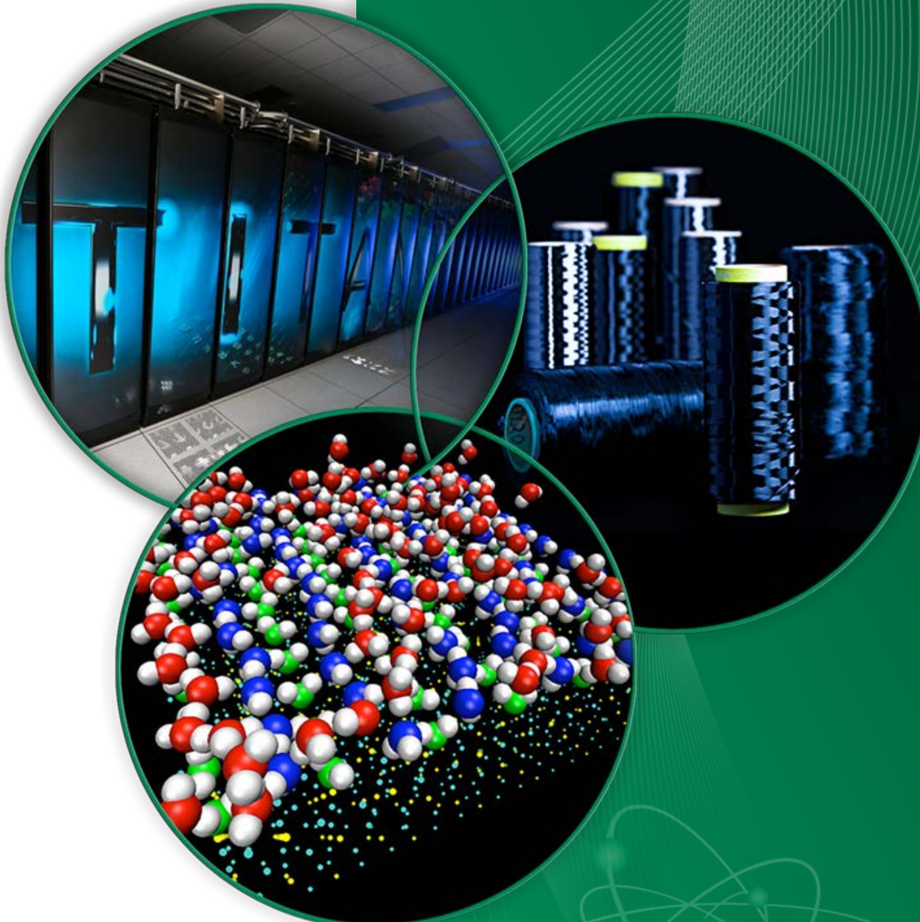
Overcoming Processing Cost Barriers of High-Performance Lithium-Ion Battery Electrodes



David L. Wood, III

Oak Ridge National Laboratory

May 14, 2013

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

Project ID
ES164

Overview

Timeline

- Project Start: 10/1/11
- Project End: 9/30/14
- Percent Complete: 45%

Barriers

- Barriers Addressed
  - **By 2015, reduce PHEV-40 battery cost to $300/kWh**
  - **By 2020, further reduce EV battery cost to $125/kWh.**
  - **Advanced Li-ion HEV/PHEV battery systems with low-cost electrode architectures.**
  - **Achieve selling price of $1700-3400 for 100,000 PHEV units/year by 2015.**

Budget

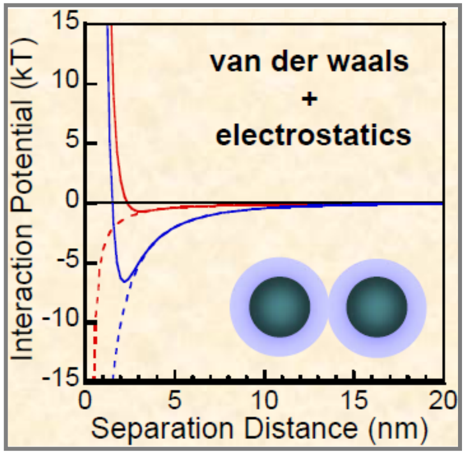
- Total project funding
  - $900k
- $300k in FY12
- $300k in FY13

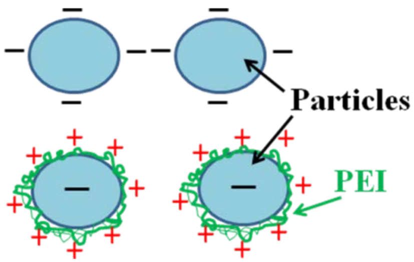
Partners

- Interactions/Collaborations
  - National Laboratories: ANL, SNL
  - Battery Manufacturers: Dow Kokam, A123 Systems, Navitas Systems
  - Material Suppliers: ConocoPhillips, Phostech Lithium, TODA America, Timcal, JSR Micro, Solvay Specialty Polymers
  - Equipment Manufacturer: Frontier Industrial Technology
- Project Lead: ORNL

Project Objectives

- Main Objective: To transform lithium ion battery electrode manufacturing by the elimination of costly, toxic organic-solvents.
  - Replace NMP processing with water-based chemistry ***for all active materials.***
  - Expand surface treatment of current collector foils to include Cu.
  - Transition from exploratory xanthan gum binder to commercially available aqueous cathode binders.
  - ***Elimination of expensive solvent recovery steps and reduction of capital equipment cost (i.e., no explosion proofing required).***
  - FY12 → $LiFePO_4$ cathode.
  - FY13 → NCM 523 cathode and ConocoPhillips A12 graphite anode.
  - FY14 → NCA and LMR-NMC cathodes.





- Relevance to Barriers and Targets
  - Implementation of low-cost, green manufacturing methodology for lithium ion battery electrodes using aqueous colloidal dispersions (to meet \$300/kWh 2015 VTO storage goal for PHEV-40s).
  - Correlation of properties of colloidal dispersions and electrode coatings to cell performance to advance energy storage manufacturing science.
  - ***Preserve*** long-term performance: achieve a lifetime of 10 years and 1000 cycles at 80% DOD for EVs and 5000 deep discharge cycles for PHEVs.

Project Milestones

Status	Milestone or Go/No-Go	Description
Complete ✓	FY12 Milestone	Development of aqueous formulations for electrodes.
Go ✓	FY12 Go/No-Go	Achieve at least 95% capacity retention through 50 cycles for half cells based on selected aqueous formulations.
Complete ✓	FY12 Milestone	Coating technique and drying protocol for aqueous electrodes.
Postponed	FY12 Milestone	Development of porosity control in electrodes with controlled settling and calendering study.
Complete ✓	FY12 Milestone	Match cell performance of aqueous dispersions (***full cell format for cathode only***) and water-soluble binder to NMP/PVDF based dispersions.
Complete ✓	FY13 Milestone	Complete round robin testing with ANL and SNL with CP A10/A12 and TODA NCM 523 electrochemical couple.
6/2013	FY13 Milestone	Match full cell performance through 100 cycles of aqueous formulations to NMP/PVDF formulations for CP A10/A12 and TODA NCM 523 electrochemical couple.
9/2013	FY13 Milestone	Match pouch cell (≥3 Ah capacity) performance through 100 cycles of aqueous formulations to NMP/PVDF formulations for CP A10/A12 and TODA NCM 523 electrochemical couple.

