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

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5/17/12

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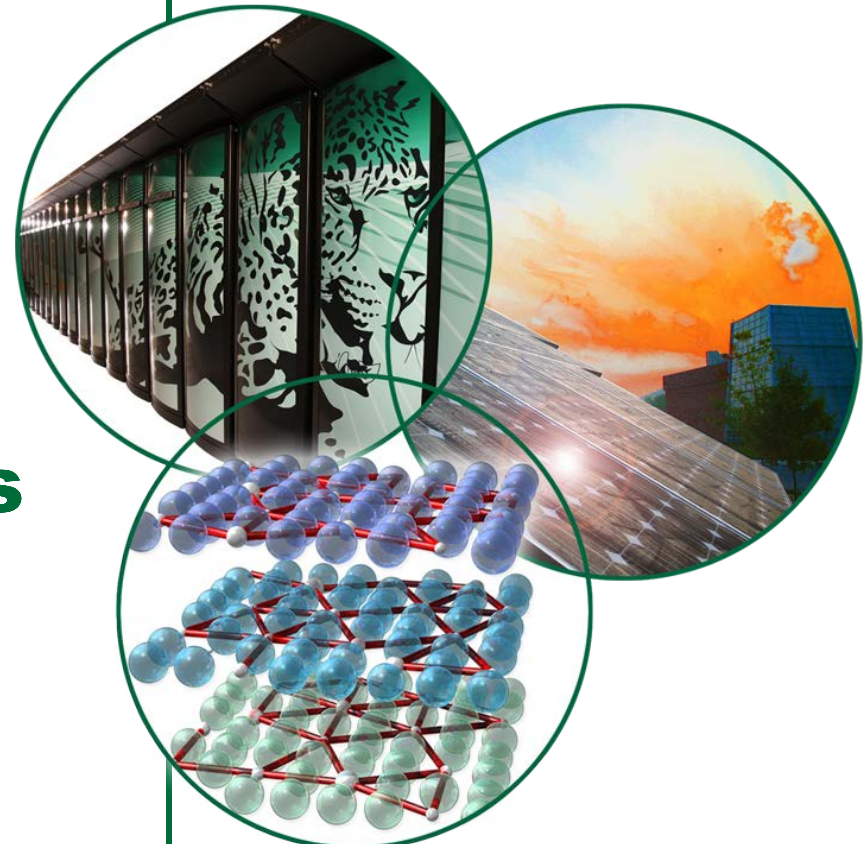

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Overview

Timeline

- ➢ Start: October 1, 2011
- ➢ End: September 30, 2014
- ➢ Percent complete: 20%

Budget

- Total project funding
  - DOE: $900k
- FY11 Funding: NA
- FY12 Funding: $300k

Barriers

- Electrode processing cost
  - By 2014, reduce PHEV battery costs to $300/kWh.
  - Advanced Li-ion HEV/PHEV battery systems with low-cost design electrode architectures.
  - Achieve selling price of $1700-3400 for 100,000 PHEV units/year by 2015.

Partners

- Collaborations:
  - Argonne National Laboratory
  - Sandia National Laboratories
- Project lead: Oak Ridge National Laboratory

Project Objectives

- Main Objective: To transform lithium ion battery electrode manufacturing by the reduction or elimination of costly, toxic organic-solvents.
  - Replace N-methylpyrrolidone (NMP) with water based chemistry.
  - Elimination of expense solvent recovery steps and capital equipment.
  - Focus on general procedure for both anode and cathode chemistries.
- Relevance to Barriers and Targets
  - Implementation of low-cost, green manufacturing methodology for lithium ion battery anodes ***and cathodes*** using aqueous colloidal dispersions (to meet $300/kWh VTP storage goal for PHEVs).
  - Correlation of properties of colloidal dispersions and electrode coatings to cell performance enabling advancement of 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

Due Date	Milestone
3/2012	Development of an aqueous formulation for cathodes.
5/2012	Development of an aqueous formulation for anodes.
6/2012	Go/no-go: Achieve at least 95% capacity retention through 50 cycles (for half cells) based on selected aqueous formulations.
7/2012	Coating technique and drying protocol for anodes and cathodes.
9/2012	Development of porosity control in electrodes with controlled settling and calendering study.
9/2012	Match cell performance in terms of initial capacity, irreversible capacity loss, and cyclability through 100 cycles of aqueous dispersions (full cell format) and water-soluble binder to NMP/PVDF based dispersions.

Project Approach

- **Problems to be solved:**
  - Excessive agglomeration and settling in aqueous dispersions.
  - Poor wetting and adhesion of water-based dispersions to current collector foils.
- **Overall technical approach and strategy:**
  - Development of complete aqueous colloidal dispersion design process including surface charge and rheology characterization, agglomerate size optimization, order of constituent addition, and tailoring of mixing protocol.
  - Coating parameter optimization for aqueous dispersion chemistry including viscosity control, substrate (current collector) surface energy optimization, and tailoring of drying protocol.
  - This project enables replacement of NMP with water by implementation of colloidal science resulting in lower electrode and drying costs.
  - Close collaboration on this project with the Argonne National Laboratory and Sandia National Laboratories ABR efforts.
- **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)
- **New project for FY12: all milestones are on schedule.**

Technical Accomplishments – Executive Summary

- Zeta potential measurement allowed for selecting the ideal *cationic* dispersant, polyethyleneimine (PEI) for $LiFePO_4$ cathode dispersions (an anionic dispersant, polyacrylic acid (PAA) has been proposed in the literature).
- Rheology studies allowed for characterization of the extent of agglomeration and surfactant concentration optimization, as well as flow optimization for slot-die coating.
- Corona plasma treatment of the cathode Al foil has been optimized at 0.4 J/cm^2 for water based $LiFePO_4$ cathode dispersions.
- Primary and secondary drying protocols have been developed for the water based $LiFePO_4$ cathode coatings, but optimization is still needed.

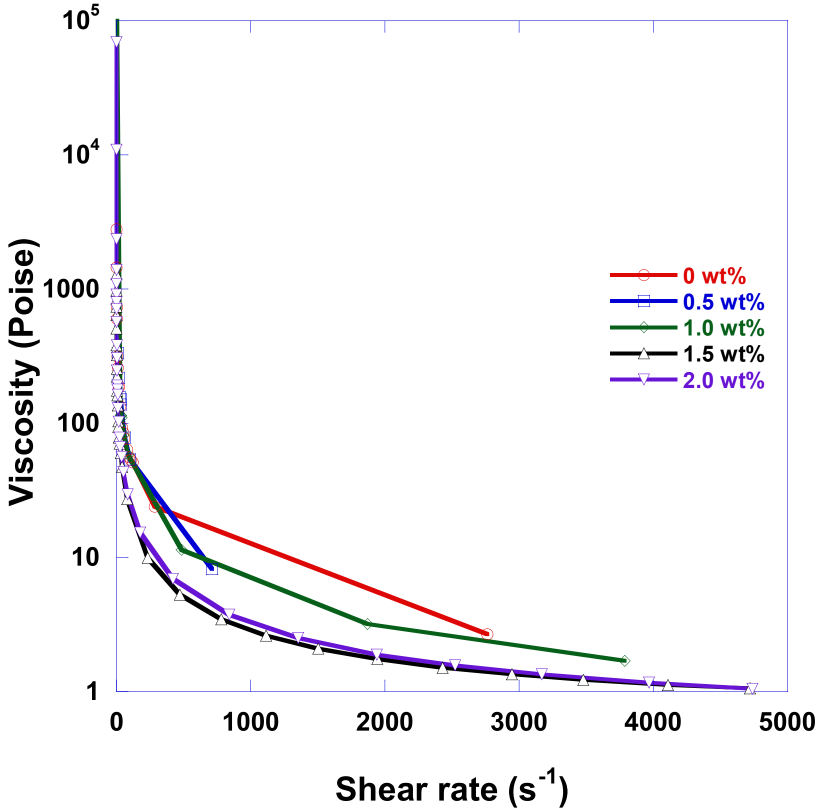
❖ Half cell performance of $LiFePO_4$ was improved by about 35 mAh/g through 50 cycles with 2 wt% PEI addition, and no capacity fade was observed.

