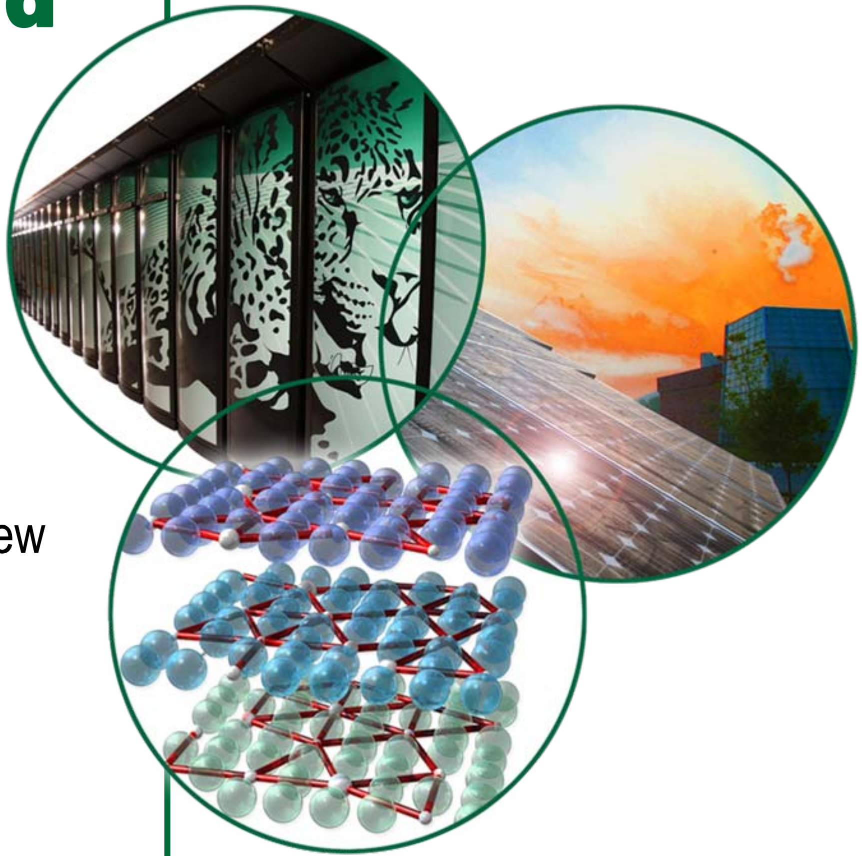
Investigations of electrode interface and architecture

Nancy Dudney

Oak Ridge National Laboratory

es_36_dudley

Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, May 21, 2009



"This presentation does not contain any proprietary, confidential, or otherwise restricted information"

U.S. DEPARTMENT OF ENERGY

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

Overview

- Timeline
  - Start July, 2007
- Budget
  - $300k FY08
  - $300k FY09
- Technical barriers for PHEV
  - Cycle and calendar life (5000 cycles EV; 300,000 cycles HEV; 15 yr.)
  - Abuse tolerance
  - Much higher energy density (40 mile system: 11.6 kWh; 120 kg; 80 liter)
- Partners
  - Oak Ridge National Laboratory
  - High Temperature Materials Lab, ORNL
    - In situ SEM, TEM
  - Collaboration
    - LBNL independent cathode testing

Objectives

- Investigate the use of highly-conductive graphite as the current collector for Li-ion battery cathodes.

- Study the properties of the SEI formed between Li or graphite anodes in aprotic electrolytes. Use these fundamental studies to identify new strategies to stabilize the interface.

