Towards Solventless Processing of Thick Electron-Beam (EB) Cured LIB Cathodes

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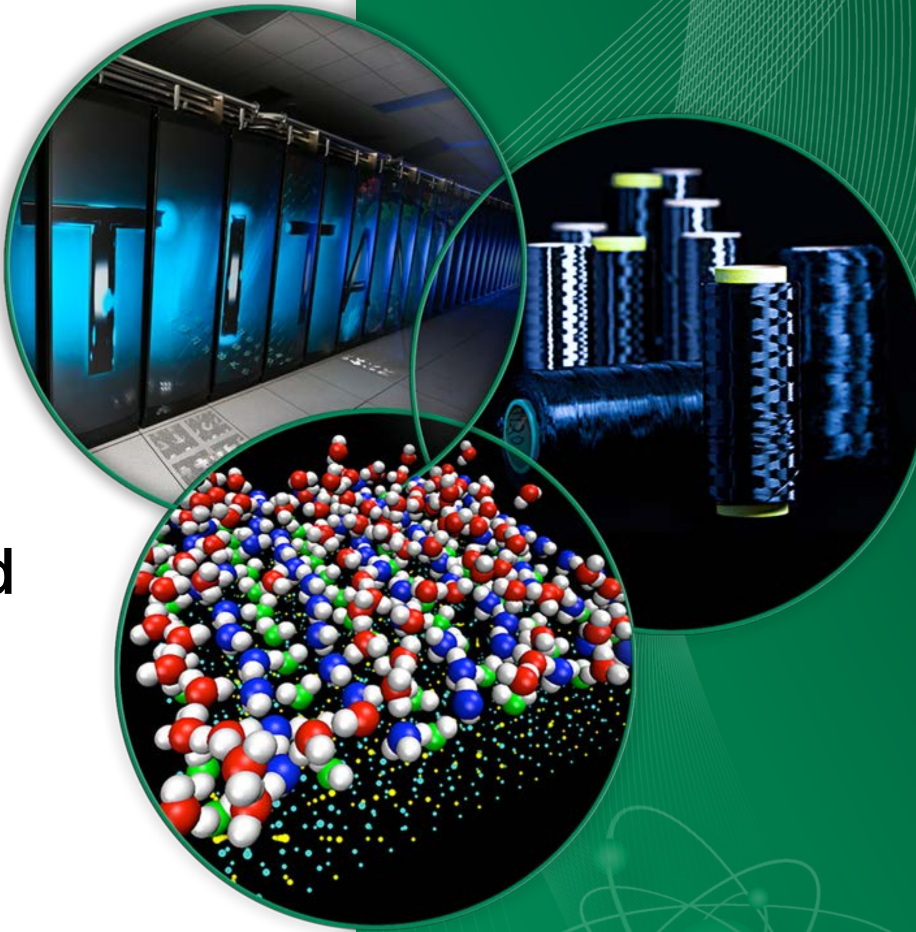

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ES207

Overview

Timeline

- Task Start: 10/1/14
- Task End: 9/30/19
- Percent Complete: 30%

Barriers

- Barriers addressed
  - By 2022, further reduce EV battery cost to \$125/kWh.
  - Materials processing cost reduction and electrode thickness increase of ≥2×.
  - Achieve deep discharge cycling target of 1000 cycles for EVs (2022).

Budget

- Total task funding
  - \$1125k
- \$125k in FY15
- \$250k in FY16

Partners

- Interactions/Collaborations
  - Equipment Suppliers: COMET-Plasma Control Technologies (PCT)
  - Battery Manufacturers: XALT Energy, Navitas Systems
  - Materials Suppliers: TODA America
- Project Lead: ORNL

Objectives & Relevance

- **Main Objective: To achieve 1) significant process energy savings; 2) ultra-high electrode processing speed; and 3) utilize much more compact equipment than conventional drying ovens.**
  - EB treatment is a fast, robust materials processing technology.
  - Low cost and excellent compatibility with high-volume materials production.
  - Unmatched throughput: ≥600 m^2/min throughput can be achieved based on ≥300 m/min line speed for roll widths up to 2 m ($1.5-2.0M installed with footprint ~10 m^2).
  - Thicker electrodes: It is expected that cathode coatings of **several hundred microns** can be processed at ~150 m/min or with a larger equipment footprint.
  - Excellent energy efficiency – Electrical efficiencies ≥60% are possible.
  - Environmentally friendly – EB processing requires no solvent and no photoinitiator and has low emissions.
- **Relevance to Barriers and Targets**
  - Significantly enabling technology for achieving ultimate EV battery pack cost of $125/kWh through substantial materials processing cost reduction.
  - *Further enables cell energy density improvement through electrode thickness increases of at least 2×.*

Advantage of EB Curing over Physical Drying

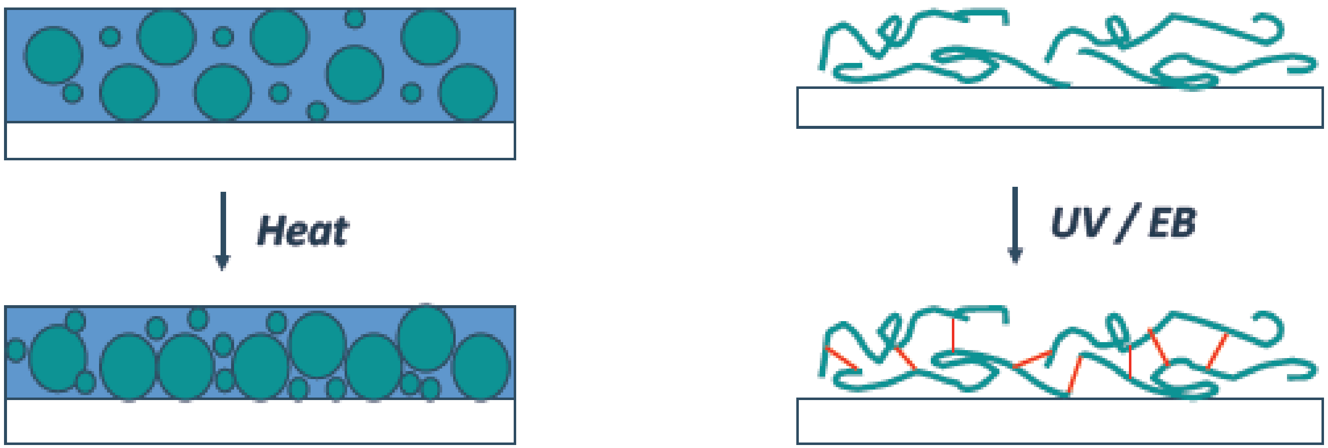
Physical drying ⟷ **Chemical curing**

Physical drying

- Solvent/water evaporation
- Physical drying
- No crosslinking
- High MW polymers

Chemical curing

- No solvent/water evaporation **(Ultimate goal)**
- Chemical polymerisation
- Crosslinking produces a rigid network
- Low MW oligomers become high MW polymers



"Conventional systems "

"Energy curing systems"

The transformation from liquid to solid is very fast (<1 second)

J. Arceneaux, UV/EB Chemistry for Non-Chemists, UV/EB Surface Curing Workshop, Atlanta, GA, Sept. 10, 2015.

Task Milestones (Only)

Status	SMART Milestones	Description
9/2015 ✓	FY15 Milestone Complete	Demonstrate no more than 20% greater first-cycle irreversible capacity loss (in half coin cell) as compared to ABR baseline cathode and electrochemical stability over 2.0-4.6 V vs. Li/Li^+ as measured by cyclic voltammetry for EB-cured NMC 532 cathode dispersion.
6/2016 ✓	FY16 Milestone Complete	Quantify capacity fade at 0.33C/-0.33C in full coin cells with down-selected EB curing NMC 532 cathode formulation; achieve at least 100 cycles.
9/2016	FY16 Go/No-Go On Schedule for Go Decision	**Go/No-Go:** EB Curing Speed and Cathode Thickness Validation: demonstrate ≥150 μm NMC 532 cathode coating thickness with full EB cure, ***down-selected electrode formulation, and selected industrial partner*** on a roll of at least 1000 m processed at ≥200 m/min. If this outcome is a no-go, then either the EB formulation will be redesigned, the industrial partner will be replaced, or both for FY17.