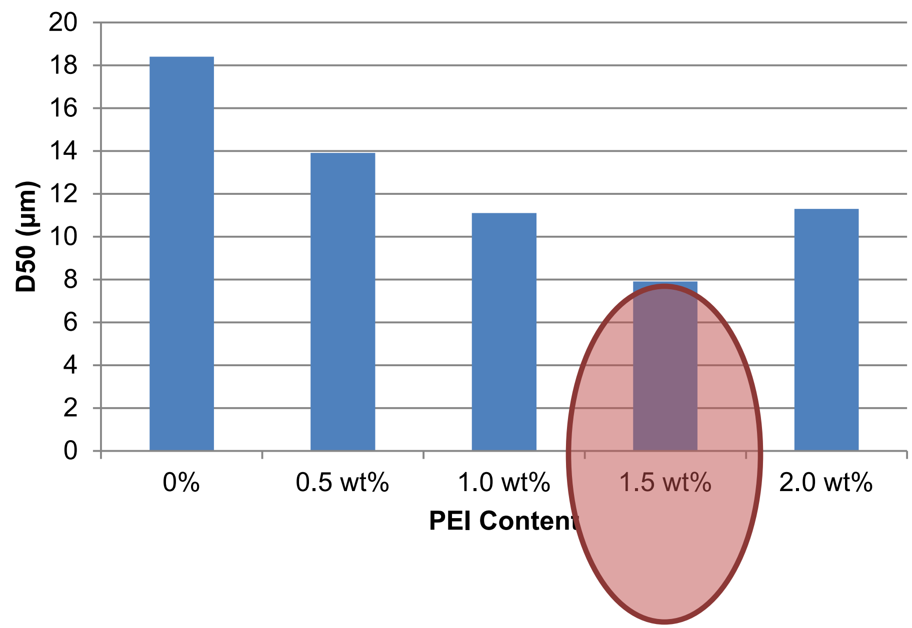
❖ Half cell performance of $LiFePO_4$ was improved by almost 25 mAh/g through 50 cycles with 0.4 J/cm^2 corona treatment.

❖ **With these two processing improvements, near theoretical capacity for a *water based* $LiFePO_4$ cathode has been achieved at 167 mAh/g.**

Full Composite Electrode Dispersion Control in Water

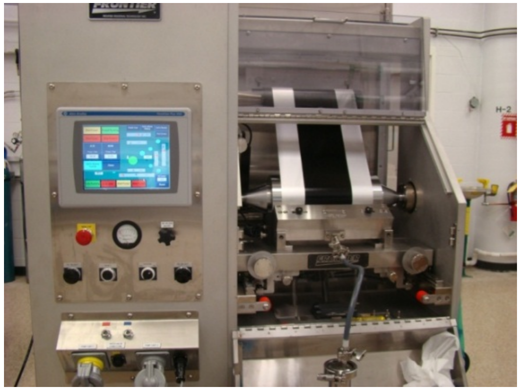
$LiFePO_4$ / C45 / Xanthan Gum / PEI / H_2O =100 / 10 / 2.5 / 0-2 / 250 wt fraction

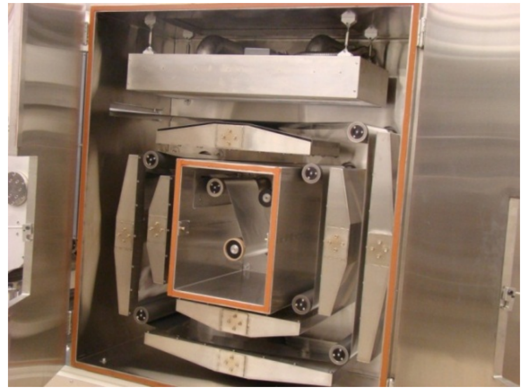




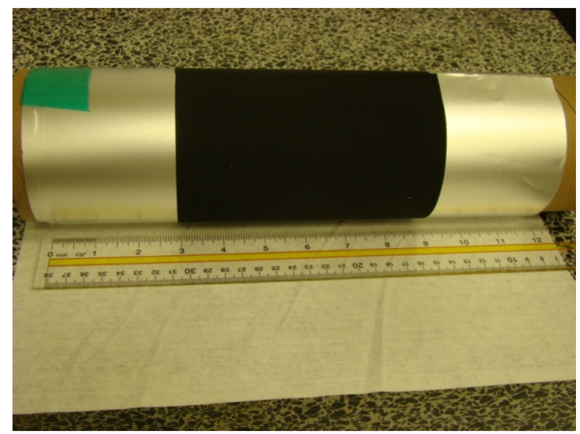
- **Viscosity and agglomerate size optimized with 1.5 wt% PEI, but performance must also be taken into account.**

Coating and Drying of $LiFePO_4$ Cathodes

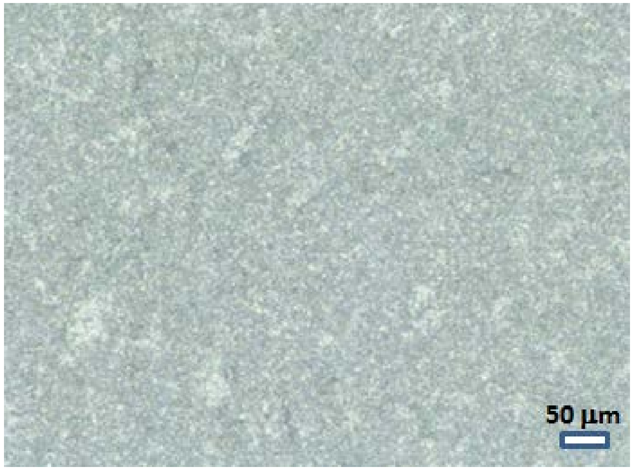




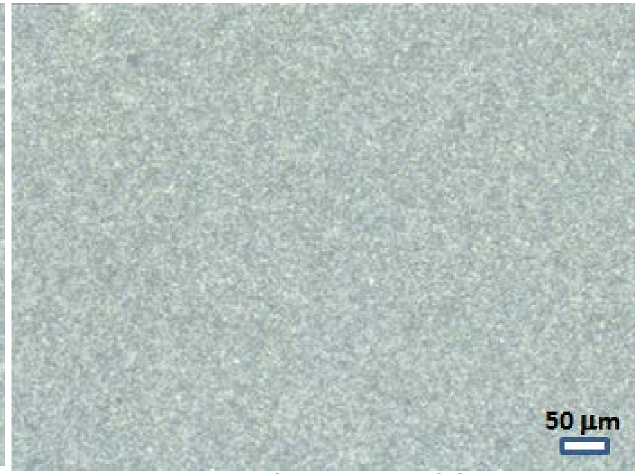
- Slot-die coating
- Pre-drying (30-90°C)
- Final vacuum drying (90°C, 2h)
- Cell assembly



