

Project ID #ES087

# Investigations of cathode architecture using graphite fibers

Nancy Dudney

Oak Ridge National Laboratory

June 9, 2010

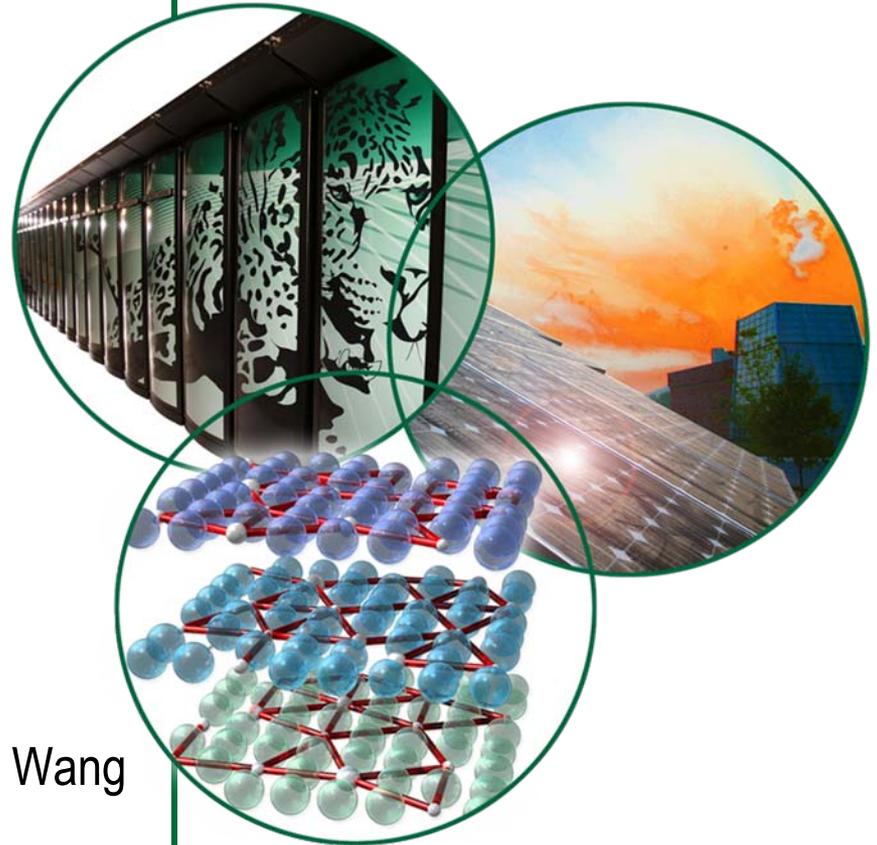
Contributors:

Jim Kiggans, Andrew Kercher, Jagjit Nanda, Hsin Wang



JUNE 7-11, 2010  
Washington, D.C.

Annual Merit Review & Peer Evaluation Meeting  
2010 U.S. Department of Energy Hydrogen Program and Vehicle Technologies Program



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



# Overview

## Timeline

- Start Oct, 2007
- End Sept, 2010
- 83% complete

## Budget

- Total project funding
  - \$900k
- Funding in FY09
  - \$300k
- Funding in FY2010
  - \$300k

**Barriers for PHEV (40miles):** Poor cycle life.  
Poor abuse tolerance. Low energy density.

## Goals:

- Cycle and calendar life (5000 cycles to deep discharge; 10+ yr.)
- Abuse tolerance
- Energy density (40 mile system: with 11.6 kWh; 120 kg; 80 liter)

## Partners

- Oak Ridge National Laboratory
- High Temperature Materials Lab, ORNL
  - Microscopy, Thermography
- Collaboration, external
  - LBNL independent cathode testing (V. Battaglia)
  - HydroQuebec for materials (K. Zaghib)

# Objective and relevance

- **Objective:**

- Investigate cathode architectures based on a highly conductive three-dimensional skeleton of bonded graphite fibers in place of the aluminum foil current collector
- Look for improvement in the cycle life and thermal conductivity of the cathodes in the absence of organic binder, aluminum foil, and microstructural features related to compaction.
- Project likely improvement in the cell energy density based on optimization of thicker cathodes with a high energy per area.
- Evaluate cost-effectiveness and manufacturability with anticipated materials advancements.

- **Relevance:**

- Addresses barriers for PHEV (40miles) of poor cycle life and low energy density.
- Electrode architectures based on fiber support and high temperature bonding of electrode materials is a promising leap frog technology for EV application.