Project Approach

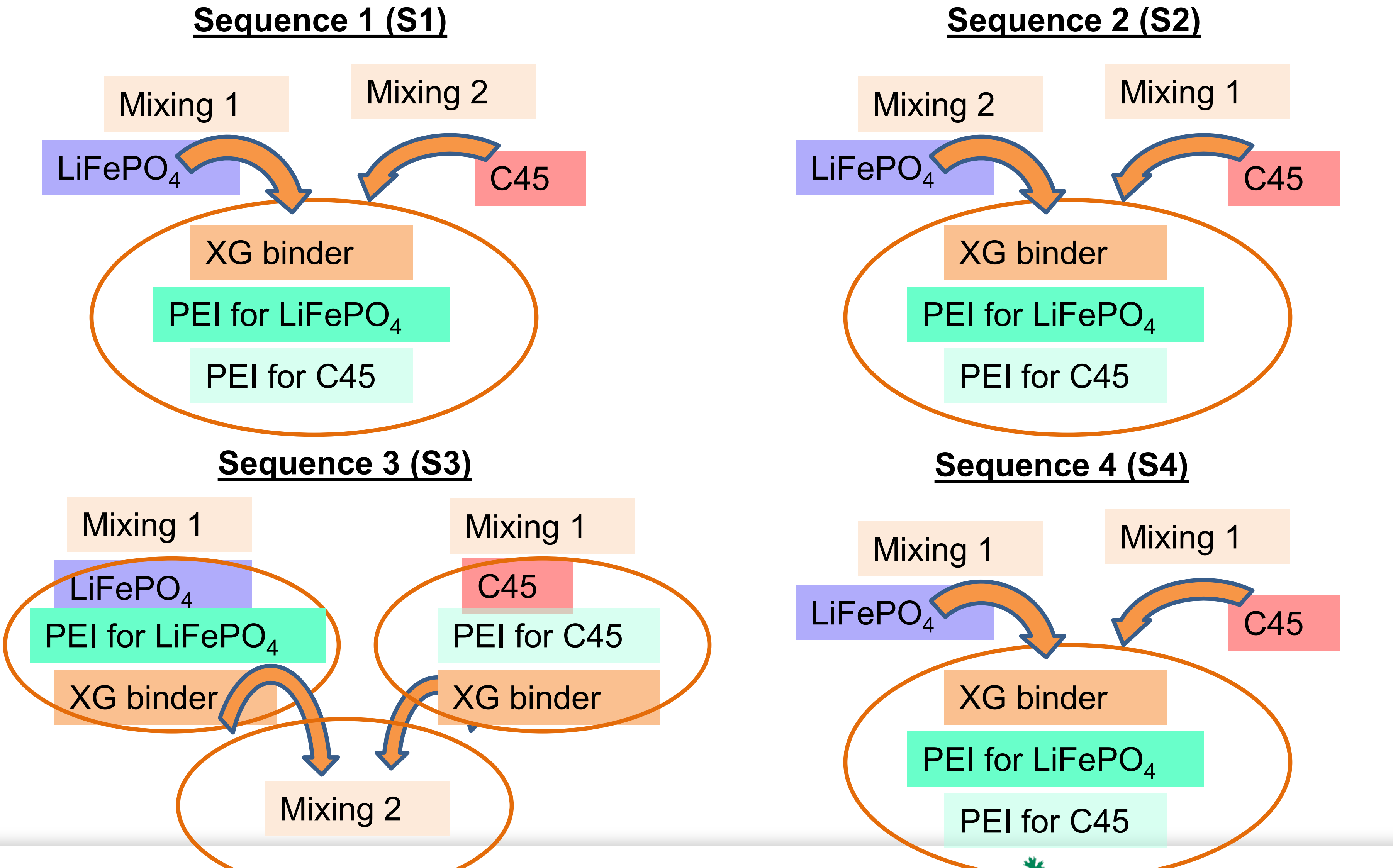
- Problems:
  - Excessive agglomeration and settling in aqueous dispersions.
  - Poor wetting and adhesion of water-based dispersions to current collector foils.
  - Solved for $LiFePO_4$ and Al foil; next materials are NCM 523, CP A12 graphite, and Cu foil.
- Overall technical approach and strategy:
  - Chemistry-specific aqueous formulation designs by standardized dispersant selection and rheological optimization methods – Tailored Aqueous Colloids for Lithium-Ion Electrodes (TACLE) → **B.L. Armstrong *et al.*, U.S. Patent Application No. 13/651,270**.
  - Surface charge measurement, rheology characterization, agglomerate size optimization, order of constituent addition, and mixing protocol optimization.
  - Coating parameter optimization for TACLE → viscosity control, current-collector surface energy optimization, and tailoring of drying protocol (solved for $LiFePO_4$).
  - Improved understanding of corona plasma surface treatment effects on current collector foils.
  - Close collaboration with the ANL and SNL ABR efforts, cell manufacturers, active material suppliers, and inactive material suppliers.
- Active materials studied
  - Anode: Conoco Phillips A10 (A12) graphite
  - Cathode: Phostech Lithium $LiFePO_4$, TODA $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM 523)
  - Future High-Voltage Cathode: TODA HE5050 $Li_{1.2}Co_{0.1}Mn_{0.55}Ni_{0.15}O_2$ (LMR-NMC).

Technical Accomplishments – Executive Summary

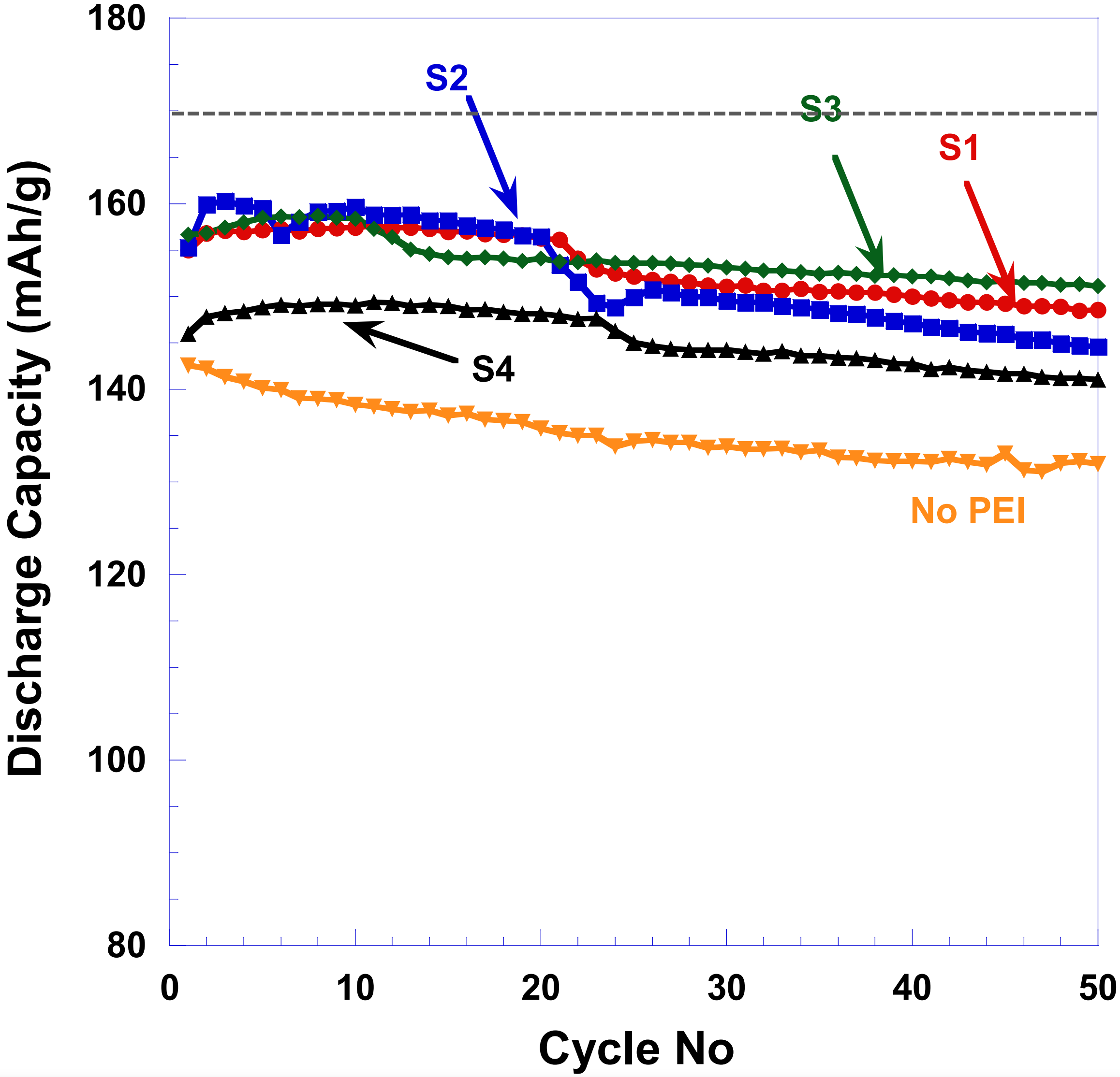
- FY12 Q1-2: Water-Based $LiFePO_4$ Half Cells (Presented at 2012 DOE AMR)
- **FY12 Q3-4: NMP-Based $LiFePO_4$ Full Cells (Following Slides)**
- **FY13 Q1-2: Water-Based $LiFePO_4$ Full Cells and Water-Based NCM 523 Initial Electrode Qualification (Following Slides)**
- FY13 Q3-4: Water-Based NMC 523 Full Cells, Water-Based CP A12 Full Cells, and Full Pouch Cells (2014 DOE AMR)
- Specific Accomplishments
  - Verified importance of electrode constituent order of addition with $LiFePO_4$ half cells.
  - Verified cathode active material stability in water for $LiFePO_4$ and NCM 523 (by ICP-MS).
  - Obtained $LiFePO_4$ half-cell CVs showing binder electrochemical stability and no effects of residual ***polyethyleneimine (PEI)***.
  - Demonstrated acceptable water content for aqueous processed NCM 523 electrodes after primary and secondary drying.
  - Obtained full cell data for aqueous and NMP processed $LiFePO_4$ cathodes through 150 total cycles (50 rate capability cycles + 100 0.2C/-0.2C cycles) with minimal capacity fade.
  - Completed first round of TODA NCM 523 and CP A12 (baseline ABR) round robin electrode performance comparison (between ANL, ORNL, and SNL).
  - ❖ All comments from FY12 DOE AMR reviewers have been addressed.

