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

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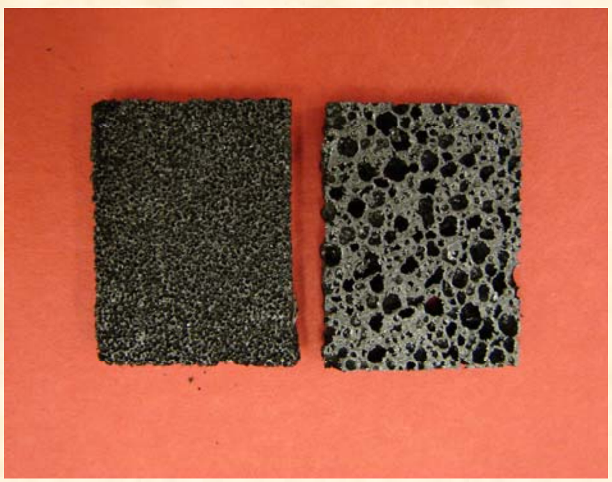
This presentation does not contain any proprietary or confidential information.

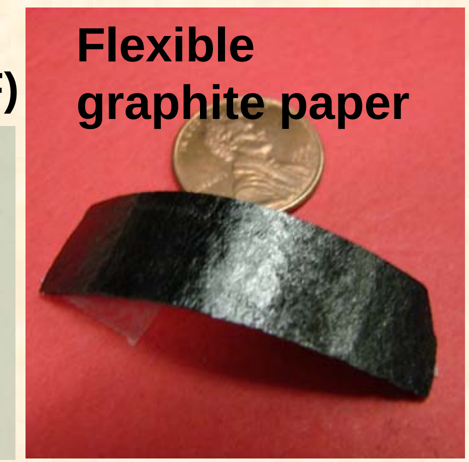
# Purpose of work *(graphite)*

- **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)**

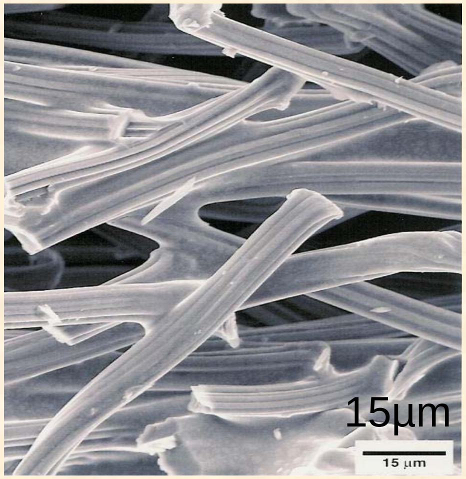
**Flexible graphite paper**

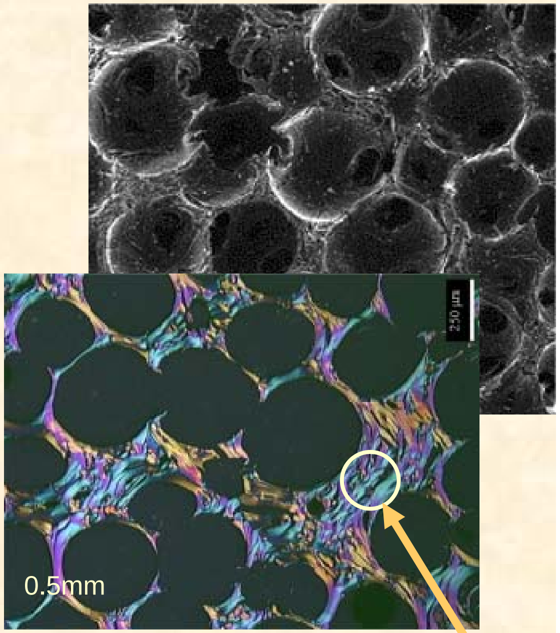


**Al foil +binder +additive (traditional)**

# 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 thermal 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*

**<u>Graphite structures</u>** (ORNL materials-commercial - collaborate with inventors)

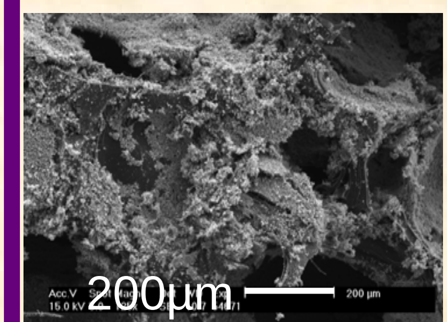
**Graphite foams** –two types AR and LQI (aromatic resin & low quinoline insoluble) *Can tailor: •pore & window sizes, •surface areas, • densities, • conductivities*

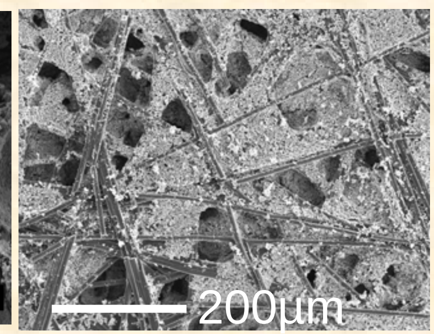
**Carbon bonded carbon fibers (CBCF)** lower density, 3D-connected 10µm fibers

**Commercial graphite fiber paper (Toray)** thinner flexible sheets

**<u>Cathode coatings</u>**
$LiFePO_4$+ 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 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