# Milestones

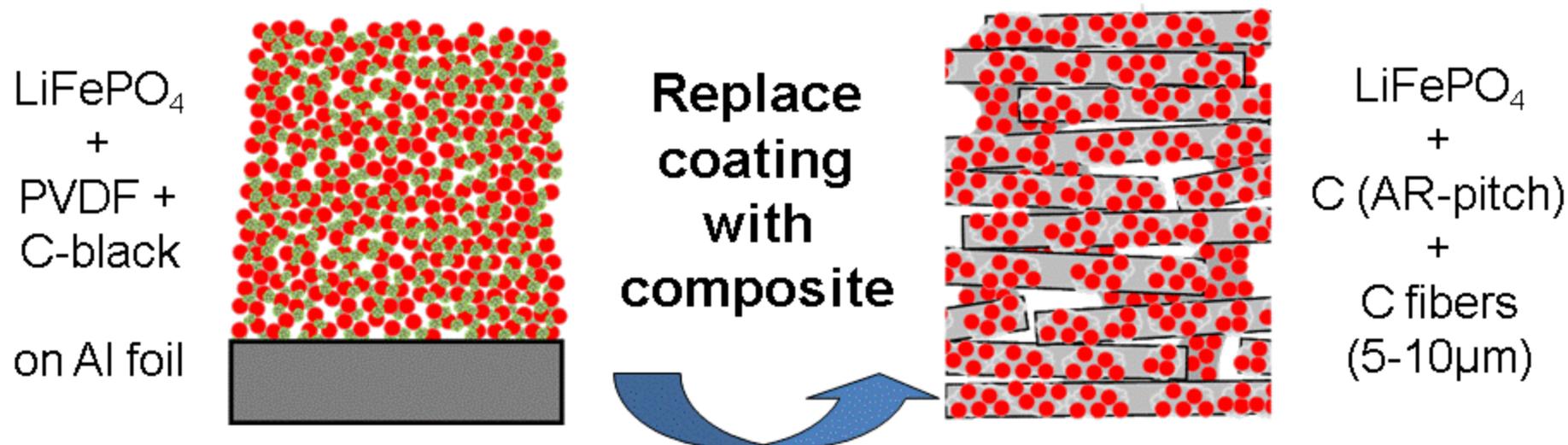
- Condensed from FY09 and FY10 AOP

Milestones:	target
1. <b>Improve the microstructure characterization and control of LiFePO<sub>4</sub>-graphite cathodes, correlating properties with simulation.</b> <i>Complete. Detailed simulation not required.</i>	<b>May 09</b>
2. <b>Evaluate cycling performance of selected cathodes at ORNL and LBNL.</b> <i>Completed.</i>	<b>May 09</b>
3. <b>Address issues of thermal conduction and mechanical robustness.</b> <i>Completed. Evaluation continuing with alternate fibers and architectures.</i>	<b>Sept 09</b>
4. <b>Provide composite cathodes of LiFePO<sub>4</sub> and carbon fibers compatible with LBNL pouch cell assembly.</b> <i>On schedule.</i>	<b>Apr 10</b>

---

# Approach

- A conductive carbon skeleton with >20-fold higher surface area improves uniformity of current and temperature in cathode - extending lifetimes and safety.
- Formation of bonds at high temperature improves electrical and mechanical contacts.



## Advantages

shorter path for electrons and heat,  
more conductive particle contacts,  
less aging from binder & corrosion  
less damage & occluded pores from pressing