Order of Constituent Addition Is Critical For Aqueous Processing Effectiveness

$LiFePO_4$/C45/Xanthan Gum(XG)/PEI/H_2O =100 / 10 / 2.5 / 2 / 350 wt fraction



Tape Cast Electrode Coatings: Superior Performance from S1-3



<u>Half Cell Construction:</u>

- Li counter electrode
- Celgard 2325 separator
- 1.2 M $LiFP_6$ in EC/DMC (3/7 wt%)
- C/5 at 25 C charge-discharge
- 2.5-4.2 V window

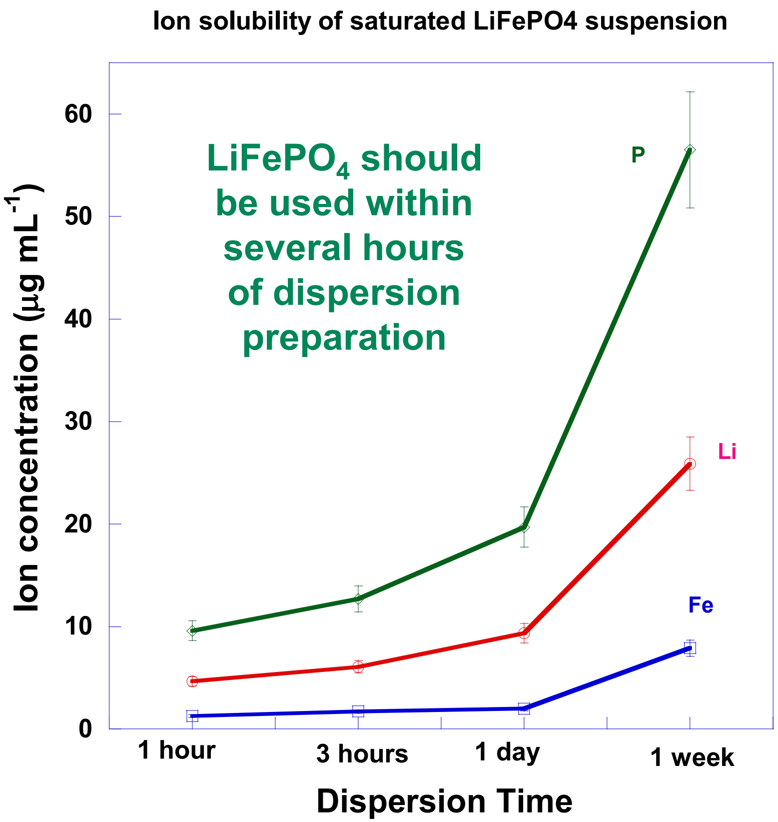
•The addition of PEI improves capacity, 10-20 mAh/g increase

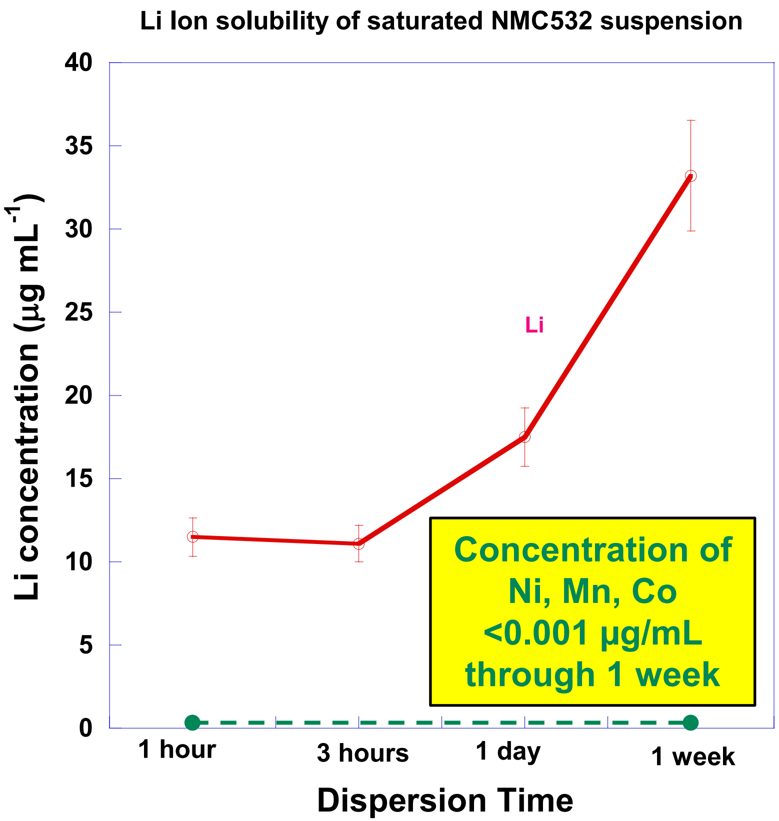
•Capacity from S4 about 10 mAh/g lower that that from S1-3

•After 50 cycles, >150 mAh/g from S1 and S3; >95% retention

J. Li et al., *Journal of Colloid and Interface Science*, Under Review, 2013.

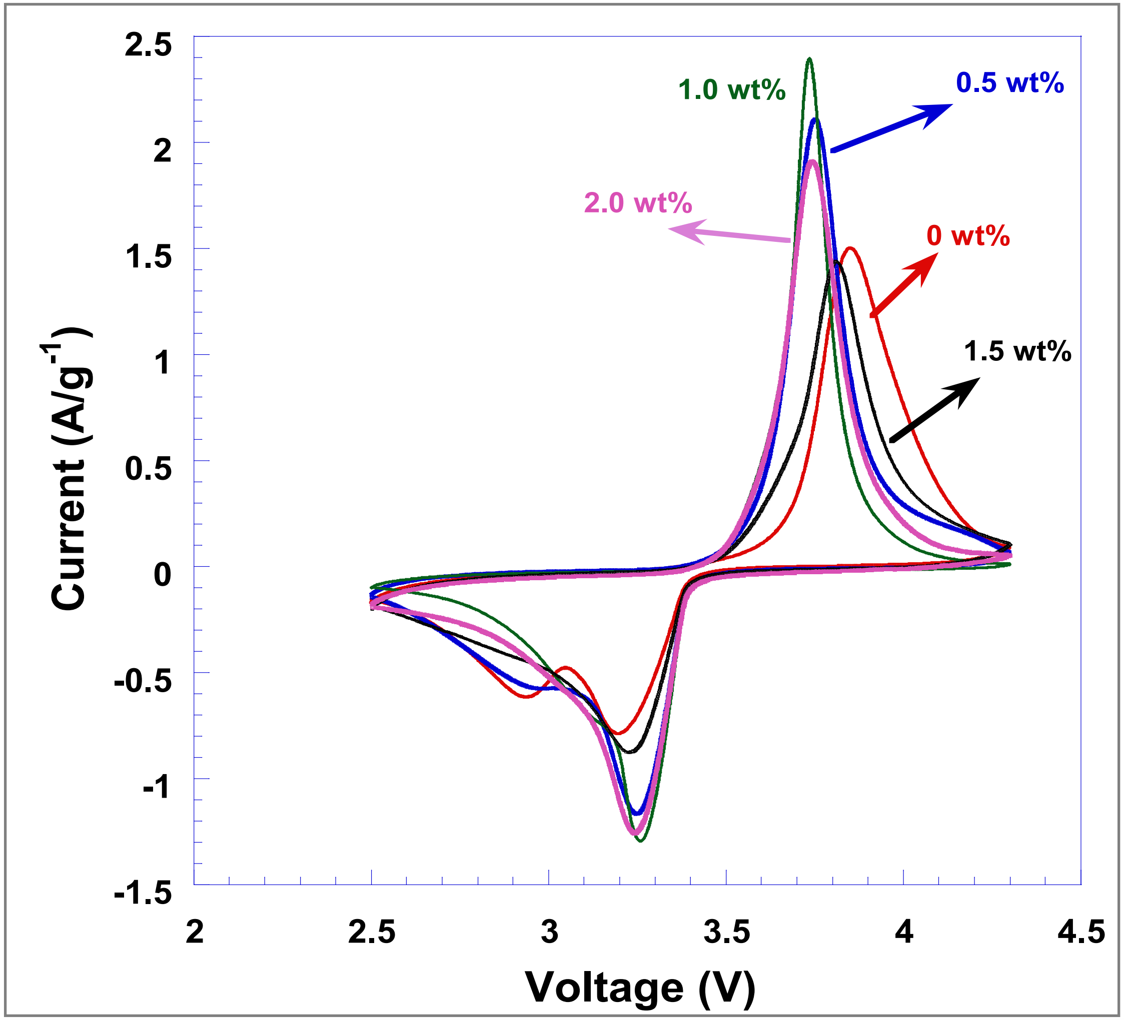
Leaching of Cathode Elements into Water Is of Minimal Concern





- Li solubility for NMC 532 is about 3× that of $LiFePO_4$ after 1 hour exposure to water (~12 ppm vs. 4 ppm, respectively).
- ***If dispersions are mixed, coated, and dried inside of 1-2 h, then exposure to water should not cause metal solubility issues.***

Xanthan Gum Binder Is Electrochemically Stable and PEI Leaves No Unstable Residue

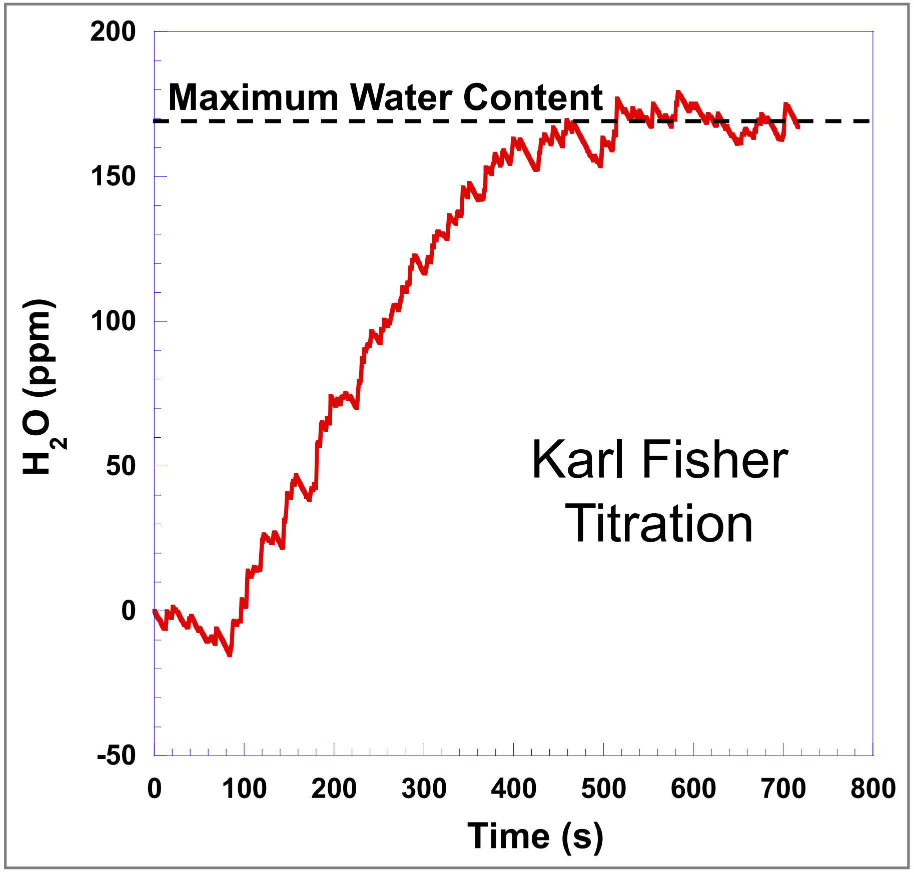


- CV scans of $LiFePO_4$ cathodes with various polyethyleneimine (PEI) concentrations (from J. Li et al., *J. Electrochem. Soc.*, **160**, A201 (2013).
- These $LiFePO_4$ cathodes contain ~2.5 wt% xanthan gum and PEI contents from 0-2.0 wt%.
- CV scans from 2.5 V to 4.3 V show no abnormal peaks indicating xanthan gum and PEI are stable within the cathode electrochemical operating regime.