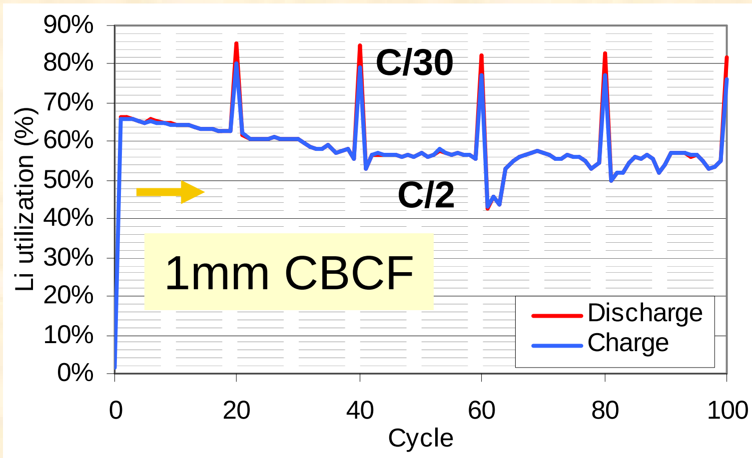
**Modified fabrication**

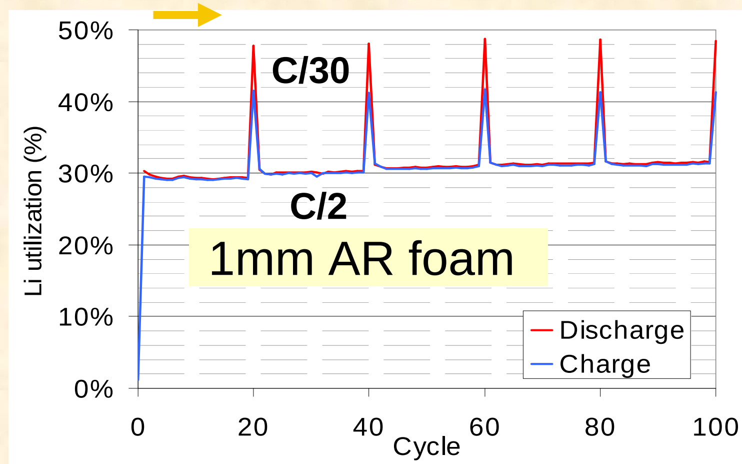
# Accomplishments *(graphite)*

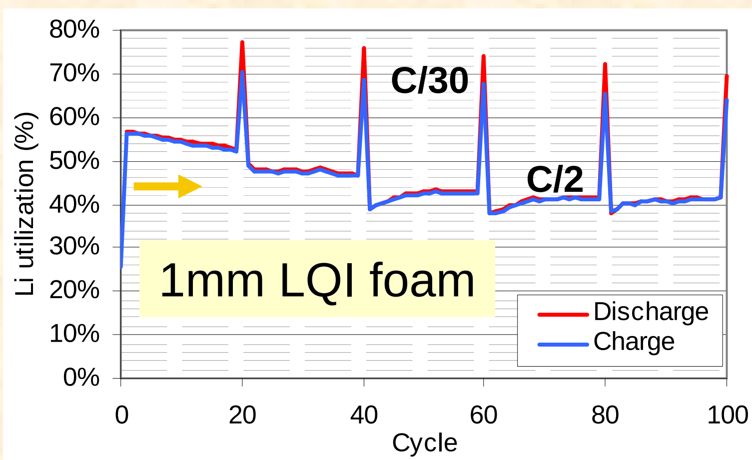
- **Good cycling, so thermal bonds of $LiFePO_4$ on graphite are robust.**
  - **Little loss of active material with >100 cycles.**
  - **Small increase of cell resistance. Lithium degradation also contributes.**
  - **Early results published, Proc. Electrochem. Soc.**

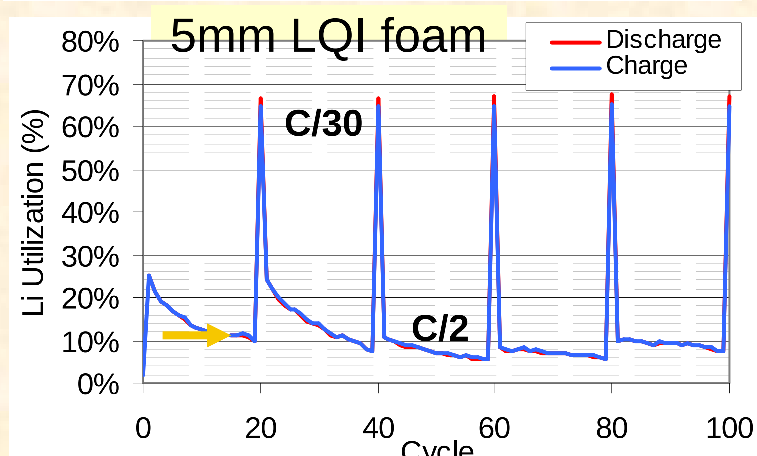
Cells are 1-6mAh/cm². Arrow shows 1mAh/cm²