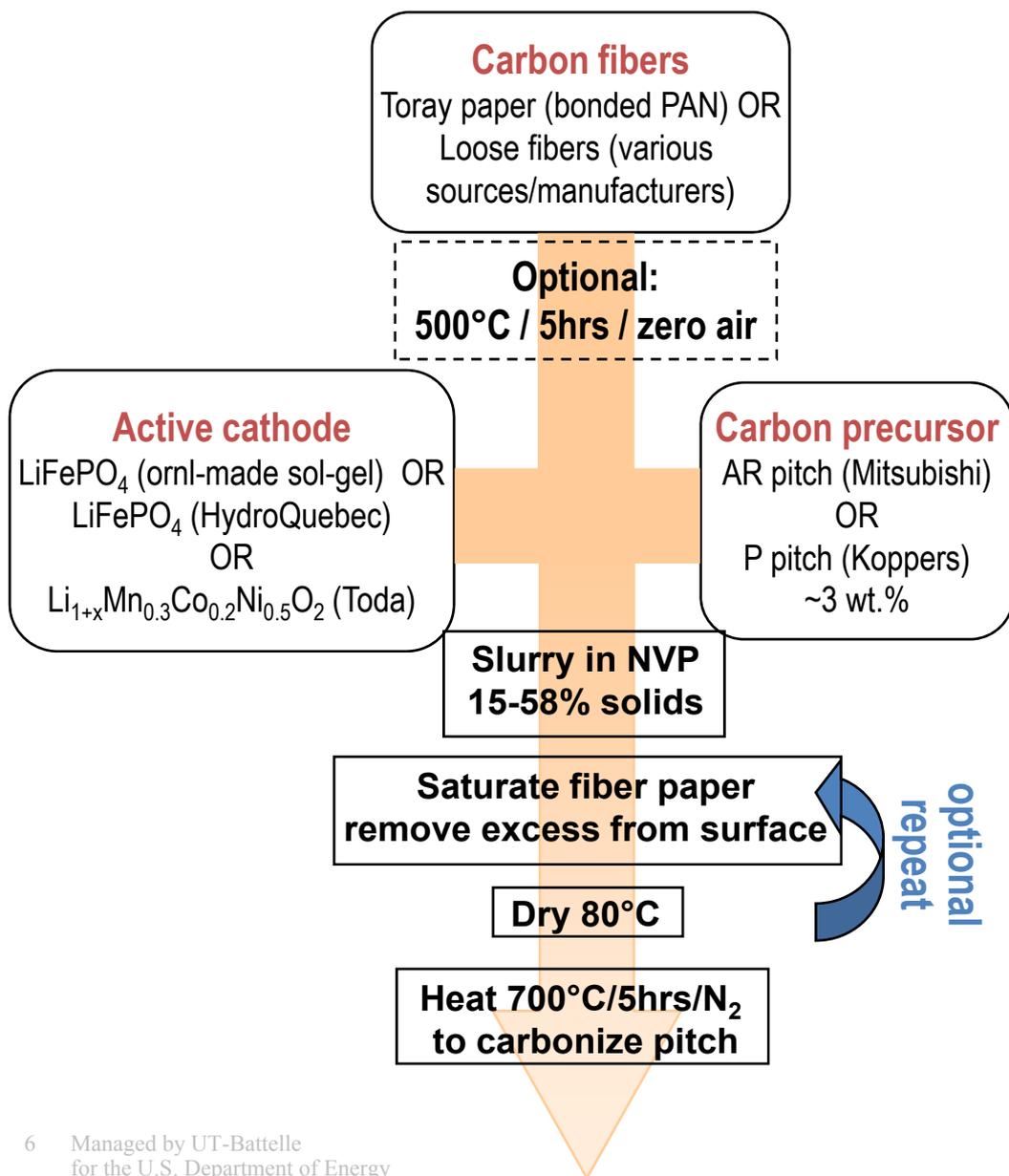
## Concerns

cost  
manufacturing

## Evaluate

half-cell cycle  
thermal  
mechanical  
metallization

# Approach (fabrication and characterization)



## Characterization

### Cycling with Li half cells (at ORNL and LBNL)

LiPF<sub>6</sub> (EC+EMC) Ferro Corp.  
Swaglok and coin cells  
(Prismatic pouch cells in progress)

Deep discharge cycle tests  
CCCV (to 4V); CC (to 2.5V)  
C/30 to 30C  
10s pulse (at high/low DOD)

**Microstructure**  
(SEM, xray tomography)

**Thermal diffusivity**  
(LaserPIT technique, in-plane transport  
using scanning pulsed laser)

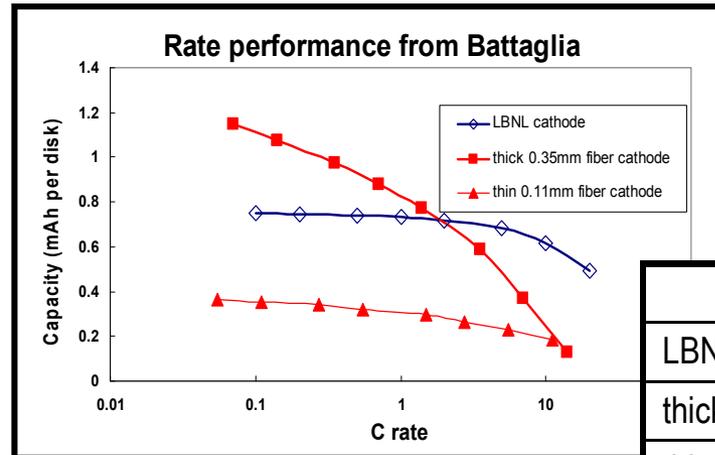
### • Important distinctions

- Free of organic binders
- Bonds formed with carbon at high temperature
- No pressure forming

# Technical Accomplishments/Progress *(next 5 slides)*

## Energy and power performance confirmed by LBNL (Battaglia) using ORNL-made $\text{LiFePO}_4$ , but noted low energy density.