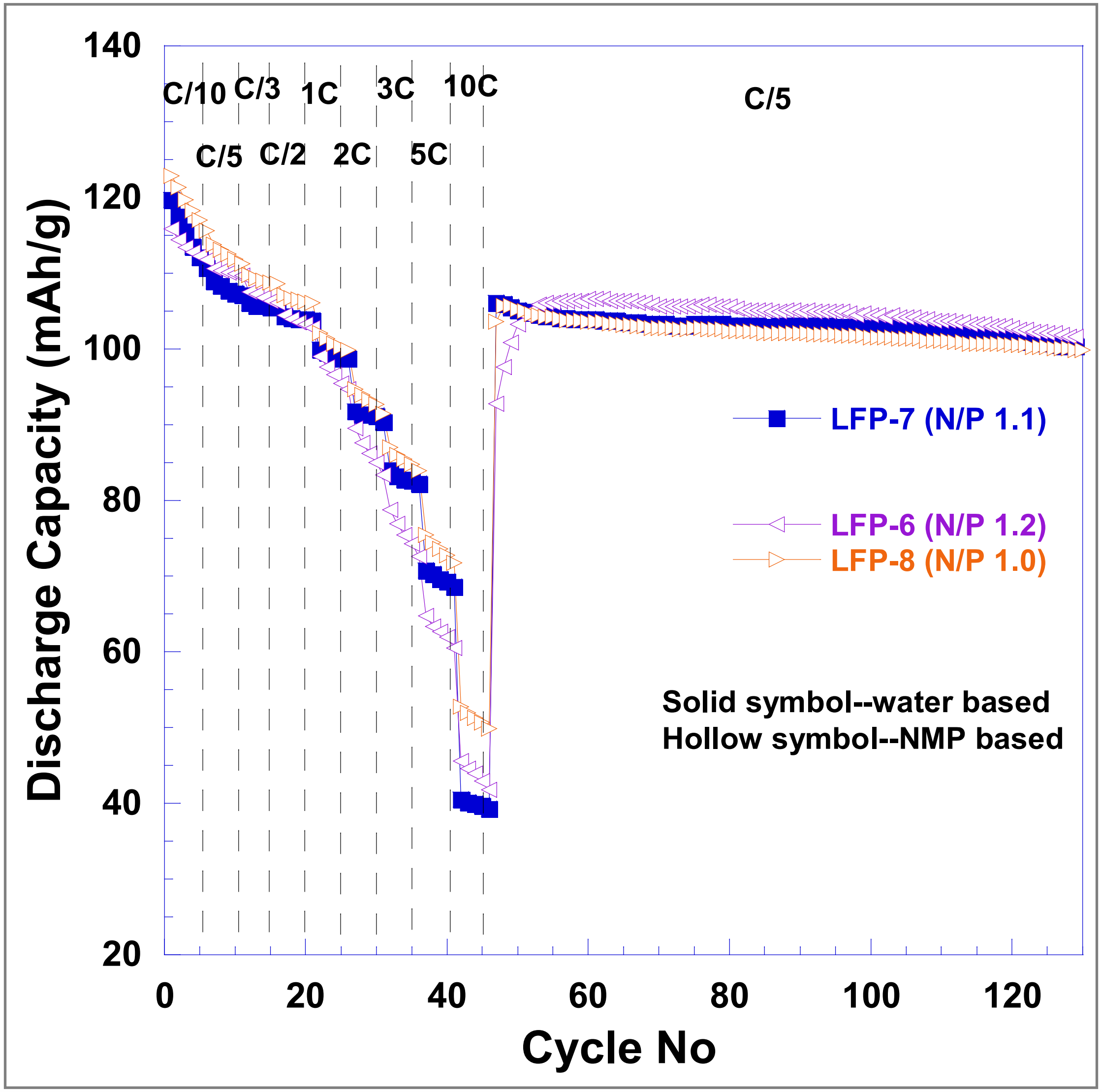
Acceptable Residual Water Content of Aqueous Processed NCM 523 Cathodes

- Hydrophilic cathode materials such as NMC and $LiFePO_4$ must be adequately dried after water-based electrode processing.
- Primary drying (post-coating deposition on ORNL slot-die coater) in 7 convection zones up to 90°C.
- Secondary drying for 2 h under 68 kPa abs. vacuum at 90°C.
- Electrode residual water content was measured by Karl Fischer titration.
- Cathode water content was reduced to 170 ppm after these drying steps, **which is below the industry standard of ~500 ppm**.
- A similar drying protocol is used for $LiFePO_4$ cathodes.

➢ **Water contents of <<500 ppm will have negligible performance effects.**



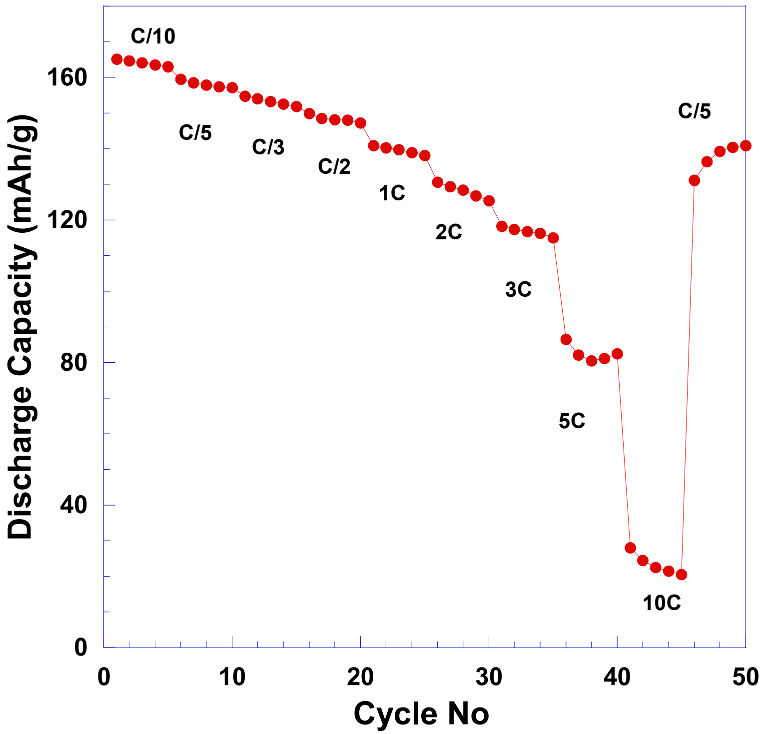
Full Cell Performance Demonstrated – 140 Cycles for $LiFePO_4$ Cathodes

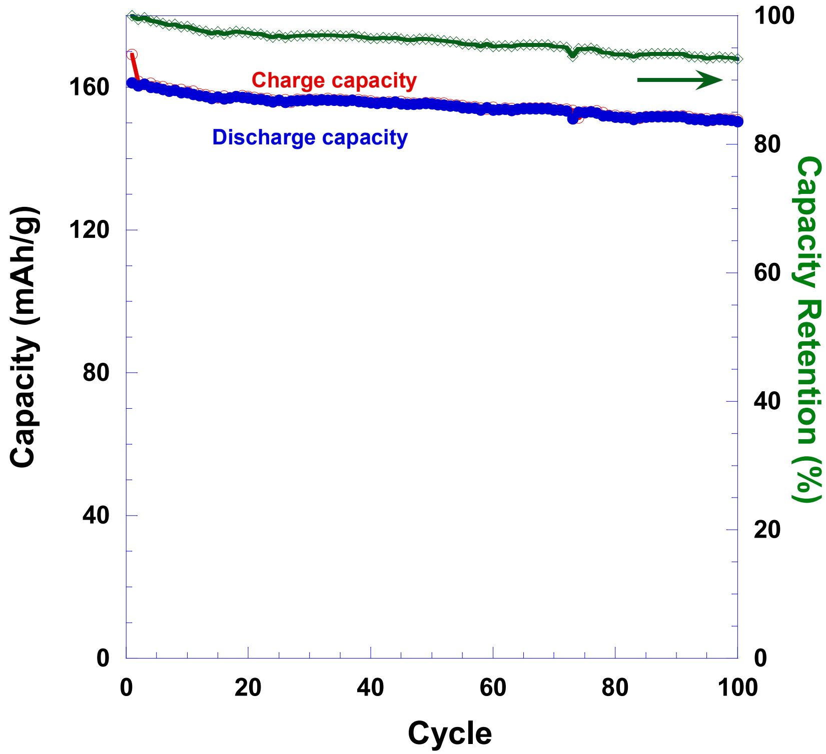


- Comparison between full cells with water- and NMP-based $LiFePO_4$ cathodes and NMP-based CP A12 graphite anodes.
- Cycled between 2.5 V and 4.2V.
- Electrode balance is between 1.0 and 1.2 (N/P).
- Water- and NMP-based cathodes demonstrate comparable performance.
- Excellent capacity retention for all cells after 100 0.2C/-0.2 cycles.