Approach

- **Major problems to be addressed:**
  - Conventional solvent primary drying ovens for lithium-ion electrodes are not compatible with high line speeds or must include long drying lines to accommodate high line speeds.
  - These drying lines are capital intensive and require a large amount of battery plant space.
  - Cost of organic solvents and solvent handling are prohibitive in terms of processing cost and capital expense.
- **Overall technical approach and strategy:**
  1. Phase 1 – Demonstrate the technology's key differentiating attributes of high throughput and thick layer processing (FY15-16).
  2. Phase 2 – Address the key challenges of binder material selection, heating effects, lithium loss, porosity control, and resulting material performance (FY17-18).
  3. Phase 3 – Demonstrate an optimized curing system in conjunction with a high-speed coating line together with a key equipment partner and battery manufacturer (FY19).
- **Verify cost savings metrics…**
  - Preliminary manufacturing cost savings report completed (12/31/15 deliverable).
  - For a 100 micron cathode, $0.056/kWh processing cost has been estimated in high volume.
  - For a 300 micron cathode, $0.023/kWh is estimated.

Phase I – Screening of Commercially Available Acrylic Polyurethanes

Pure resin films & curing:

- Film formation quality
- Cross-linking vs. dose

NMC coating formation quality:

- Adhesion
- Uniformity
- Flexibility

Electrode electrochemical performance:

- Voltage profiles
- Irreversible capacity loss
- Cycling performance

Technical Accomplishments – Executive Summary

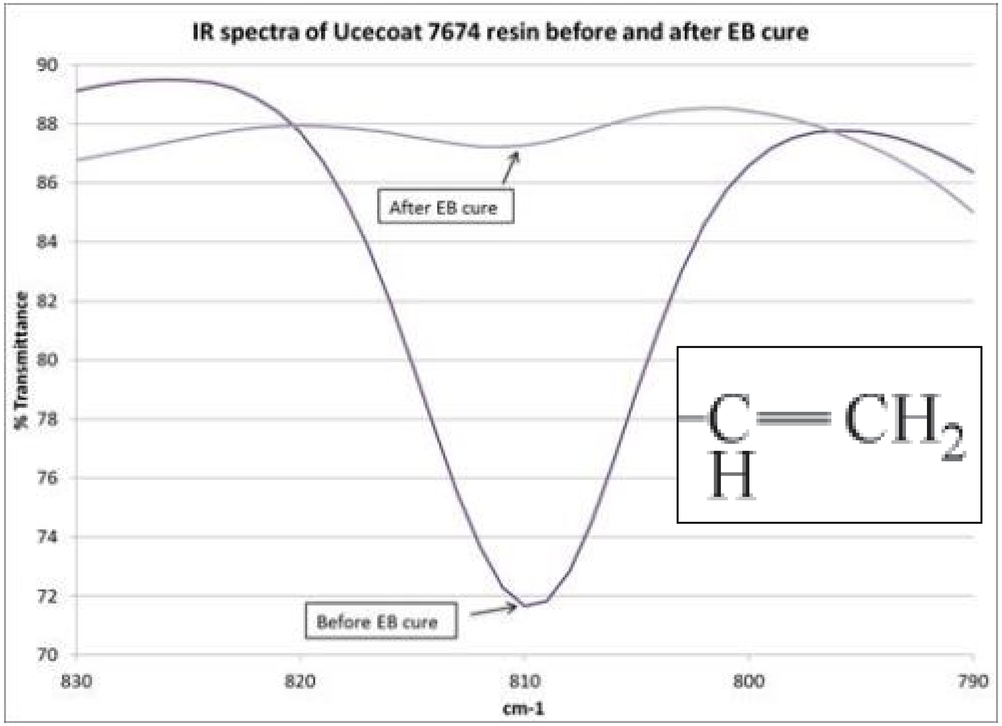
- FY15Q3:
  - ✓ Planning discussions were held with some of the world's leading acrylate resin manufacturers.
  - ✓ Major dispersion chemistry and formulation variables such as dispersing, solvent selection, wetting, cohesion, adhesion, etc. were selected for study.
- FY15Q4:
  - ✓ First coating formulations were prepared and dried at ORNL and subsequently cured at NEO Beam and the Georgia Power Customer Center.
  - ✓ First task milestone of post-curing electrochemical stability was met by 12/31/15.
- FY16Q1:
  - ✓ Second round of water and alcohol-based formulations were tested in collaboration with COMET-PCT at Georgia Power Customer Center.
  - ✓ Extent of cross-linking was verified by FT-IR.
- FY16Q2:
  - ✓ The six best performing formulations (four waterborne and 2 alcohol based) based on 100 full coin cell cycles (two separate tests) were down-selected for scale-up trials at COMET-PCT's Davenport, IA pilot coating facility.
  - ✓ Successful curing demonstrated at 100 m/min line speed for multiple samples (extent of cross-linking and cell performance at 600-800 ppm O_2 to be verified).

Screening: Coating Quality of Pure Resins

Pure resins were applied onto Al foil using a doctor blade. The resultant films were closely observed.

Ucecoat 7699 developed cracks after drying and was not tested. All other resins form good coatings on Al foil.

Measurement of Resin Cross-Linking via FTIR



- **Ucecoat 7674 resin was cured under 60 KGy.**
- **Disappearance of C=C double bonds due to the cross-linking.**

$$1\ \mathrm{Gy} = 1\ \frac{\mathrm{J}}{\mathrm{kg}} = 1\ \frac{\mathrm{m}^2}{\mathrm{s}^2}$$

Pure resin films were cured under different doses: 15 KGy, 30 Kgy, 45 KGy, 60 KGy, 90KGy (75 samples). Full FTIR analysis is in progress.