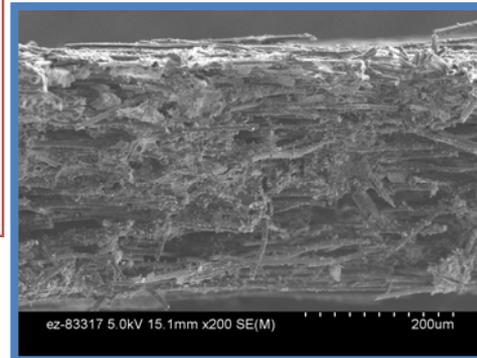
- Cathodes supplied to LBNL for coin cell
  - 0.11 & 0.37 mm thick
  - Toray carbon fiber + ORNL  $\text{LiFePO}_4$  (made with low conc 26% slurry)
  - designed to match typical LBNL size and capacity
- LBNL confirmed our measurements
  - LBNL notes low specific and volumetric energy
- Other evaluation of these cathodes
  - Good uniformity observed by sem\* and xray tomography
  - Good cycling\*
  - Thermal transport dominated by fibers
- \*initiated last review



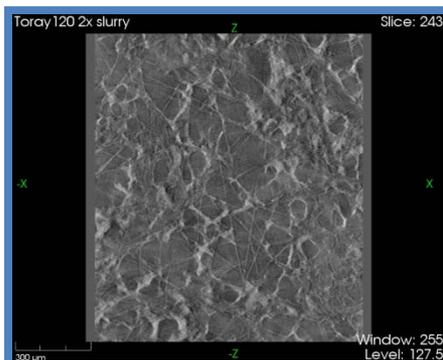
Comparison of fiber composites and typical LBNL cathodes

	mAh/g	mAh/cm <sup>3</sup>
LBNL	50 **	122 **
thick	24	17
thin	30	20

\*\* includes Al foil in mass and vol.