Electrodes (Average of Three Cells)	Capacity Retention after 100 Cycles
NMP based	94%
Water based	93%

Round Robin Electrode Performance (ANL, ORNL, and SNL Collaboration)



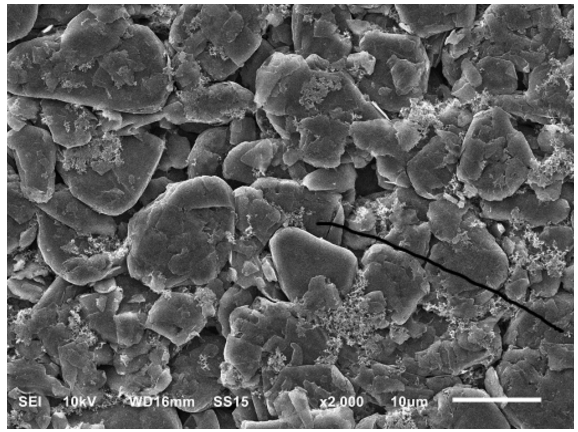


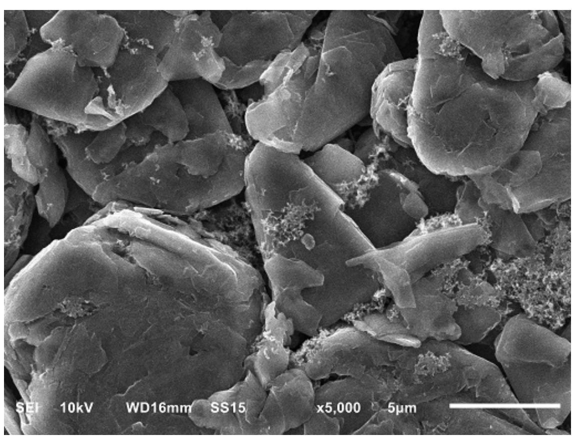
- ORNL evaluation of VTO ABR baseline anode (ConocoPhillips A10/A12 graphite) and cathode (TODA NCM 523).
- Excellent capacity retention of ***full cells*** after 150 charge-discharge cycles.
- Electrode rolls were supplied to ANL and SNL for subsequent evaluation.

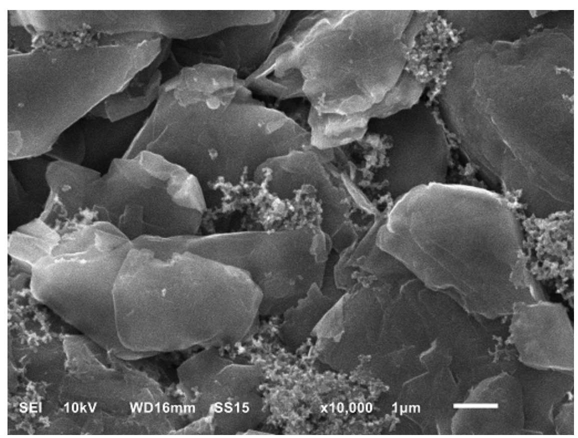
Inter-Laboratory Round Robin: ANL Evaluation of ORNL Anode (CP A12)

Anode Electrode Surface

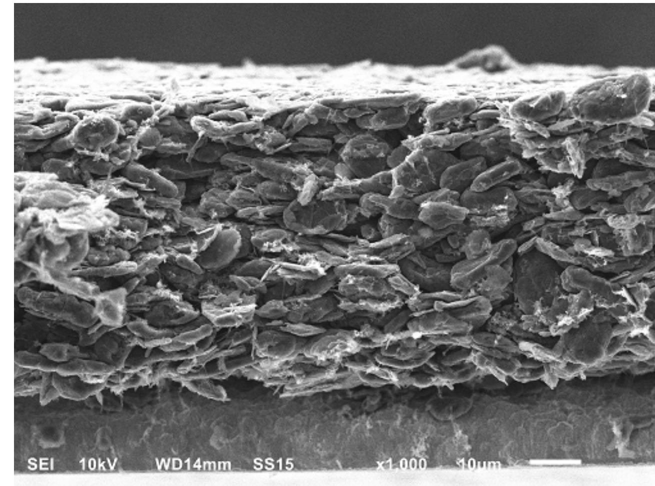
Anode Composition
- 92 wt% Phillips 66 C-Preme A12
- 2 wt% Super P Li Carbon
- 6 wt% Kureha 9300 PVdF Binder

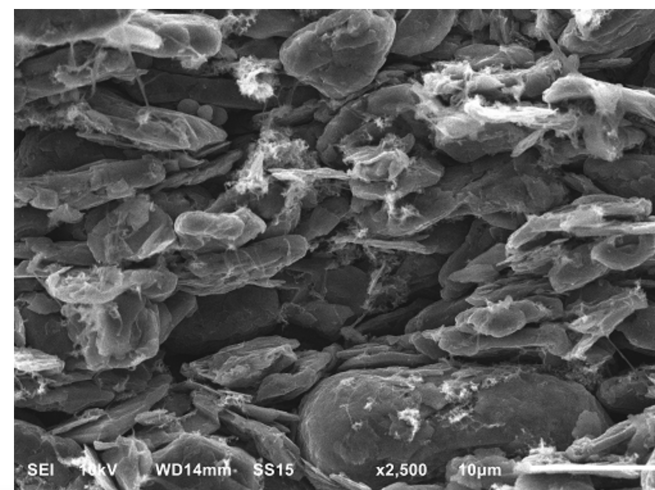






Anode Electrode Cross Section

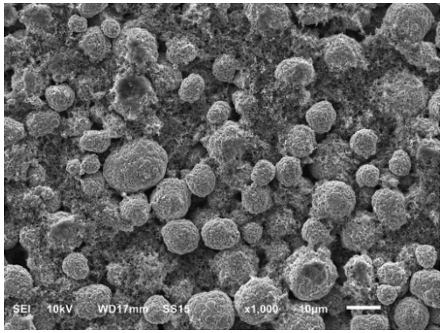


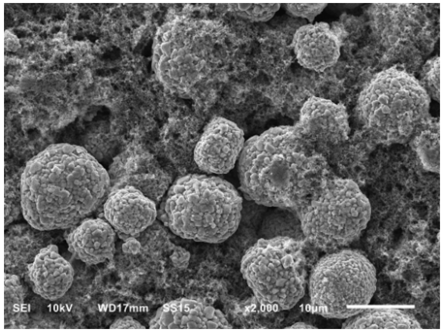


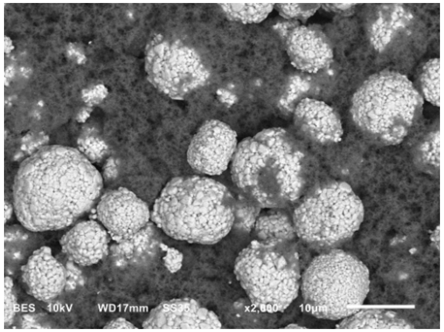
Inter-Laboratory Round Robin:
ANL Evaluation of ORNL Cathode (TODA NCM 523)

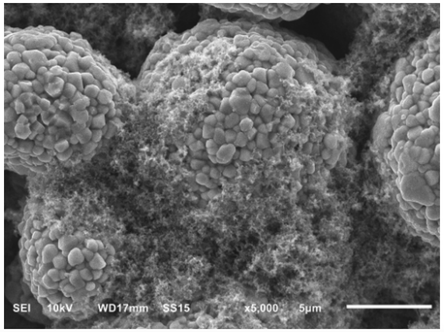
Cathode Electrode Surface

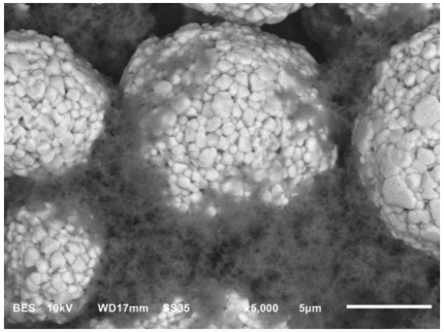
Cathode Composition
- 90 wt% Toda 523 ($LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$)
- 5 wt% Denka Carbon Black
- 5 wt% Solvay 5130 PVdF Binder



