Fundamental Approach to Electrode Fabrication and Failure Analysis

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LBNL

May 11, 2011

es081_battaglia_2011_o

Overview

Timeline

- October 2008
- September 2012
- 65 % Complete

Budget

- Total project funding
  - DOE share = 100%
  - Contractor share = 0%
- Funding received in FY10
  - $865 k
- Funding for FY11
  - $865 k

Barriers

- Barriers addressed
  - A. Cost
  - C. Performance
  - E. Life
- Targets
  - 205 $/kWh
  - 207 Wh/l
  - 15 years

Partners

PIs	Companies
V. Srinivasan	Conoco Phillips
B. Lucht	Daikin, Japan
M. Doeff	NEI
J. Cabana	SWeNT
G. Ceder	Nippon Denko
K. Zaghib	HydroQuebec
A. Manthiram	
A. Angell	

Relevance: General

Objectives

To make "good" electrodes.

– What does this entail?
  - Correlate electrode performance with the fundamental properties of its constituents.
  - Provide fundamental understanding of key electrode processing steps.
  - Provide fundamental understanding of electrode failure, *i.e*. is it a result of the electrode formulation/processing or of the active material properties?
  - Test materials to evaluate their full potential.
  - Provide quality electrodes to other BATT researchers.

Relevance: 2010 to 11

Objectives

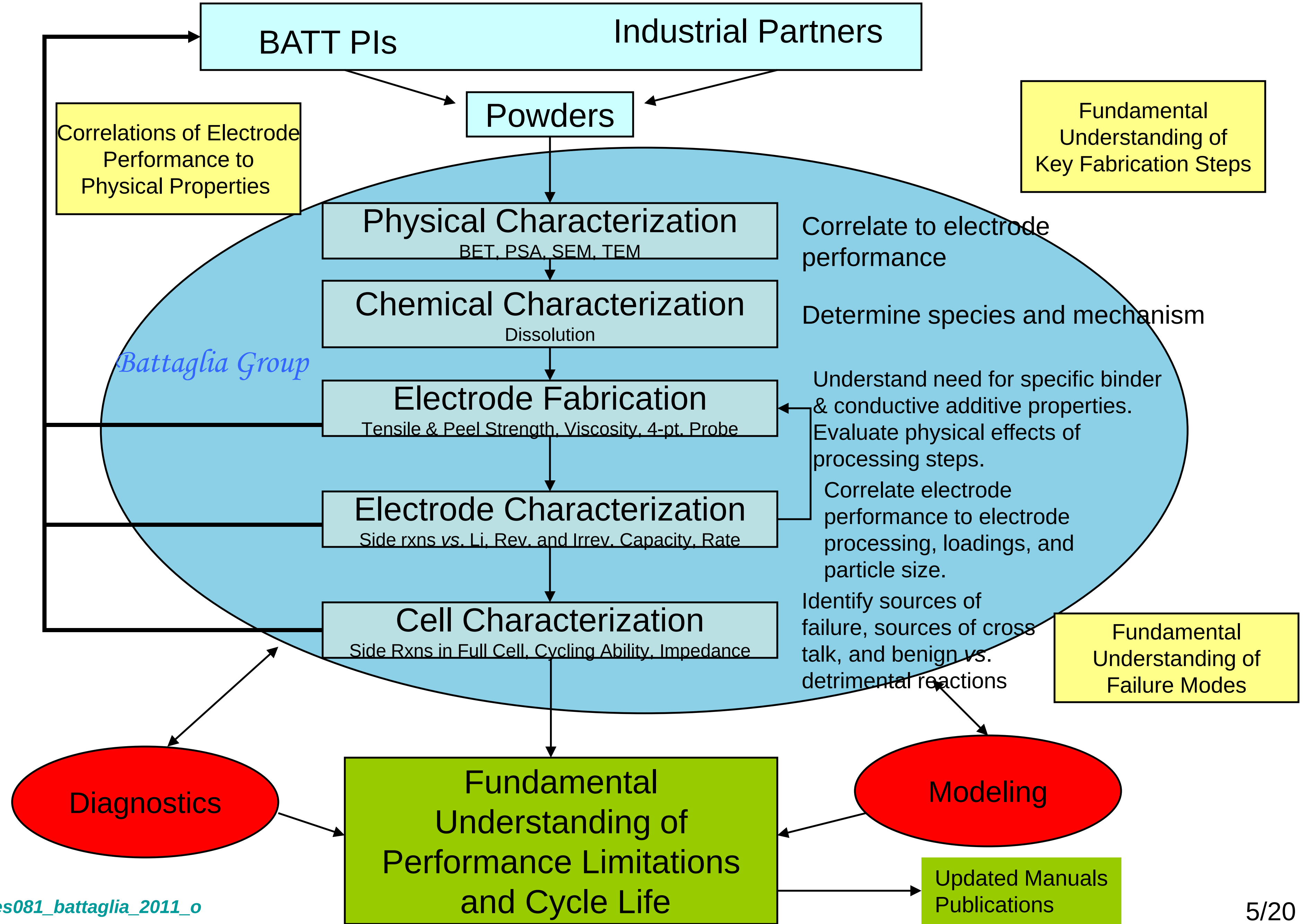
Specific to 2010/11 –

- Develop a sealed cell with a reference electrode that allows long-term cycling outside of a glove box and does not require an additional separator. (Critical to understanding cycle life issues.)

- Understand the electrode performance of an off-stoichiometric material as compared to a carbon-coated material. (A material tested in the ABR Program but moved to the BATT Program for in-depth analysis.)

To meet OVT's Targets of Cost, Performance, and Life it is essential that we have electrodes that exhibit maximum energy density, adequate pulse-power capability, and long life.

Approach/Strategy



Approach/Strategy

DOE Reportable Milestones 2010 thru 2011

Distribute electrodes cycled to different cut-off voltages to BATT program members. (Apr. 10)

Complete

Report results of mechanical properties *vs.* cycling capability of NCM-PVdF-based cells. (Sep. 10)

Complete

Procure 20 g of high-quality $LiNi_{1/2}Mn_{3/2}O_4$. (Jan. 11)

Complete

Supply laminates of $LiNi_{1/2}Mn_{3/2}O_4$ that survive 100 cycles. (Apr. 11)

On schedule

Report the solubility of Mn compounds. (Apr. 11) **On schedule**

On schedule

Report side-reaction rates of NCM *vs*. Li and *vs*. Graphite. (Jul. 11)

On schedule

Report the rate of side reaction of $LiNi_{1/2}Mn_{3/2}O_4$ *vs*. Li. (Sep. 11)

