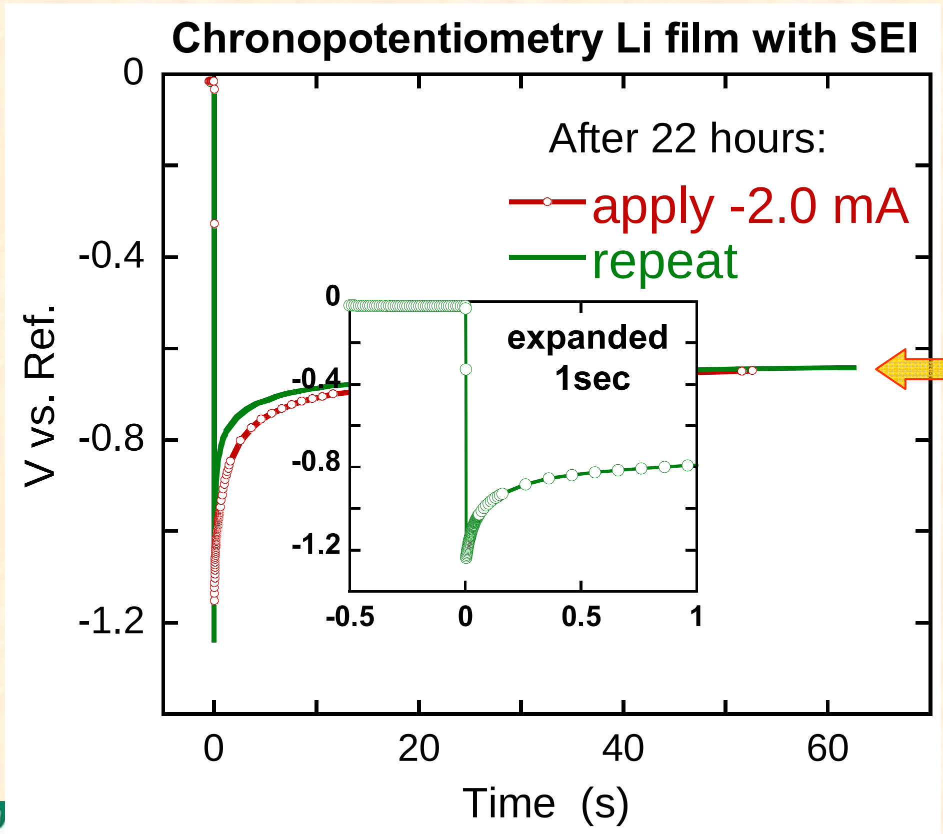


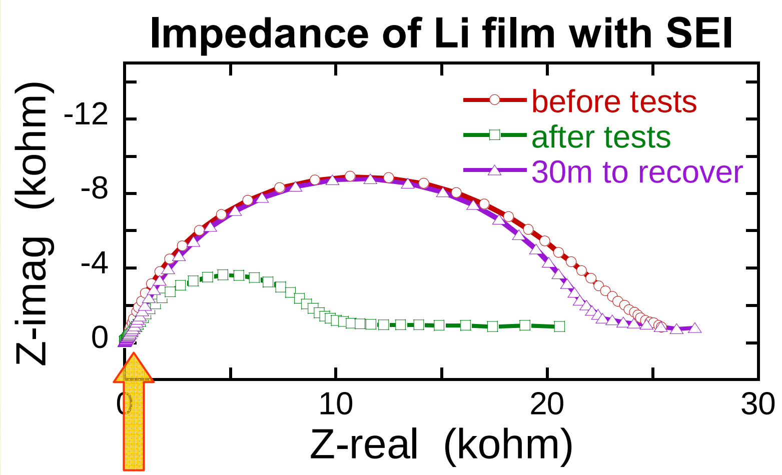
Fracture edge
Ta coated



Accomplishments *(lithium anode)*

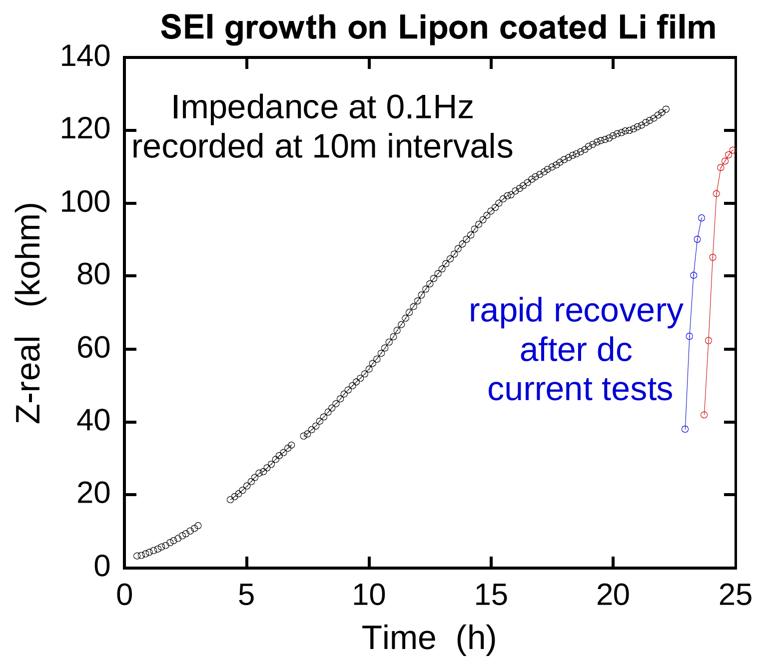
- **Breakdown of resistive SEI barrier occurs ~ instantly when higher current applied**
- **Does barrier become porous? More conductive?**
- **At open circuit, resistive barrier recovers rapidly.**