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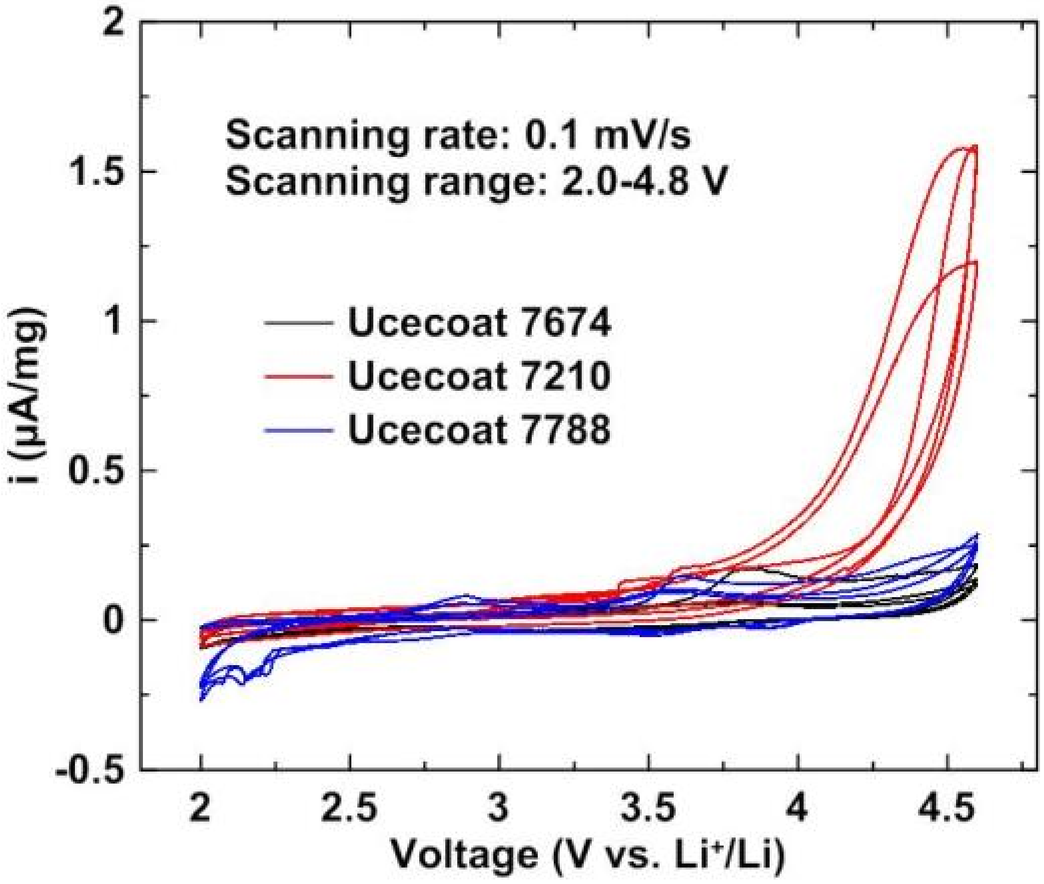
FY15 Milestone (9/30/15) Results – Cyclic Voltammetry on Waterborne Acrylate Binders Cured under N_2



0.1 mV/s from 2 V to 4.8 V (current per mass of binder).

7674 and 7788 resins show <u>no reactivity</u> towards lithium in scanned range.

The peak current at 4.5 V for 7210 resin is only 1.5 μA/mg. 7210 is <u>also considered inactive.</u>

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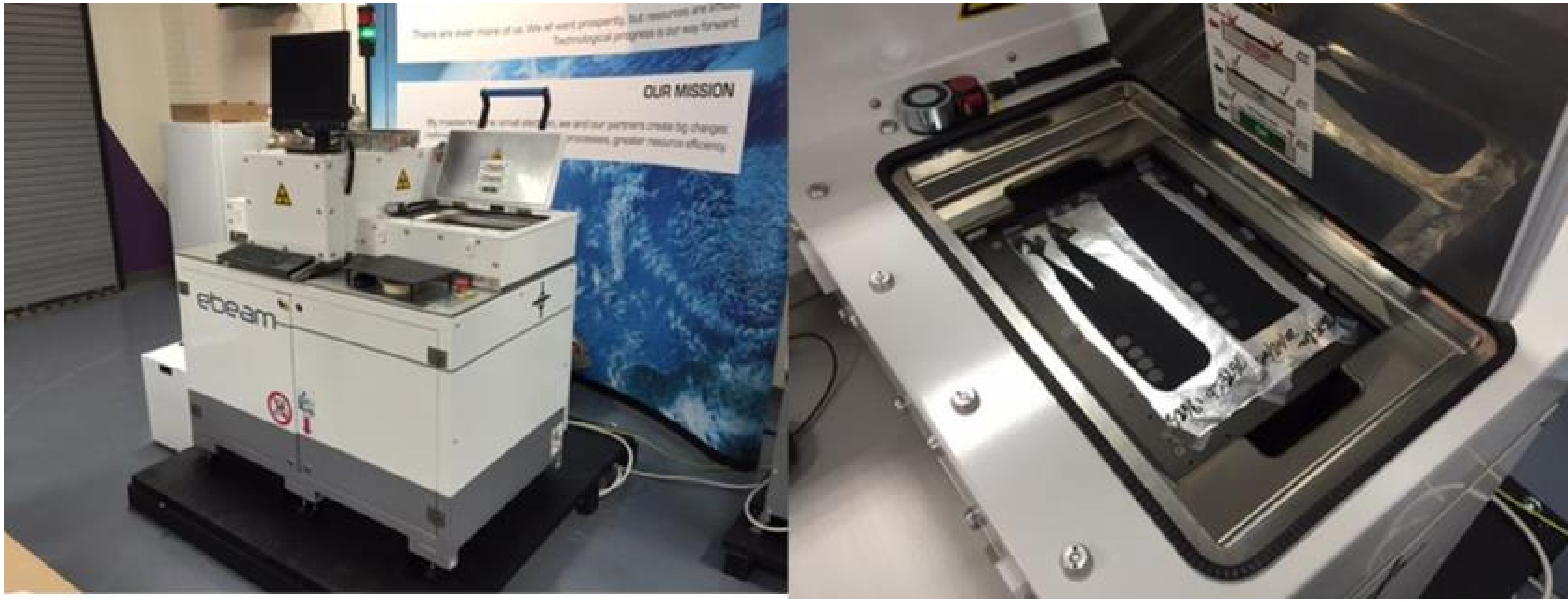
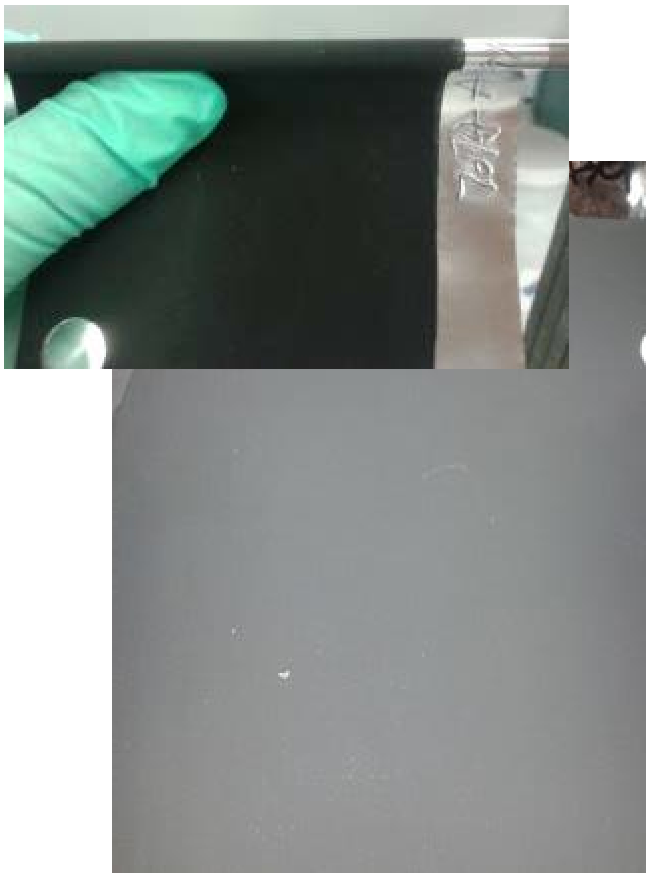
EB Curing of Coatings Using COMET-PCT Lab-Scale Unit



EBLab200 at the Georgia Power Customer Center - 200 keV, self-shielded, N_2 inerted EB machine (left); coated samples in sample holder prior to EB cure (right).