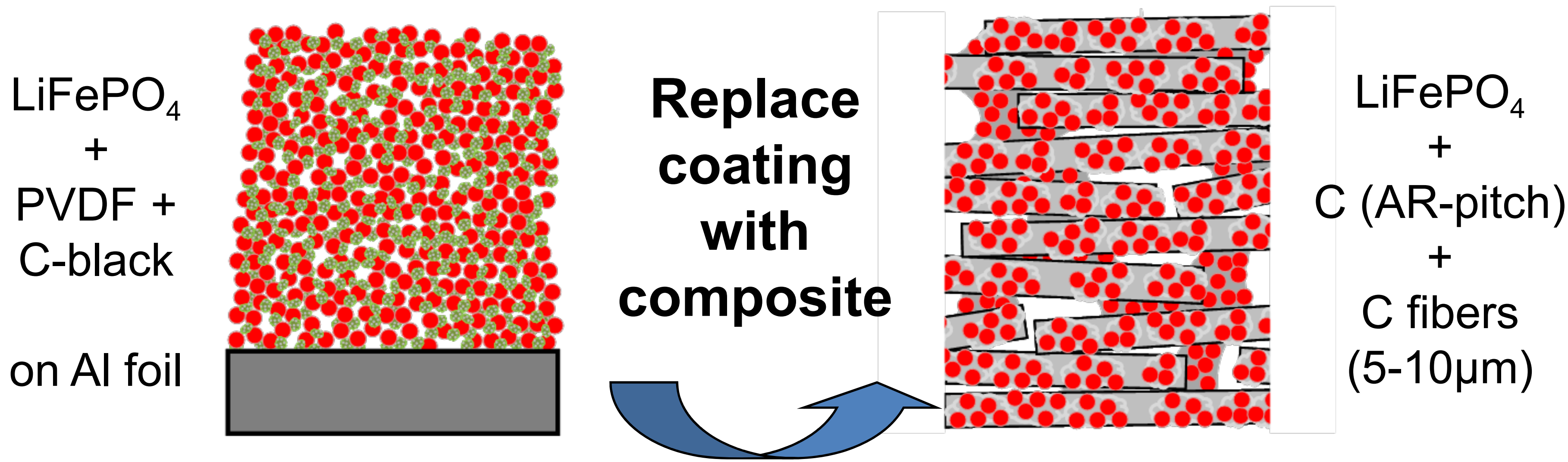
Milestones

- Condensed from FY08 and FY09 AOP

	Milestones:	target
1.	Project the energy and power densities for batteries with graphite current collectors	Sept 08
2.	Improve the microstructure characterization and control of $LiFePO_4$-graphite cathodes, correlating properties with simulation.	May 09
3.	Evaluate cycling performance of selected cathodes at ORNL and LBNL.	May 09
4.	Address issues of thermal conduction, mechanical robustness, and cost.	Sept 09
5.	Continue in situ studies revealing the nature and transport of SEI at the Li-electrolyte interface	Sept 09

Approach - *graphite current collector*

- A conductive carbon skeleton will improve uniformity of current and temperature in cathode - extending lifetimes and safety.

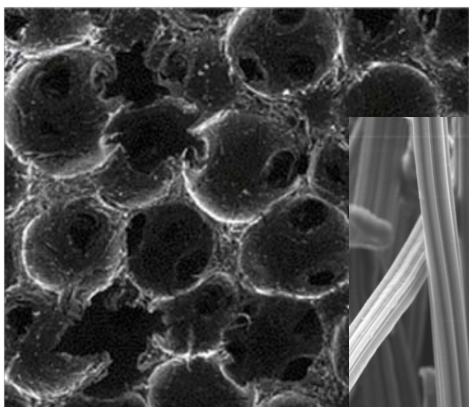


advantages	concerns	evaluate
shorter path for electrons and heat,	cost	half-cell cycle
more conductive particle contacts,	manufacturing	thermal
less aging from binder & corrosion		mechanical

Technical Progress – *choosing material*

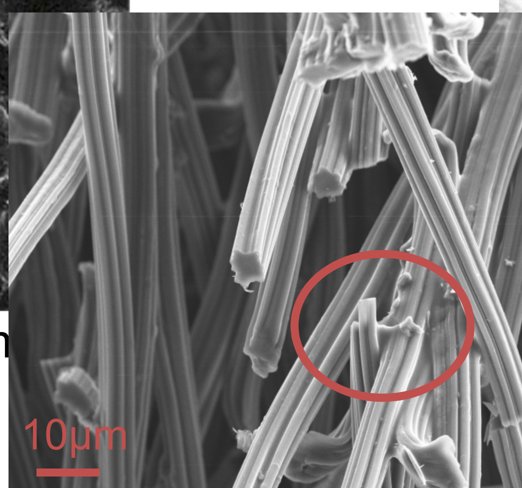
- **Many new graphite and carbon nanotube products are being developed.**
- **Materials are still too expensive, but prices have dropped dramatically. This is expected to continue.**
- **Estimated cost of carbon for 1.4 Ah battery is $0.40 to $1.70**
- **Some fiber papers and mats can be rolled for coating. (100µm and up)**

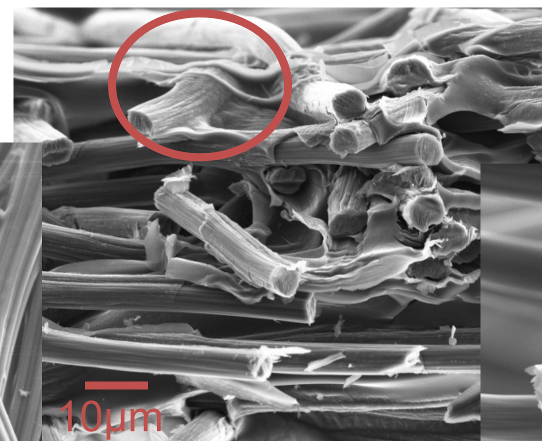
foams → **bonded fibers** → **unbonded fibers**



