Thick Low-Cost, High-Power Lithium-Ion Electrodes via Aqueous Processing

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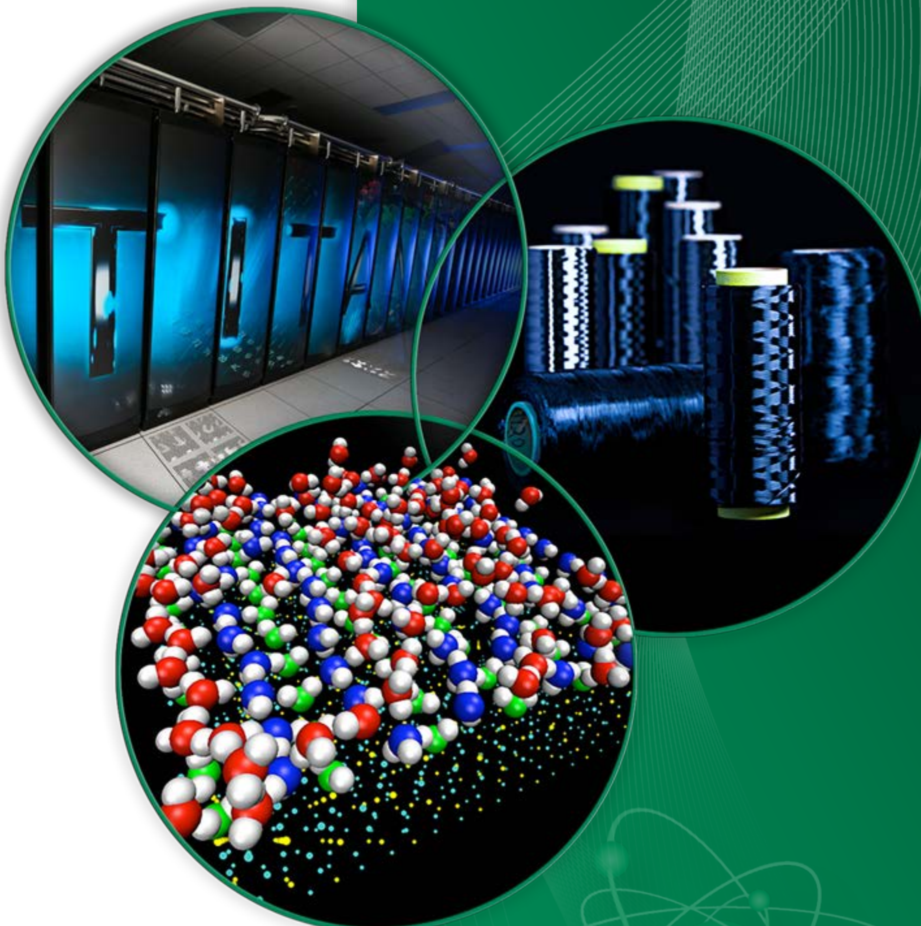

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ES164

Overview

Timeline

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

Barriers

- Barriers Addressed
  - **By 2020, further reduce EV battery-pack 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.**

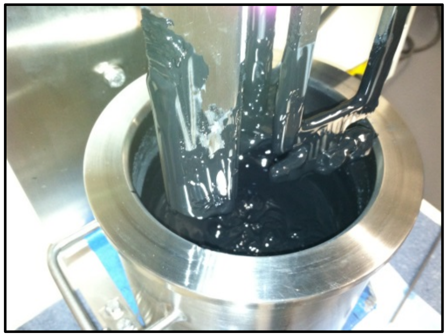
Budget

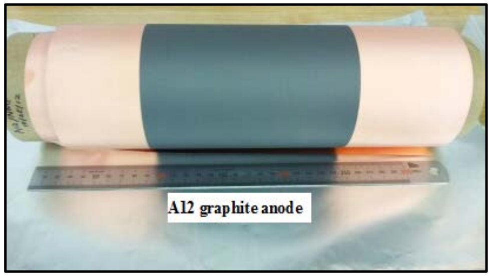
- Total project funding
  - $9050k
- $1475k in FY15

Partners

- Interactions/Collaborations
  - National Laboratories: ANL, SNL
  - Battery Manufacturers: XALT Energy, Navitas Systems
  - Material/Process Suppliers: PPG Industries, Phostech Lithium, TODA America, Superior Graphite, Zenyatta Ventures, GrafTech International, Timcal, JSR Micro, Solvay Specialty Polymers, SABIC Global Technologies, Ashland, XG Sciences
  - Equipment Manufacturer: Frontier Industrial Technology
- Project Lead: ORNL

Relevance & Objectives





- Main Objective: To transform lithium ion battery electrode manufacturing by the elimination of costly, toxic organic-solvents, and double energy density.
  - Replace NMP processing with water-based chemistry ***NMC532 cathode and graphite anode***.
  - Evaluate different commercially available waterborne binders and water-dispersible conductive carbon additives for increased power density.
  - Investigate effect of doubling electrode thicknesses (i.e. develop a thick, high-power cathode architecture).
  - ***Elimination of expensive solvent recovery steps, reduction of capital equipment cost, and elimination of expensive inactive components.***
  - Enhance wetting and adhesion of electrode coating on current collectors
  - Optimize power density by controlling particle size distribution, electrode porosity, pore size distribution, and porosity gradient in electrodes
- Relevance to Barriers and Targets
  - Implementation of low-cost, green manufacturing methodology for lithium ion battery electrodes using aqueous colloidal chemistry (to meet $300/kWh 2015 VTO storage goal for PHEV-40s).
  - Correlation of ***aqueous*** colloidal dispersion properties and ***thick*** electrode coatings to cell performance to reduce LIB pack cost by **~22% ($110/kWh-usable reduction)**.
  - ***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	SMART Milestones	Description
3/2015 ✓	FY15 Milestone	Establish 1.5-Ah pouch cell rate performance, low-rate capacity fade (50 0.2C/-0.2C cycles), and high-rate capacity fade (150 1C/-2C cycles) for baseline ABR anode/cathode active material ***with aqueous electrode processing*** → achieve state-of-the-art gravimetric energy density for graphite/NMC 532 cells of 160±30 Wh/kg (cell level).
12/2015 On Schedule	FY16 **Stretch** Milestone	Complete 1.5-Ah pouch cell rate performance, low-rate cycling (50 0.2C/-0.2C cycles), and high-rate cycling (150 1C/-2C cycles) for cells with ABR anode and first design of graded cathode architecture with NMC 532 → improve gravimetric energy density of baseline cell design to ≥200 Wh/kg (cell level) and demonstrate no more than 10% capacity fade through 100 additional 0.2C/-0.2C cycles in 1.5-Ah full pouch cells.

Project Approach

- Problems:
  - Excessive agglomeration and settling in aqueous dispersions.
  - Poor wetting and adhesion of water-based dispersions to current collector foils.
  - Poor electrode flexibility, integrity, and power density of thick electrodes.
- Overall technical approach and strategy:
  1. Cost reduction analysis in thick electrode manufacturing via aqueous processing
  2. Chemistry-specific aqueous formulation designs by standardized dispersant selection and rheological optimization methods – Tailored Aqueous Colloids for Lithium-Ion Electrodes (TACLE) → **J. Li *et al.*, U.S. Patent No. 8,956,6888 (UT-Battelle, LLC)**.
  3. Surface charge measurement, rheology characterization, agglomerate size optimization, order of constituent addition, and mixing protocol optimization.
  4. Novel binder development beneficial to electrode conductivity and power density
  5. Coating parameter optimization for TACLE → viscosity control, current-collector surface energy optimization, and tailoring of drying protocol.
  6. Dual slot-die coating and calendering optimizing electrode architecture (pore structure gradients for better liquid-phase Li^+ transport) for high energy and power electrodes.
  7. Close collaboration with the ANL and SNL ABR efforts, cell manufacturers, active material suppliers, and inactive material suppliers.
  8. ***Scale TACLE methodology with key industry partner.***
  9. Systematic study of effects of electrolyte volume on battery performance, formation protocol on SEI properties, and battery performance with ANL.