Cell:
Li anode (Ni)
$LiPF_6$(EC+EMC) or (EC+DMC)
Celgard
$LiFePO_4$-C,
Al wire



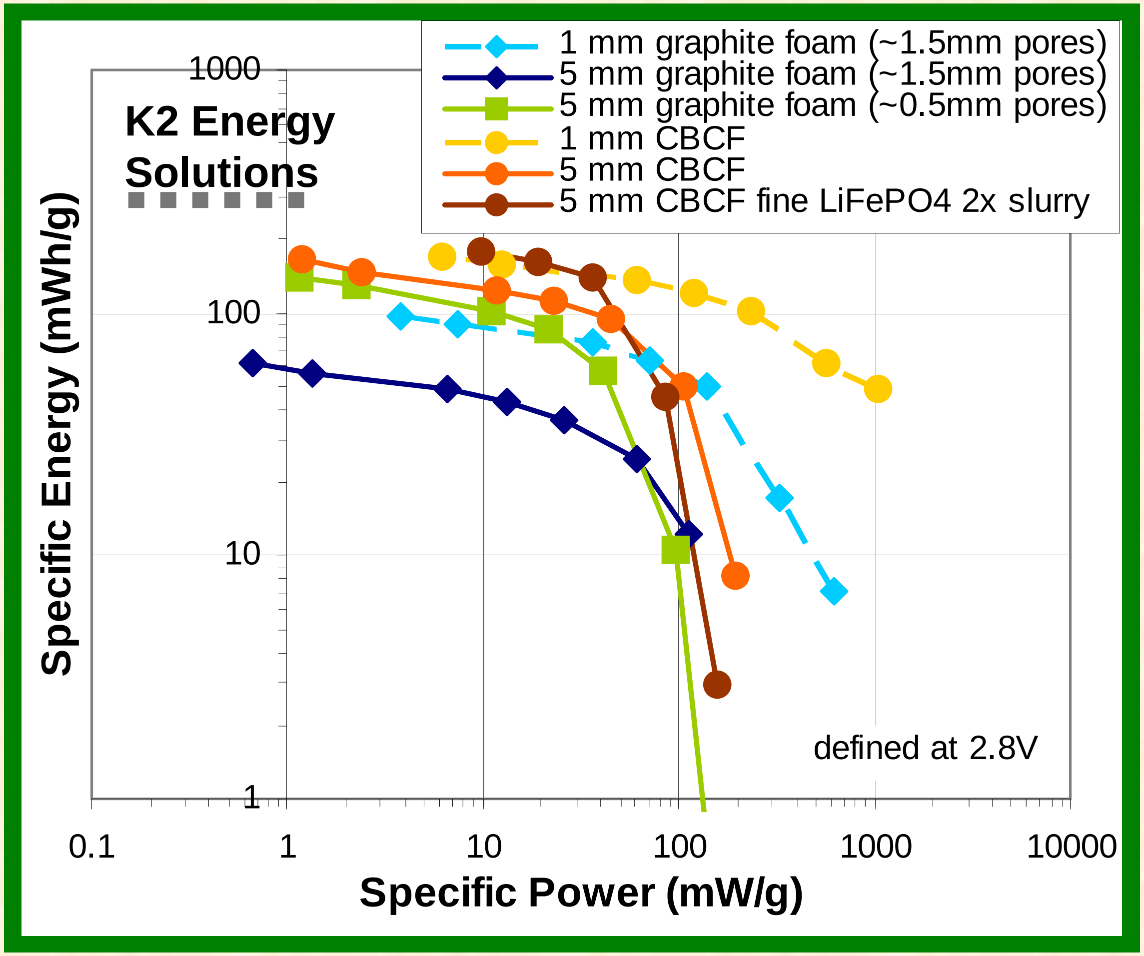



# Accomplishments *(graphite)*

- **Energy and power assessed**
- **Power is best for**
  - **thin samples (1mm)**
  - **fibers structures**
- **Max. energy varies as:**
  - **Wt% of $LiFePO_4$ (15-58%)**
  - **$LiFePO_4$ utilization (85-140 mAh/g)**
  - **Source of 2 wt% carbon**
- **More concentrated slurries will further increase wt %**