Koppers foam
$0.44/g

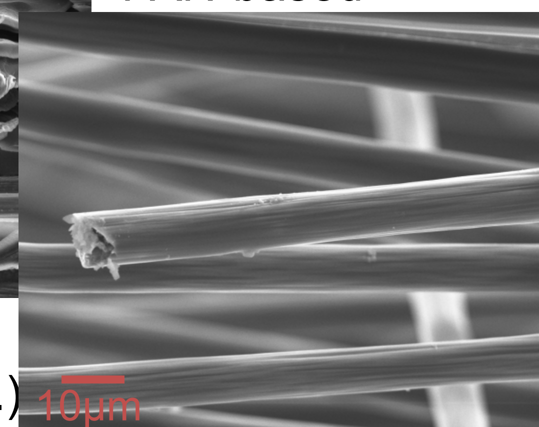
Calcarb CBCF
$0.16/g





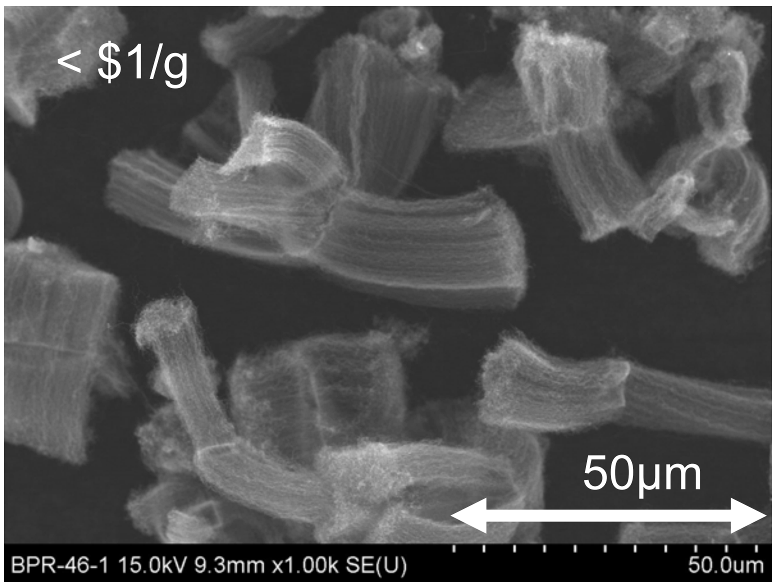
Toray paper
$3/g (10x dec. proj.)
pitch-based

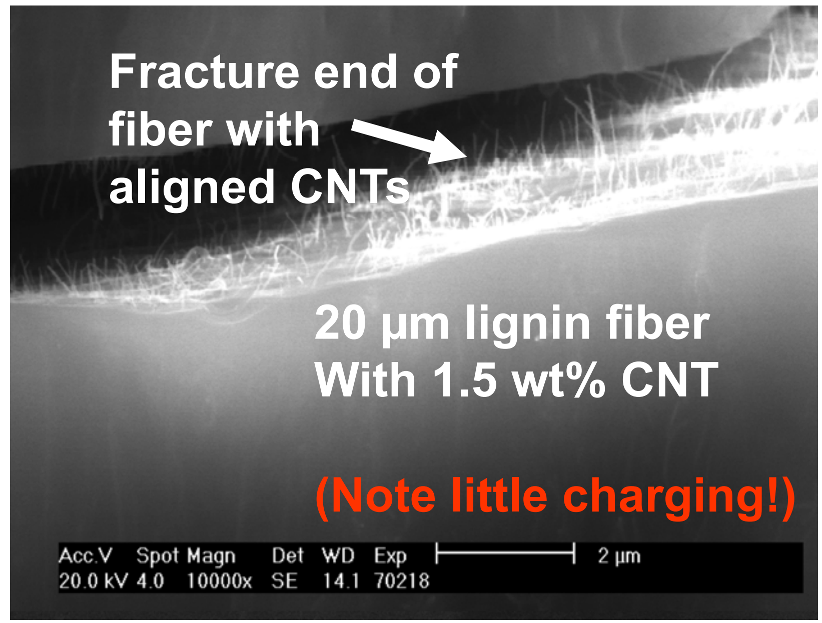
Hollingsworth and
Vose, $0.16/g
PAN-based



Technical progress – *cost effective materials*

- **Lower cost MWCNTs by CVD "Cratos V Nano-Wool" an ORNL R&D 100 award**
- **Small (1-5%) addition of CNT greatly enhance properties of less costly carbon fibers and foams**
- **Cost of CNT-reinforced lignin fibers may approach 2 to 7 ¢/g**





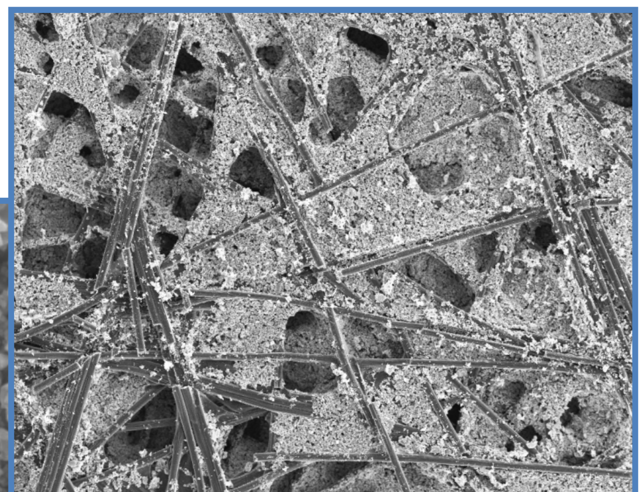
WTEC Report on International Assessment of R&D of Carbon Nanotube Manufacturing and Applications, June 2007

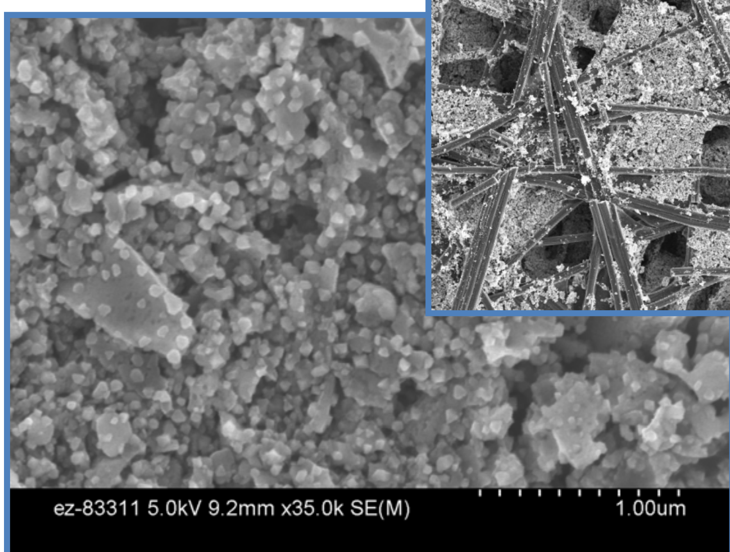
> Li-ion batteries will be 2nd major commercial success for CNTs.