Project Approach – Pilot-Scale Electrode Processing and Pouch Cell Evaluation: DOE Battery Manufacturing R&D Facility (BMF) at ORNL

Planetary Mixer (≤2 L)

Corona Plasma Treater (Surface Energy Modification)

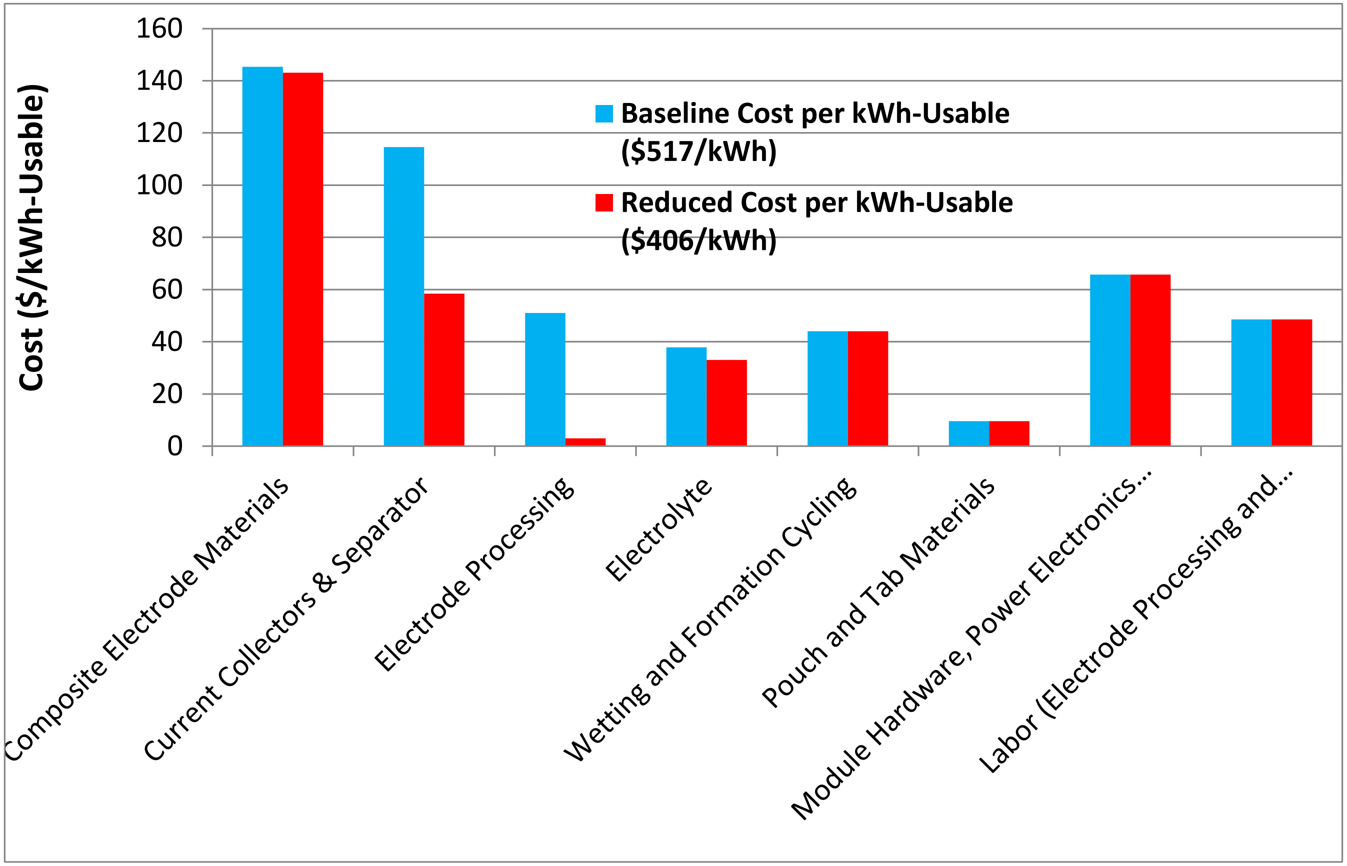
<u>Dry room for pouch cell assembly</u>

- Largest open-access battery R&D facility in US.
- All assembly steps from pouch forming to electrolyte filling and wetting.
- 1400 ft^2 (two 700 ft^2 compartments).
- Humidity <0.5% (-53°C dew point maintained).
- Pouch cell capacity: 50 mAh – 7 Ah.
- Single- and double-sided coating capability.
- Current weekly production rate from powder to pouch cells is 20-25 cells.

Technical Accomplishments – Executive Summary

- Cost reduction analysis on aqueous processed electrode with 2× electrode thicknesses.
- Repeatability and durability of 1.5-Ah pouch cells with ABR baseline electrodes.
- ***All-aqueous*** NMC 532 and CP A12 graphite scale-up and assembly of 1.5-Ah pouch cells.
- Effect of surface properties of current collector on electrode performance.
- Specific Accomplishments
  - Obtained **1.5-1.7 *Ah pouch cell*** data for aqueous and NMP processed NMC 532 cathodes through 250+ total cycles (40 rate capability cycles + 250 1C/-2C capacity fade cycles).
  - Improved pouch cell cyclability via calendering of electrodes.
  - Enhanced coating wettability, electrode adhesion, and performance via corona treatment of Al foils.
  - Scale-up and fabrication of NMC 532 and $LiFePO_4$ cathodes via aqueous processing with key industry partner.
  - Initiated systematic electrolyte volume and SEI properties study with ANL to determine effects on battery performance and calendar life.

Technical Accomplishments – Cost Reduction Potential



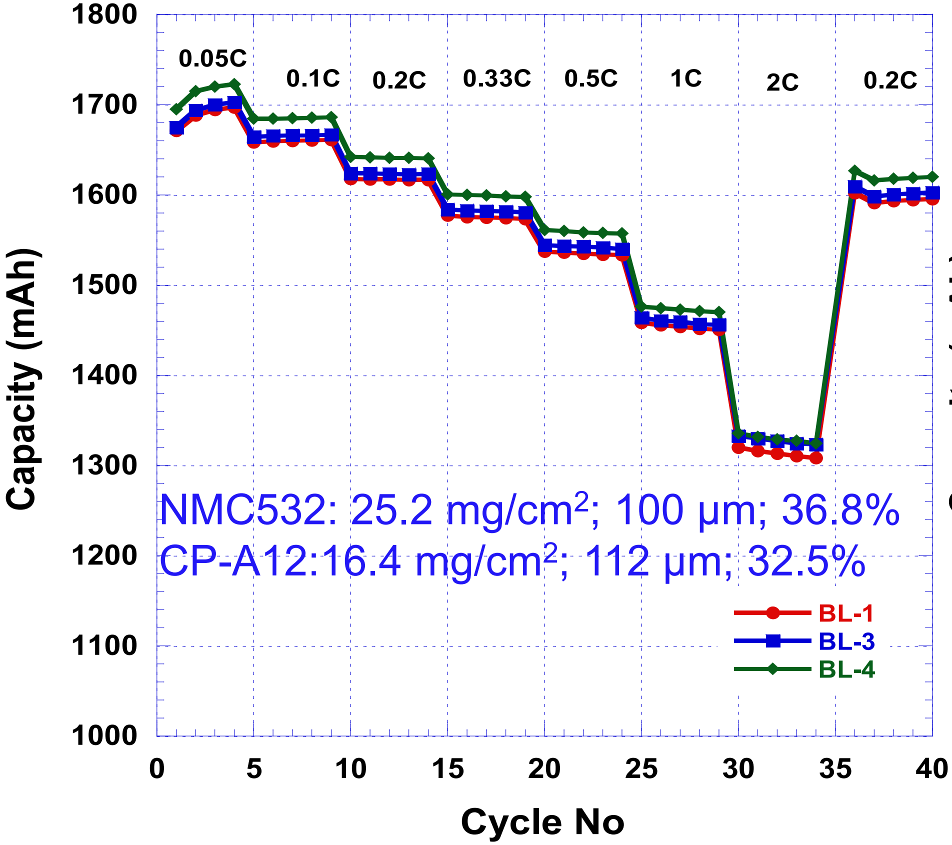
Physics make water much easier to remove!

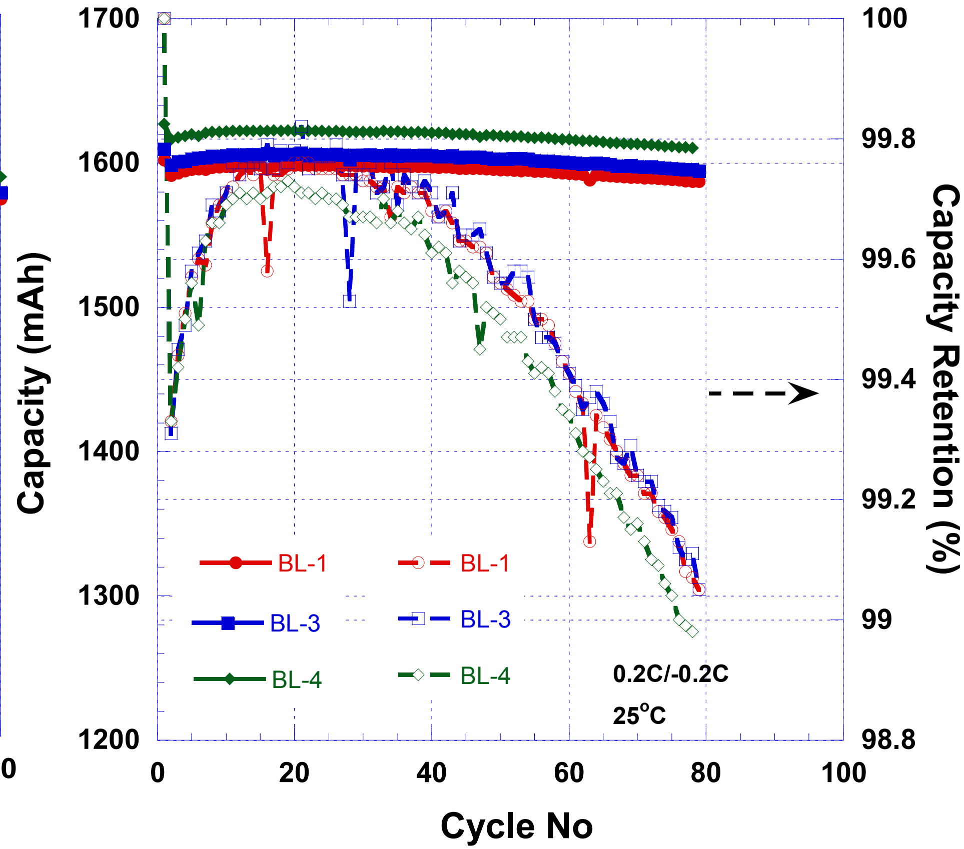
Property	NMP	Water
Heat of Vaporization at 100°C (kJ/mol)	50.6	40.7
Boiling Point (°C)	204.3	100.0
Vapor Pressure at 40°C (mm Hg)	1.0	55.3