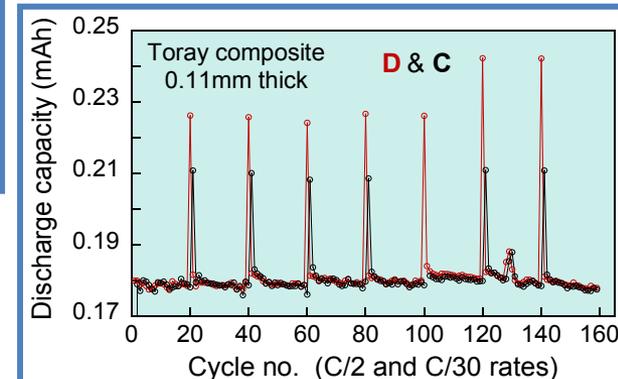


SEM fracture cross section



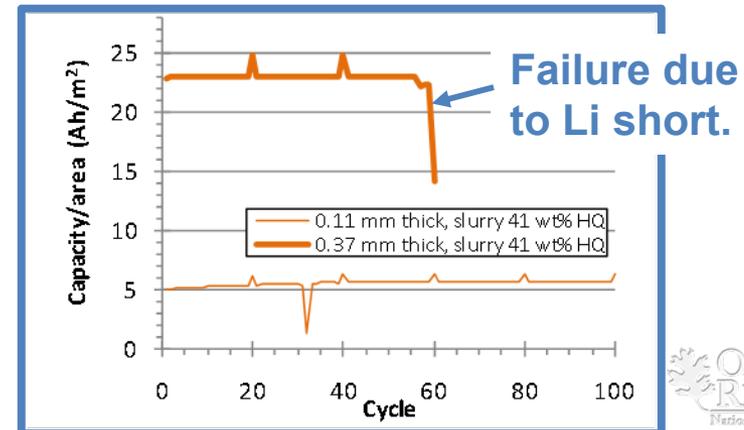
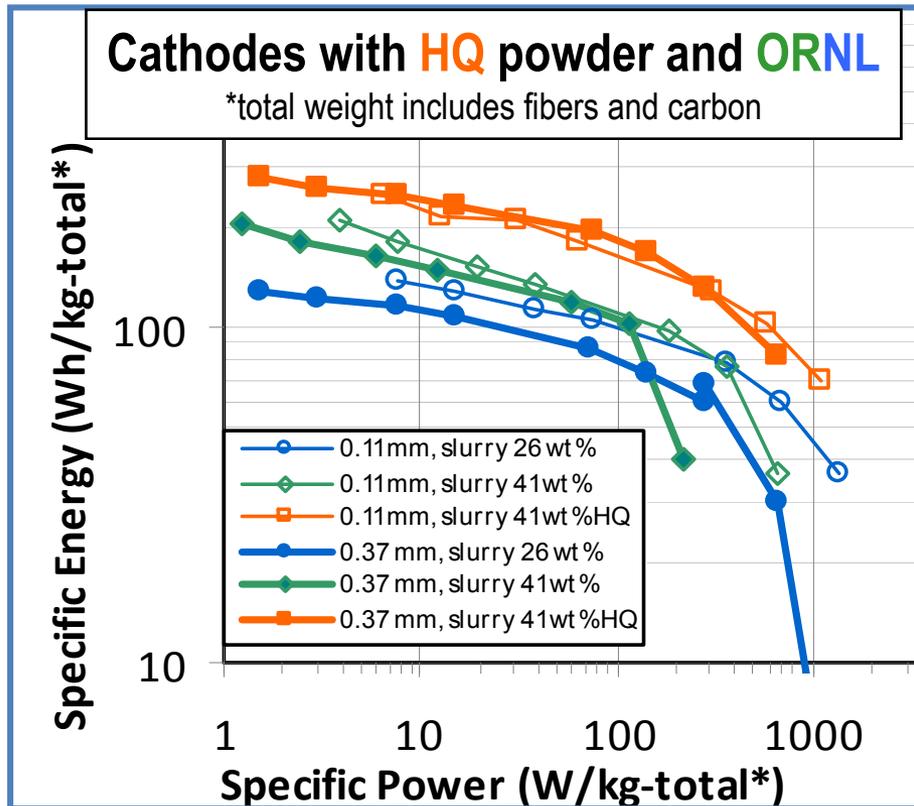
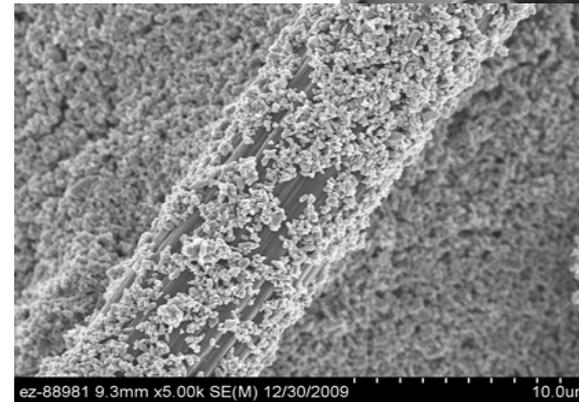
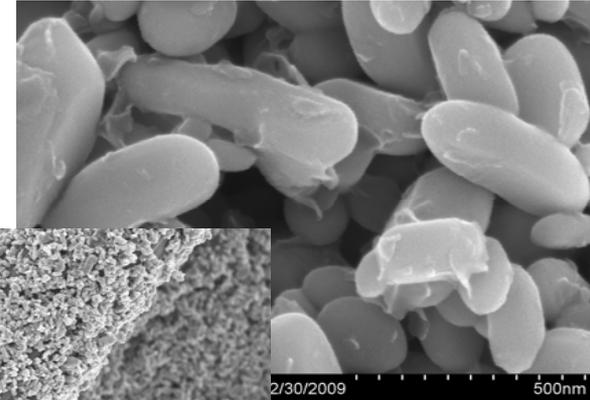
X-ray tomograph of midsection

### Excellent capacity retention



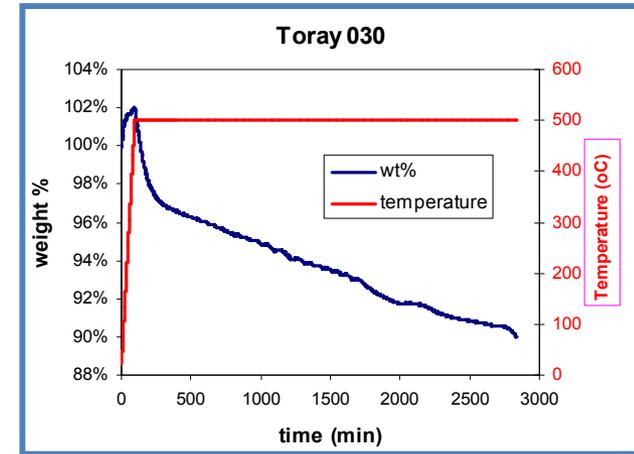
# Cathodes with $\text{LiFePO}_4$ from HydroQuebec have *improved* utilization and power performance. Specific energy now comparable to typical LBNL cathodes.