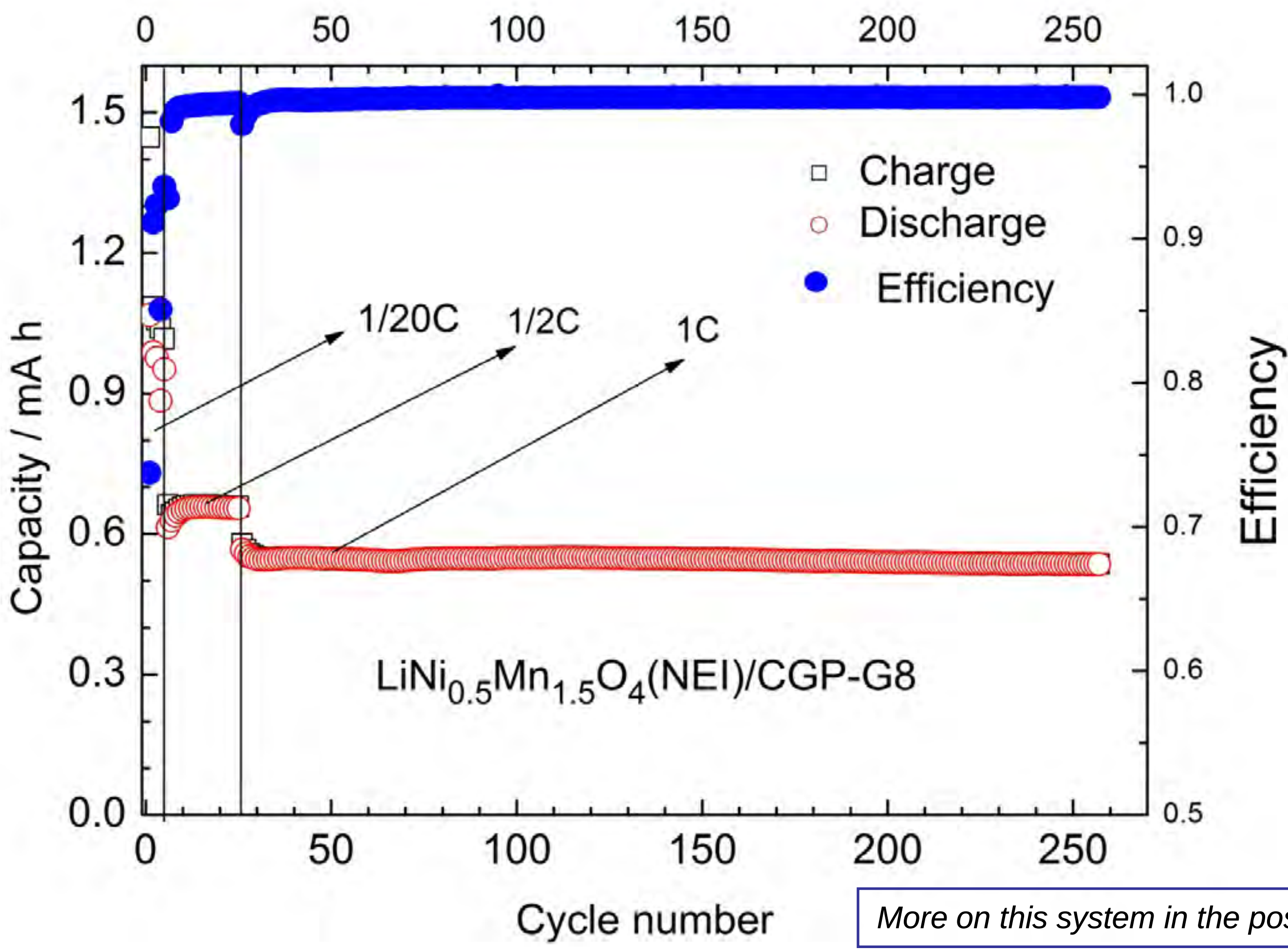
On schedule

Technical Accomplishments and Progress:

1. *Battery Fabrication Manual published online Dec. 17, 2010*

Y. Fu

LNMO(NEI)/CGP-G8



Following the manual, a visiting researcher was able to achieve this level of performance in 4 months.

More on this system in the poster – es029_battaglia_2011_p

Technical Accomplishments and Progress:

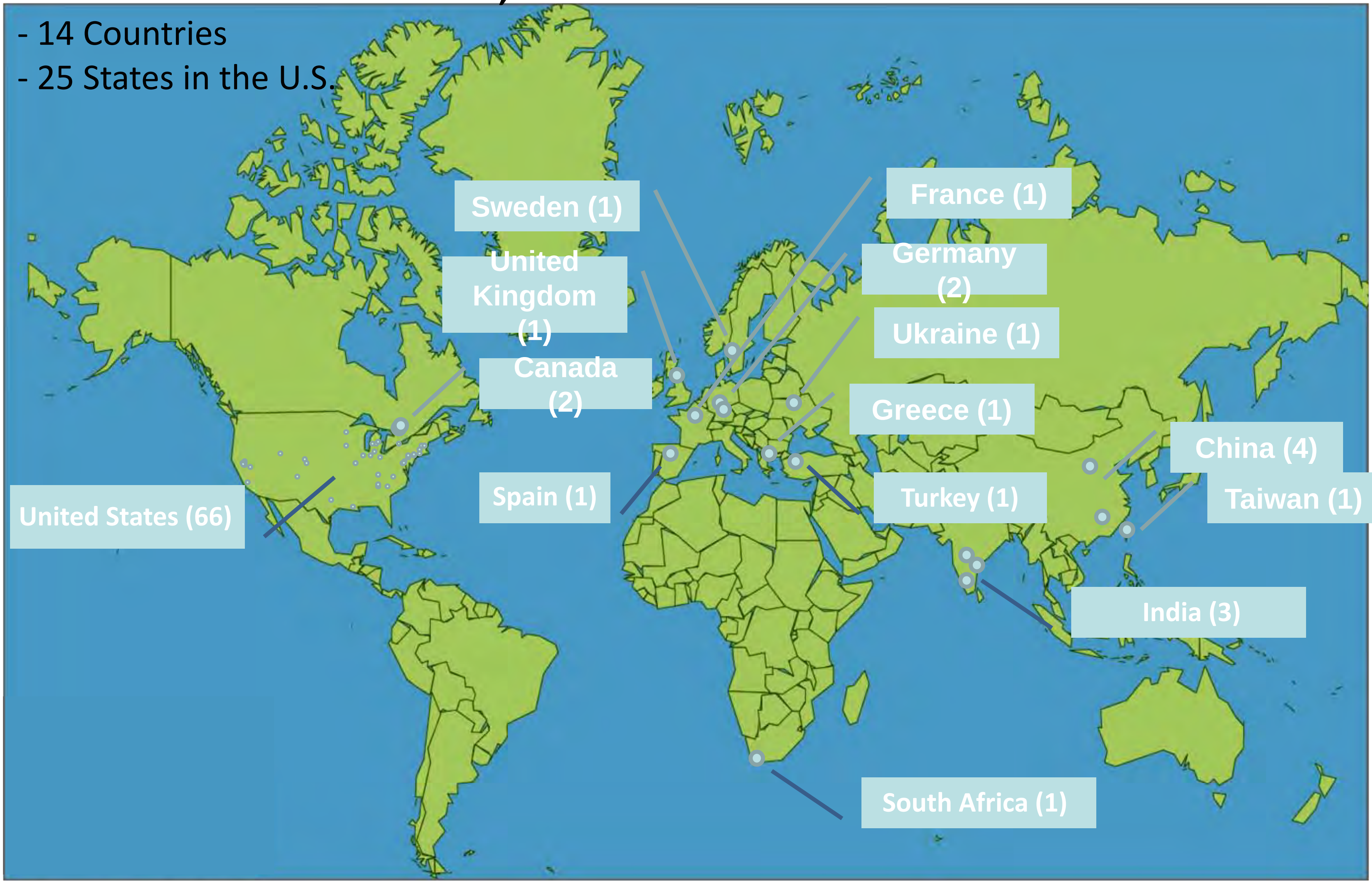
1. *Battery Fabrication Manual published online Dec. 17, 2010*