- Combination of all-water-based processing plus 2× thicker electrodes has potential of saving $111/kWh-usable of the ***total pack cost*** (based on 70% depth of discharge limit).
- Cost of electrode processing could be cut to $3/kWh-usable primarily due to fast drying of water (i.e. higher solids loading, lower drying T, lower air flow rate & higher volatility than for NMP) and ***no solvent recovery costs***.

1. D.L. Wood et al., "Prospects for Reducing the Cost of Lithium Ion Electrode Processing and Pouch Cell Formation Steps," J. Power Sources, 275, 234-242 (2015).
2. D. Howell, "U.S. Battery R&D Progress and Plans," DOE Annual Merit Review, May 14, 2013.
3. K.G. Gallagher et al., "PHEV Battery Cost Assessment," DOE Annual Merit Review, May 9-13, 2011.

Technical Accomplishments – Excellent Reproducibility in Baseline PVDF/NMP Pouch Cells





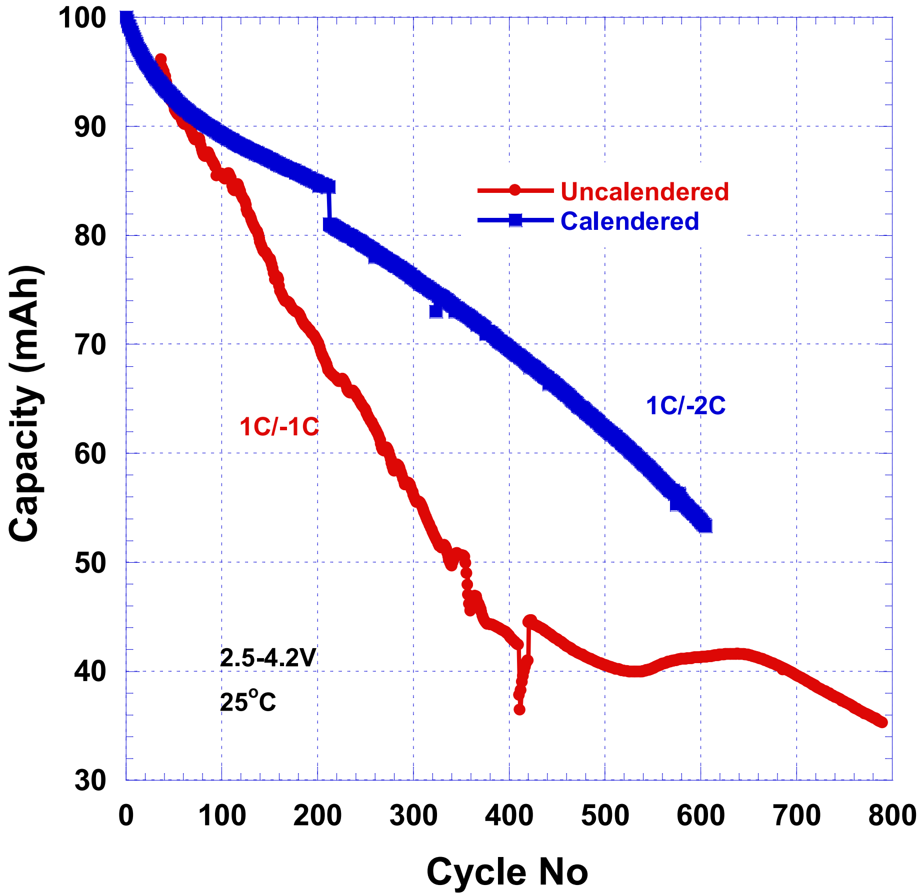
- Cell testing at 25°C; 2.5-4.2V
- 4 formation cycles at 0.05C/-0.05C
- 5 cycles at each C-rate

➢ Excellent cell reproducibility
➢ Excellent rate performance

- Capacity retention normalized to the initial capacity

➢ >99% capacity retention after 80 cycles at 0.2C/-0.2C

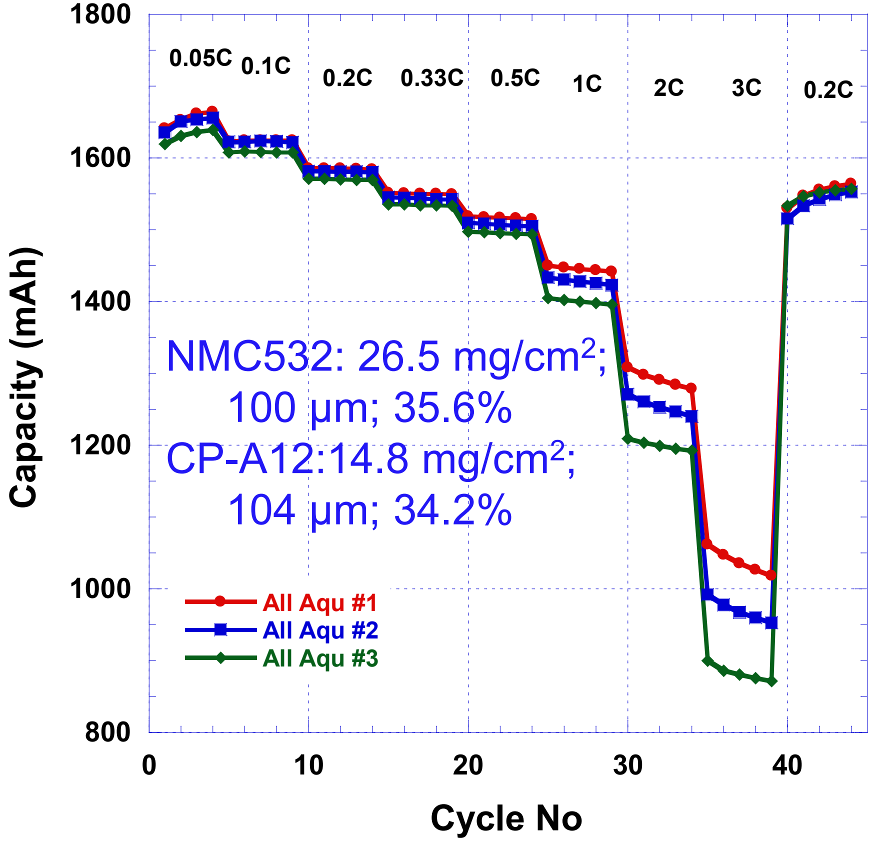
Technical Accomplishments – Improved Cyclability via Electrode Calendering in Baseline PVDF/NMP Pouch Cells