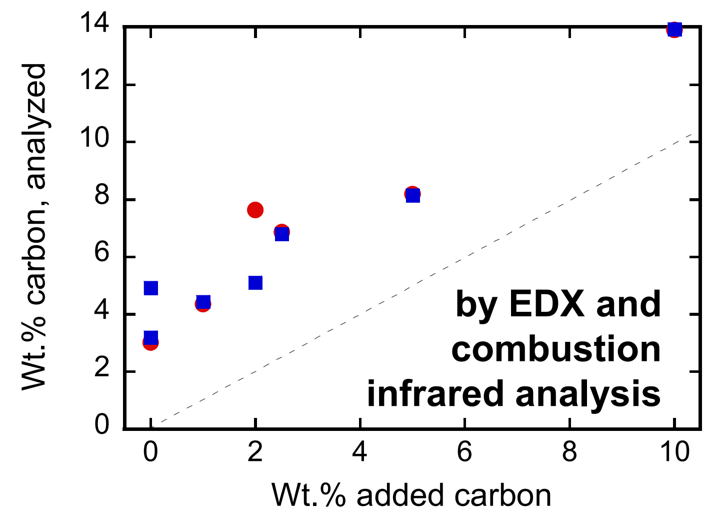
> Showa Denko, Japan producing >100 tons/yr, mainly for battery application.

Technical Progress *– control of microstructure and composition*

- **Coating from solution of finely ground $LiFePO_4$ + AR pitch. Pitch forms conductive graphitic bonds when treated at 500-700°C.**
- **Carbon analysis larger than expected. 3-5% residual from solvents and precursors.**
- **Solution dries as web rather than coated fibers. Geometry complex.**
- **Challenge to increase density without pressing. Slurry 0.2 to 1.3 g/cc solids.**

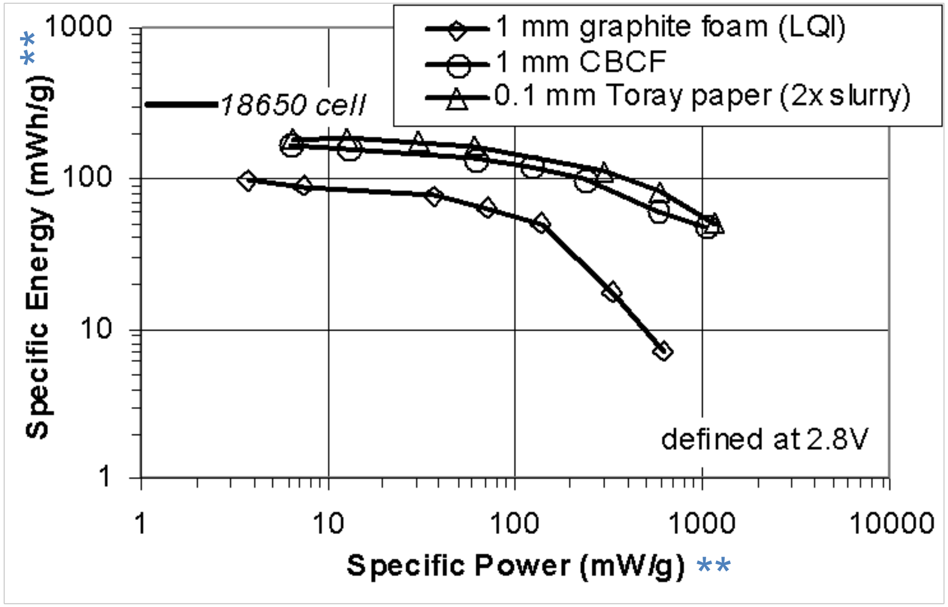






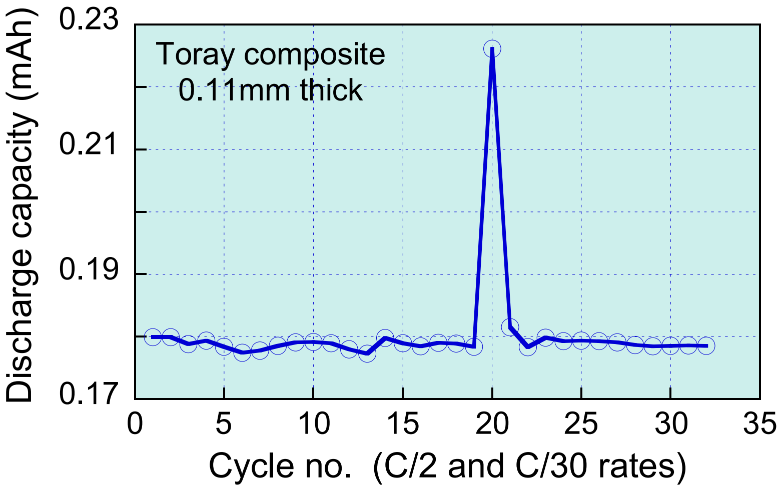
Technical Progress *–cycling and rate performance*