Visually Improved Coatings with PEI

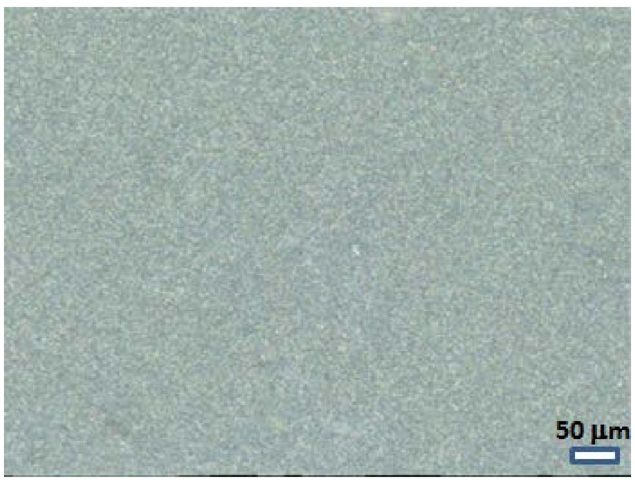


a) 0%

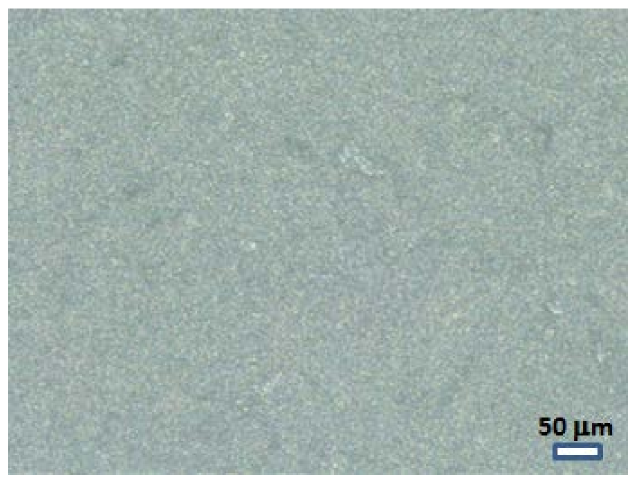


b) 0.5 wt%

c) 1.0 wt%



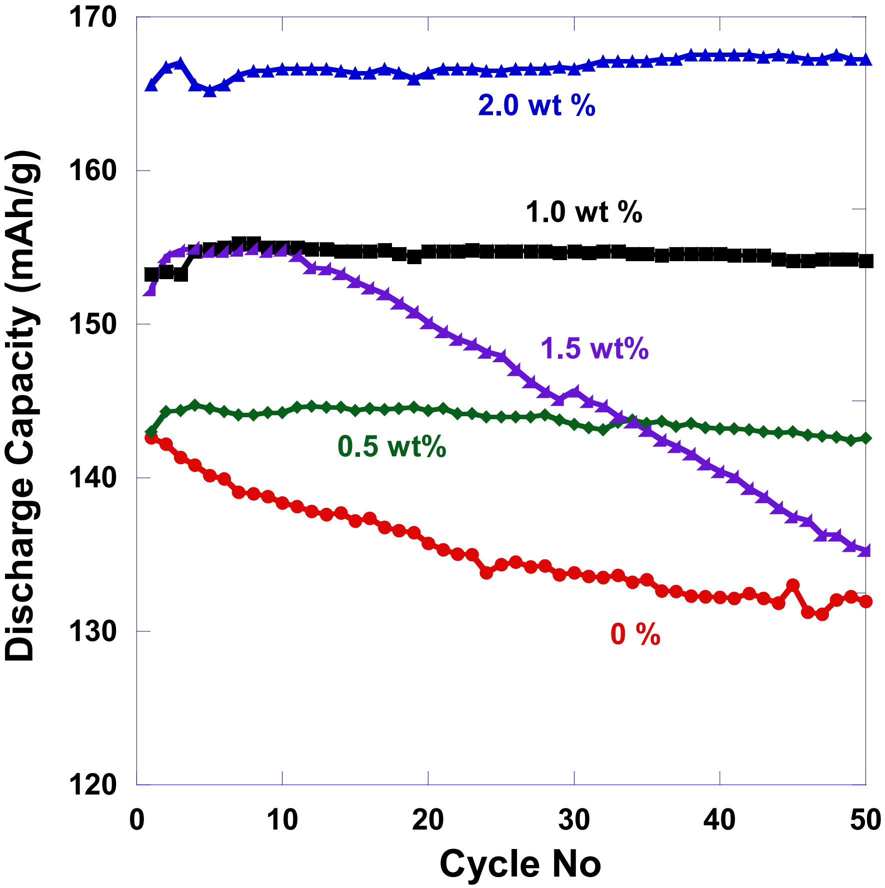
d) 1.5 wt%

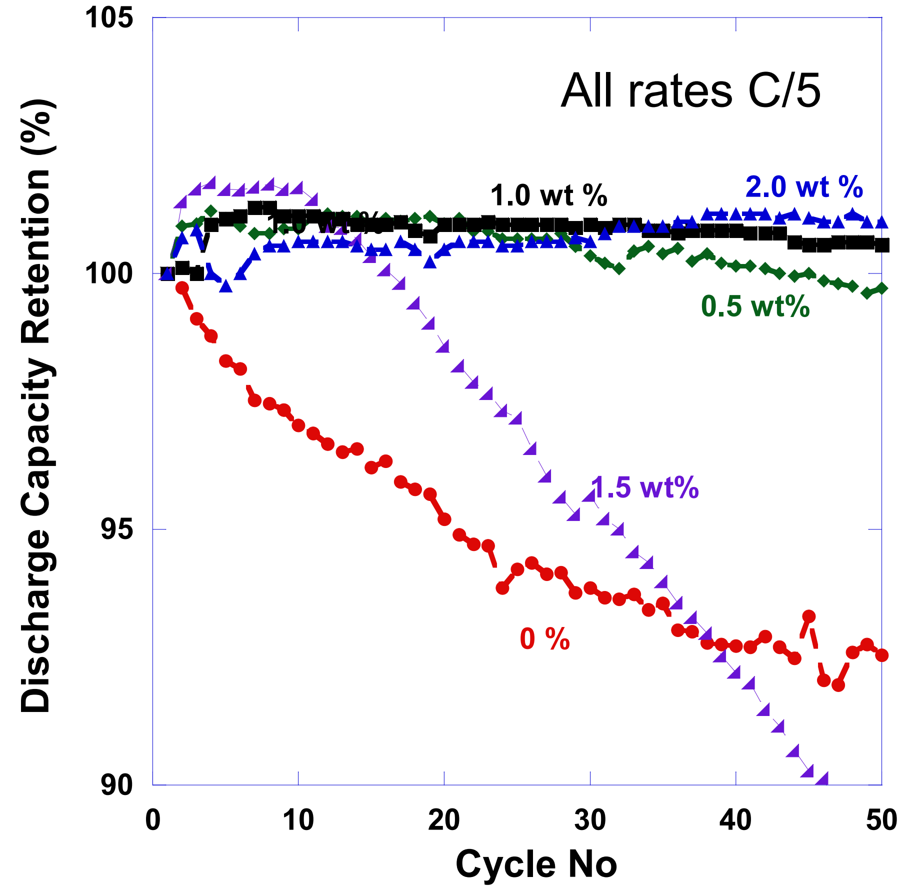


e) 2.0 wt%

- Without PEI, agglomerates and micro-cracking
- With PEI, better integrity and dispersion

Optimized Performance Realized with 2.0 wt% PEI





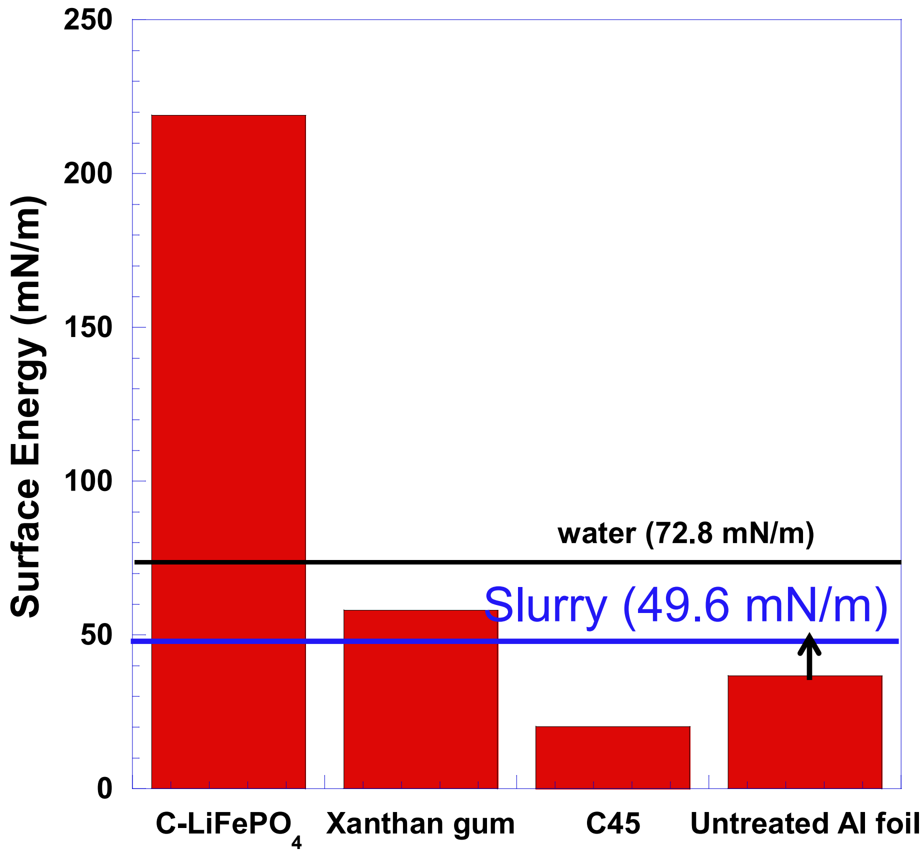
<u>Half cell:</u>

- Li counter electrode
- Celgard® 2325
- 1.2 M $LiFP_6$ in EC/DMC (3/7 wt fraction)

Slurry Surface Energy Too High for Coating

Materials: C-$LiFePO_4$, Super P® C45 (C45, Timcal), Xanthan Gum (XG, Nuts Online), Polyetheneimine (PEI, Mw=25 kg/mol, Sigma-Aldrich), Al foil (MTI), distilled water.

Slurry composition: $LiFePO_4$/C45/PEI/XG/H_2O=100/10/1.0/2.5/350 wt.
Mixing by high shear mixer at 2k RPM: 1) Xanthan Gum in PEI solution; 2) $LiFePO_4$ in suspension; 3) C45 in suspension



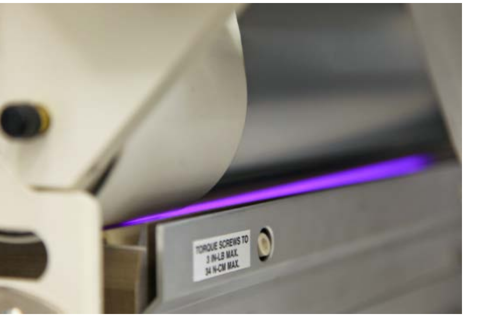
Slurry surface energy was measured using mercury and diiodomethane.

Surface tension of the slurry not governed by $LiFePO_4$.