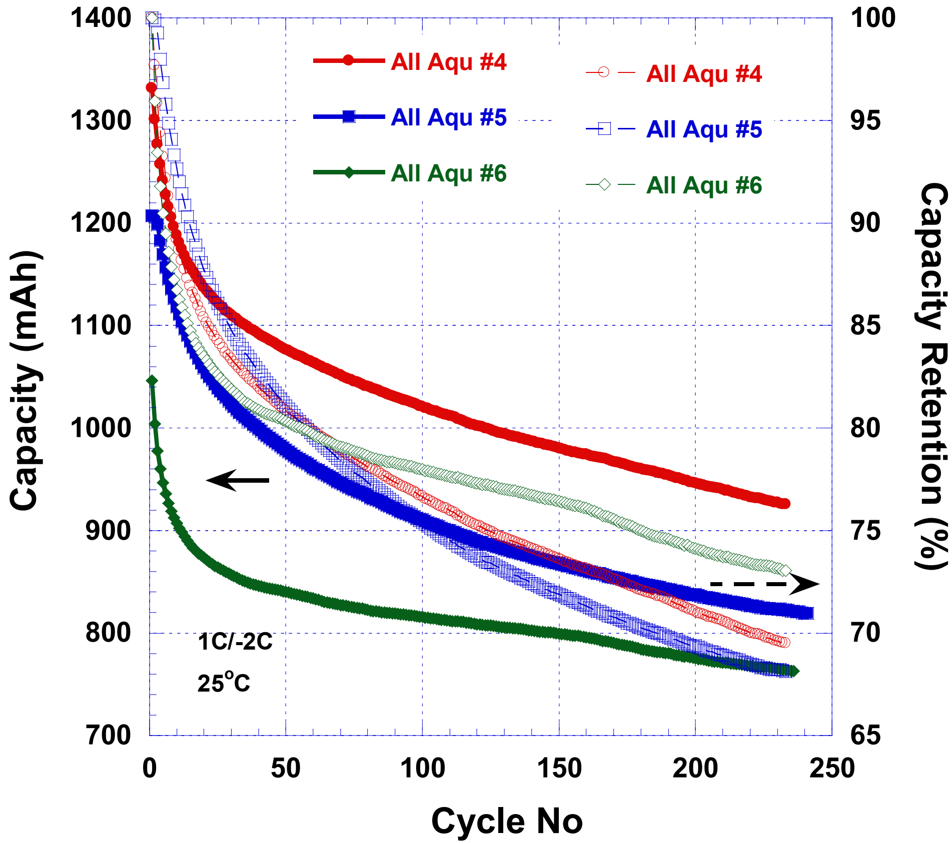


- NMC532 & CP-A12 graphite
- Uncalendered electrodes: 53-55% porosity
- Calendered electrodes: 33-37% porosity
- 3 pouch cells each condition

- ➢ Excellent cell reproducibility
- ➢ Significant improvement in cyclability after calendering

Technical Accomplishments – Durability of *All-Aqueous* Processed 1.6-Ah Pouch Cells at High-Rate (1C/-2C Cycling)



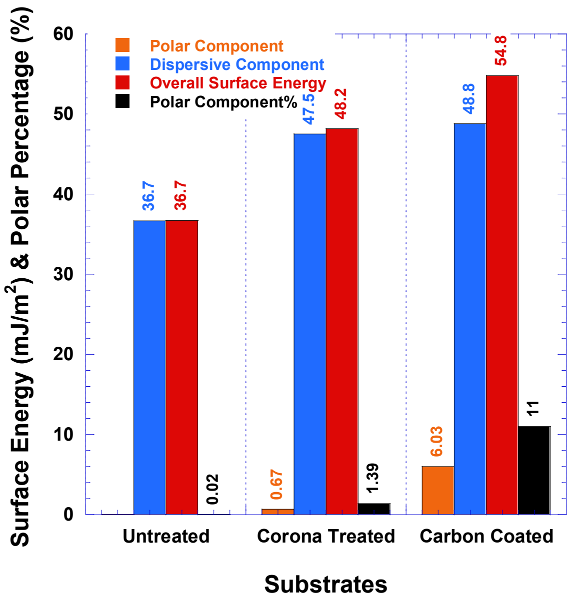


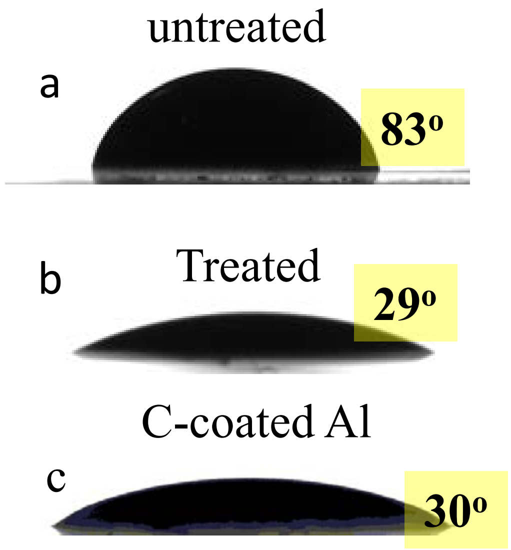
- Excellent cell reproducibility
- Excellent rate performance
- >70% capacity retention after 200 cycles at 1C/-2C

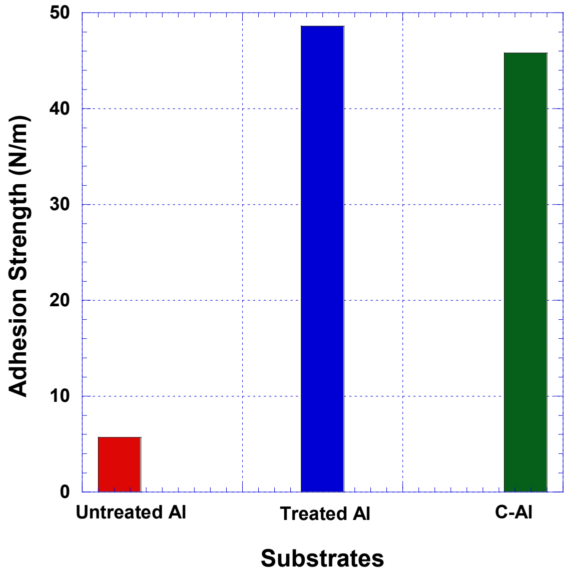
To improve cyclability

- Further removal of residual moisture
- Modification of formation protocol

Technical Accomplishments – NMC 532 Cathode Coating Performance on Different Substrates—Electrode Processing



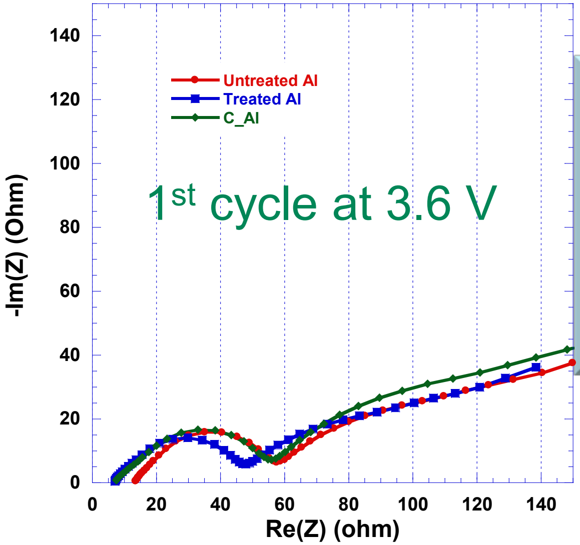




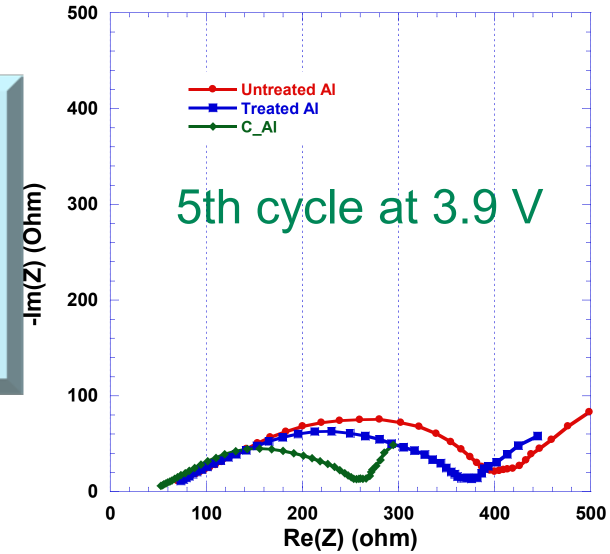
Corona treated and carbon coated Al foils:

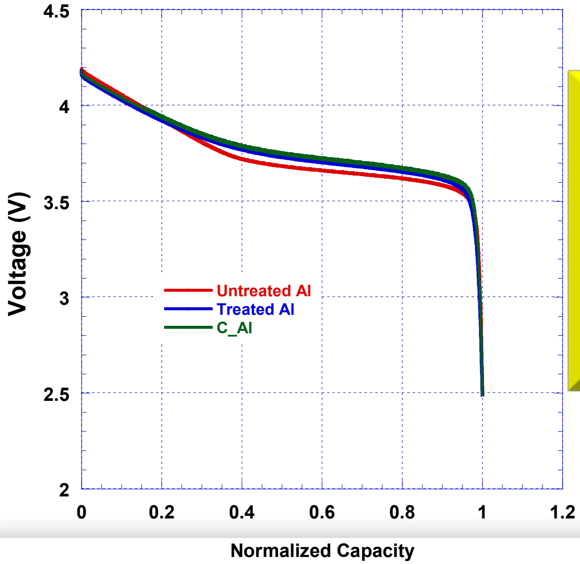
- Surface energy improved
- Wetting of aqueous NMC 532 coating improved
- Order-of-magnitude increase in adhesion strength between NMC 532 and Al foils

Technical Accomplishments – NMC 532 Cathode Coating Performance on Different Substrates—Electrode Performance