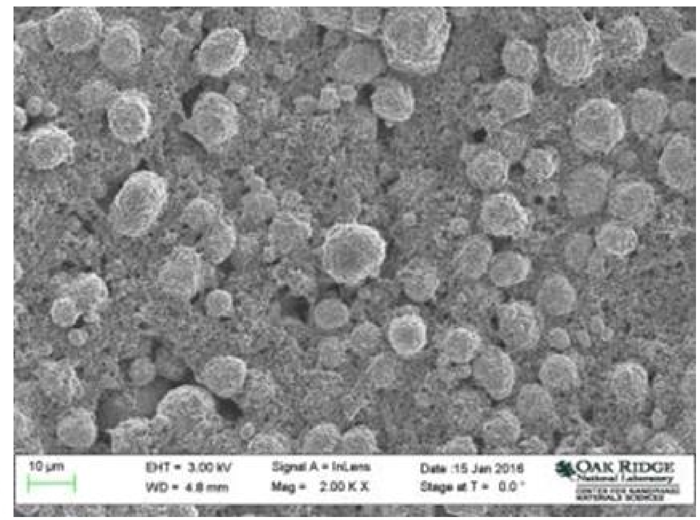
Screening: Coating Adhesion and Active Material Dispersion (Aqueous Processing)

- 43A, 43B, 43D, 43G, 43H exhibited good adhesion and flexibility.
- Adhesion for 43C, 43E and 43F was inferior.
- Dispersion of NMC in good coatings was uniform.



Good adhesion

Bad adhesion



Good dispersion in the coating

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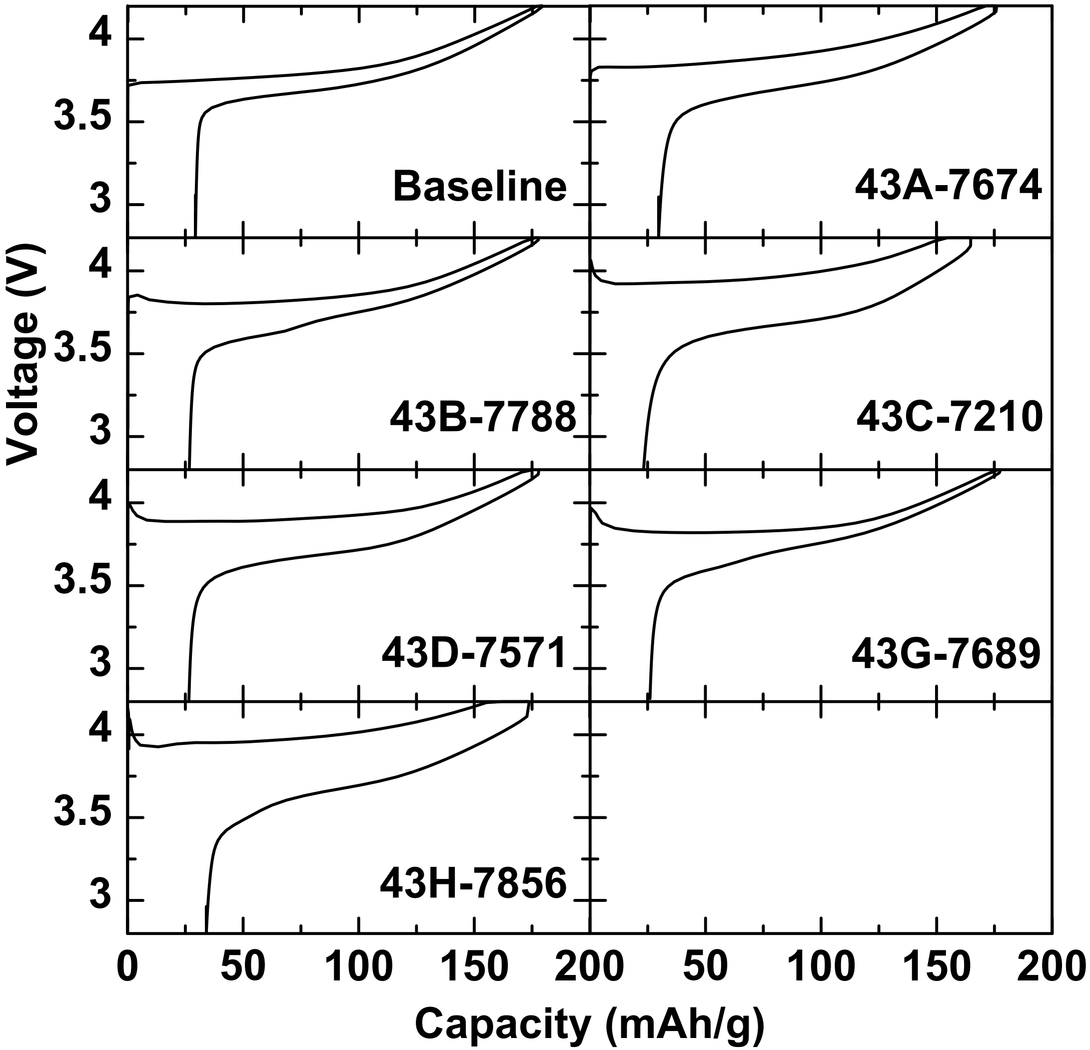
First Cycle Half-Cell Results (Aqueous Formulation)



- Cells showed typical NMC features indicating EB resins do not affect the lithiation/delithiation process.
- Typical first Coulombic efficiencies were about 86% with reversible capacity of 150 mAh/g, which is comparable to the NMP/PVDF processed coatings (baseline).
- Coatings 43C and 43H had slightly higher hysteresis in charge/discharge voltage compared to other EB resins and the baseline coating.