M. Wang
K. Striebel

88 Downloads as of March 9, 2011

http://berc.lbl.gov/vbattaglia/cell-analysis-tools/

- 14 Countries
- 25 States in the U.S.

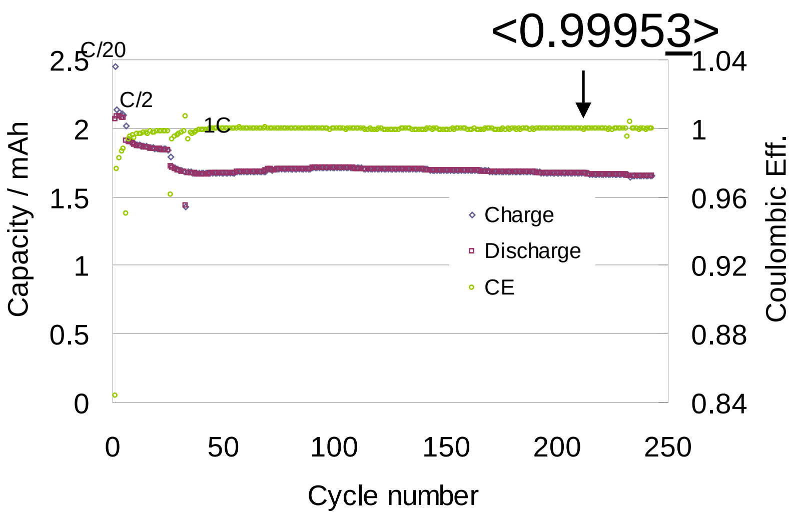


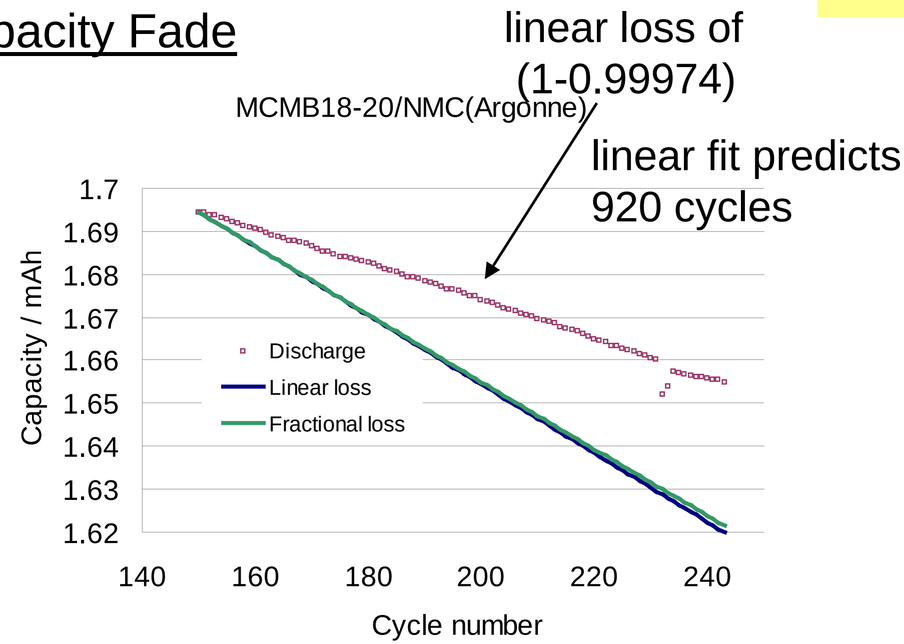
Technical Accomplishments and Progress:

2. A tool for assessing capacity fade and resistance rise.

Y. Fu

Modeling Capacity Fade





- Coulombic efficiency is fairly constant from 50 cycles onward.
- Capacity fade begins at ~ 150 cycles.
- Consider two models for capacity fade:
  - Linear – $Q = Q_o - Q_o(1-\eta)*(N_{cycle} - 150)$ where η = cycle efficiency
  - Fractional – $Q = Q_o\eta^{(Ncycle - 150)}$
- The 2 models are indistinguishable w/ η = 0.99953; under predicts by a factor of 1.7.
- Only 40% of the side reaction is detrimental. Goal is 0.99996 efficient.

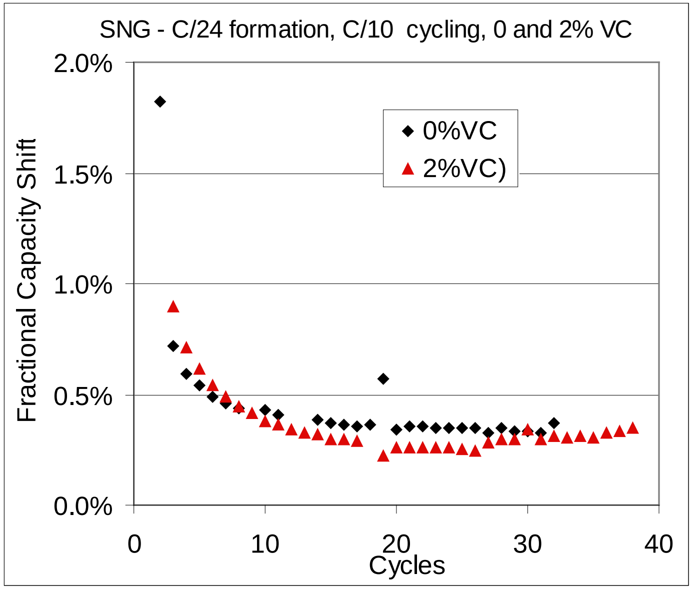
It is critical to understand these side reactions.