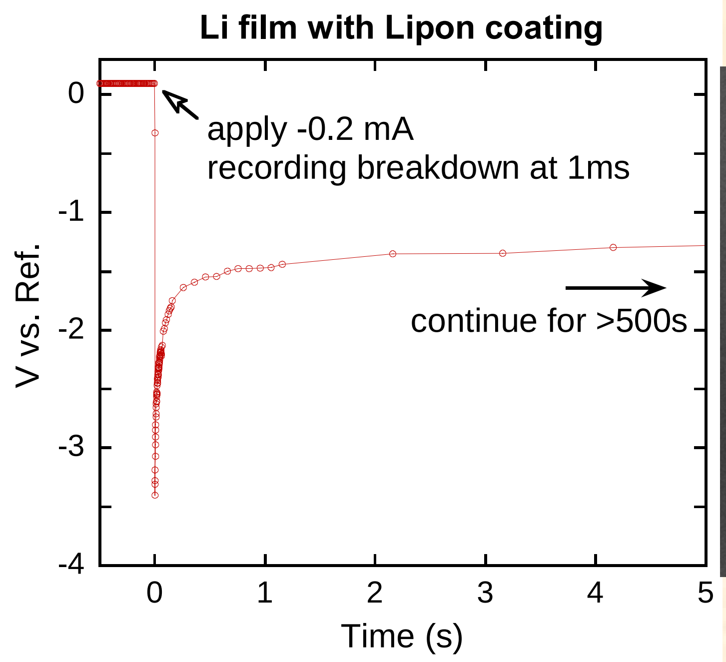


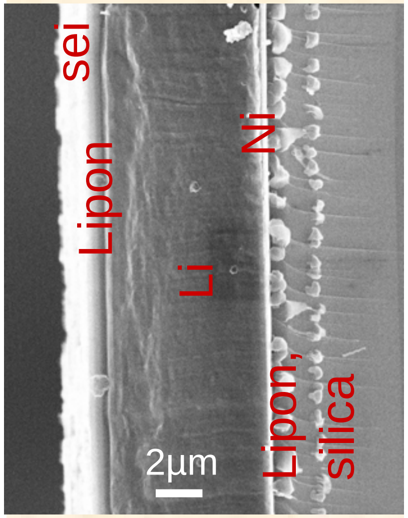


Accomplishments *(lithium anode)*

- **Passivating layers and protective barrier films added. So far, these do not impede reaction.**
  - **Li carbonate film formed by CO_2 treatment following deposition**
  - **Lipon film formed by sputter deposition onto fresh Li film**
    - **'Lipon' is: a glassy solid electrolyte, electronic insulator, stable with lithium. (Invented at ORNL; commercial)**







Future work and Tech Transfer *(lithium)*

- **Evaluate the SEI formation for Li in contact with an organic electrolyte.** ★
  - **Model for lithium roughening based on SEI breakdown**
  - **Resolve effect of Lipon barrier as SEI**
- **New techniques for lithium and SEI study**
  - **Load lock to XPS, FTIR, dual beam FIB+SEM**
  - **In-situ or 'wet' study by electron microscopy (collaboration with High Temperature Materials Laboratory staff)**
- **Collaborate with teams designing and testing new electrolytes**

★ **Milestones for FY08**

Summary (graphite and lithium anode projects)

- **Enable the next generation Li-based batteries**
- **Graphite current collectors for thermal management and improved safety and cycle life**
  - **Initial results of $LiFePO_4$ on graphite cathodes promising**
  - **Projections → competitive energy density & good thermal transport**
  - **Modeling → optimum structure**
  - **Graphite foams/fiber materials from ORNL are commercial**
- **Lithium metal anodes for much higher energy density.**
  - **Insight into roughening of interface, by focusing on SEI formation and breakdown and the effect of Lipon barrier**
- **Apply resources of ORNL's High Temperature Materials Laboratory, in particular electron imaging, to both projects**
- **FY08**
  - **Investigate sintered bonds of cathode particles coating graphite**
  - **Use models and experiments to project performance of optimized cathode coating and graphite structure**
  - **Determine impact of SEI formation on roughening of lithium**