*Selected samples – illustrate trends for different supports and slurries*



# 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 (cm$^2$) | | 1250 | 470 |
| 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 bonds with active material ★**
  - **Use electron microscopy and dual beam FIB**
  - **Extend electrical cycling beyond 100 cycles (need to add fresh Li and electrolyte)**
- **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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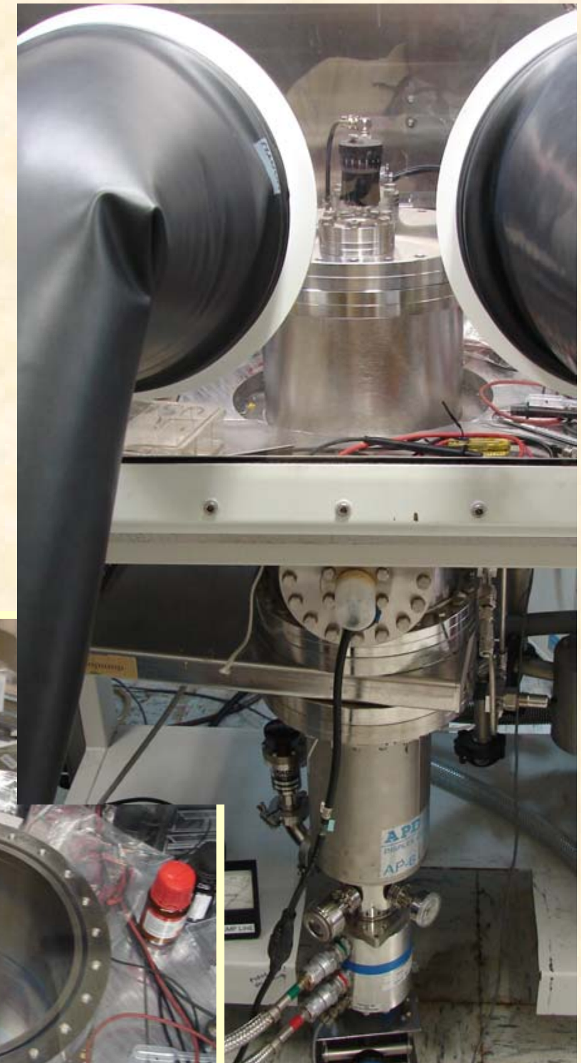
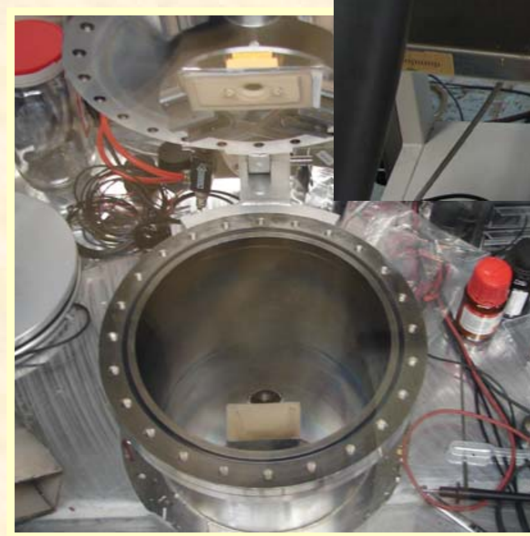
# Purpose of work *(lithium anode)*

- **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.**

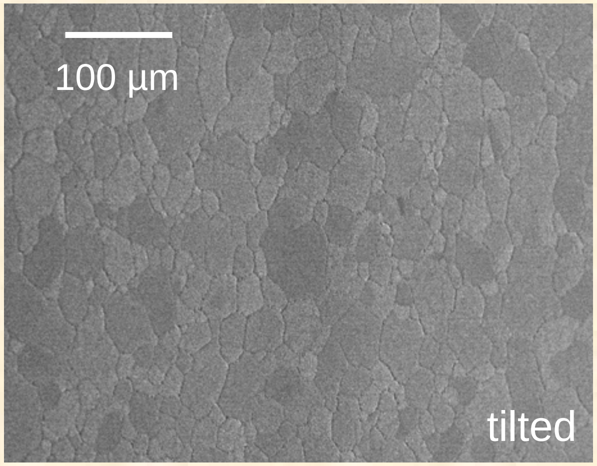




# Technical barriers *(lithium anode)*

- **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**
- **Solution will enable next generation battery and petroleum savings for transportation**

# Approach FY08 *(lithium anode)*

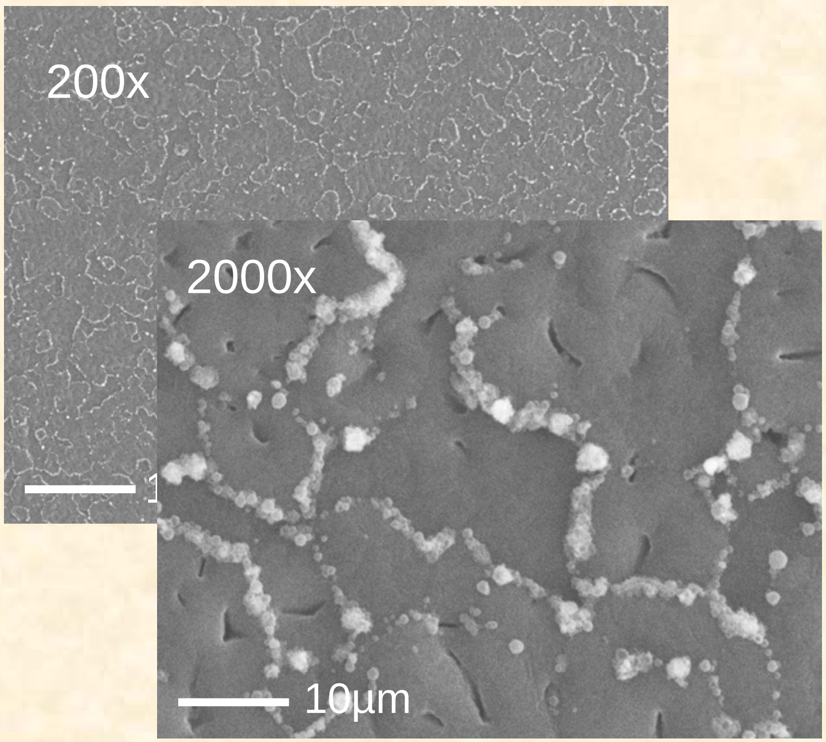



- **Approached has changed.**
- **Initial approach**
  - **Study dendrite initiation on very smooth and clean Li**
    - **Emphasize current density, time, surface features**
- **New approach – recognize effect of SEI**
  - **Study growth and 'breakdown' of SEI layer at Li – electrolyte interface**
    - **Use very smooth surfaces. replace when roughened**
    - **Incorporate surface coatings and barrier layers**
    - **Use electrochemical & quartz crystal microbalance tests**
    - **SEM observation of 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**