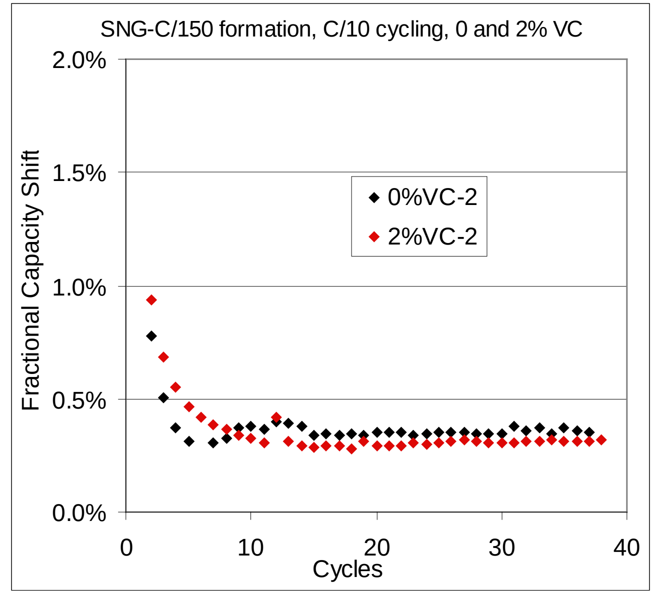
Technical Accomplishments and Progress:

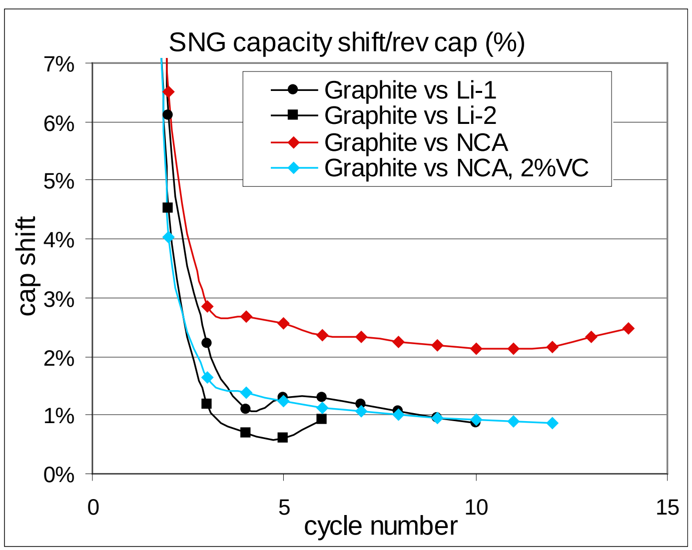
2. *A tool for assessing capacity fade and resistance rise.*

P. Ridgway

Side Reactions







- No effect of vinylene carbonate (VC) or formation protocol on graphite side-reaction rates when cycled against Li.
- Coulombic inefficiency of graphite doubled when cycled against NCA, suggesting the presence of a high-voltage shuttle.
- VC appeared to deactivate the shuttle and thereby improve coulombic efficiency.

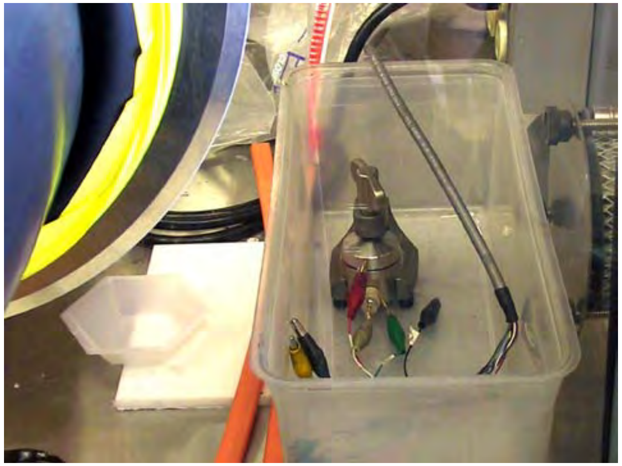
Technical Accomplishments and Progress:

2. A new tool for assessing capacity fade and resistance rise.

P. Ridgway

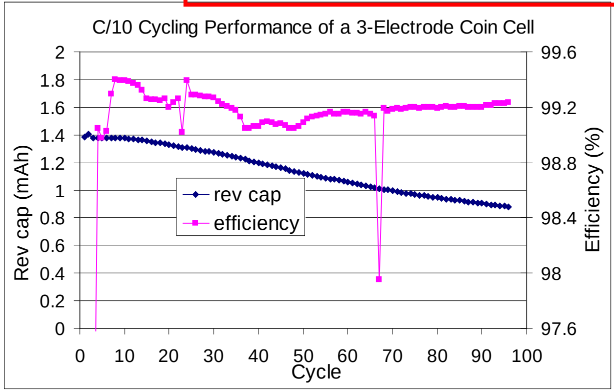
3-electrode Cell

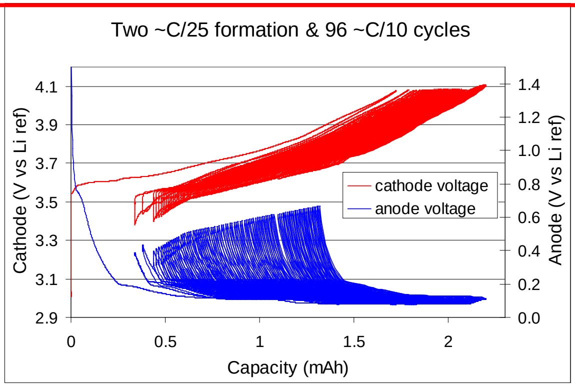
Traditional

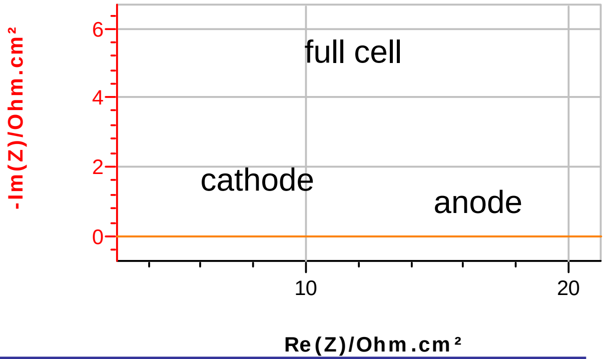


New Coin Cell

We have developed a novel 3-electrode coin cell to simultaneously study long-term cycling effects and side reactions of both electrodes.







We expect this cell to be very helpful in assessing cell failure!