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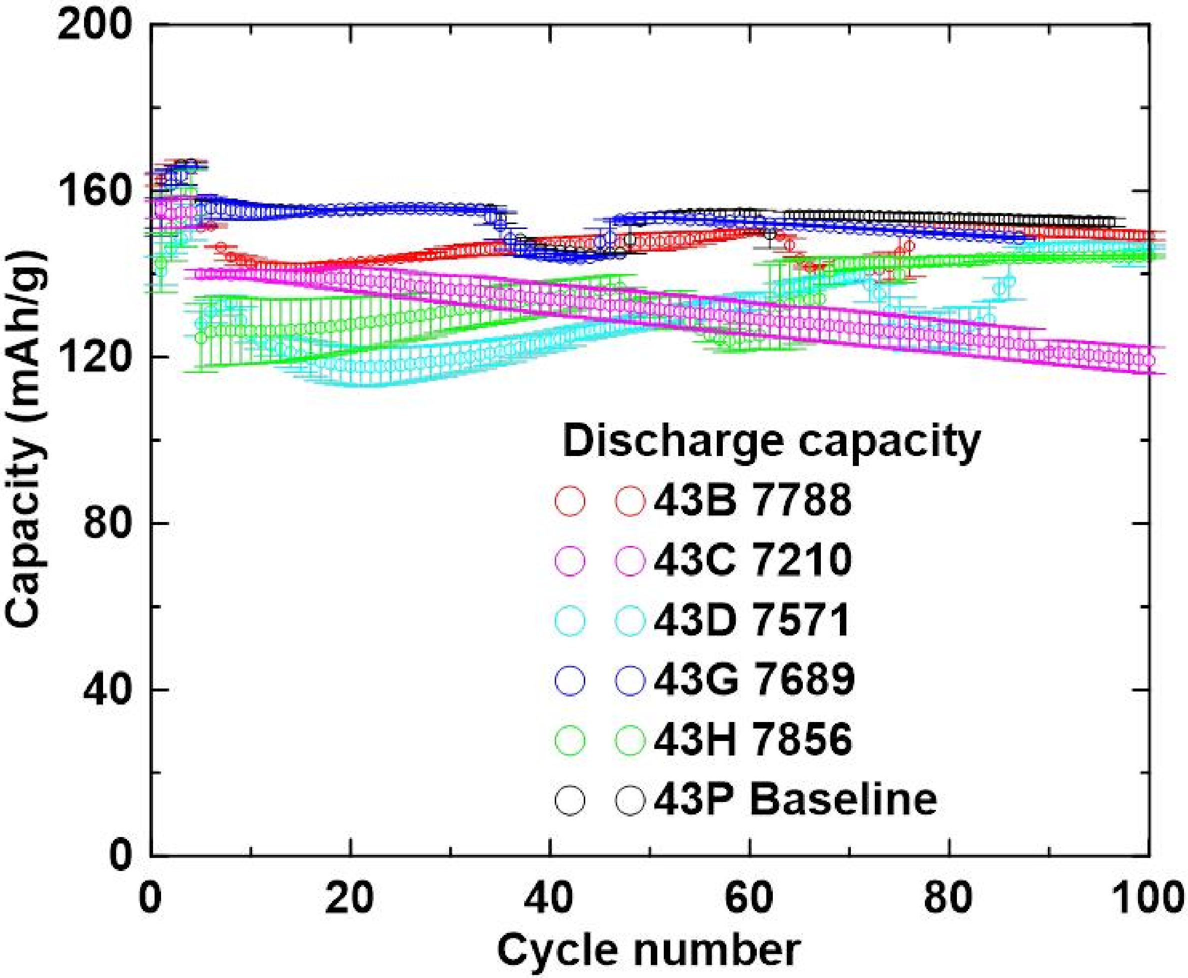
Good Full-Coin-Cell Cycling Performance for Most Aqueous Formulation



- 43B and 43G showed comparable performance to the NMP/PVDF baseline and were selected for pouch cell scaling.
- 43D and 43H likely require longer formation time to obtain stabilized capacity.
- 43C showed continuously decreasing capacity.

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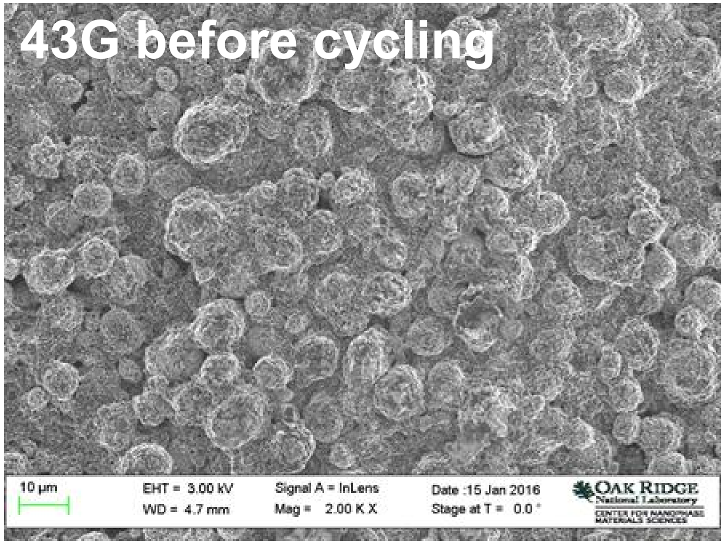
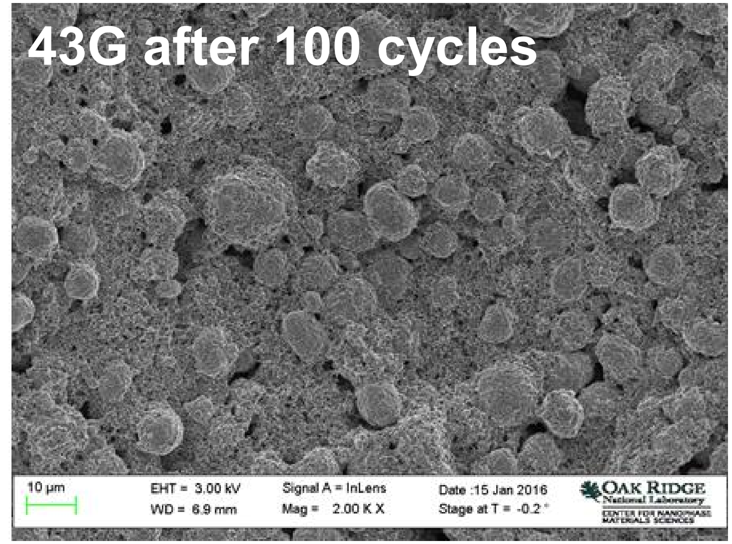
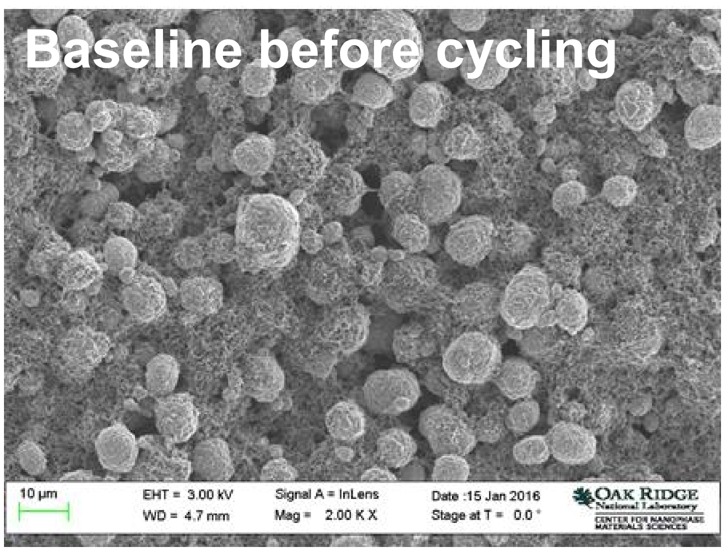
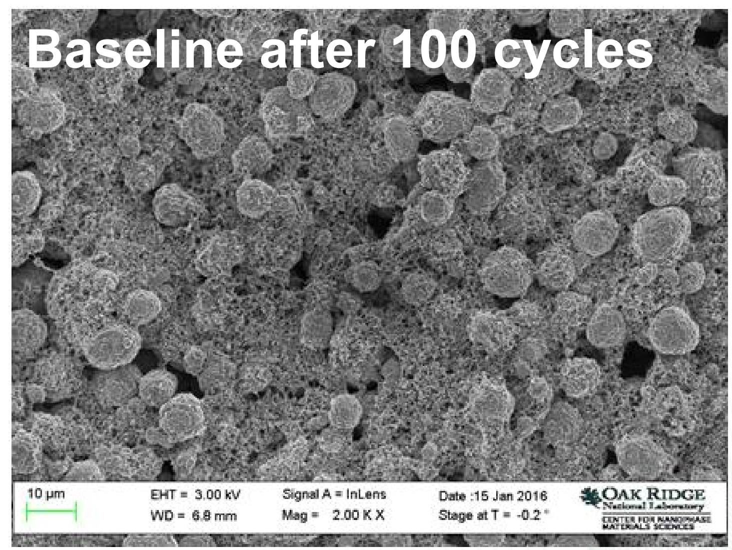
Good Electrode Integrity After Cycling