- Higher solids loading in slurry + higher capacity utilization → adequate specific capacity (see orange data)
- HQ powder from Karim Zaghbi (LifePower  $\text{LiFePO}_4$ ) has smaller and more uniform particles than ORNL-made
- Full utilization ~170 mAh/g- $\text{LiFePO}_4$  (for fiber cathodes with HQ powder)
- Performance thick ≈ thin sheets (for HQ cathodes)
- Cycle life good for all cathodes. Degradation and failures due to Li anode
- Need further increase in density for better volumetric energy density

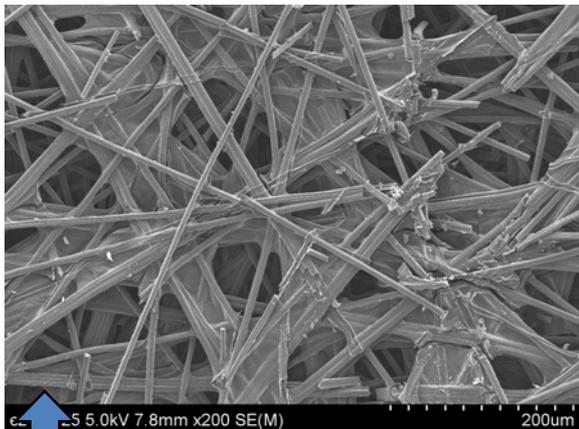


# Uniformity of the $\text{LiFePO}_4$ particles on the carbon fibers is improved by oxidation of the carbon before slurry coating

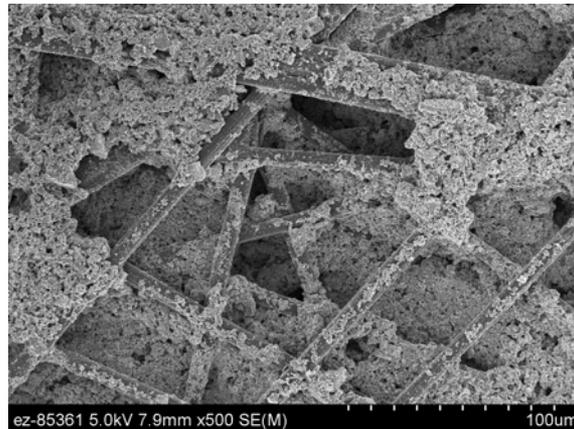
- Carbon fibers from Toray oxidized at  $500^\circ\text{C}$  with 3% weight loss
- Oxidation of carbon fibers  $\longrightarrow$  uniform coating, not higher loading
- Oxidation of carbon fibers  $\not\longrightarrow$  higher loading
  - Weight loading of  $\text{LiFePO}_4$  limited by slurry concentration. Above 53% is too viscous.
  - Tests of multiple slurry coating underway. Expected to increase loading of  $\text{LiFePO}_4$
  - Targets: 55 wt%  $\text{LiFePO}_4$  and 40 vol% porosity



