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

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Oak Ridge National Laboratory

National Transportation Research Center

2019 U.S. DOE Vehicle Technologies Office Annual Merit Review

June 11, 2019 **Project ID: BAT164**

ORNL is managed by UT-Battelle for the US Department of Energy

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Overview

Timeline

- Task Start: 10/1/14
- Task End: 9/30/22
- Percent Complete: 60%

Barriers

- Barriers Addressed
  - **By 2022, further reduce EV battery-pack cost to $80-100/kWh.**
  - **Advanced Li-ion xEV battery systems with low-cost electrode architectures.**
  - **Achieve deep discharge cycling target of 1000 cycles for EVs by 2022.**

Budget

- Total task funding
  - $3600k
- $700k in FY18
- $400k in FY19
- $600k in FY20 (planned)

Partners

- Interactions/Collaborations
  - National Laboratories: ANL, SNL, INL
  - Universities: KIT, SUNY-Binghamton
  - Battery Manufacturers: XALT Energy, Navitas Systems
  - Material/Process Suppliers: PPG Industries, TODA America, Superior Graphite, ConocoPhillips, IMEYS, JSR Micro, Solvay Specialty Polymers, Ashland, PneumatiCoat
  - Equipment Manufacturer: Frontier Industrial Technology, B&W MEGTEC, DataPhysics
- Project Lead: ORNL

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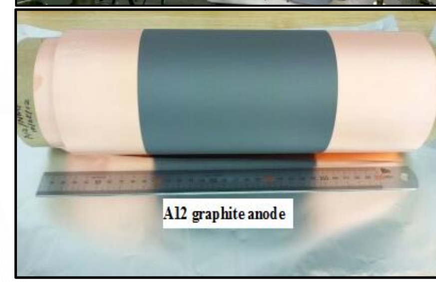
Relevance & Objectives

- Main Objective: To improve cell energy and power density and reduce battery pack cost by manufacturing thick electrodes with tailored electrode architecture via aqueous processing and utilizing high energy high voltage cathode materials.

- Objectives in this period
  - Apply aqueous processing to Ni-rich NMC (NMC811)
  - Fabricate thick (6-8 mAh/cm^2) and crack-free composite NMC811 cathode via aqueous processing
  - Create laser structured electrodes
  - Characterize electrolyte imbibition rate and understand the electrolyte imbibition-processing relation
  - Assemble pouch cells with NMC811 and tailored electrode architecture
  - Demonstrate energy density ≥225 Wh/kg (cell level)



Project Milestones

Status	SMART Milestones	Description
12/31/18 ✔	Quarterly Progress Measure (Regular)	Optimize NMC811 aqueous dispersion formulations, and quantify dispersion constituent zeta potentials; obtain rate capability data and quantify capacity through at least 500 USABC 0.33C/-0.33C cycle while demonstrating an initial cell energy density rating of 225-250 Wh/kg.
3/31/18 To be completed by June	Annual Milestone (stretch)	Quantify impedance (via AC impedance technique) of Gen 3 structured, multilayer anode and cathode coatings (6 mAh/cm^2) with different individual layer thickness and different total thickness to achieve 225-250 Wh/kg improvement in cell energy density.
6/30/19 In Progress	Annual Milestone (stretch)	Quantify impedance of (via AC impedance technique) of Gen 3 structured, multilayer anode and cathode coatings (8 mAh/cm^2) with different total thickness to achieve > 250 Wh/kg improvement in cell energy density. Verify long-term performance by achieving no more than 40% capacity fade through at least 500 USABC 0.33C/-0.33C cycles. Demonstrate 40% of rated capacity at 2C discharge rate to show preservation of power density.
9/30/19 In Progress	Go/No-Go Decision	Complete 1.5-Ah pouch cell rate performance for cells with combined Gen 3 graphite anode and NMC811 cathode structured designs. Improved gravimetric energy density of baseline cell design to > 250 Wh/kg (cell level) and demonstrate no more than 40% capacity fade through 500 USABC 0.33C/-0.33C cycles. Demonstrate 40% of rate capacity at 2C discharge rate verifying high power density

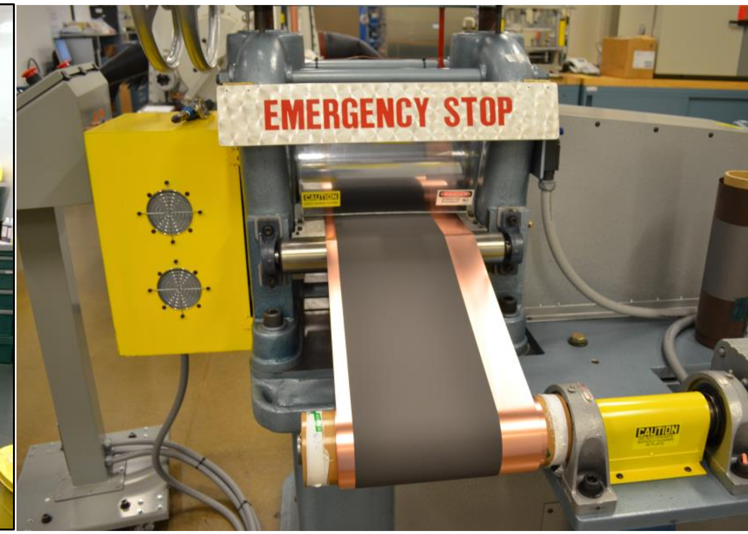
Project Approach

- Problems:
  - Electrode cracking in thick electrodes
  - Mass transport limitations thick electrodes