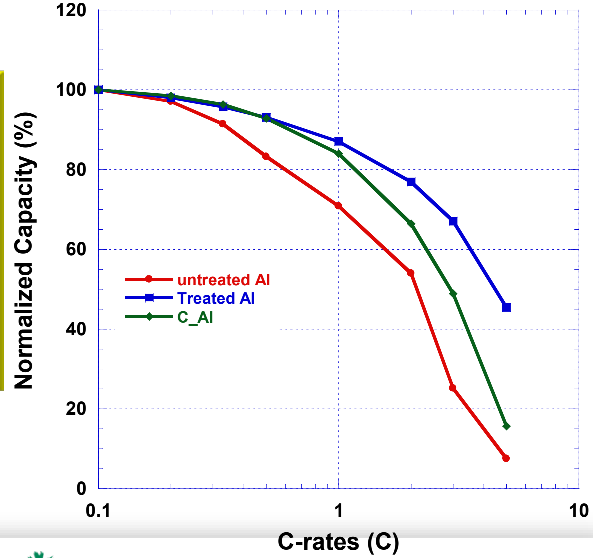


- Corona treatment and carbon coating reduce impedance
- Further reducing impedance can be realized via controlling corona treatment conditions

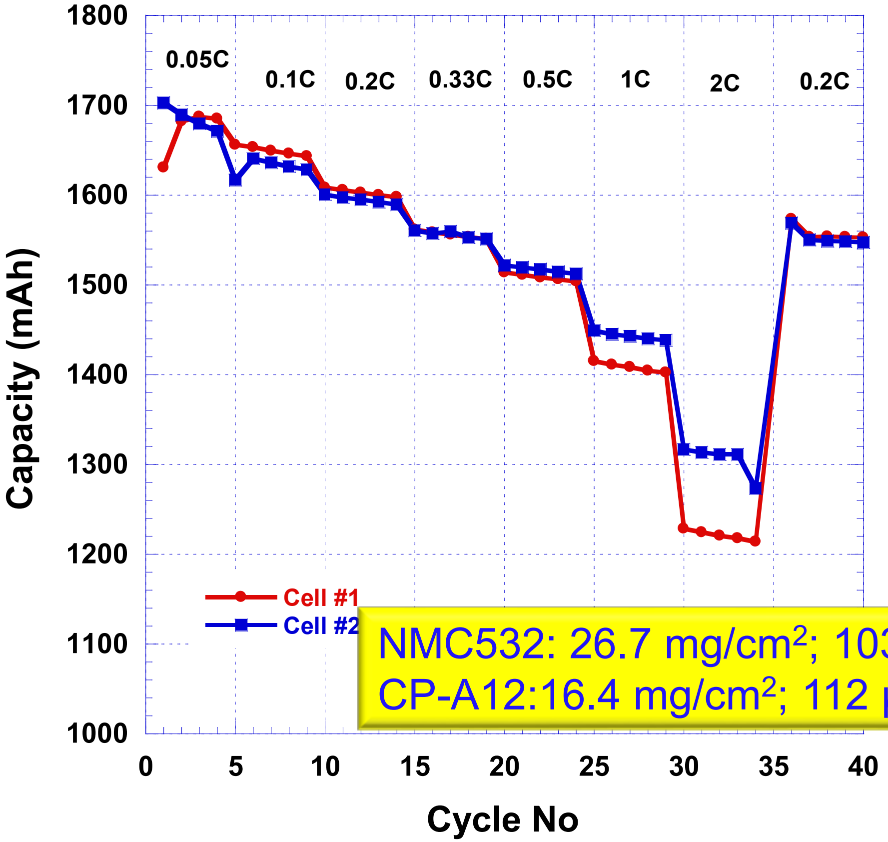


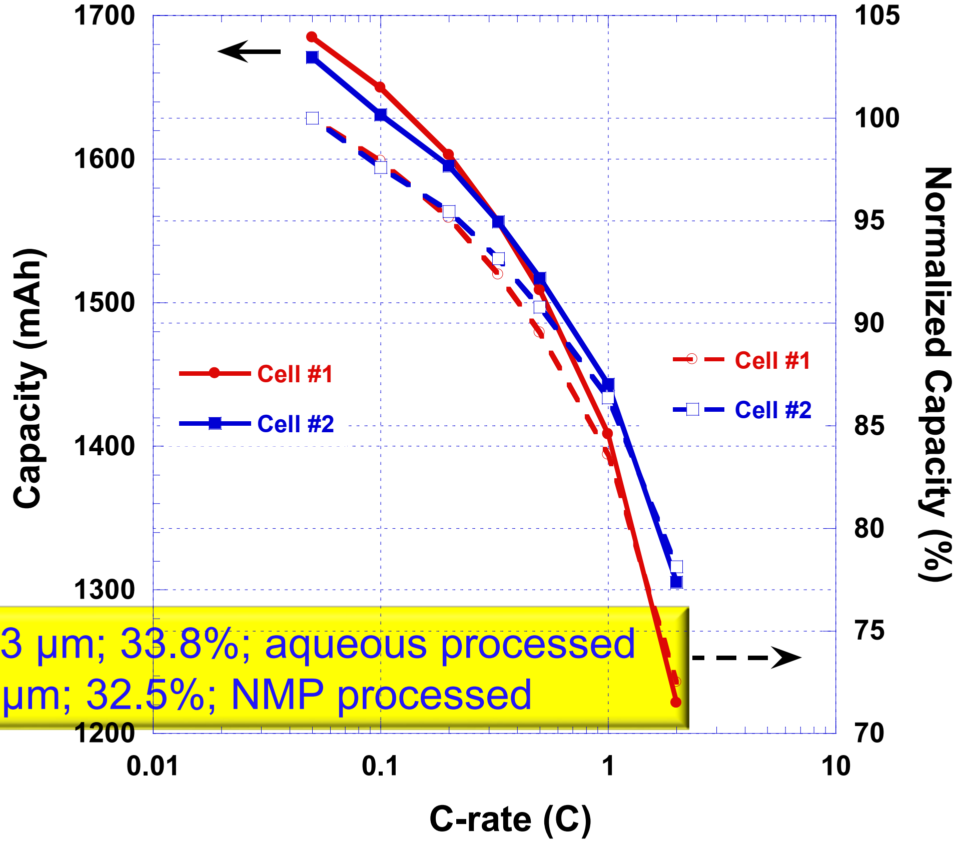


- Corona treatment and carbon coating reduce polarization and improve rate performance
- Electrodes on corona treated Al foils show the best rate performance



Technical Accomplishments – *Initial* Cathode Aqueous Processing Scale-Up with Key Industry Partner (1)