Technical Accomplishments and Progress:

3. HQ's $LiFePO_4$ is as high rate as G. Ceder's (MIT) with the addition of acetylene black.

J. Chong
X. Song

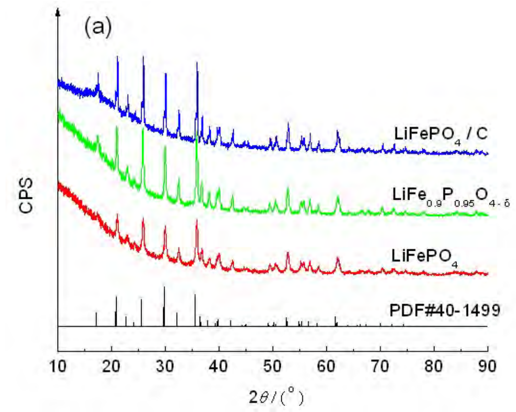
The Materials

Three $LiFePO_4$ materials were evaluated

a) Ceder's off-stoichiometric, nano-material: $LiFe_{0.9}P_{0.95}O_{4-\delta}$

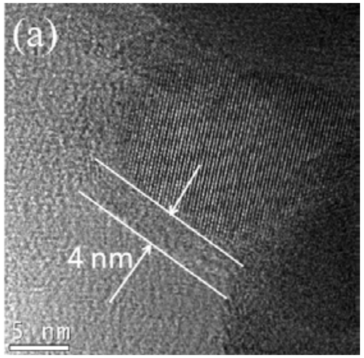
b) LBNL's stoichiometric, nano-material: $LiFePO_4$

c) HQ's carbon coated material: $LiFePO_4$ / C



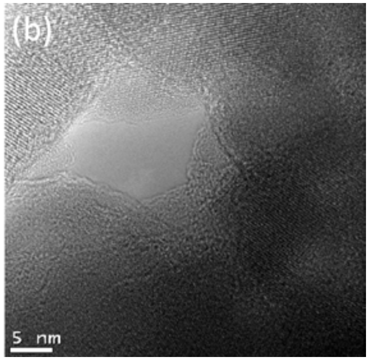
X-ray signatures are similar

$LiFe_{0.9}P_{0.95}O_{4-\delta}$

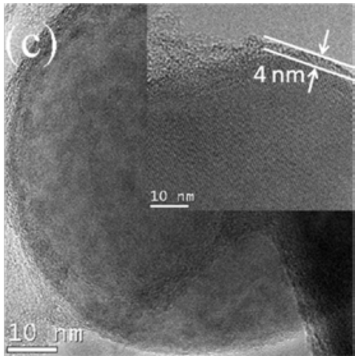


Amorphous film is visible with HRTEM

$LiFePO_4$



$LiFePO_4$ / C



Carbon film is visible with HRTEM

The Ceder material was pre-evaluated in the ABR Program.

Technical Accomplishments and Progress:

3. HQ's $LiFePO_4$ is as high rate as Ceder's with the addition of acetylene black.

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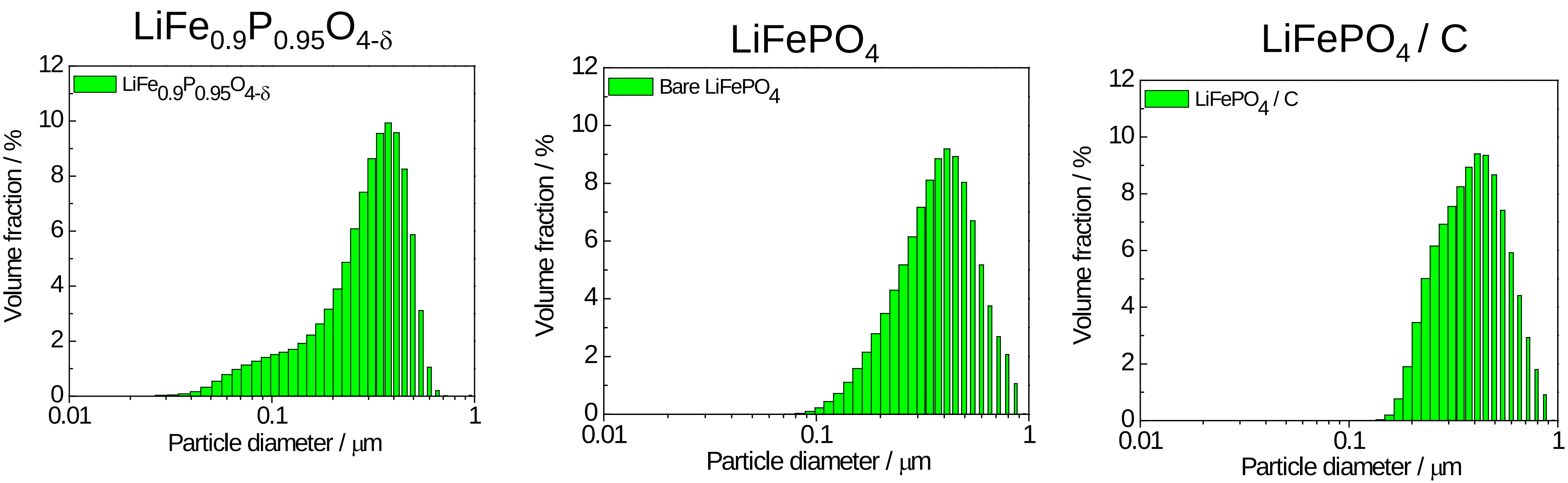
X. Song

Particle Size Distribution



Sample	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)	BET ($m^2 \cdot g^{-1}$)	Eqv. Dia. (mm)
$LiFe_{0.9}P_{0.95}O_{4-\delta}$	0.135	0.333	0.498	33.9551	0.049
Bare $LiFePO_4$	0.219	0.402	0.651	47.3239	0.035
$LiFePO_4$ / C	0.252	0.415	0.657	12.9335	0.12

PSA detects secondary particles;
BET detects primary particles

Technical Accomplishments and Progress:

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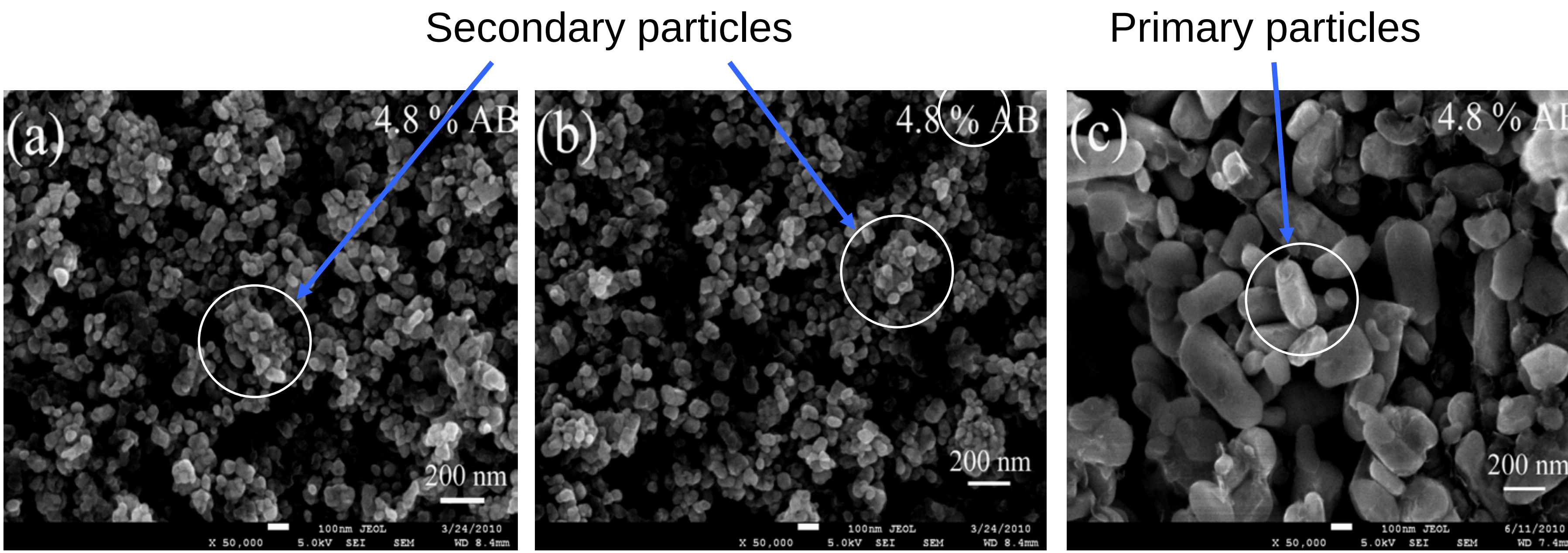
SEM's of Electrodes



The MIT and LBNL nano-particles agglomerate into secondary particles.