- Rate performance
  - Better for carbon fibers than foams
  - 1mm-thick CBCF with transverse fibers equals thinner paper composites
  - Have not identified maximum loading, where density impedes cycling



** Normalized by total weight of cathode: $LiFePO_4$ + carbon skeleton

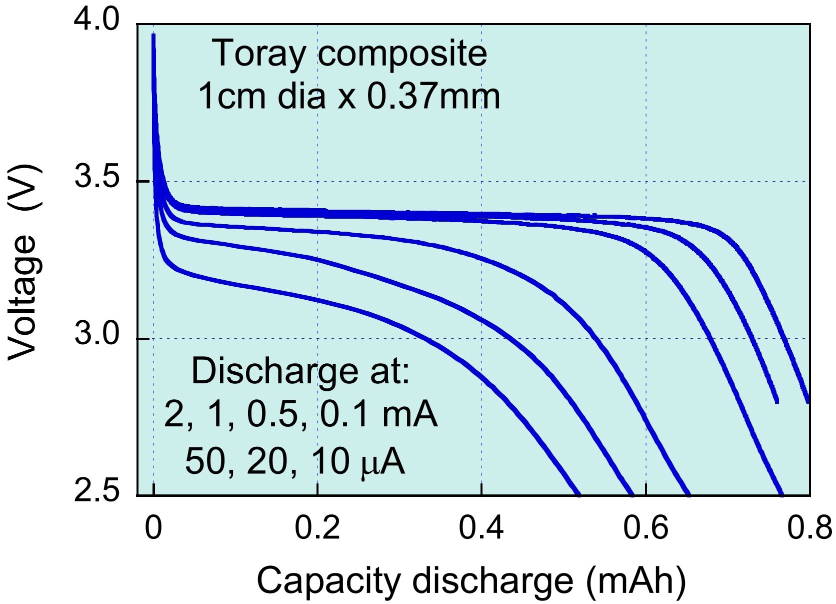
- Energy density
  - Up to 30 mWh/cm^2 for 5mm CBCF
  - Only 120 mWh/cm^3
  - Improvement requires much higher $LiFePO_4$ loading
- Cycle life
  - Better for thin composites
  - Limited by Li degradation.

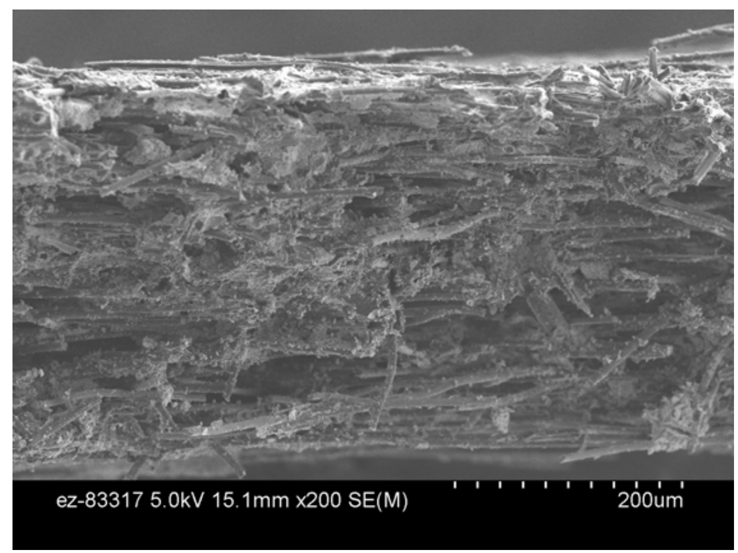


Technical Progress *– evaluate by V. Battaglia*

- **Samples prepared matching dimensions and capacity of typical LBNL samples***
  - **9/16” diameter, 1-2.5 mAh/cm^2 (1.6-4 mAh)**
  - **$LiFePO_4$ composites with Toray paper, 0.37mm and 0.11mm thick**
- **Results LBNL are TBD**
- **Sister cells at ORNL (1 cm diameter)**

	LBNL samples		projection high loading
thickness (mm)	0.37 mm	0.11 mm	0.37 mm
loading (wt.% LFPO)	35 %	45 %	70 %
capacity (mAh)	2.5 mAh	0.6 mAh	12 mAh
vol.% porosity	62 %	70 %	~30%

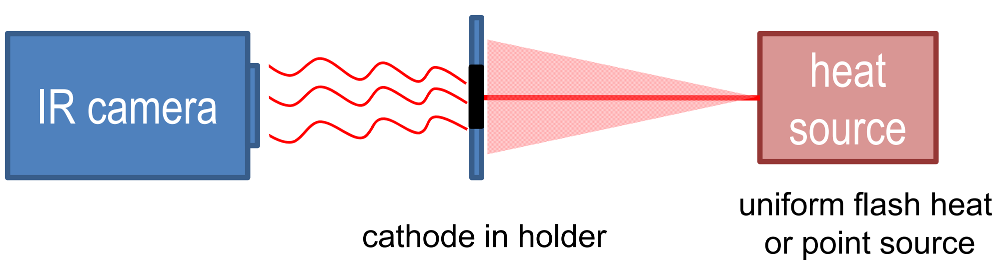




*H. Zheng, V. Battaglia, JECS 155 (2008) A887.