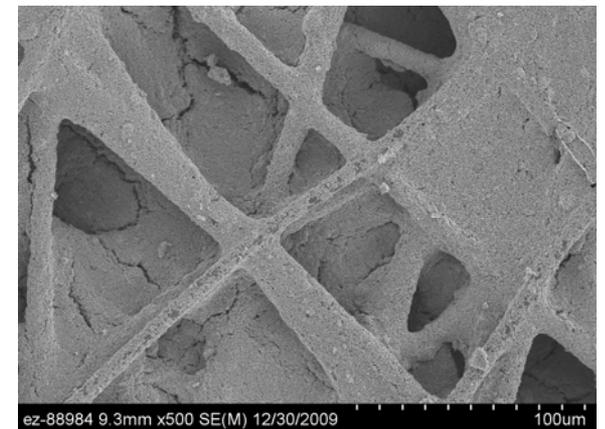
Toray fiber paper, untreated



Coated with ORNL- $\text{LiFePO}_4$



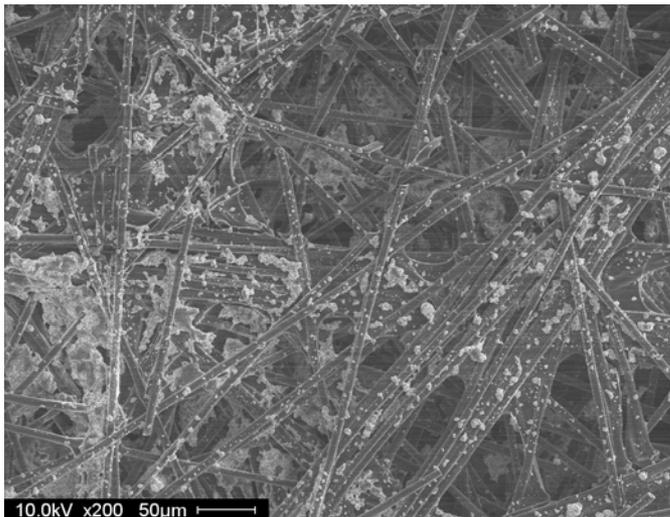
Oxidized fibers with HQ  $\text{LiFePO}_4$



# Approach (slurry coat + anneal) is applicable to other cathodes and carbon binders

- Aim to achieve higher energy density by using high voltage cathodes.
- Excess lithium compound,  $\text{Li}_{1+x} \text{Ni}_{0.5} \text{Co}_{0.2} \text{Mn}_{0.3} \text{O}_2$  (NCM) from Toda Materials Corp.
- Alternative carbon pitch (from Koppers) for 700 C bonding with carbon fiber
- Using the same dispersing procedure as  $\text{LiFePO}_4$  yielded non uniform coating

NCM on Toray paper

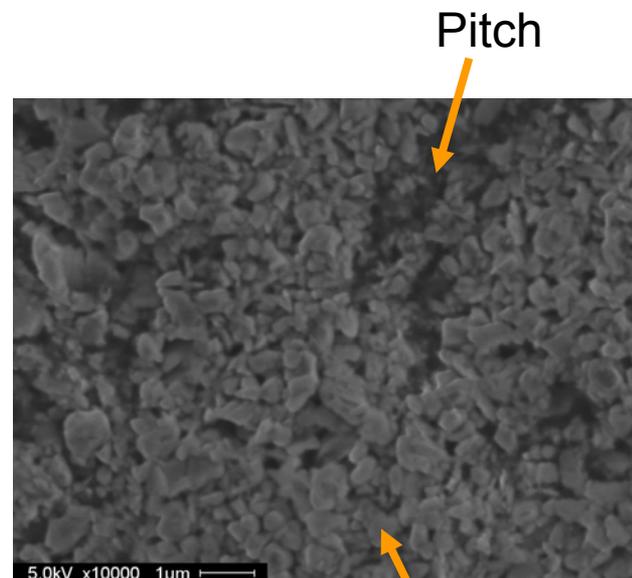


Poor non-uniform coating

Solution



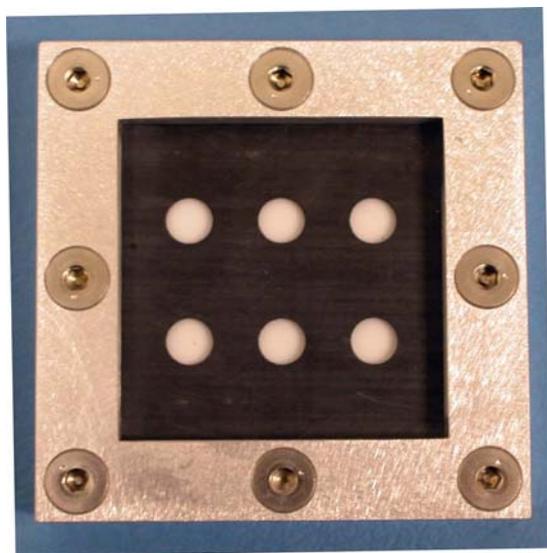
Increased milling media and time (X 2) for uniform slurry dispersion