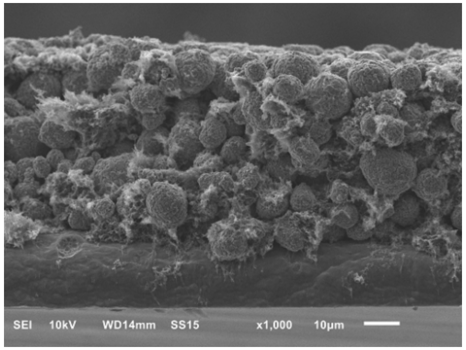


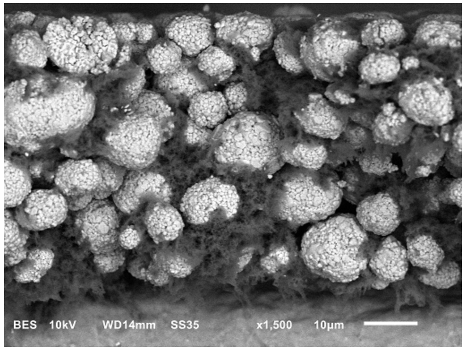


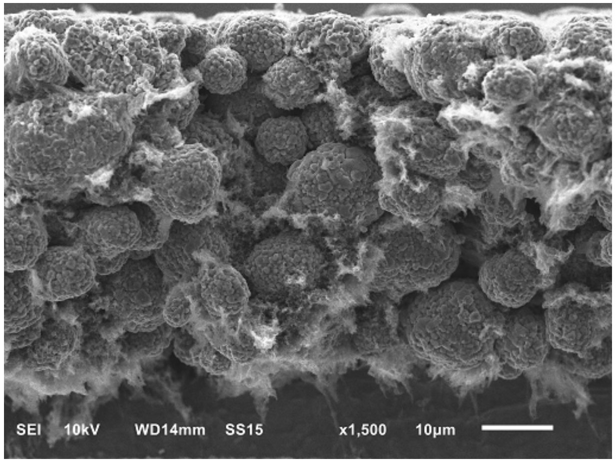




Cathode Electrode Cross Section





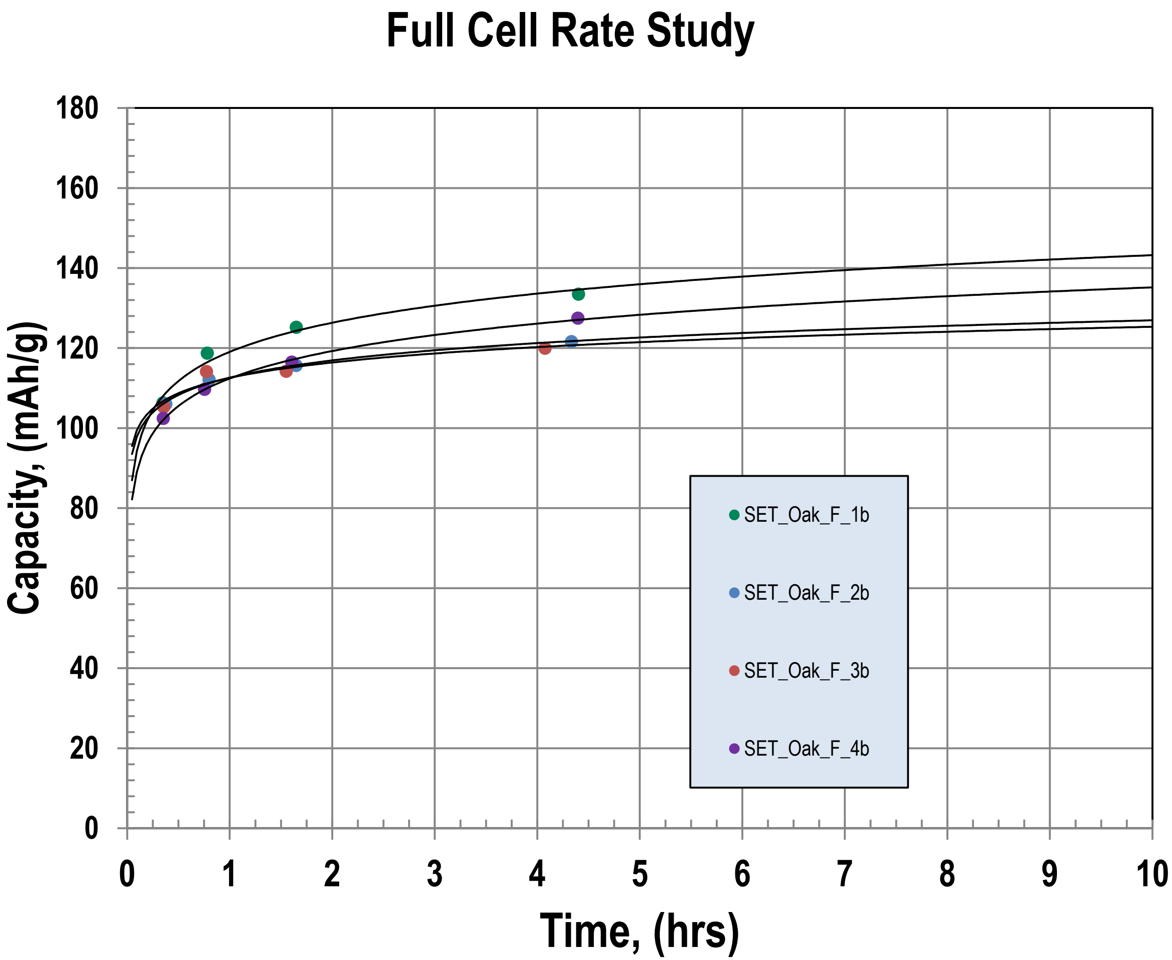


Inter-Laboratory Round Robin: ANL Rate Capability Study on ORNL Electrodes

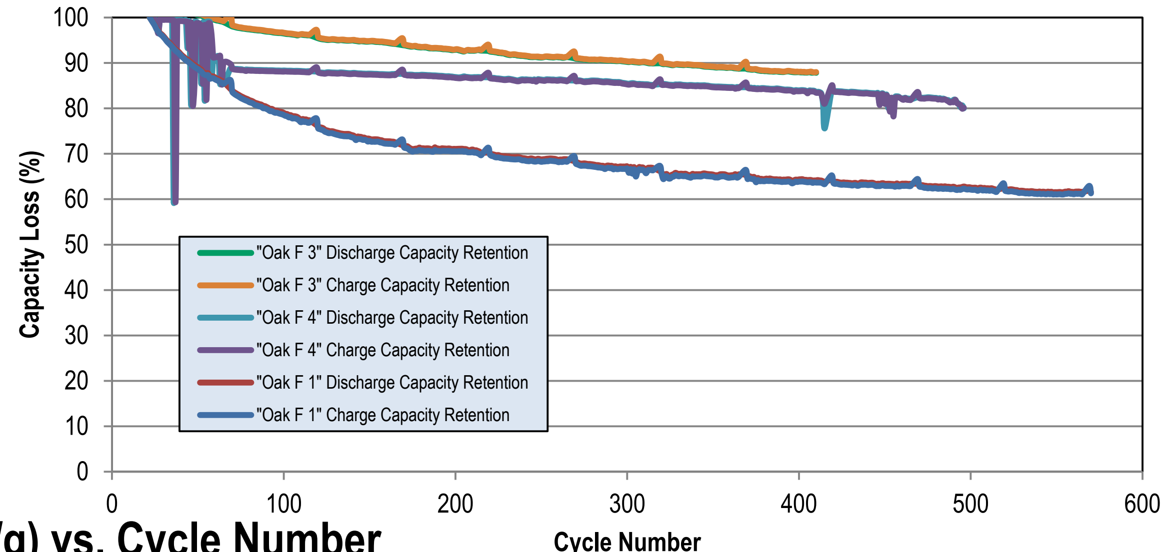
Testing Procedure

1. Voltage Window (3.0-4.1V)
2. Estimated 1 C rate of 3.0 mAh
3. Charged and discharged at C/5 (0.6 mA), C/2 (1.5 mA), 1C (3.0 mA) and 2C (6.0 mA) rates
4. 3 cycles at each rate

SET_Oak_F_4a		
C-rate	mAh	mAh/g of 523
C/5	2.64	127
C/2	2.41	116
1C	2.27	110
2C	2.12	102

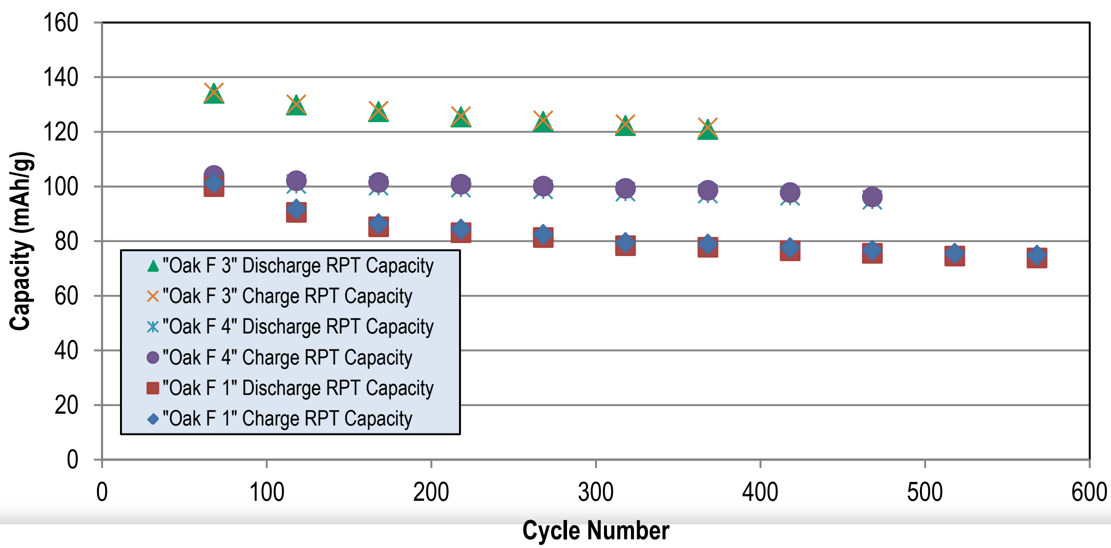


Inter-Laboratory Round Robin: ANL Life and Performance Study on ORNL Electrodes



Testing Procedure

1. Voltage Window (3.0-4.1V)
2. **C/2 Rate after cycle 19**
3. HPPC every 50 cycles
4. RPT (C/24) every 50 cycles
5. 1C value of 2.5 mAh



Capacity fade ranged from 12-36% through 400 cycles.