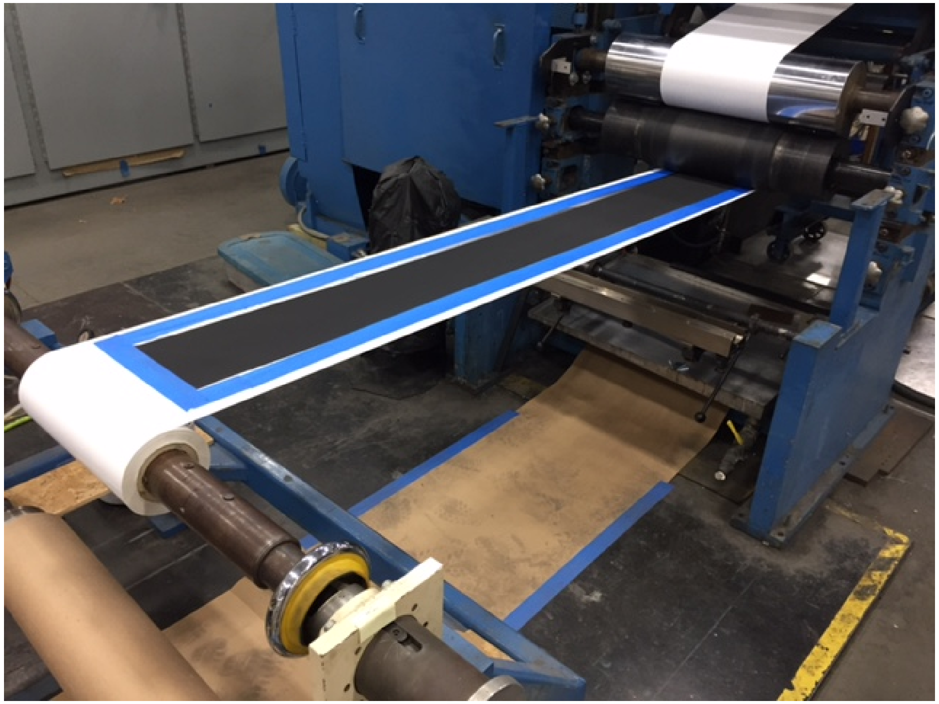








Successful Equipment and Line Speed Scaling



- 150 m/min line speed successfully demonstrated with coatings produced at ORNL BMF.
- High speed coating technique (gravure, curtain, etc.) needs to be developed for up to 85% formulation solids loadings.
- Trapped O_2 in pores at even higher line speeds needs to be addressed.

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Collaborations

- Partners
  - Equipment Suppliers: COMET-PCT, B&W MEGTEC, Eastman Kodak
  - Battery Manufacturers: XALT Energy, Navitas Systems
  - Raw Materials Suppliers: TODA America

- Collaborative Activities
  - Extensive EB curing trials were completed at NEO Beam and Georgia Power Customer Center with COMET-PCT lab-scale unit in fall 2015 and winter 2016.
  - Coating and curing trials are currently being scaled to COMET-PCT pilot coating and curing line in Davenport, IA.
  - Plans to investigate high-speed gravure coating with high solids (low solvent) content with either COMET-PCT, B&W MEGTEC, or Eastman Kodak.

Conclusions & Future Work

- Conclusions
  - In total, over 100 different slurries and coatings were made together with 150 coin cells to screen acrylic polyurethane resins (9/15 – 2/16).
  - FTIR confirmed the curing of resins under EB exposure.
  - Two waterborne and 2 alcohol-based (IPA) resins were selected in the screening process due to excellent coating quality and electrochemical performance comparable to the baseline.
- Future Work (F16-17)
  - Thickness-dose
    - Vary electrode thickness
    - Vary electron dose
  - Scale-up
    - Decrease solvent (water and/or IPA) content
    - Slot-die coating at ORNL and COMET-PCT
    - Gravure coating at COMET-PCT, MEGTEC, or Eastman Kodak

Summary

- **Objective:** To achieve 1) significant process energy savings; 2) ultra-high electrode processing speed; and 3) utilize much more compact production equipment.
- **Approach:** Three-phase approach from formulation chemistry to full-scale production.
    1. Phase 1 – Demonstrate the technology's key differentiating attributes of high throughput and thick layer processing (FY15-16).
    2. Phase 2 – Address the key challenges of binder material selection, heating effects, lithium loss, porosity control, and resulting material performance (FY17-18).
    3. Phase 3 – Demonstrate an optimized curing system in conjunction with a high-speed coating line together with a key equipment partner and battery manufacturer (FY19).
- **Technical:** Preliminary binder selection, aqueous formulation chemistry (60% solids), electrochemical stability, full coin cell short-term capacity fade, and pilot-scale equipment trials completed.
- **Collaborators:** Coating and curing trials are currently being scaled to COMET-PCT pilot coating and curing line in Davenport, IA with plans to investigate high-speed gravure coating with high solids (low solvent) content with either COMET-PCT, B&W MEGTEC, or Eastman Kodak.
- **Commercialization:** High likelihood of technology transfer because of strong industrial collaboration, significant electrode production cost reduction, and impact on cell energy density (≥2× thicker cathodes).

Acknowledgements

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

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Technical Collaborators

- Tony Carignano
- Michael Bielmann
- Jeff Quass
- Dave Ventola
- Kevin Dahlberg
- Fabio Albano
- Mike Wixom
- Dan Occorr

B&W MEGTEC

Kodak

XALT Energy

TODA AMERICA

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NAVITAS SYSTEMS

COMET Technology with Passion

Information Dissemination and Commercialization

Refereed Journal Papers and Presentations

- D.L. Wood, III, “Overview of Lithium-Ion Cell R2R Processing at ORNL: Current and Future Opportunities,” NAATBatt Annual Meeting & Conference, Indian Wells, California, February 29 – March 3, 2016 (Invited).
- Z. Du, C.J. Janke, J. Li, C. Daniel, and D. L. Wood III, “Electron beam curable acrylated polyurethanes as novel binders of Li-ion battery electrodes” *J. Power Sources*, In Preparation (2016).