Technical Progress – *initial thermal testing*

- **Thermography:**
  - **flash diffusivity system: through thickness measurement of thermal diffusivity**
    - **comparison of through-thickness thermal diffusivity of carbon supported cathodes and conventional cathodes**
  - **In-plane diffusivity using continuous (laser) point-source heating**
    - **comparison of in-plane thermal diffusivity of carbon supported cathodes and conventional cathodes**
    - **clear demonstration of heat dissipation due to point source heating, which is representative of localized thermal failure in lithium ion cells**



Future work *- carbon skeleton current collectors*

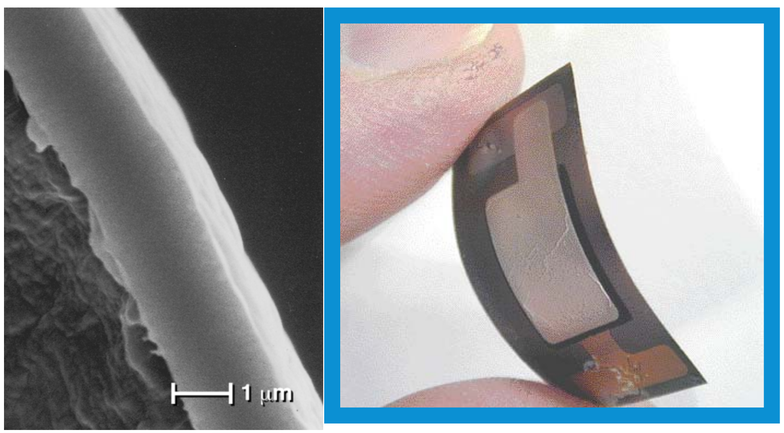
- Immediate
  - Thermal conductivity study
  - Wrap up study with commercial foams and fiber papers, publish results
- Continuing effort - for much higher $LiFePO_4$ loading & dense structure, (also lower cost & better control)
  - Use loose carbon fibers. Cast dispersion of fibers with AR-pitch + $LiFePO_4$ powders; bond with one step heating (poss. microwave).
- Vision for a future project
  - Coated continuous carbon fibers for interwoven battery architecture
    - $LiFePO_4$-coated graphitized fibers
    - Si-plated or bare graphitized fibers
    - Need highly conductive skeleton for 3D architecture with high aspect ratio electrodes
    - Potential for multifunctional use, another route to system mass and volume efficiency
      - (J. Snyder, Army Research Lab, JECS 156 (2009) A215.)

Approach –*Studies of SEI at Li metal anode*

- Why do we need further work on SEI layer? Is a Li anode possible?

Background:

No Li dendrites for thin film battery with ORNL electrolyte (Lipon ~1µm).

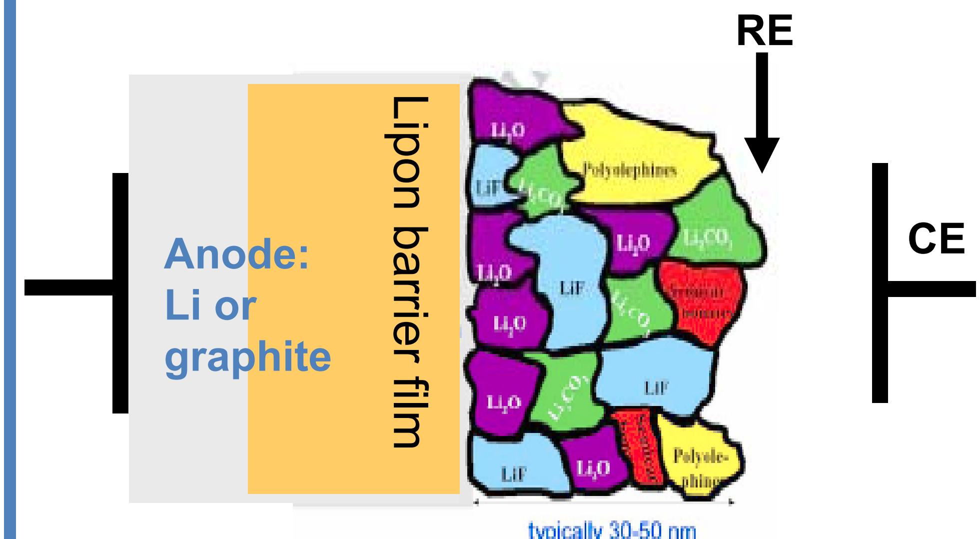


But unsupported Lipon barrier on Li → cracks if volume change is uneven.

Polyplus's study of Lipon on Li anode → improvement, but flaws develop leading to dendrites.

Approaches for engineering solution:

- ➢ Reinforce thin Lipon film
- ➢ Engineer SEI layer
  - promote uniform Li plate/removal
  - enhanced mobility for smoothing interface.