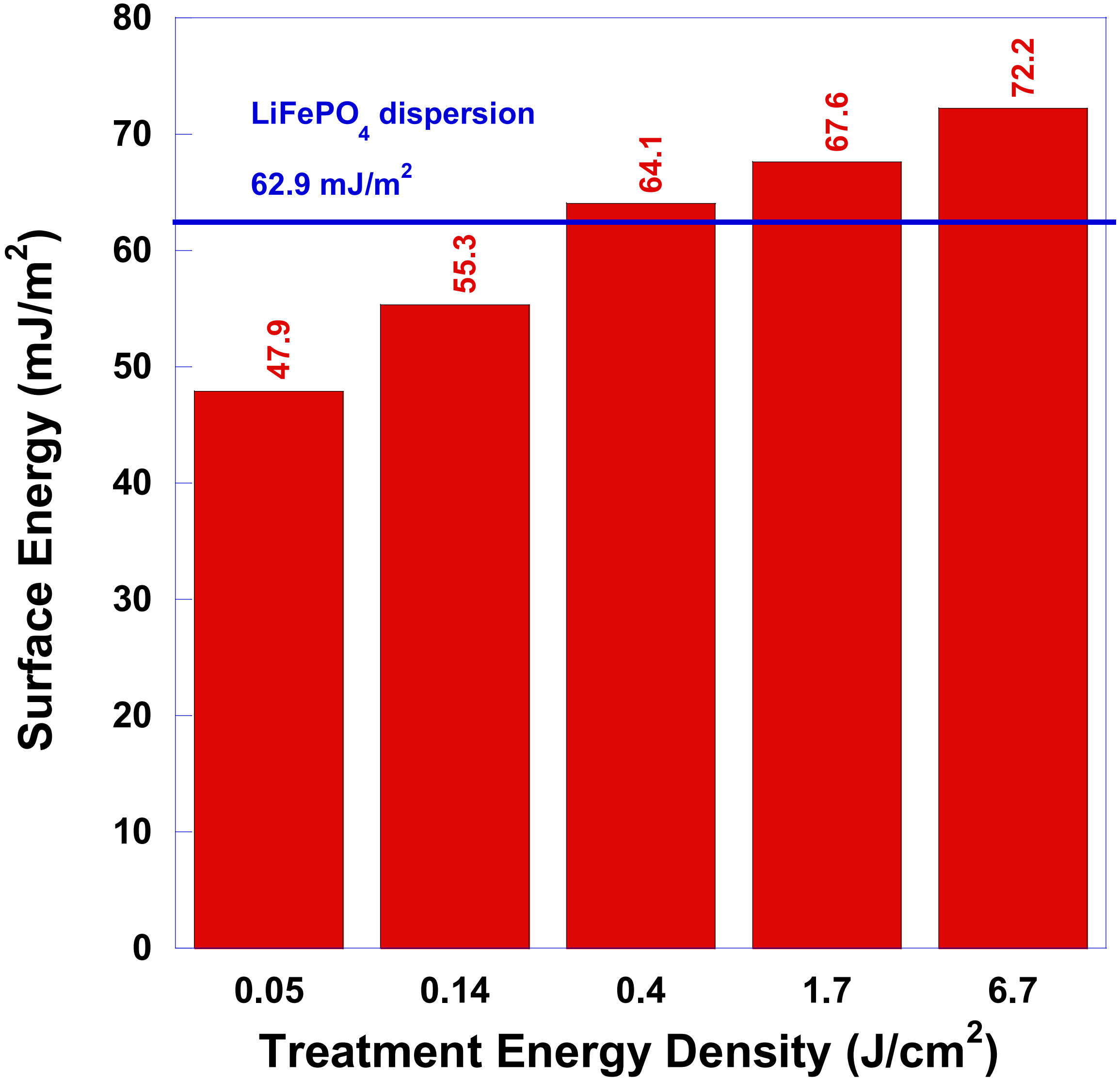
For a good coating, substrate surface energy must be greater than slurry surface energy.

Surface Energy Change by Discharge Corona Plasma

- Invented by Verner Eisby in 1951
- Generated by application of high voltage to sharp electrode tips
- Removes adsorbed hydrocarbon
- Treatment conditions:
  0.14, 0.4, 1.7, 6.7 J/cm^2



Surface Energy of Al Foil Increased by Corona Treatment

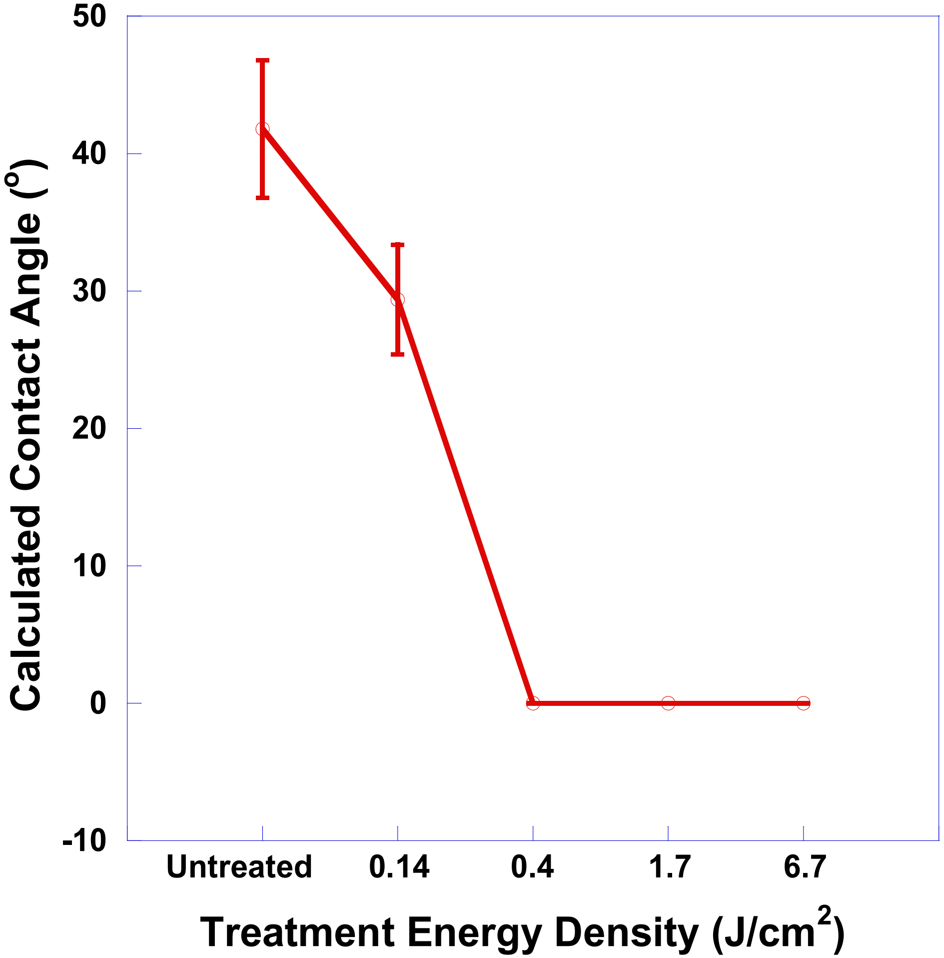


Surface Energies Measured Using Water and Diiodomethane.

A corona treatment energy density of 0.4 J/cm^2 raises the Al foil surface energy **above** the surface tension of the dispersion.