Thank you for your attention!

Reviewer Comment Slides
(Task Not Reviewed in FY15)

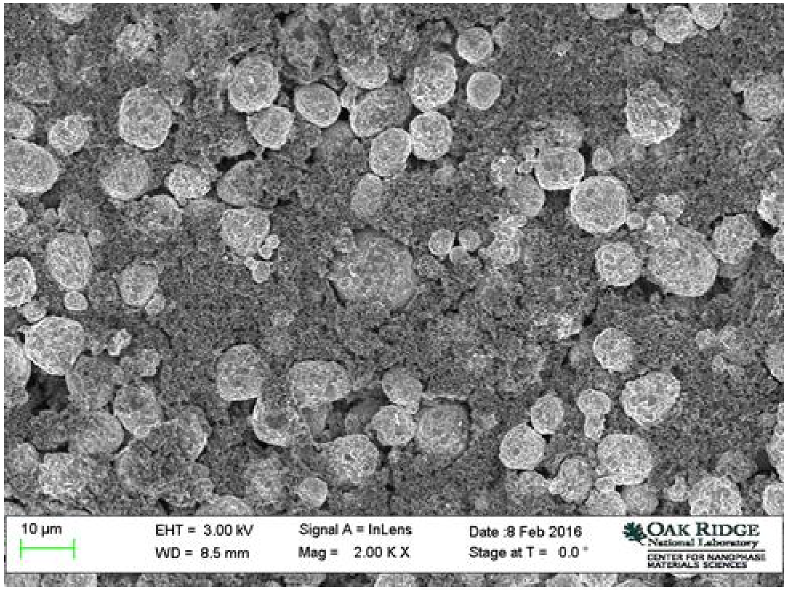
Back-up Slides

Screening: Coating Adhesion and Active Material Dispersion (IPA Processing)

- 43K, 43L, 43N, 43O exhibited good adhesion and flexibility.
- Adhesion for 43I, 43J and 43M was inferior.
- Dispersion of NMC in the coating was uniform.

Good adhesion

bad adhesion



Good dispersion in the coating

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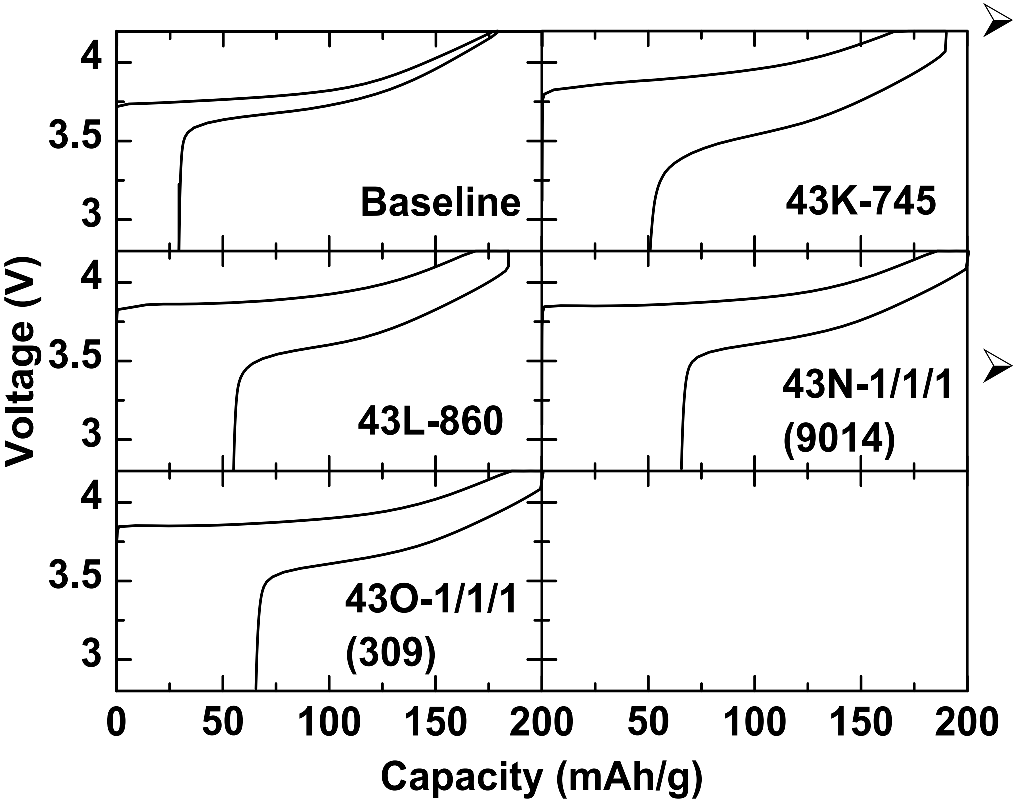
First cycle voltage curves-half cell IPA formulation



- Typical first Coulombic efficiencies were about 69% with reversible capacity of 135 mAh/g, which was not as good as NMP/PVDF processed coatings (baseline).

- These results demonstrate that alcohol-based (IPA) EB curable resins can be used as binders for NMC coatings. Coating 43K had slightly higher hysteresis in charge/discharge voltage compared to other EB resins and the baseline coating.