Collaborations

- Partners
  - National Labs: Argonne National Laboratory, Sandia National Laboratories
  - Battery Manufacturers: Dow Kokam, A123 Systems, Navitas Systems
  - Active Material Suppliers: Phostech Lithium, TODA America, ConocoPhillips
  - Inactive Material Suppliers: JSR Micro, Solvay Specialty Polymers, Timcal
  - Equipment Supplier: Frontier Industrial Technology
- Collaborative Activities
  - Electrode formulation, coating standardization, and round robin electrode testing with VTO ABR baseline active and inactive materials.
  - ORNL's unique contribution is modification of baseline NMP/PVDF formulation and develop an aqueous dispersion for evaluation by ANL and SNL.
  - Selection of appropriate dispersants and water-soluble binders for aqueous processing and thick electrode development.
  - Scale-up logistics and manufacturing cost savings of aqueous electrode processing with key battery developers and raw materials suppliers.

Future Work

- Remainder of FY13
  - Demonstrate pilot-scale coating capability with drying protocol optimization for CP A12 anode and TODA NCM 523 cathode formulations (Summer 2013).
  - Verify success of drying protocol through quantitative water-content study (Karl Fischer titration) of aqueous processed electrodes (Summer 2013).
  - Demonstrate comparable performance of CP A10 anode / Toda NCM 523 aqueous formulations to NMP-formulations in combined full coin cells and large-format (3 Ah) pouch cells (Sept. 2013).
- Into FY14
  - Aqueous processing of LMR-NMC cathodes to support high-energy cell commercialization.
  - Assist binder suppliers with commercialization of water-soluble binders.
  - Scale-up trials with a select battery-supplier partner's equipment.
  - Supply ANL, SNL, and industry partners with 100-ft rolls with 8" coating width of water-based anodes and cathodes.

Summary

- **Objective:** this project facilitates lowering the unit energy cost of EVs and PHEVs by addressing the expensive electrode coating and drying steps.
- **Approach:** blends colloidal and surface science with manufacturing science (coating, drying, etc.) to enable implementation of aqueous processed electrodes.
  - Raw material (solvent and binder) and processing costs are addressed.
  - $LiFePO_4$ → NCM 523 and CP A12
  - Ease of technology scale-up (capital costs reduced and solvent-recovery costs eliminated).
- **Technical:** Demonstrated cycling performance in full cells with water-based $LiFePO_4$ and in half-cells with water-based NCM 523 cathodes with simultaneous verification of dispersant/binder electrochemical stability and electrode water content.
- All FY13 milestones are on schedule.
- **Collaborators:** Extensive collaborations with national laboratories, lithium-ion battery manufacturers, and raw materials suppliers.
- **Commercialization:** Highly engaged with potential licensees; high likelihood of technology transfer because of significant cost reduction benefits and equipment compatibility.

Acknowledgements

- U.S. DOE Office of Energy Efficiency and Renewable Energy (EERE) Vehicle Technologies Office (Program Managers: David Howell and Peter Faguy)

- ORNL Contributors:
  - Claus Daniel
  - Jianlin Li
  - Jim Kiggans
  - Beth Armstrong
  - Brad Brown
  - Debasish Mohanty

Technical Collaborators:

- Andrew Jansen
- Bryant Polzin
- Chris Orendorff
- Maneesh Bahadur
- Erin O'Driscoll
- James Banas
- Mike Wixom
- Mark Ewen
- Gregg Lytle

Information Dissemination and Commercialization

- Patent
  - B.L. Armstrong, C. Daniel, D.L. Wood, and J. Li, "Aqueous Processing of Composite Lithium Ion Electrode Material," Filed October 12th, 2012, U.S. Patent Application No. 13/651,270 (UT-Battelle, LLC).
- Refereed Journal Papers and Book Chapter
  - J. Li, C. Daniel, and D.L. Wood, "Cathode Manufacturing for Lithium-Ion Batteries," in *Handbook of Battery Materials*, C. Daniel and J.O. Besenhard, Editors, 2nd Edition, pp. 939-960, Wiley-VCH, Weinheim, Germany (2011).
  - J. Li, C. Daniel, and D.L. Wood, "Materials Processing for Lithium-Ion Batteries," *Journal of Power Sources*, **196**, 2452–2460 (2011).
  - J. Li, C. Rulison, J. Kiggans, C. Daniel, and D.L. Wood, "Superior Performance of $LiFePO_4$ Aqueous Dispersions via Corona Treatment and Surface Energy Optimization," *Journal of The Electrochemical Society*, **159**, A1152–A1157 (2012).
  - J. Li, B.L. Armstrong, J. Kiggans, C. Daniel, and D.L. Wood, "Optimization of $LiFePO_4$ Nanoparticle Suspensions with Polyethyleneimine for Aqueous Processing," *Langmuir*, **28**, 3783–3790 (2012).
  - J. Li, B.L. Armstrong, J. Kiggans, C. Daniel, and D.L. Wood, "Lithium Ion Cell Performance Enhancement Using Aqueous $LiFePO_4$ Cathode Dispersions and Polyethyleneimine Dispersant," *Journal of The Electrochemical Society*, **160**, A201–A206 (2013).
  - J. Li, B.L. Armstrong, J. Kiggans, C. Daniel, and D.L. Wood, "Optimization of Multicomponent Aqueous Suspensions of $LiFePO_4$ Nanoparticles and Carbon Black for Lithium Ion Battery Cathodes," *Journal of Colloid and Interface Science*, Under Review, 2013.
- Selected Presentations (5 out of 9)
  - D.L. Wood, "Advanced Materials Processing for Lithium Ion Battery Applications," Oak Ridge National Laboratory Materials & Chemistry Seminar, Oak Ridge, TN, March 14, 2012 **(Invited)**.
  - J. Li, B. Armstrong, J. Kiggans, C. Daniel, and D. Wood, "Dispersant and Mixing Sequence Effects in $LiFePO_4$ Processing," 221st Meeting of The Electrochemical Society, Seattle, Washington, Abstract No. 164, May 6-11, 2012.
  - D. Wood, J. Li, D. Mohanty, S. Kalnaus, B. Armstrong, and C. Daniel, "Advanced Materials Processing for Lithium Ion Battery Applications," 222nd Meeting of The Electrochemical Society, Honolulu, Hawaii, Abstract No. 1052, October 7-12, 2012.
  - D. Wood, J. Li, D. Mohanty, S. Kalnaus, B. Armstrong, C. Daniel, and B. Brown, "Advanced Materials Processing and Novel Characterization Methods for Low-Cost, High Energy-Density Lithium-Ion Batteries," Advanced Automotive Battery Conference 2013, Pasadena, California, February 4-8, 2013. **(Invited)**.
  - C. Daniel, D. Wood, J. Li, B. Armstrong, J. Kiggans, D. Mohanty, and S. Kalnaus, "Electrification of Transportation – Cost and Opportunities", Bridging the Gap Conference 2013, Oak Ridge, Tennessee, March 5-6, 2013 **(Invited)**.

Made in USA
美国制造

Pictured Left to Right above:
David Wood (ORNL), Mike Wixom (A123 Systems), Erin O'Driscoll (Dow Kokam), Claus Daniel (ORNL), and Secretary of Energy Steven Chu at the ORNL Battery Manufacturing Facility (BMF)

Jianlin Li
(Staff Researcher)

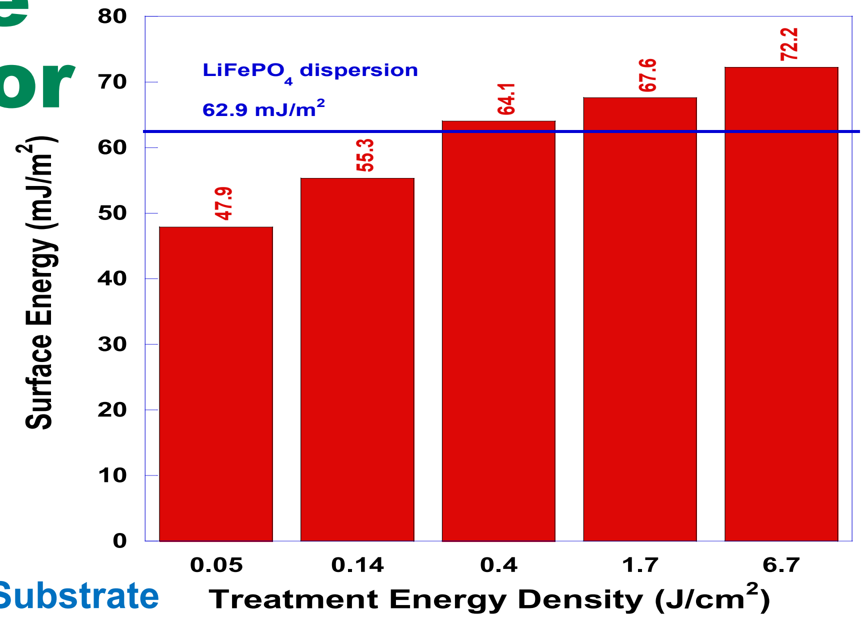
Bradley Brown
(Lab Technician)

Thank you for your attention!