The HQ carbon-coated material segregates as primary particles.

Technical Accomplishments and Progress:

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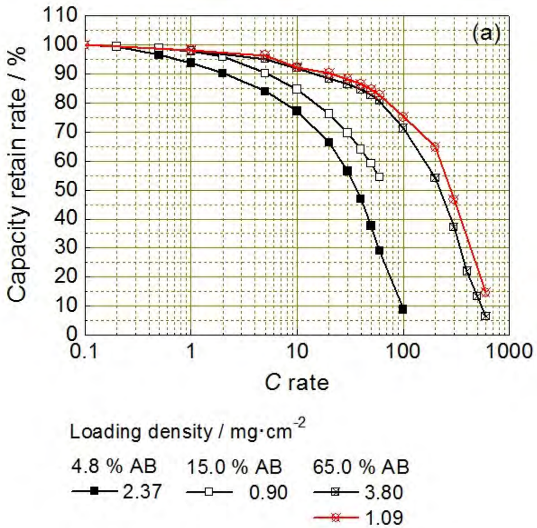
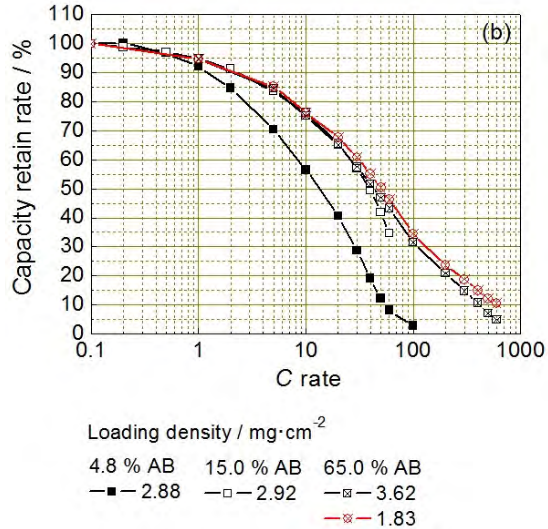
C-rate Capability

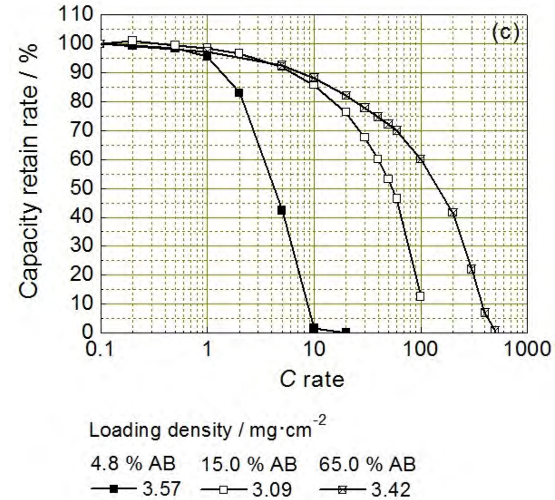
$LiFe_{0.9}P_{0.95}O_{4-\delta}$



$LiFePO_4$



$LiFePO_4$ / C



- At 65% carbon, the electrode thickness does not affect the rate performance.
- For the bare material and HQ material, 15% carbon additive is essentially all that is needed.
- With large amounts of conductive additive (65%) the rate is mostly limited by solid-state diffusion of Li in $FePO_4$.
- Solid state diffusion is much slower for the bare material than either the MIT LiPO-coated nanomaterial or the HQ carbon coated material.

Technical Accomplishments and Progress:

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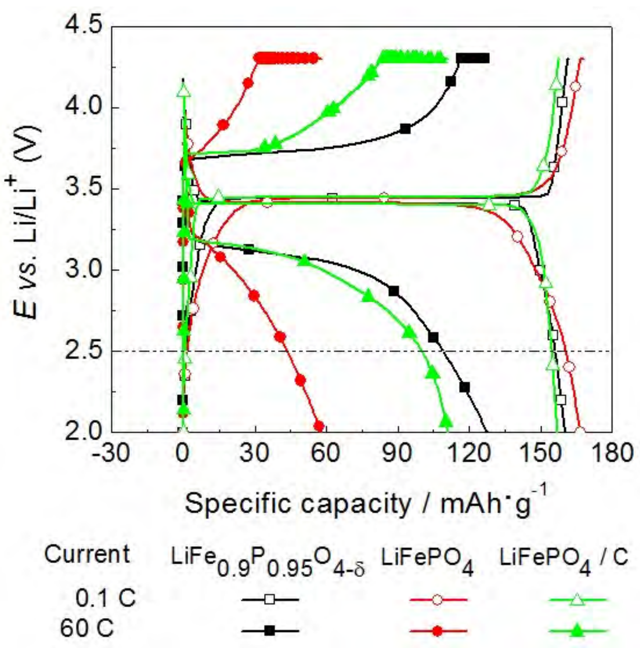
65% Carbon Additive



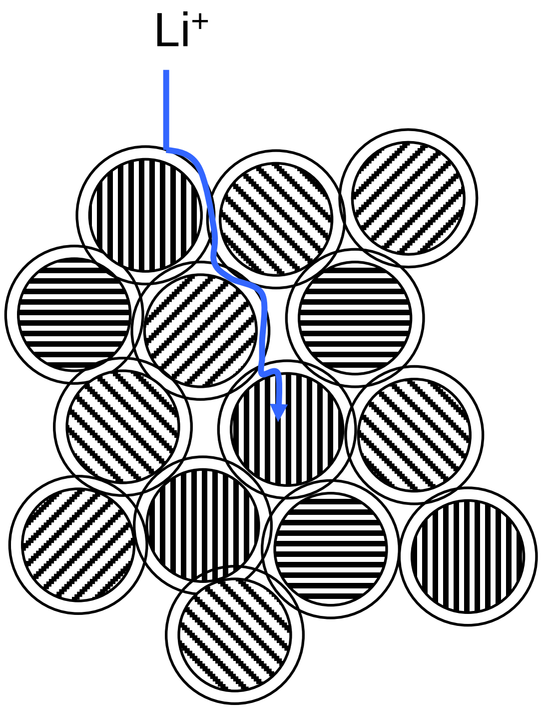
With 65% carbon additive, the materials are rate limited by solid-state diffusion.