Better Wettability Between Cathodes and Treated Al Foil

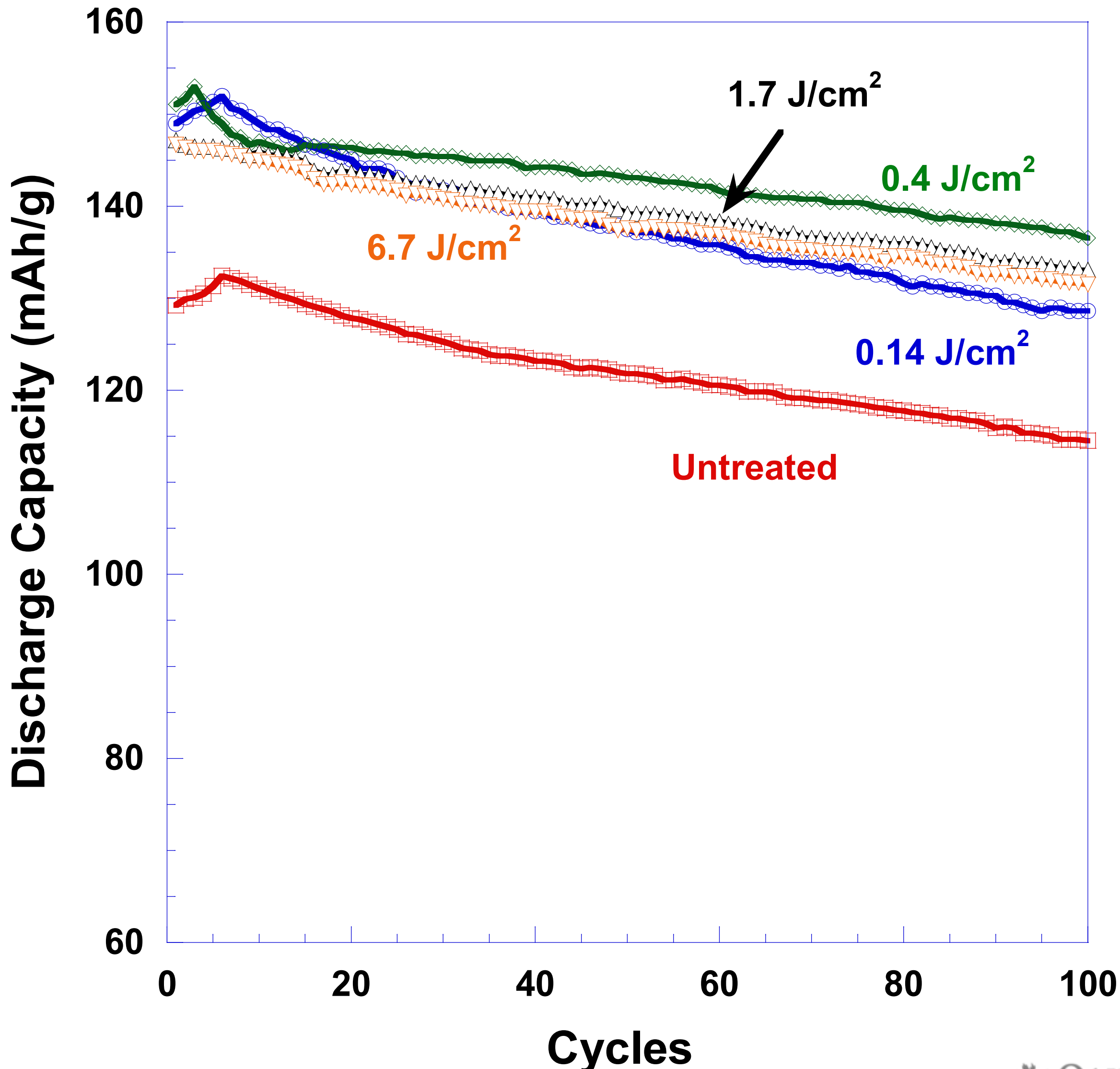
Fowkes Theory: $$\left(\sigma_L^D\right)^{1/2}\left(\sigma_S^D\right)^{1/2}+\left(\sigma_L^P\right)^{1/2}\left(\sigma_S^P\right)^{1/2}=\frac{\sigma_L(\cos\theta+1)}{2}$$



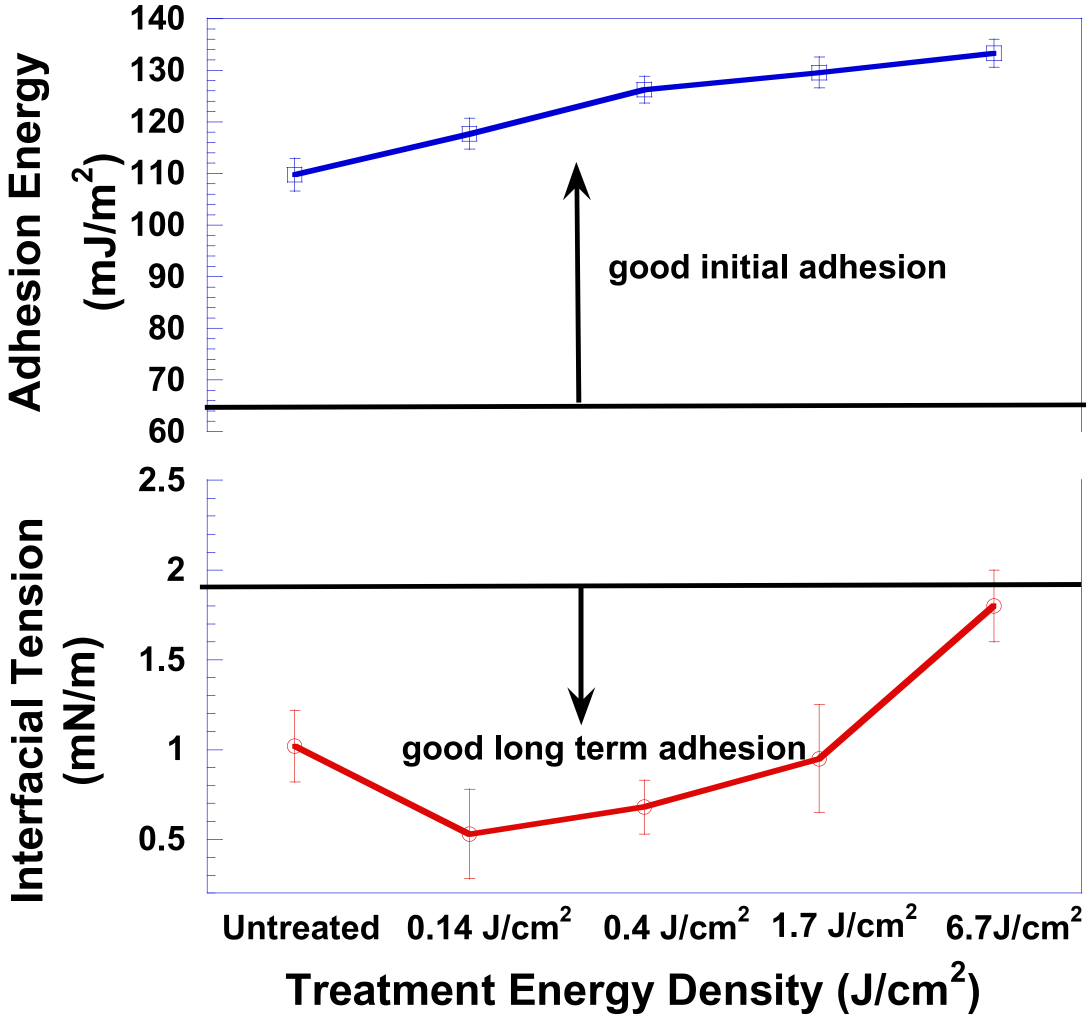
- **Contact angle of $LiFePO_4$ dispersion with Al foil decreases with increasing energy density.**
- **Optimum wetting of dispersion is achieved at 0.4 J/cm^2 or higher, but cell performance must also be taken into account.**

Better Performance with Treated Al Foil (1 wt% PEI Added to Dispersion)

- Over two orders of magnitude of corona treatment energy density were examined.
- All treatment energy densities showed higher capacity than with no corona treatment.
- Capacity fade was less with 0.4 J/cm^2 than for the higher energy densities, as well as for the case with no surface treatment.