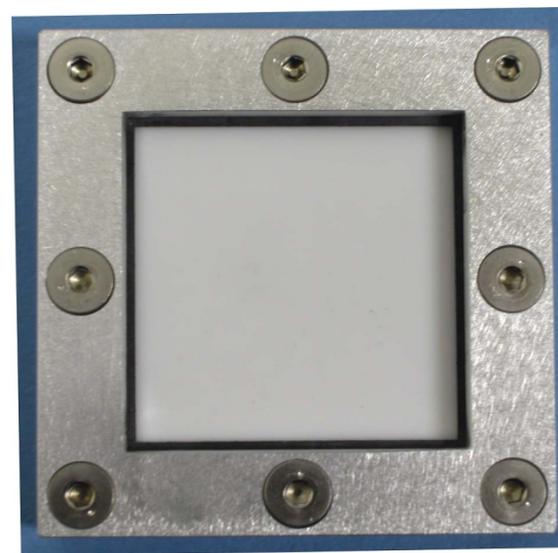
NCM

# Investigation of cathodes prepared with loose fibers are underway

- Casting sheets and disks in Teflon molds
- Loose fibers are a means to reduce cost of carbon component
- Anticipated differences from cathodes prepared with Toray paper – under investigation
  - Electronic pathways may not be a continuous carbon skeleton
  - Cathode will be higher density. Porosity needs to be controlled and aligned.



Mask for casting 9.3 mm discs  
From carbon fiber slurries

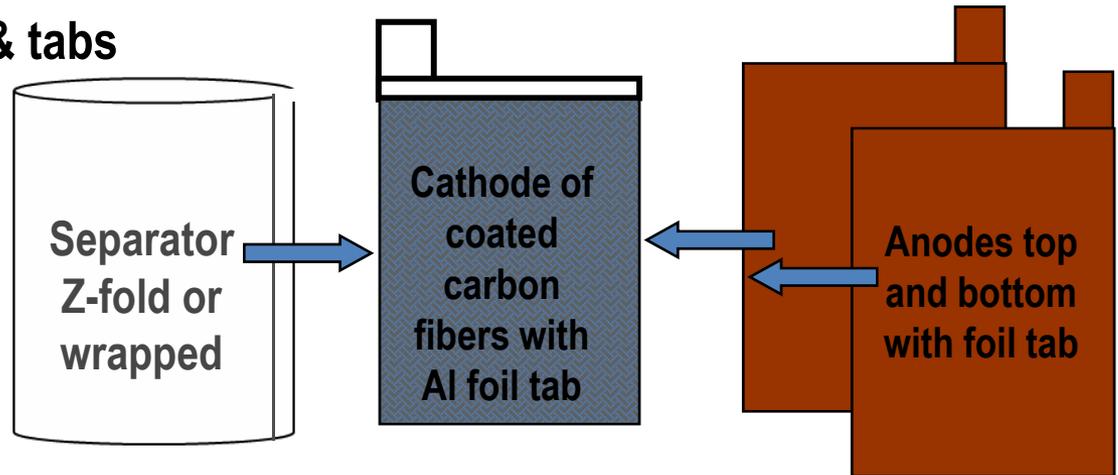


Mask for casting rectangular  
Parts for two pouch cell geometries

# Future work

- Next 6 months

- Improve  $\text{LiFePO}_4$  loading & density with controlled porosity
- Include 10 sec pulses in cycle tests
- Prepare cathodes for prismatic pouch cell assembly (LBNL evaluation)
  - Include metallization & tabs
  - Test as double-sided



- Explore alternative cathodes and fibers
  - Loose, unbonded & low-cost carbon fibers

- Vision of future projects:

- (1) composite with low-cost fibers fabricated at ORNL
- (2) structural batteries based on coated fibers

# Summary

- **Relevance:** Batteries for PHEV require improvements in the cycle life, energy density and safety.
- **Approach:** Cathodes are formed as composites with a highly-conductive carbon fiber skeleton replacing the Al foil as the current collector. Electrical contacts are formed or carbonized pitch, rather than pressing with organic binder.
- **Accomplishment and progress:**
  - Energy and power performance confirmed by LBNL using *ORNL-made*  $\text{LiFePO}_4$ . Cathodes cycled with no significant fade, but energy density was low.
  - Cathodes with  $\text{LiFePO}_4$  from HydroQuebec have near 100% utilization, good power performance even for 0.4mm, and good cycling. Specific energy is acceptable; volumetric energy density is low.
  - Oxidation of the carbon improves wetting and uniformity of the  $\text{LiFePO}_4$  particles on the carbon fibers. Multiple re-coating should further improve energy density.
  - This approach to fabricate electrode is applied to  $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$  with modification in slurry formulation.
  - Investigation of cathodes prepared with non-bonded low-cost fibers are underway.
- **Future work:** Remaining program effort will focus on increasing the density and fabricating prismatic pouch cells for LBNL validation and utilization of low-coat loose fibers.