- The single-crystal HQ material has straight paths to the center of the particles.
- The coating on the MIT primary particles appears to facilitate diffusion to the center of the secondary-particle
- The LBNL material exhibits slower diffusion through the tortuous secondary particle.

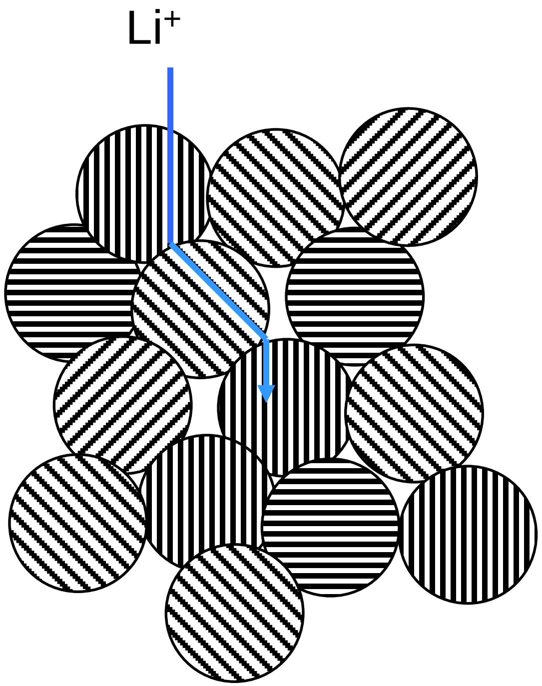
Technical Accomplishments and Progress:

3. HQ's $LiFePO_4$ is as high rate as Ceder's with the addition of acetylene black.

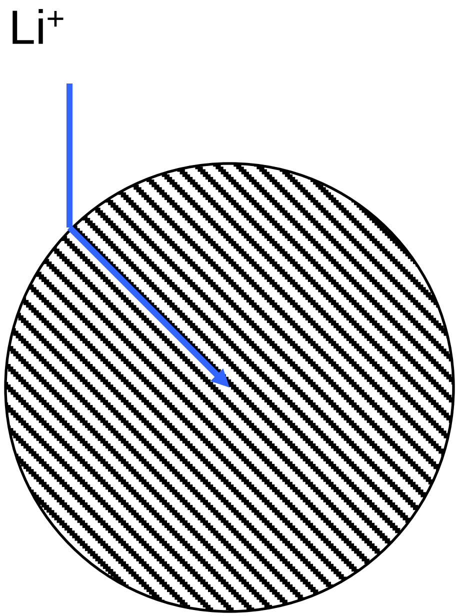
Schematic of Solid State Diffusion Limitation



Fast but tortuous



Slow and tortuous



Slow but non-tortuous

Work in progress.

Collaborations and Coordination with Other Institutions

Companies

- Daikin, Japan will send their newest high-voltage electrolytes
- Conoco Phillips provided baseline graphite and will send CGP-A12 shortly
- NEI will provide a baseline $LiNi_{1/2}Mn_{3/2}O_4$ spinel material for distribution to BATT PIs through Y.-M. Chiang's Group
- Daikin, America will provide a baseline electrolyte for distribution to BATT PIs
- HydroQuebec will provide $LiNi_{1/2}Mn_{3/2}O_4$ spinel material

Principal Investigators

- Receive powders from G. Ceder (MIT)
- Make laminates for the V. Srinivasan Group (LBNL)
- Make laminates for the J. Cabana Group (LBNL)
- Provide TEM for the T. Richardson/G. Chen Groups (LBNL)
- Provide electrodes to the B. Lucht Group (URI)
- Make laminates with the M. Doeff Group (LBNL)
- Receive LTO laminates and new $LiNi_{1/2}Mn_{3/2}O_4$ materials from the K. Zaghib Group (HQ)
- Provide powders and electrolyte to A. Manthiram Group (UT)
- Provide powders and electrolyte to J. Zhang Group (PNNL)
- Provide powders and electrolyte to A. Angell Group

Proposed Future Work

- Electrode design optimization
- Electrode failure analysis
  - $LiNi_{0.5}Mn_{1.5}O_4$ has been identified as a focus area; we will use our approach to provide a fundamental understanding of its limitations.
    - Optimize the design of high-energy electrodes, investigate the fabrication of high-loading electrodes that cycle well, and study the roles of inactive material chemistry and material physical structure
    - Study the side reactions of all components, including the binder, conductive additive, and the current collector, and identify reaction products
    - Investigate dissolution as a function of SOC, and determine its mechanism.
    - Compare the performance of active material from various sources, and correlate performance to differences in physical properties such as crystallography, degree of metals disorder, and particle structure.
    - Distribute powders, electrolytes, and laminates of baseline systems to BATT partners.
    - Investigate the effect of Daikin high-voltage electrolyte on rate of side reactions, and identify reaction products with help from Diagnostics team.

Summary

We are an integral part of a comprehensive team to assess electrode materials from a fundamental perspective.

- We have developed a robust methodology for making electrodes that is proven to be transferable to BATT researchers and other institutions.
- Side reactions play a pivotal role in cell lifetime; we have developed a sealed 3-electrode cell that will allow us to rigorously study these effects and decouple the anode and the cathode for long-term studies.
- We conducted a rigorous assessment of two BATT $LiFePO_4$-based materials and determined mechanisms for their inherent limitations.