Better Adhesion Between Cathodes and Treated Al Foil



Adhesion energy by Fowkes theory:

$$\varphi_{SL} = 2\left(\sigma_L^D\right)^{1/2}\left(\sigma_S^D\right)^{1/2} + 2\left(\sigma_L^P\right)^{1/2}\left(\sigma_S^P\right)^{1/2}$$

Interfacial tension by Good's expression:

$$\gamma_{SL} = \sigma_S + \sigma_L - 2\left(\sigma_L^D\right)^{1/2}\left(\sigma_S^D\right)^{1/2} - 2\left(\sigma_L^P\right)^{1/2}\left(\sigma_S^P\right)^{1/2}$$

Collaborations

- Partners
  - Argonne National Laboratory (ANL)
  - Sandia National Laboratories (SNL)
- Collaboration is within the Vehicle Technologies Applied Battery Research (ABR) Program.
- Collaborative activities
  - Electrode formulation standardization with baseline active and inactive materials.
  - Electrode coating standardization at multiple sites.
  - Round robin evaluation of coated electrodes.
  - ORNL's unique contribution is to modify baseline NMP formulation and develop an aqueous dispersion for evaluation by ANL and SNL.

Future Work

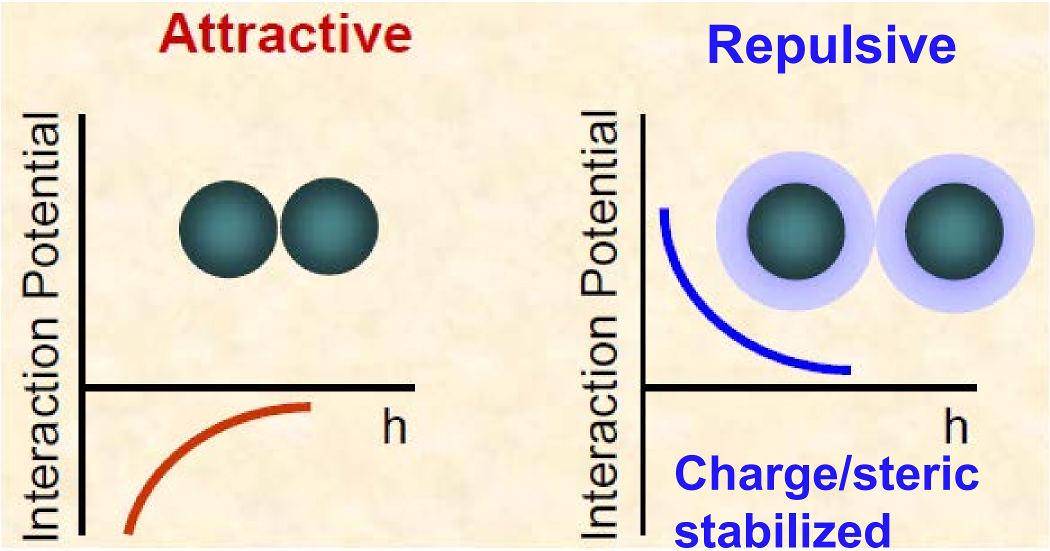
- Remainder of FY12
  - Complete development of CP A10 anode and Toda NCM 523 cathode formulations (by May 2012).
  - Demonstrate pilot-scale coating capability with drying protocol optimization for each formulation and ship materials to ANL and SNL for performance validation (July 2012).
  - Optimize porosity of electrode coatings through solids loading and settling control and calendering study (Sept. 2012).
  - Validate performance of full coin cells with pilot-scale aqueous electrode coatings through 100 cycles (Sept. 2012).
- Into FY13
  - Multistage drying investigation and water content study.
  - Long-term, full coin and pouch cell cycling study with rate dependence.
  - Scale-up trials with a select industry partner's equipment.

Summary

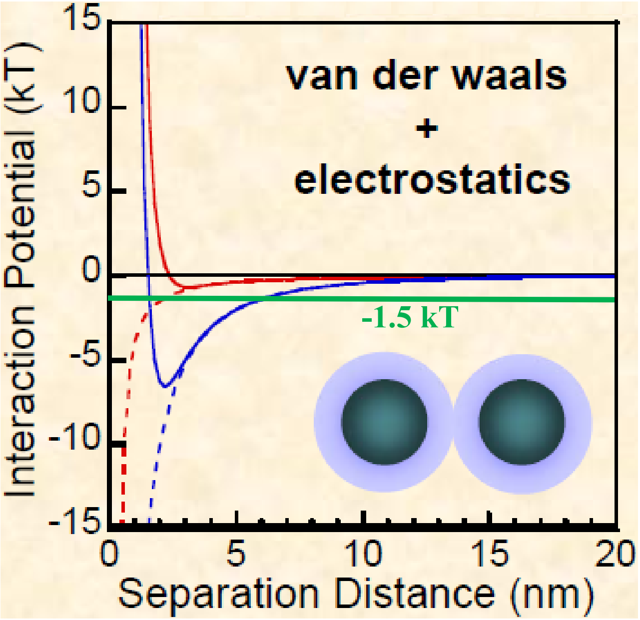
- This project facilitates lowering the unit energy cost of EVs and PHEVs by addressing the expensive electrode coating and drying steps.
- Our approach blends colloidal and surface science to enable implementation of aqueous dispersion chemistry.
  - Raw material (solvent) and processing costs are addressed.
  - Ease of implementation of technology (capital costs reduced).
  - $LiFePO_4$ performance was increased using both technologies of project.
- All FY12 milestones are on schedule.
- High likelihood of technology transfer because of significant cost reduction benefits and equipment compatibility.
- Addition of industrial partner by the end of FY12 positions the project well for continuation and expansion into FY13.

Technical Back-Up Slides

Interactions Between Colloidal Particles



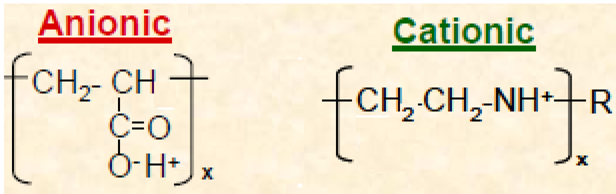
Attractive – van der vaals force
Repulsive– coulomb force



Average molecular kinetic energy: 3/2kT

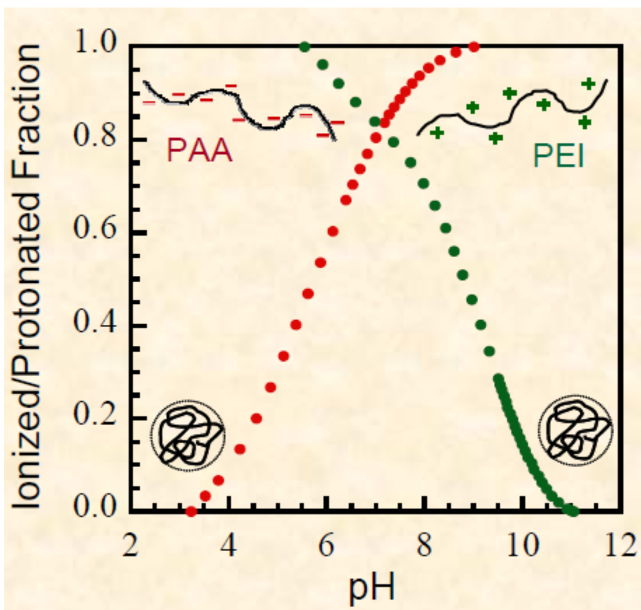
Agglomeration of colloidal particles can be controlled by adjusting the charge on the particle surface.