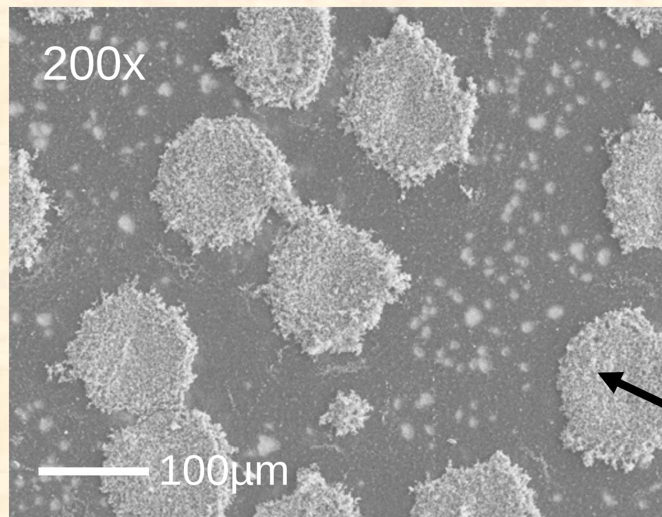
Cell details: WE=Li film on Ni, CE=Li ribbon or film; RE=Li on Ni wire
$LiPF_6$(EC+EMC) or (EC+DMC); no separator - 0.5mm gap; Teflon

# Accomplishments *(lithium anode)*

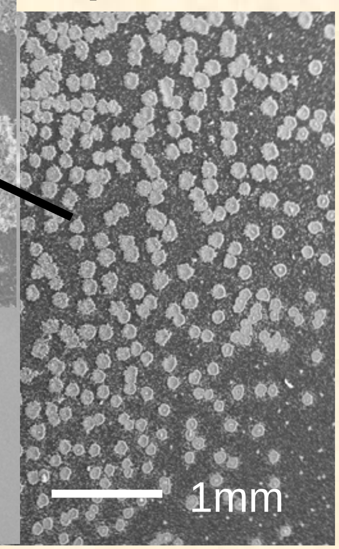
- **Abandoned investigation focused on initiation and growth of dendrites**
  - **Inconclusive results of current density, time to initiation, surface feature investigation**
  - **Form and location of dendrites varied**
  - **Deposition and also Li removal initiated at spots on surface**