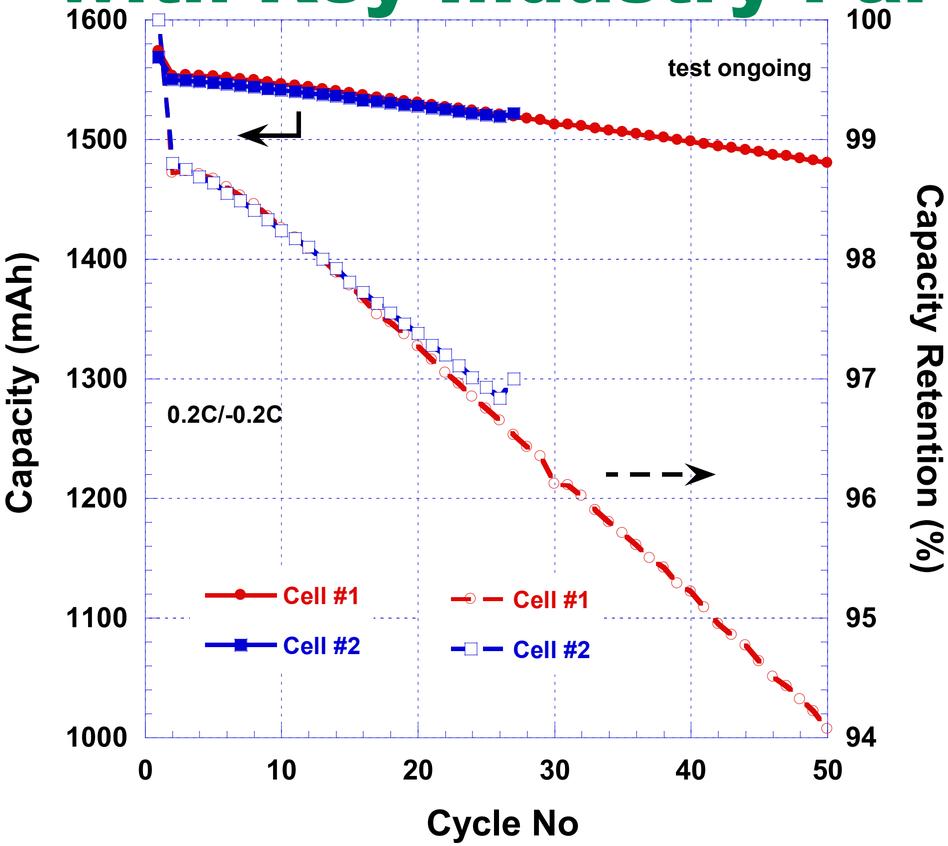


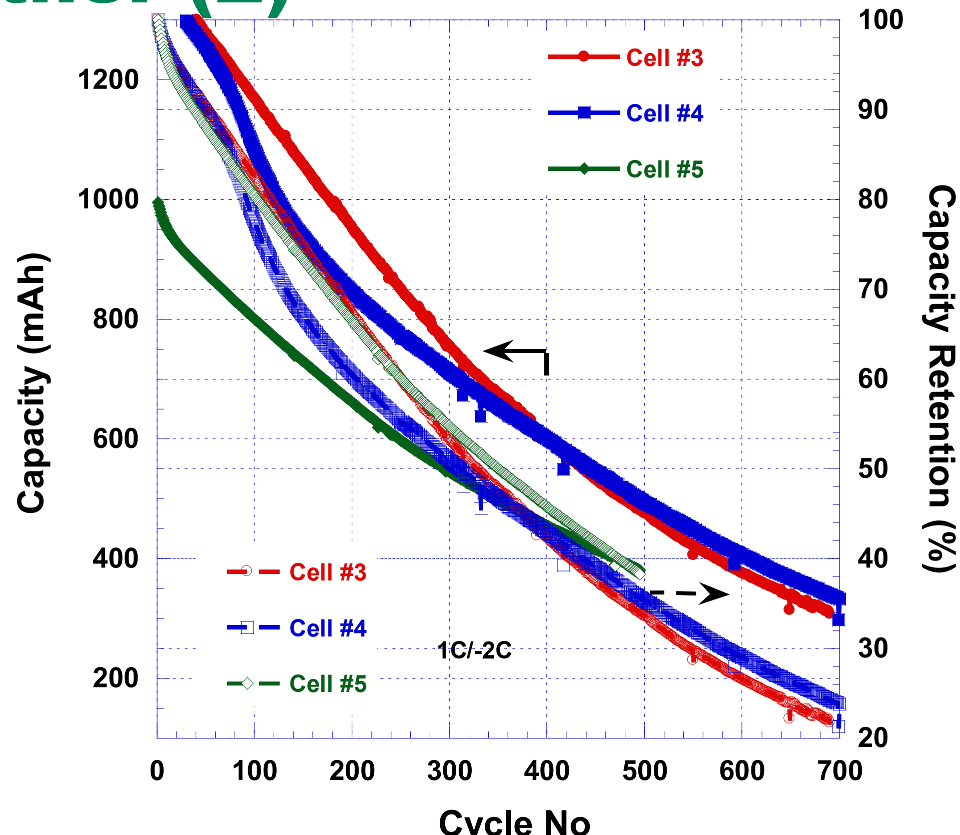
NMC532: 26.7 mg/cm^2; 103 µm; 33.8%; aqueous processed
CP-A12:16.4 mg/cm^2; 112 µm; 32.5%; NMP processed

- Cell testing at 25^{o}C; 2.5-4.2V
- 4 formation cycles at 0.05C/-0.05C
- 5 cycles at each C-rate

➢ Excellent cell reproducibility
➢ Excellent rate performance

Technical Accomplishments – *Initial* Cathode Aqueous Processing Scale-Up with Key Industry Partner (2)



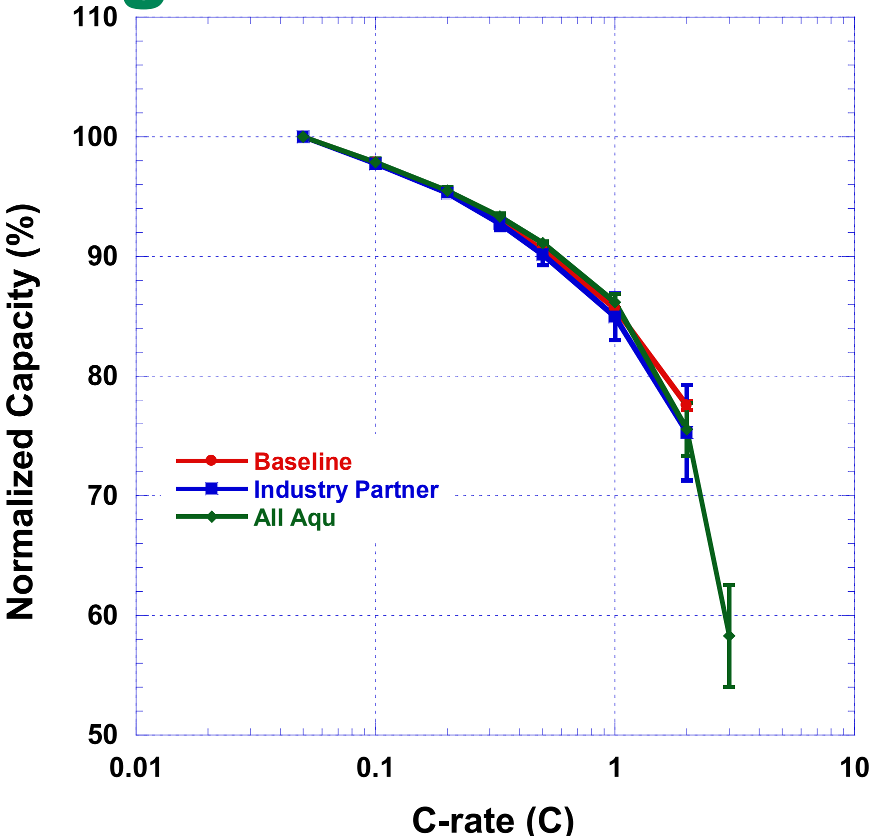


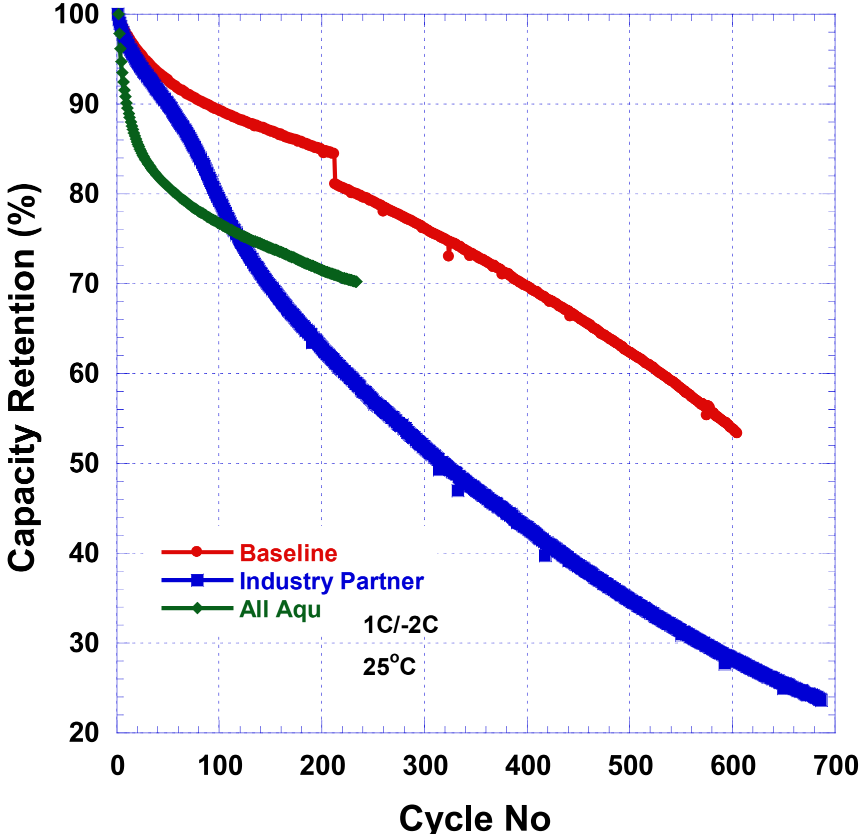
- Cell testing at 25°C; 2.5-4.2V
- 4 formation cycles at 0.05C/-0.05C
- Capacity retention normalized to the initial capacity at the same condition

*Cell #5 with fewer electrodes and lower capacity

- Good cyclability— >94% retention after 50 cycles at 0.2C/-0.2C; >22% after 700 cycles at 1C/-2C

Technical Accomplishments – Capacity Fade Comparison at Accelerated Degradation Conditions





NMC532 & CP-A12 graphite

- Baseline-all NMP based processed electrodes
- Industry partner-NMC cathode via aqueous processing
- All aqu—all aqueous processed electrodes

- ➢ Similar rate performance
- ➢ Baseline cells—best cyclability
- ➢ Slope changes indicate different degradation mechanisms.

Technical Accomplishments – ORNL Receives LIB Aqueous Electrode Processing Patent

- J. Li, B.L. Armstrong, C. Daniel, and D.L. Wood "Aqueous Processing of Composite Lithium Ion Electrode Material," Filed October 12th, 2012, U.S. Patent No. 8,956,688 (UT-Battelle, LLC).
- **Available for licensing.**

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ISSUE NOTIFICATION

The projected patent number and issue date are specified above.