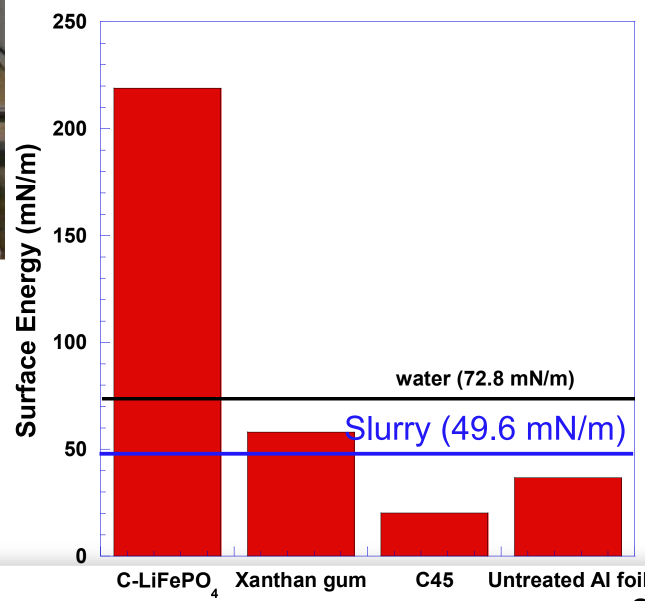
Technical Back-Up Slides

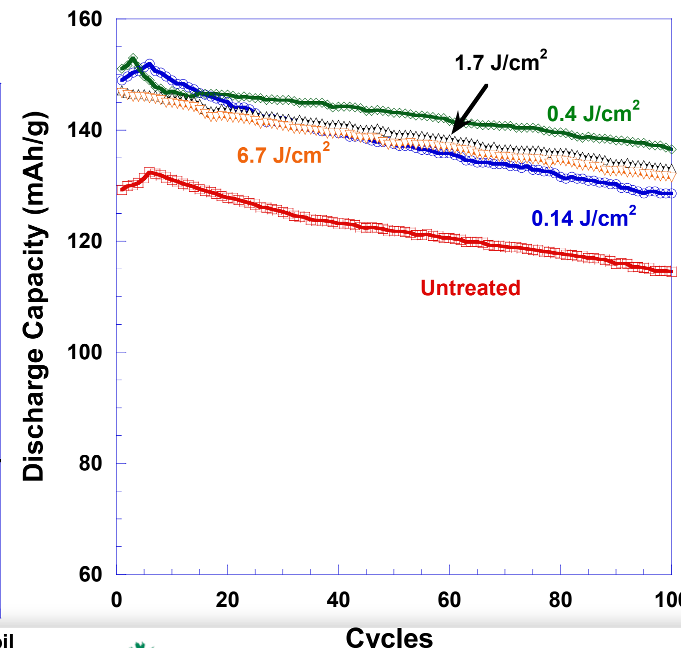
Corona Plasma Surface Treatment Optimized for Cathode Al Substrates

0.4 J/cm² → Optimum Energy Density



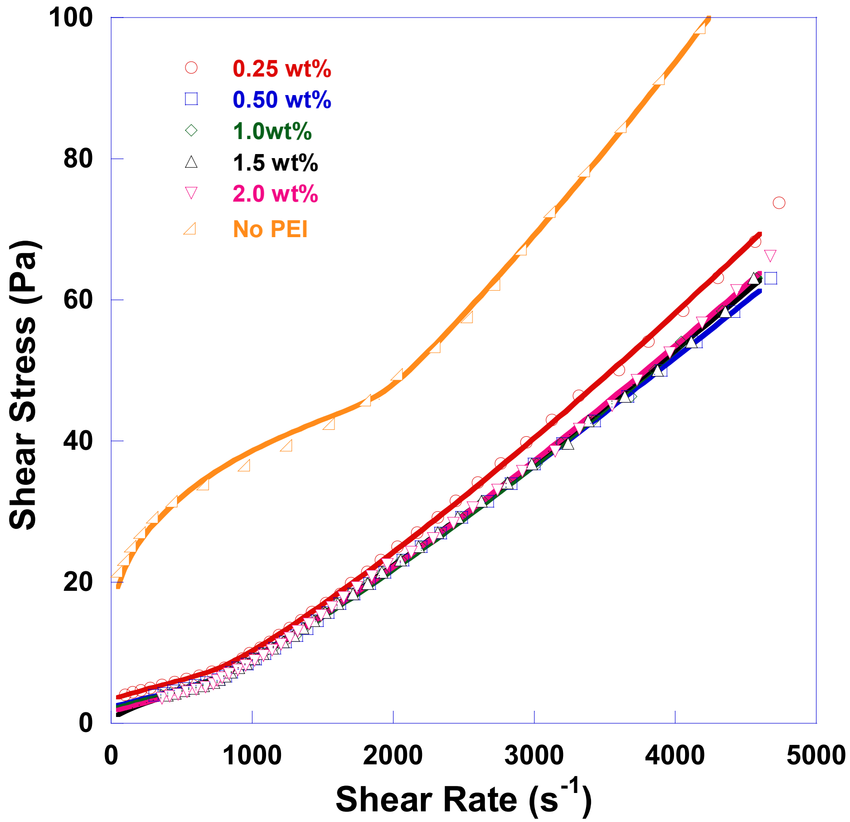
Surface Energy of Substrate Must Be Greater Than Surface Tension of Solvent!





Newtonian Behavior with PEI > 0.25 wt%

$LiFePO_4$ / PEI / H_2O = 100 / 0-2 / 350 wt fraction, **MW=600 g/mol**



Herschel-Bulkley (H-B) model

$$\begin{cases} \tau = \tau_0 + K\,\dot{\gamma}^n & \text{if } \tau > \tau_0 \\ \dot{\gamma} = 0 & \text{if } \tau \le \tau_0 \end{cases}$$

where τ, τ_0, K, $\dot{\gamma}$ and n are the shear stress, yield stress (stress needed to initiate the flow), consistency index, shear rate and power-law index, respectively

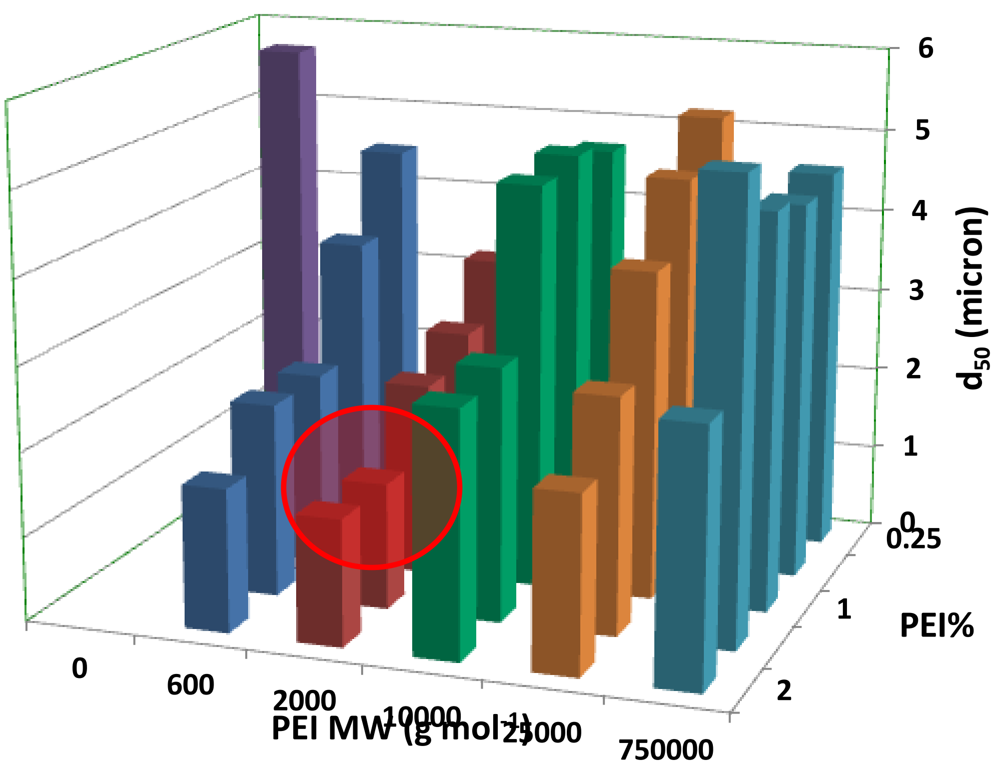
$$\begin{cases} n<1 & \text{shear thinning} \\ n=1 & \text{Newtonian} \\ n>1 & \text{shear thickening} \end{cases}$$

Power-Law Index

	0%	0.25%	0.50%	1.00%	1.50%	2.00%
Low $\dot{\gamma}$	0.32	0.87	0.92	0.94	0.96	0.99
high $\dot{\gamma}$	1.37	1.27	1.18	1.28	1.21	1.25

J. Li et al., ***Particle & Particle Systems Characterization*, Under Review, 2013.**

Optimal PEI Conditions: 1.5 wt% PEI (MW=2,000 g/mol)



J. Li et al., *Particle & Particle Systems Characterization*, Under Review, 2013.

<u>PEI is based on $LiFePO_4$ weight fraction</u>

- The addition of PEI dramatically reduces agglomerate size
- Agglomerate size decreases with increasing PEI%
- Agglomerate size decreases with increasing PEI MW from 600 to 2000 g/mol and mostly increases with further increasing PEI MW
- Minimum agglomerate size obtained at 1.5 wt% and 2.0 wt% PEI with MW = 2,000 g/mol

Lithium-Ion Binders Have Been Found to Be Stable at High Temperatures

- Comparison of binder thermal stability via TGA (F. Courtel *et al.*, "Water Soluble Binders for Graphite Anodes, Application in Lithium-Ion Batteries," 219th ECS Conference, May 1-6, 2011).
- Based on these results, xanthan gum and PVDF are stable up to ~200°C and ~350°C, respectively (much higher temperature than required for water solvent drying).

➢ **Therefore, residual electrode water can be removed to a safe level without damaging the binder.**