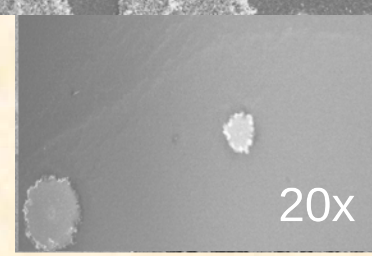

**Li deposition at grain boundaries**




**Li deposition**

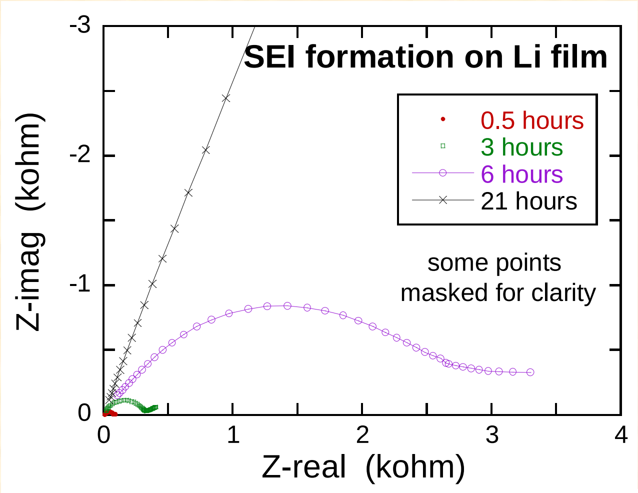


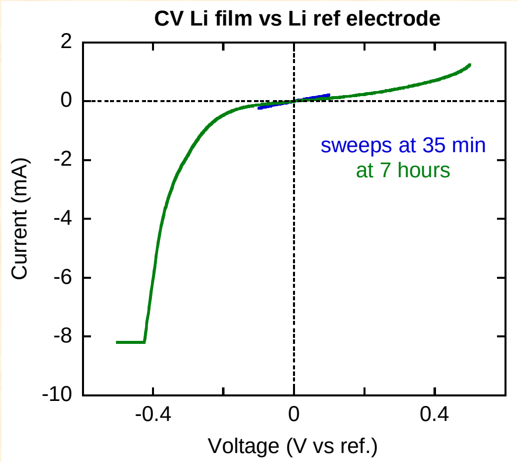

**Li removal**

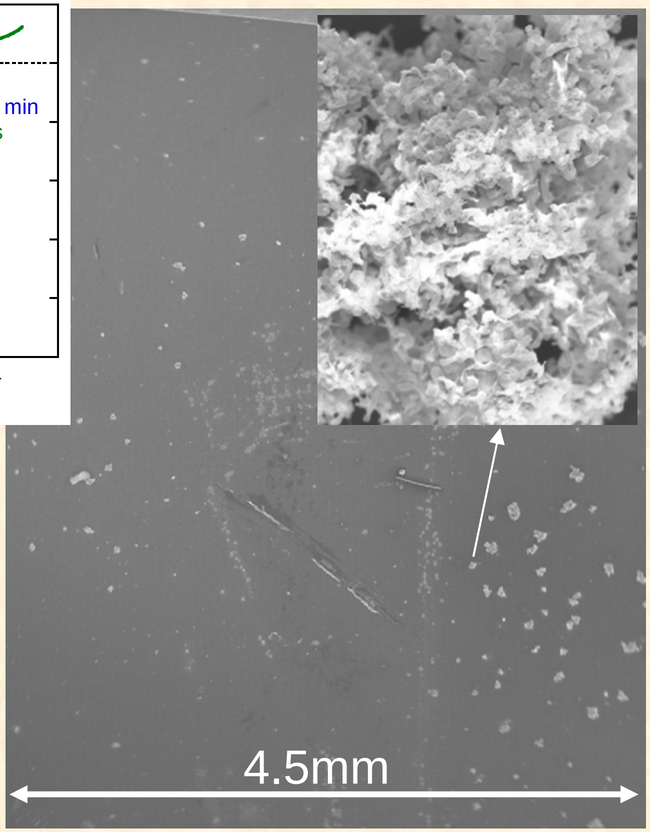


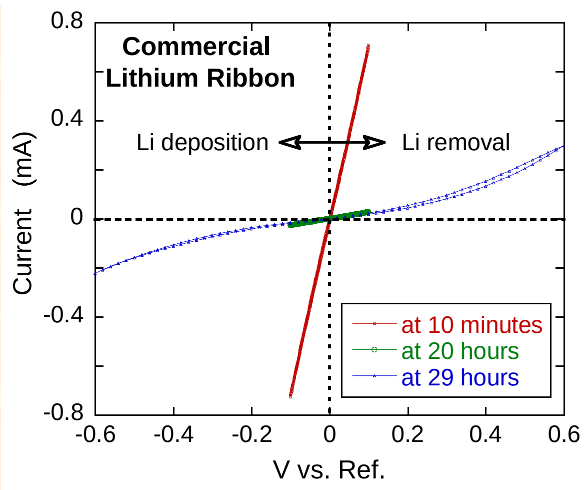
# Accomplishments *(lithium anode)*

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



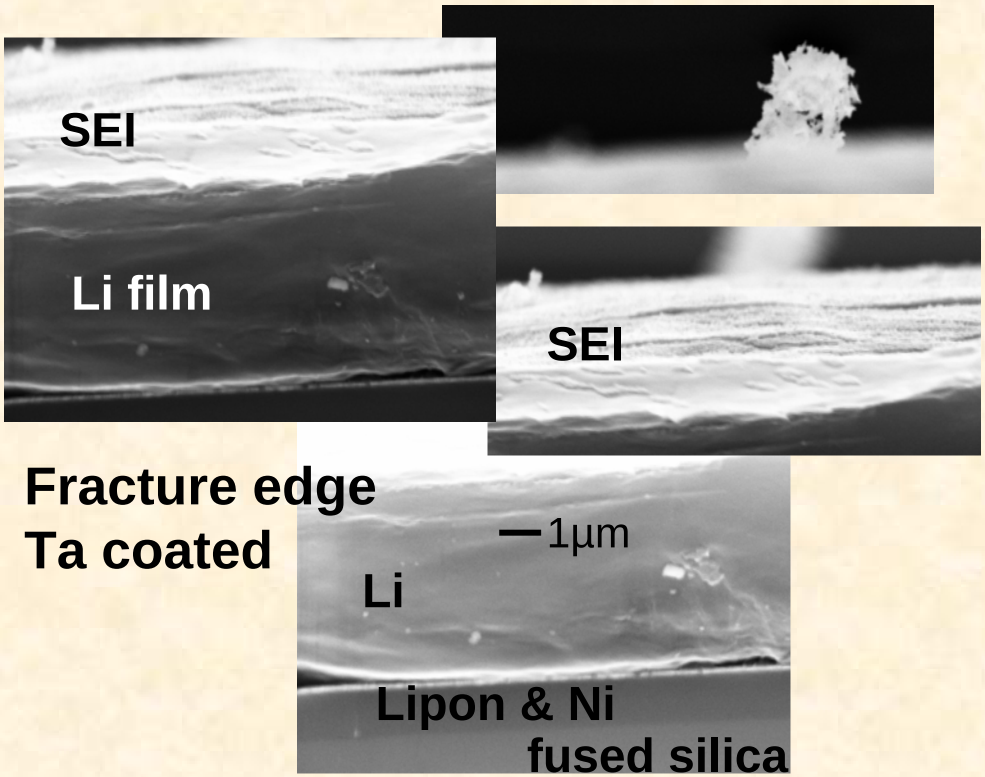



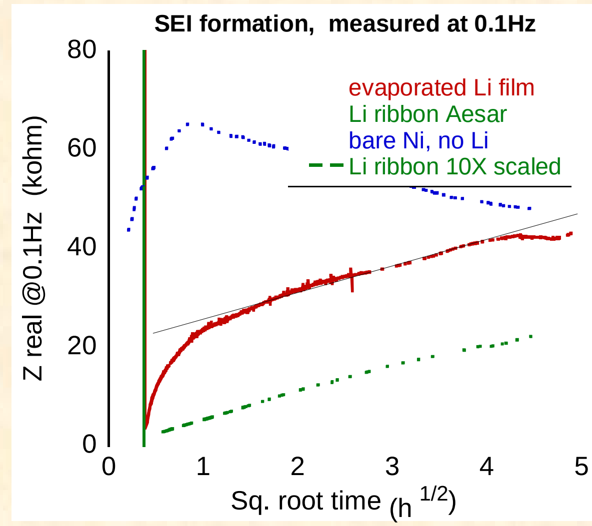



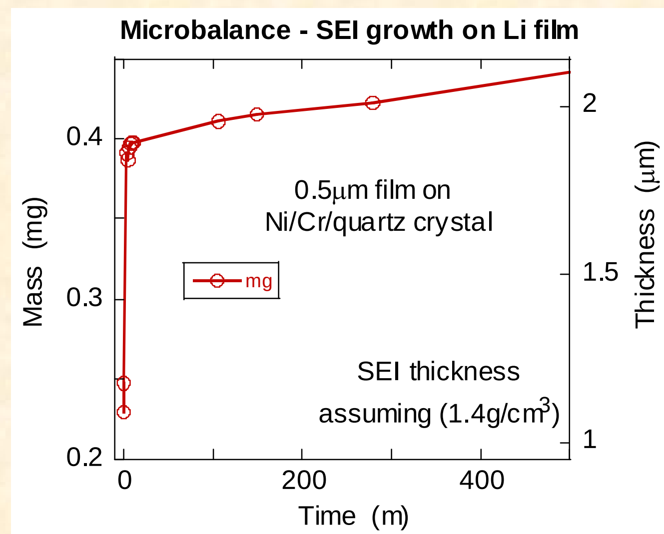
# Accomplishments *(lithium anode)*

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



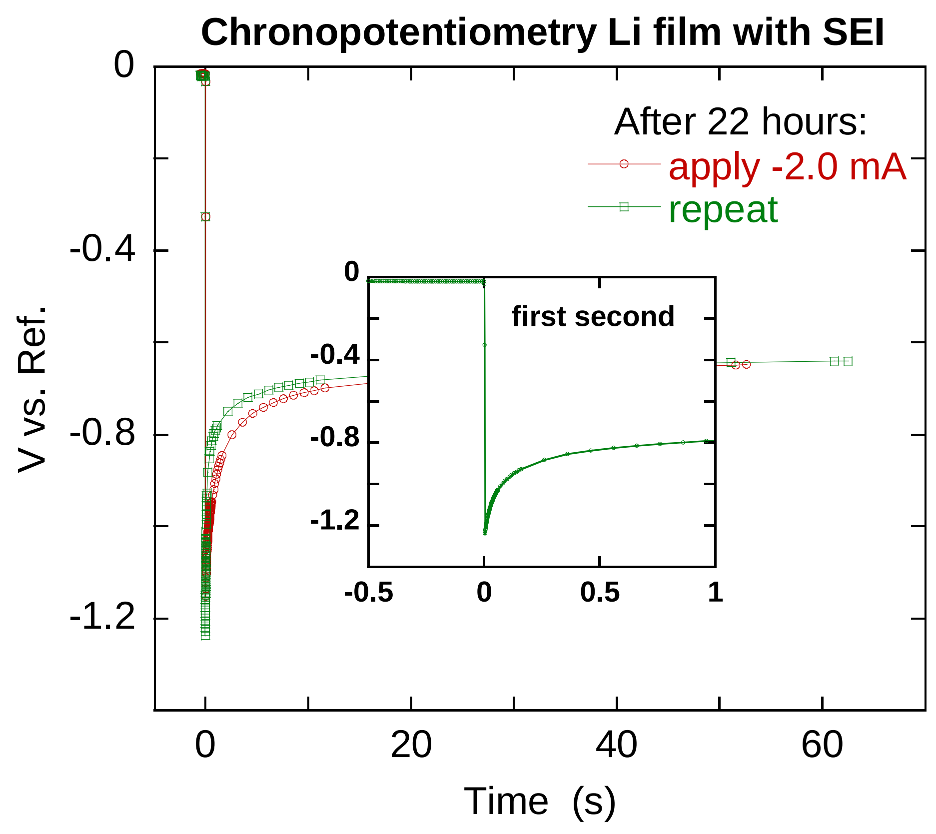

**Fracture edge**
**Ta coated**

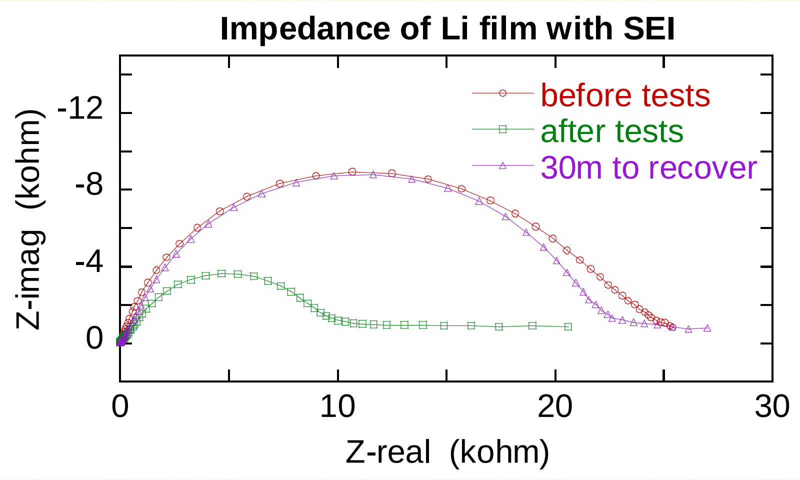


# Accomplishments *(lithium anode)*

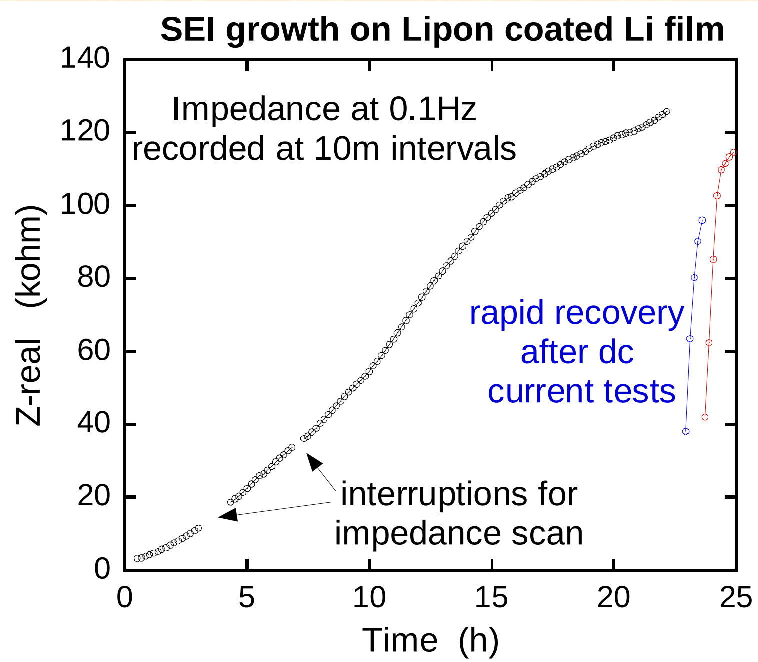