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(application filed on or after May 29, 2000)

The Patent Term Adjustment is 172 day(s). Any patent to issue from the above-identified application will include an indication of the adjustment on the front page.

If a Continued Prosecution Application (CPA) was filed in the above-identified application, the filing date that determines Patent Term Adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Application Information Retrieval (PAIR) WEB site (http://pair.uspto.gov).

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Application Assistance Unit (AAU) of the Office of Data Management (ODM) at (571)-272-4200.

APPLICANT(s) (Please see PAIR WEB site http://pair.uspto.gov for additional applicants):

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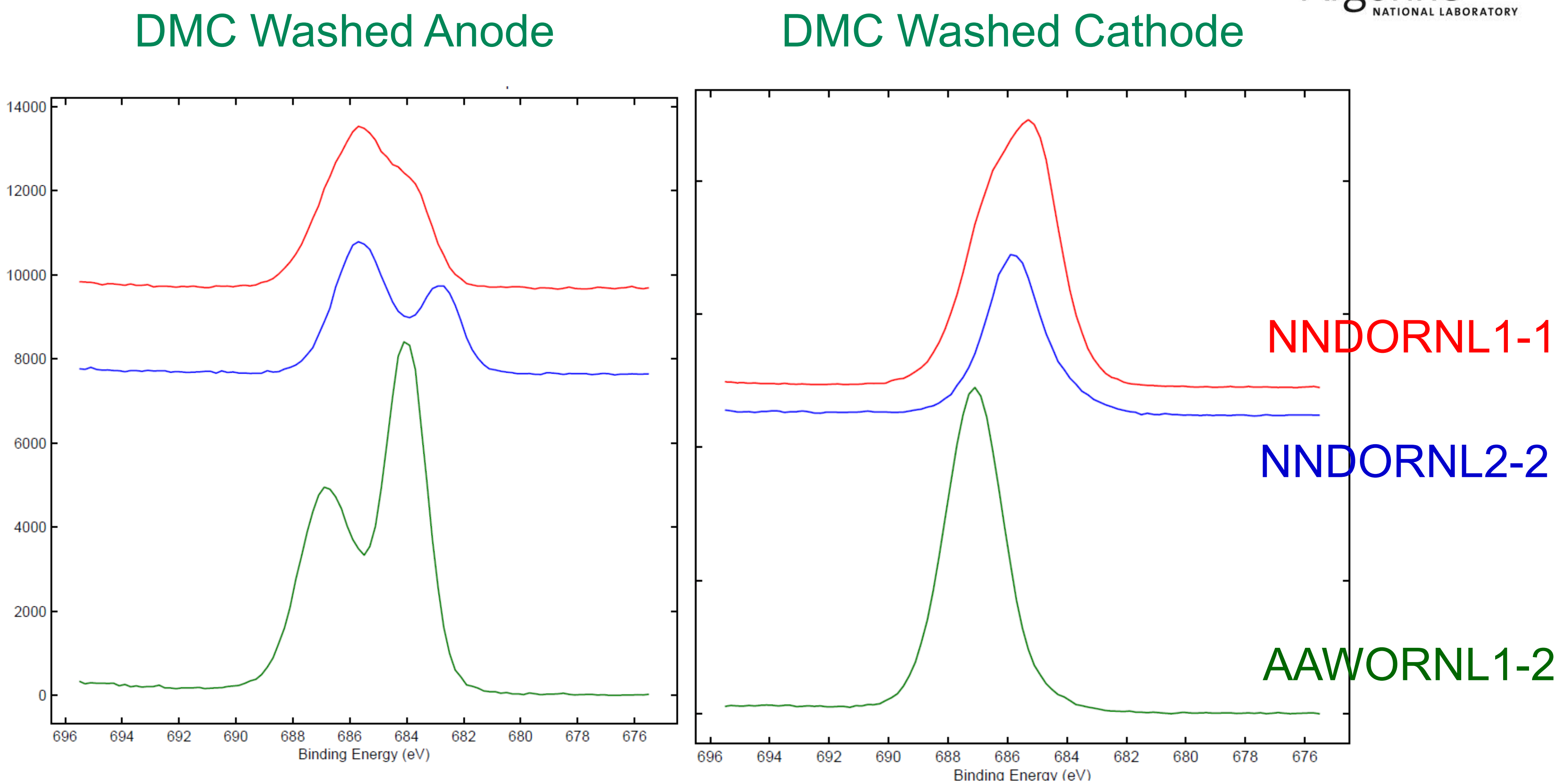
IR103 (Rev. 10/09)

Technical Accomplishments – Analysis of SEI Layer Composition and Morphology with ANL (1)

- Cell chemistry (ABR anode and cathode baseline):
  - Anode: ConocoPhillips A12
  - Cathode: TODA America NMC 532
  - Electrolyte: Novolyte 1.2 M $LiPF_6$ in (3:7 EC/DEC) by weight
- ORNL BMF pouch cells with one unit cell:
  - NMP/PVDF baseline processing WITH secondary drying (NND)
  - NMP/PVDF electrodes equilibrated with ambient dew point (NNW)
  - ORNL aqueous processing WITH secondary drying (AAD)
  - ORNL aqueous processing equilibrated with ambient RH (AAW)
- Formation Protocol 1 (ORNL1):
  - Tap charge to 2.5 V for 5 min
  - Rest at 45°C for 24 hours
  - 3 shallow cycles between 2.5-3.3 V at 0.1C/-0.1C
  - 2 full-range cycles between 2.5-4.2 V at 0.1C/-0.1C
  - Rest at room temperature for 48 hour
- Formation Protocol 2 (ORNL2):
  - Tap charge to 2.5 V for 5 min
  - 4 full-range cycles between 2.5-4.2 V at 0.05C/-0.05C at room temperature

Technical Accomplishments – Analysis of SEI Layer Composition and Morphology with ANL (2): XPS of F1s Region