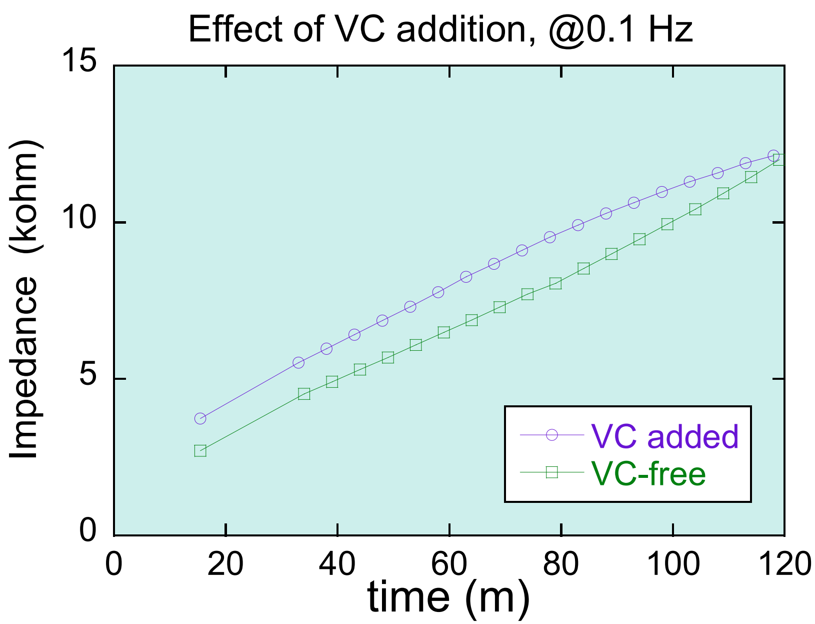


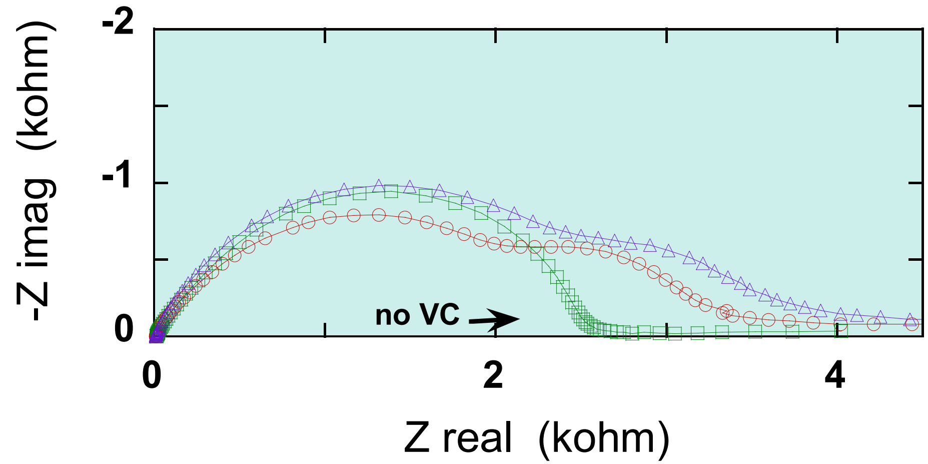
Understanding is lacking.
What is transport path for Li across SEI?
How is SEI growth passivated?

 Managed by UT-Battelle
for the U.S. Department of Energy

Technical Progress – *SEI formation*

- **Characterization by Electrochemical Impedance Spectroscopy (5 or 10mV signal) to minimize perturbation of the interface**
- **SEI forms rapidly but continues to age and become more resistive for many hours**
- **Results of side-by-side tests show vinylene carbonate addition to $LiPF_6$ (EC+EMC) electrolyte contributed another dispersion (layer of SEI), but did not reduce resistivity or non-linear behavior.**