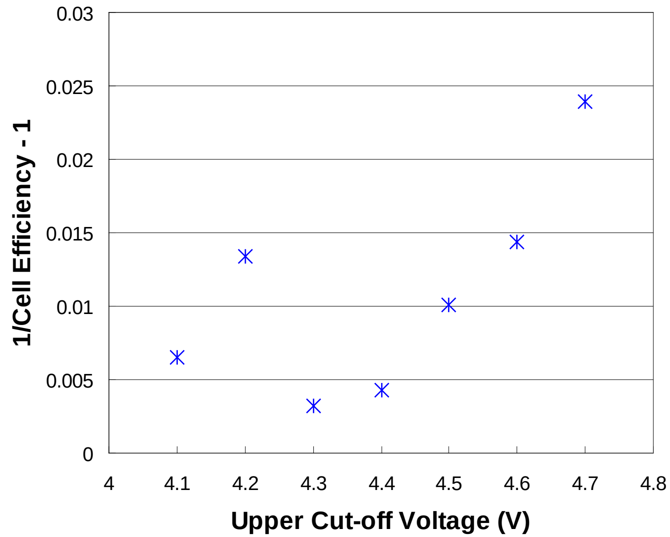
Technical Back-Up Slides

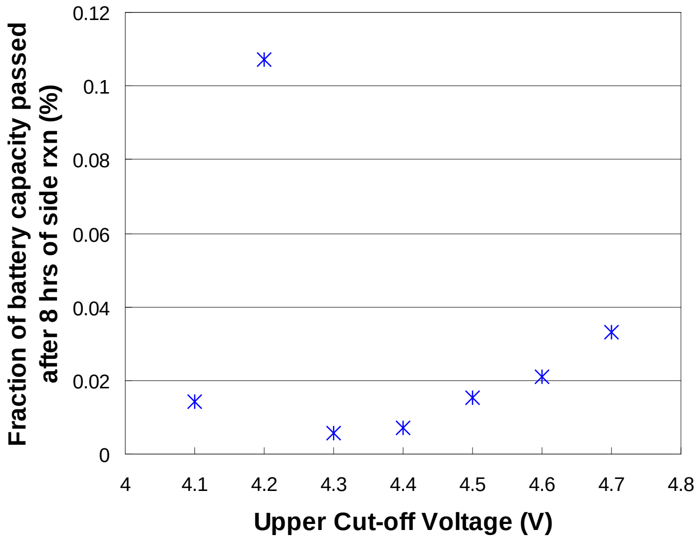
Technical Accomplishments and Progress:

2. A new tool for assessing capacity fade and resistance rise.

Y. Fu

Side Reaction and Cell Balancing





Rate of side reaction is a function of cell voltage.

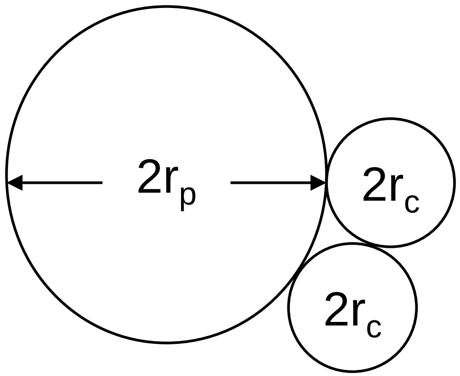
Demonstrates how much capacity a cell can be balanced during an 8 hr trickle charge.

Demonstrates that if Gr./NCM is held at 4.2 V, there is 10.7% capacity available for cell balancing without the need for electronics!

Technical Accomplishments and Progress:

3. HQ's $LiFePO_4$ is as high rate as Ceder's with the addition of acetylene black.

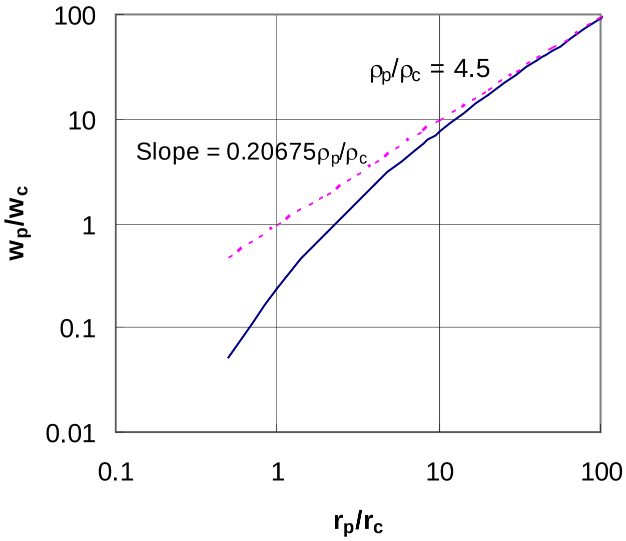
Weight of active material *vs.* weight of conductive additive?



One can derive through geometric arguments the weight ratio of one material needed to cover another material:

$$\frac{w_p}{w_c} = b\left(\frac{\lambda}{1+2/\lambda + 1/\lambda^2}\right)$$

where, $\lambda = \frac{r_p}{r_c}$ and $b = \frac{\rho_p}{\rho_c}\frac{3\sqrt{3}}{8\pi} = \frac{\rho_p}{\rho_c}0.20675$



If λ = 0.4/0.05 and ρ_p/ρ_c = 3.6/(0.4*2) then w_c/w_p > 0.17

Gives an electrode of 14% carbon, 81% $LiFePO_4$, and 5 % binder.

Technical Accomplishments and Progress:

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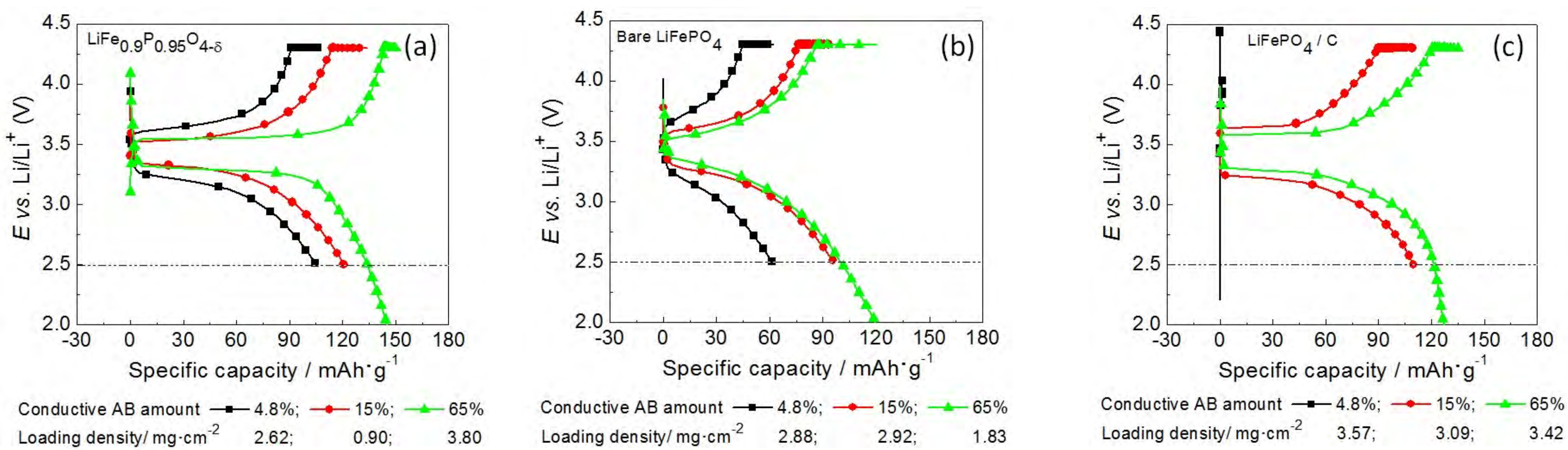
J. Chong

The Addition of Carbon Additive to the 3 Materials

$LiFe_{0.9}P_{0.95}O_{4-\delta}$ | $LiFePO_4$ | $LiFePO_4$ / C



- MIT material requires the least amount of carbon additive to attain high rates.
- Ohmic and kinetic resistance not much improved beyond 15% carbon additive.

The addition of conductive carbon facilitates access to the particles beyond just an improvement in kinetics or ohmic resistance!