Argonne NATIONAL LABORATORY

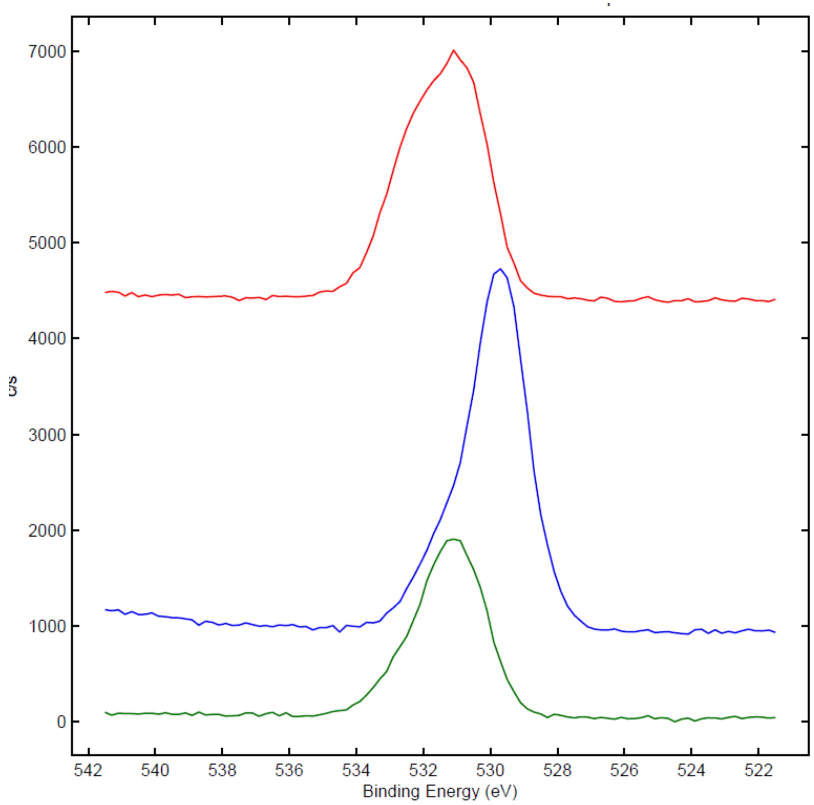


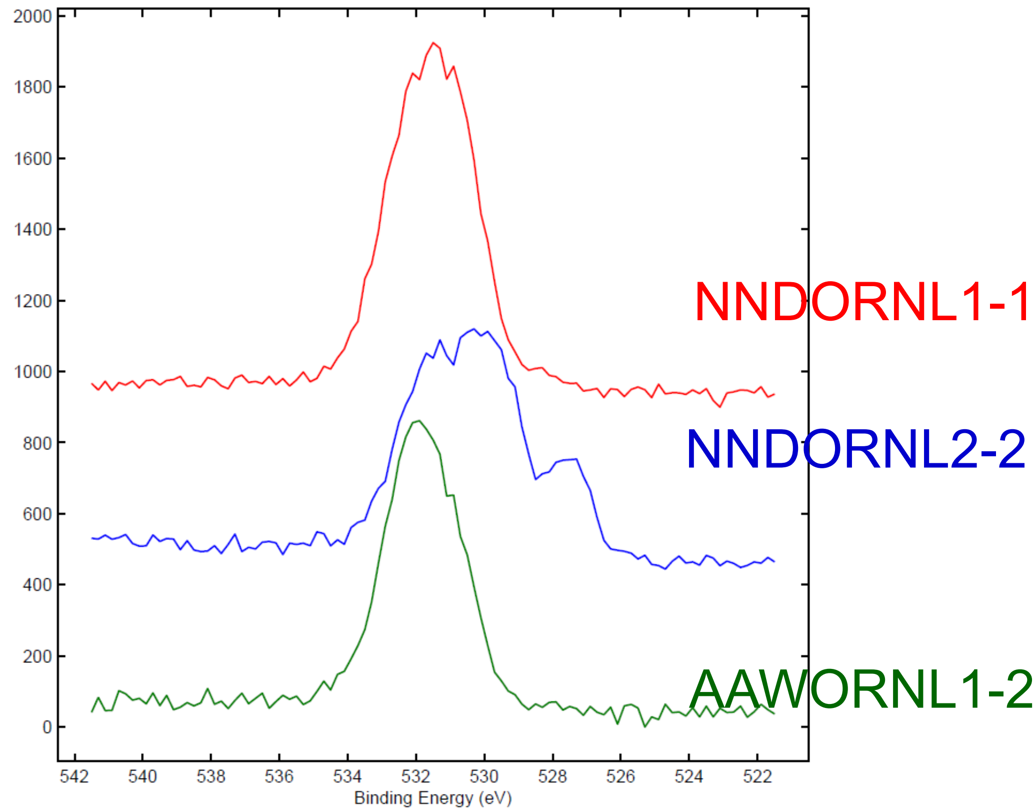
Anode organic and inorganic F contents were found to be different for different formation and secondary drying protocols.

Technical Accomplishments – Analysis of SEI Layer Composition and Morphology with ANL (3): XPS of O1s Region

Argonne NATIONAL LABORATORY

DMC Washed Anode | DMC Washed Cathode





Different amounts of organic and inorganic O were found for both anode and cathode surfaces.

Collaborations

- Partners
  - National Labs: Argonne National Laboratory, Sandia National Laboratories
  - Battery Manufacturers: XALT Energy, Navitas Systems
  - Active Material Suppliers: Phostech Lithium, TODA America, Superior Graphite, GrafTech International, Zenyatta Ventures
  - Inactive Material Suppliers: JSR Micro, Solvay Specialty Polymers, SABIC Global Technologies, Ashland, Timcal, XG Sciences
  - Equipment/Coating Suppliers: PPG Industries, Frontier Industrial Technology
- Collaborative Activities
  - Electrode thickness and electrolyte volume effect, cell assembly standard, and formation protocol effect on SEI with ANL.
  - Selection of appropriate dispersants and water-soluble binders for aqueous processing and thick electrode development (with Solvay Specialty Polymers, JSR Micro and Ashland).
  - Scale-up logistics and manufacturing cost savings of aqueous electrode processing with key coating experts (PPG Industries and Frontier Industrial Technologies).

Future Work

- Remainder of FY15
  - Fabricate thick electrodes via NMP-based processing
  - Collect data from pouch cells with thick, NMP-based electrodes as benchmark
  - Develop electrode formulation for thick electrodes via aqueous processing
  - Investigate calendering effect on graded and non-graded electrode pore structures
  - Finish study on electrolyte volume effect on cell performance
  - Investigate compression effect on pouch cell performance
  - Supply ANL cells undergone various formation protocols to optimize formation protocols
- Into FY16
  - Continue formulation development and scale-up work with PPG Industries.
  - Develop initial aqueous formulations for dual slot-die coated (graded) thick electrodes.
  - Begin obtaining 2000 USABC capacity fade cycles at 0.33C/-0.33C for baseline PVDF/NMP and all-aqueous processed pouch cells.

Summary

- **Objective:** this project facilitates lowering the unit energy cost by up to $110/kWh-usable of EVs and PHEVs by addressing the expensive electrode coating and drying steps and increasing electrode thickness.
- **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.
  - Ease of technology scale-up (capital costs reduced and cell production costs eliminated).
  - Electrode formula and processing are developed to enable thick electrode manufacturing.
  - Electrode architecture is optimized for appropriate power density.
- **Technical:** Scale up manufacturing water-based NMC532 and CP A12 electrodes; Demonstrated cycling performance in 1.6-Ah pouch cell with both NMP and water-based NMC 532 and CP A12; Improved electrode wetting, adhesion and performance with corona treated Al foils.
- All FY15 milestones are on schedule.
- **Collaborators:** Extensive collaborations with national laboratories, lithium-ion battery manufacturers, raw materials suppliers, and coating producer.
- **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:
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  - Seong Jin An
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Technical Collaborators:

- Andrew Jansen
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- Feng Gao
- Alan Goliaszewski
- Mike Wixom
- James Banas
- Gregg Lytle
- Jack Burgman
- Stuart Hellring
- Randy Daughenbaugh
- Chong Chen

Information Dissemination and Commercialization

- Patent
  - J. Li, D. L. Wood, C. Daniel, and B.L. Armstrong, "Aqueous Processing of Composite Lithium Ion Electrode Material," U.S. Patent No. 8,956,688 (UT-Battelle, LLC), February 17, 2015.
- Refereed Journal Papers and Book Chapter
  1. J. Li, C. Daniel, and D.L. Wood, "Aqueous Processing and Performance of $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ Cathodes," *Journal of the Electrochemical Society,* In Preparation, 2015.
  2. J. Li, C. Daniel, D. L. Wood, et. al., "Processing and Performance of $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ Cathode on Various Current Collectors", *Journal of Power Sources*, In Preparation, 2015.
  3. D. L. Wood, J. Li, and C. Daniel, "Prospects for Reducing the Cost of Lithium Ion Electrode Processing and Pouch Cell Formation Steps," *Journal of Power Sources*, **275**, 234-242 (2015).
  4. J. Li, D. Mohanty, B. Brown, C. Daniel, and D.L. Wood, "Fabrication and Performance of $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ cathodes through aqueous processing with various binders," Advanced Automotive Battery Conference (AABC) 2014, LLIBTA Symposium Track A, Atlanta, GA, February 3-7, 2014.
- Selected Presentations
  1. D.L. Wood, J. Li, C. Daniel, and B. L. Armstrong, "Aqueous Colloidal Chemistry for Low-Cost, Green Manufacturing of Lithium-Ion Battery Electrodes," MS&T' 14, Pittsburgh, PA, October 12-15, 2014 **(Invited)**.
  2. J. Li, D. L. Wood, and C. Daniel, "Enabling Manufacturing Composite Cathodes through Aqueous Processing for Lithium-Ion Batteries," 3rd International Conference and Exhibition on Materials Science & Engineering, San Antonio, TX, October 6-8, 2014.
  3. J. Li, C. Daniel, and D. L. Wood, "Effect of Interface Between Current Collector and $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ Composite Cathodes on the Electrode Performance,", 227th ECS meeting, Chicago, IL, May 24-28, 2015.

Thank you for your attention!

Back-up Slides

Additional Reviewer Response – Electrode Processing Cost Reduction Potential[1]

Cost Component	Baseline Cost per kWh-Total ($/kWh)	Baseline Cost per kWh-Usable ($/kWh)	Reduced Cost per kWh-Total ($/kWh)	Reduced Cost per kWh-Usable ($/kWh)
Composite Electrode Materials	101.7	145.3	100.2	143.1
Current Collectors & Separator	80.2	114.6	40.9	58.4
Electrode Processing	35.7	51.0	2.1	3.0
Electrolyte	25.9	37.0	23.1	33.0
Wetting and Formation Cycling	24.1	34.4	24.1	34.4
Pouch and Tab Materials	6.7	9.6	6.7	9.6
Module Hardware, Power Electronics & Pack Cooling[2]	46	65.7	46	65.7
Labor (Electrode Processing and Cell/Pack Construction)[3]	34	48.6	34	48.6
Total =	354.3	506.2	**277.1**	**395.8**

- Combination of all-water-based processing plus 2× thicker electrodes has potential of saving $110/kWh-usable of the ***total pack cost*** (based on 70% depth of discharge limit).
- Cost of electrode processing could be cut to $3/kWh-usable primarily due to fast drying of water (i.e. higher solids loading, lower drying T, lower air flow rate & higher volatility than for NMP) and ***no solvent recovery costs***.

1. D.L. Wood et al., "Prospects for Reducing the Cost of Lithium Ion Electrode Processing and Pouch Cell Formation Steps," J. Power Sources, 275, 234-242 (2015).
2. D. Howell, "U.S. Battery R&D Progress and Plans," DOE Annual Merit Review, May 14, 2013.
3. K.G. Gallagher et al., "PHEV Battery Cost Assessment," DOE Annual Merit Review, May 9-13, 2011.