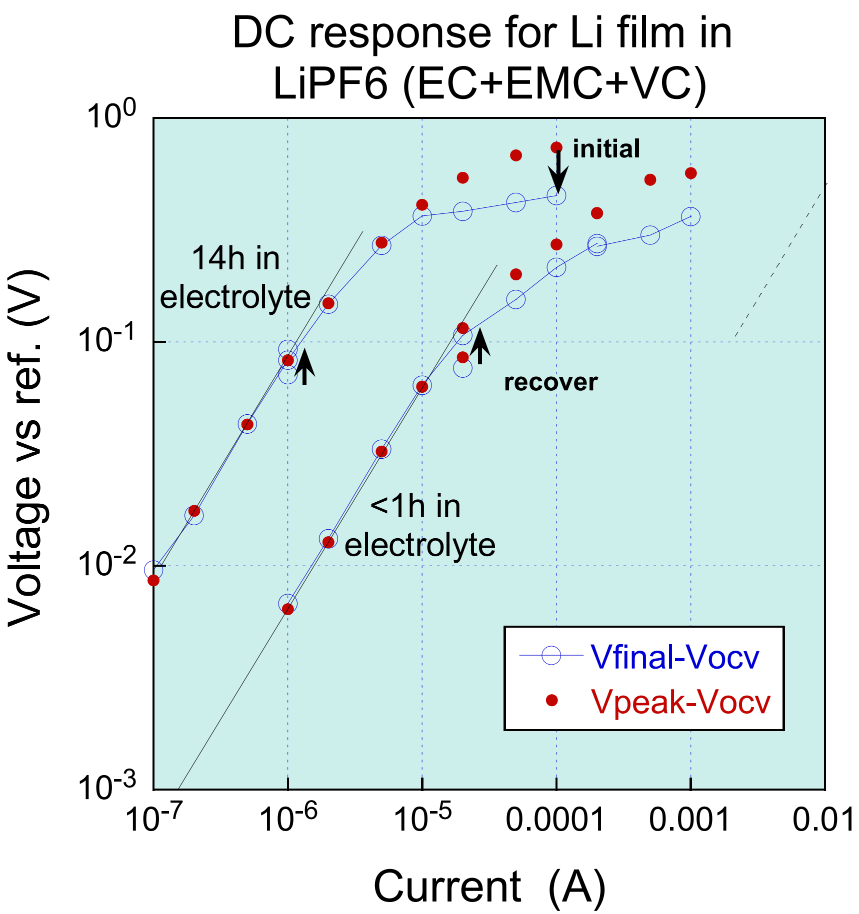


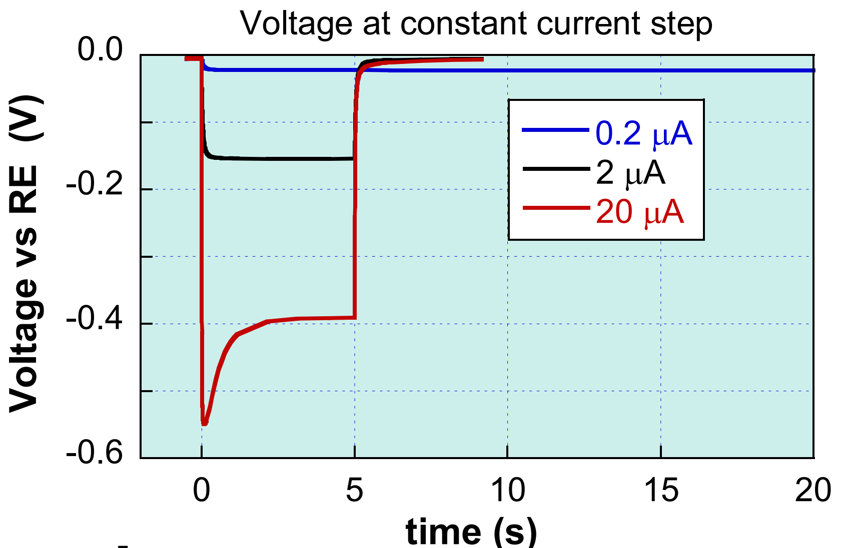


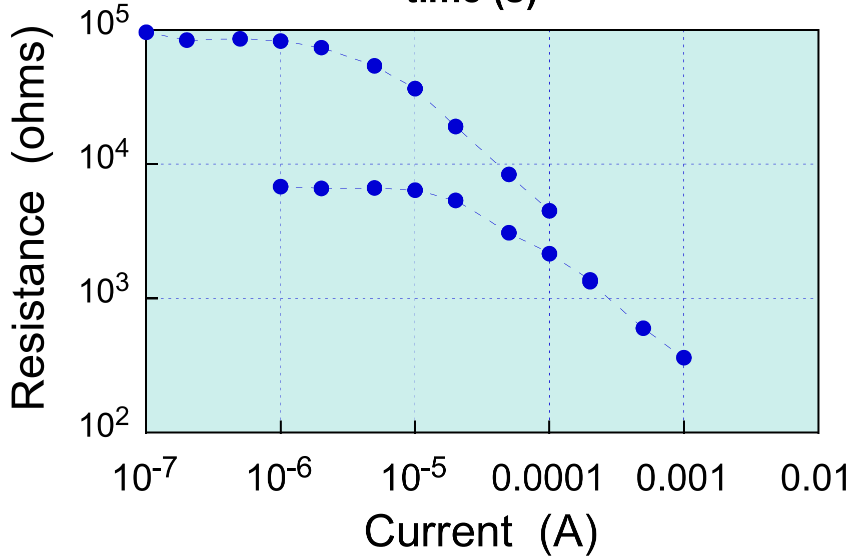
 Managed by UT-Battelle
for the U.S. Department of Energy

Technical Progress *– transport properties of SEI*

- **DC chronopotentiometry reveals highly non-linear electrical response**







Future work – *Li transport at SEI in relation to surface roughening*

- **Expand investigation of non-linear electrical response**
  - Goal is to understand mechanism, gain new insight
  - Evaluate distribution of current
    - (IR thermography, electrochemical scanning probe)
  - Evaluate alternative electrolytes, additives, or anodes (Si, C)
    - silane (Song) or chlorosilane derivatives (Dunn, Wudl),
    - dioxolane (Aurbach) or propylene carbonate
    - roughened Li surface or carbon
- **Reevaluate – what is promising route to stabilize Li interface?**

Summary

- Composites of carbon fibers + $LiFePO_4$ form effective cathodes. Advantages include more uniform current and temperature distribution. The remaining challenge is to increase the density and $LiFePO_4$ loading in the composite by alternative processing routes. Continued reduction in the cost of carbon fibers will make this cost effective.

- Non-uniform transport due to the morphological and compositional heterogeneity of the SEI may cause degradation of interface for both lithium and lithium-ion electrodes. A non-linear electrical response of the SEI formed in a carbonate electrolyte has been observed for the first time. Understanding the creation and distribution of high current paths will suggest new strategies to engineer protective barriers and stabilize the interface.