- **'Breakdown' of resistive SEI barrier occurs instantly when higher current applied**
- **After 'breakdown' resistive SEI recovers rapidly.**

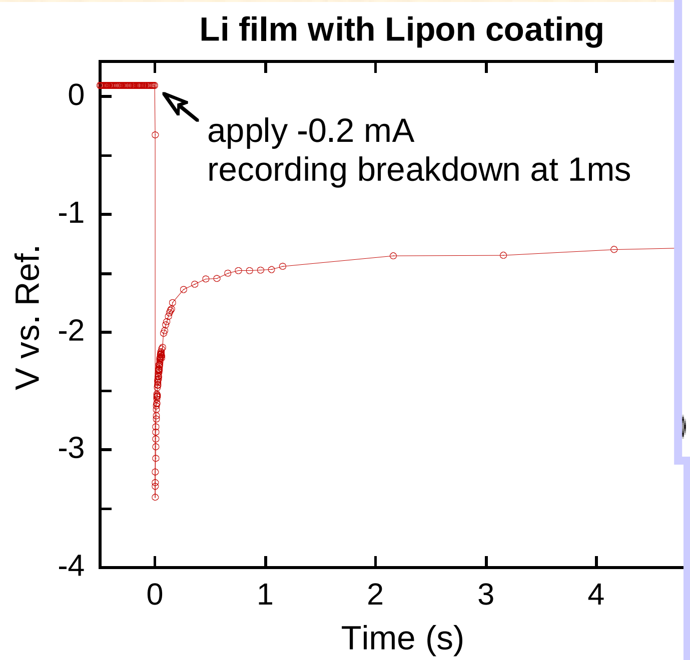


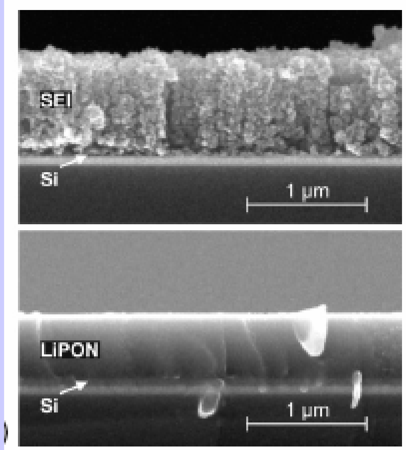



# Accomplishments *(lithium anode)*

- **Passivating layers and protective barrier films added. So far, these do not impede SEI formation. Why?**
  - **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)**




After 60 cycles with conventional organic electrolyte. Adv. Mat. 2007, by PHL Notten et.al.

# 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 on SEI**
- **New techniques for lithium and SEI study**
  - **Load lock to XPS, FTIR**
  - **Dual beam FIB**
  - **In-situ or 'wet' study by electron microscopy (collaboration with HTML staff)**
- **Initiate collaboration with teams designing new electrolytes**

★ **Milestones for FY08**

# Summary *(graphite and lithium anode projects)*

- **Potential – enable the next generation Li-based batteries**
- **Graphite current collectors for thermal management and improved safety**
  - **Initial results of $LiFePO_4$ on graphite cathodes promising**
  - **Projections → competitive energy density & good thermal transport**
  - **Graphite foams/fiber materials from ORNL are commercial**
- **Lithium metal anodes for much higher energy density.**
  - **Insight into roughening of interface, by shifting focus to SEI formation and breakdown and effect of Lipon barrier, rather than dendritic growth**
- **Apply resources of ORNL's High Temperature Materials Laboratory, in particular electron imaging, to both projects**
- **FY08**
  - **Investigate thermal 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**