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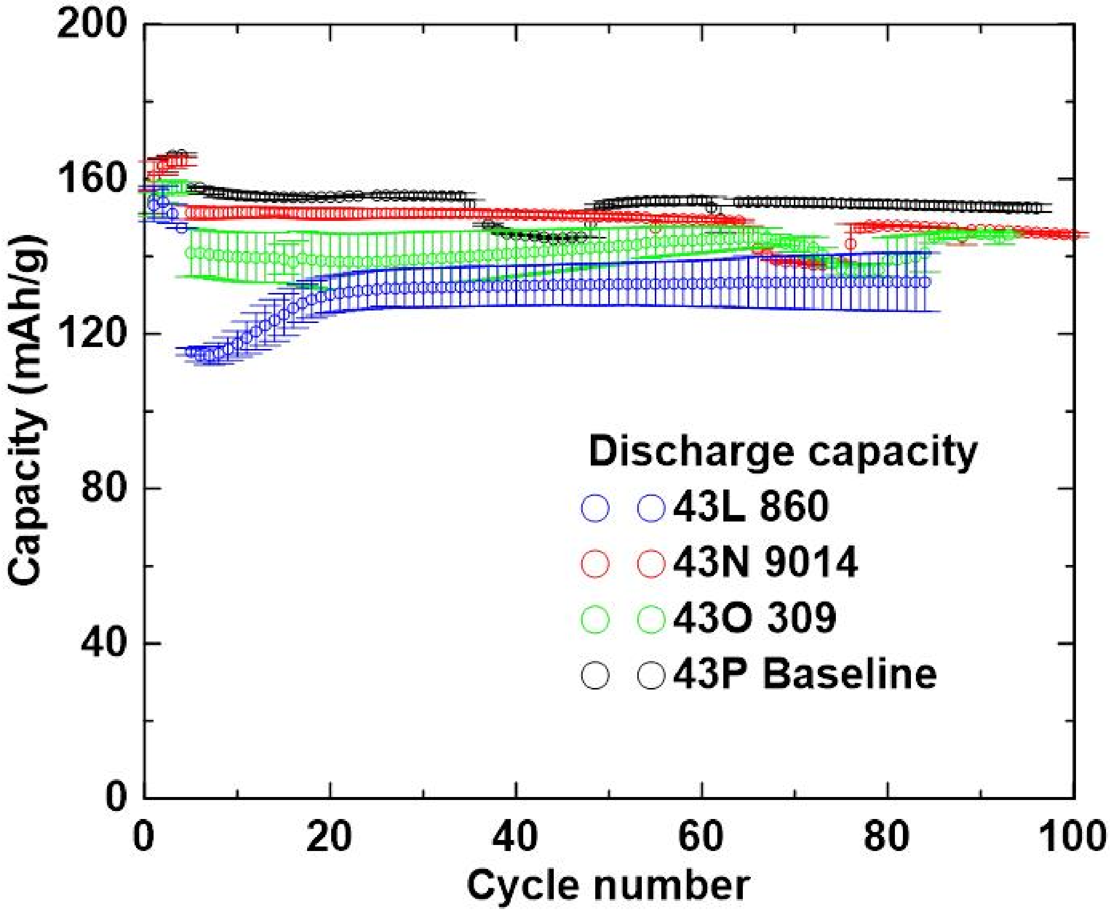
Good Cycling Performance for IPA Formulations



- 43N and 43O showed good cycling performance comparable to the NMP/PVDF baseline.
- 43 L showed slightly lower capacity than the other EB resins and the baseline coating.

Screening result: 43N and 43O are promising for the next step.

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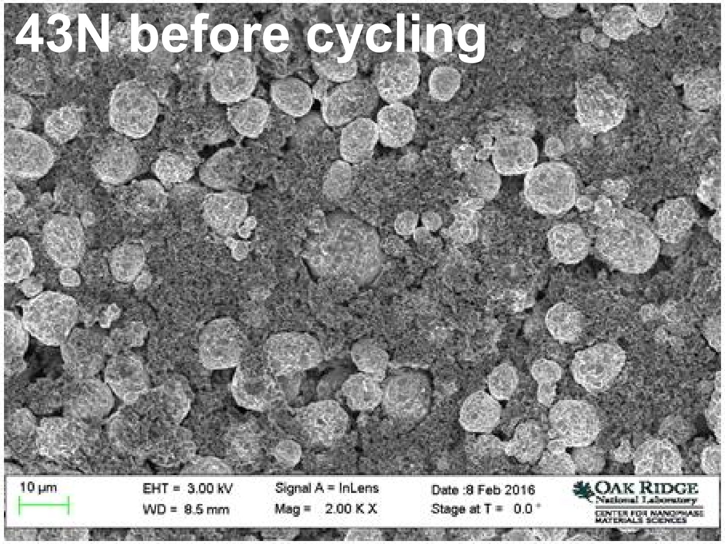
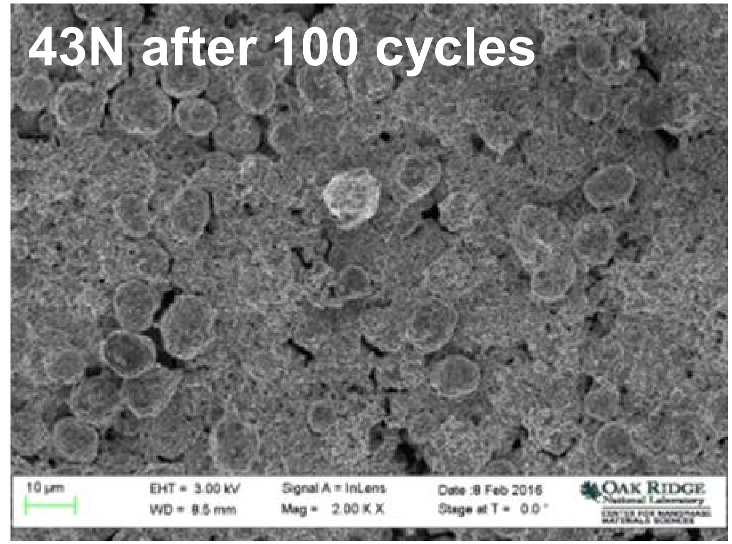
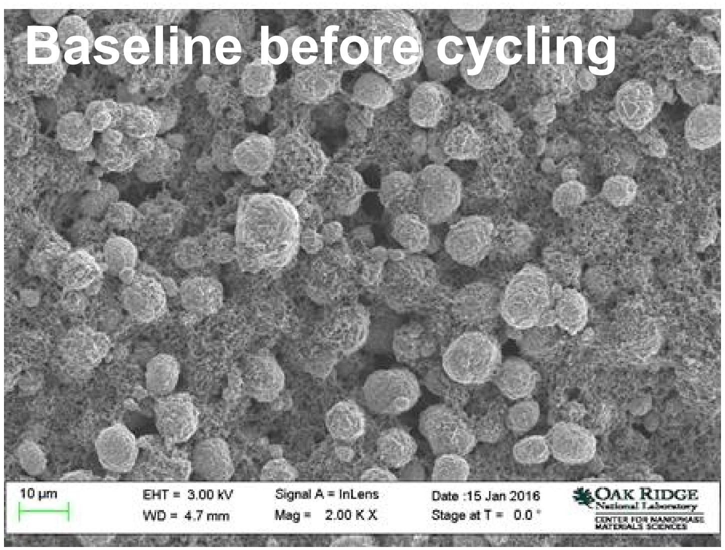
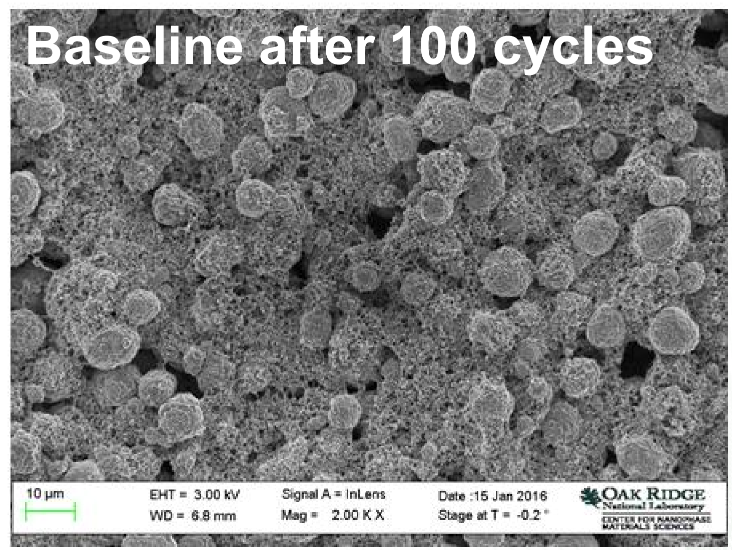
Good Electrode Integrity after Cycling









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