PEI is an Effective Dispersant for $LiFePO_4$ Suspensions



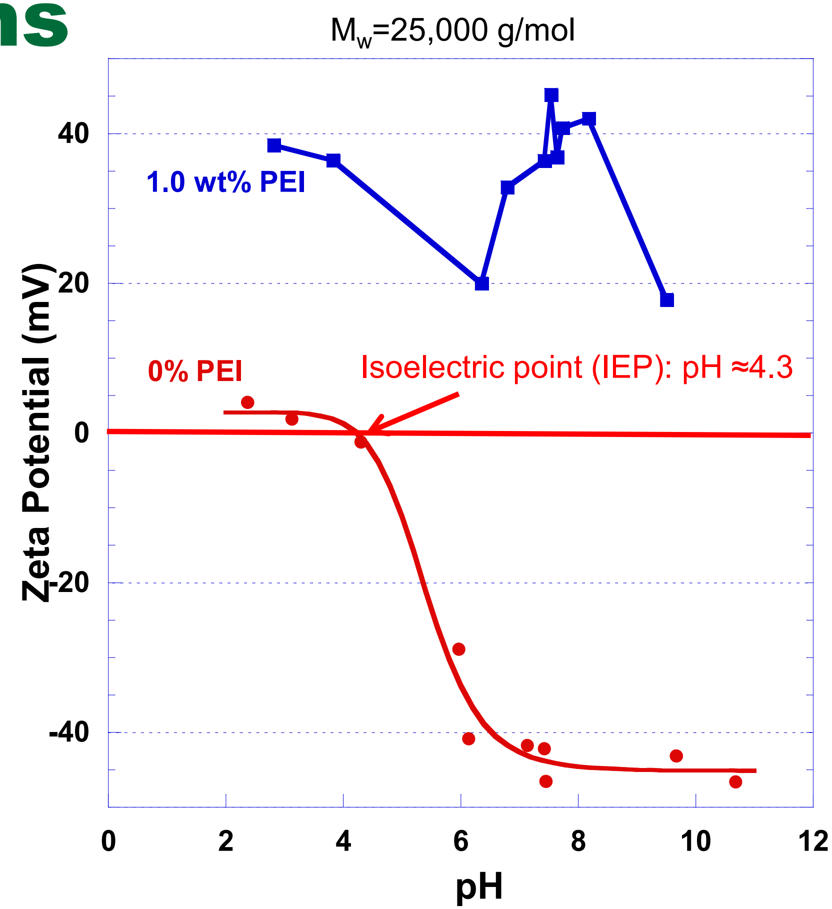
Poly(acrylic acid) (PAA)

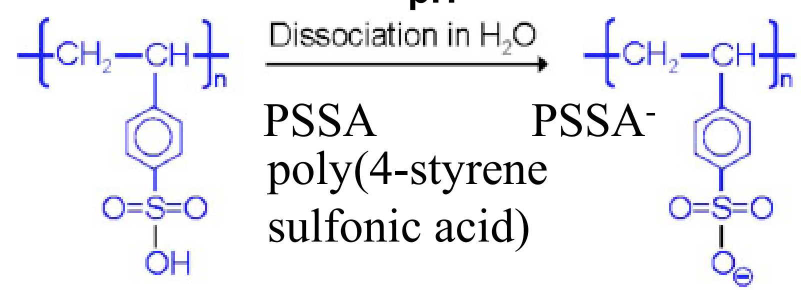
Poly(ethylene imine) (PEI)



Guideline for absorption:

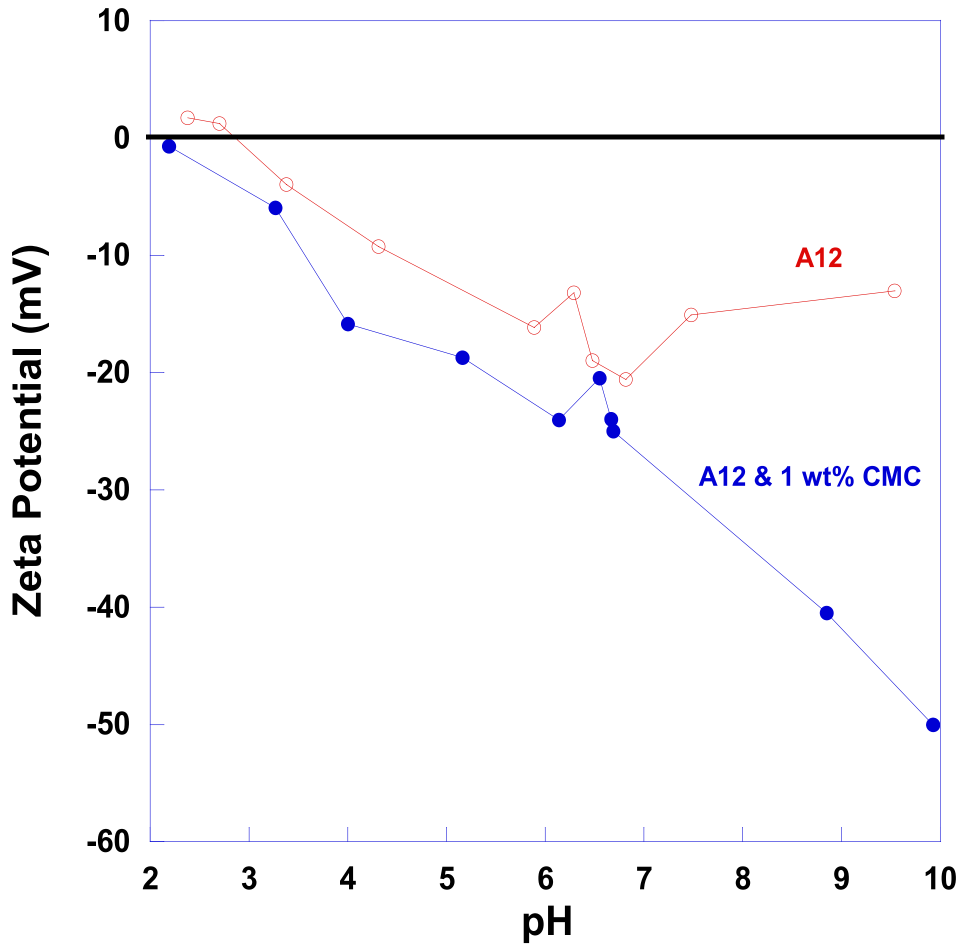
IEP <6	PEI
IEP 6-8	PAA or PEI
IEP >8	PAA





Chia-Chen Li *et al.*, *J. Electrochem. Soc.*, **157** (2010), A517

CMC Dispersant Effect on CP A10 (A12)



- Isoelectric point (IEP) for A12 graphite was pH = 3, which indicates that a cationic dispersant should be used.
- Addition of 1 wt% carboxymethylcellulose (CMC), *an anionic dispersant*, has been investigated by ConocoPhillips.
- ORNL has confirmed a shift in the zeta potential to more negative values, indicating an improvement in dispersion quality.
- An even better dispersion is expected with a cationic dispersant such as PEI.