- Technical approach and strategy:
  - Evaluate stability of high energy and high voltage cathodes (NMC622 and NMC811) during aqueous processing
  - Incorporate aqueous processing to fabricate NMC811 cathodes
  - Fabricate crack-free NMC811 cathodes with high areal loading (6-8 mAh/cm^2) via aqueous processing
  - Create laser structured electrodes to overcome mass transport limitation
  - Simulate energy and power density in laser structured electrodes
  - Characterize surface energy of composite electrodes and electrolyte imbibition in porous electrodes
  - Characterize electrode microstructure
  - Evaluate rate performance and long term cyclability at room temperature and high temperature in pouch cells

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

Planetary Mixer (≤2 L)



Dry room for pouch cell assembly

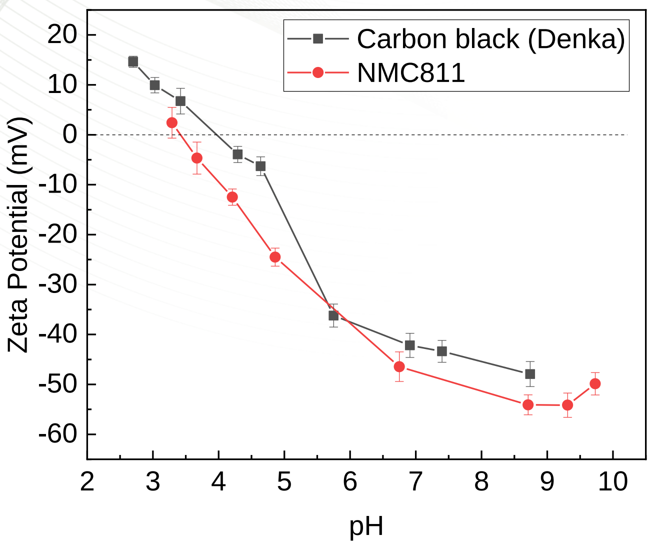
- Largest open-access battery R&D facility in US.
- All assembly steps from pouch forming to electrolyte filling and wetting.
- 1400 ft^2 (two 700 ft^2 compartments).
- Humidity <0.5% (-53°C dew point maintained).
- Pouch cell capacity: 50 mAh – 7 Ah.
- Single- and double-sided coating capability.
- Current weekly production rate from powder to pouch cells is 50-100 cells.

Technical Accomplishments – Executive Summary

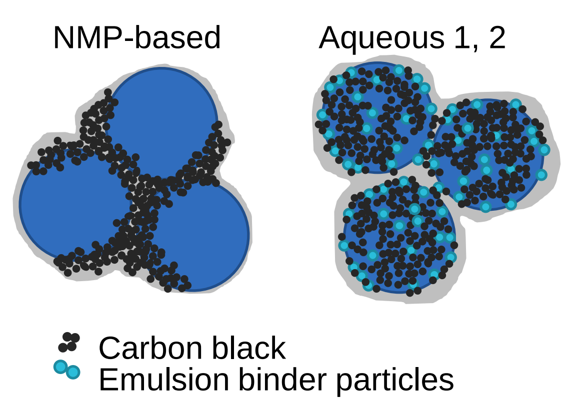
- Applied aqueous processing to fabricate NMC811 cathodes.
- Demonstrated >70% capacity retention over 1000 cycles in NMC811 cathodes processed via aqueous processing with various water soluble binders.
- Fabricated thick NMC811 (6 mAh/cm^2) through aqueous processing
- Discovered variation in binder coverage on NMC811 between NMP-based and aqueous processing.
- Created laser structured NMC811 cathodes (6 mAh/cm^2) in collaboration with KIT, Germany.
- Synthesized 6-7 µm NMC811 particles for Gen 3 electrode design
- Demonstrated 225 Wh/kg in 14-Ah pouch cells with laser structured and all aqueous processed electrodes.
- Characterized area specific impedance of pouch cells with NMC811 and graphite at various temperatures
- Identified lower rate performance observed in aqueous-processed cells mostly due to formulation rather than structural changes
- First time characterization of electrolyte imbibition through 2D model and determination of coefficient of permeation and solid permeability coefficient

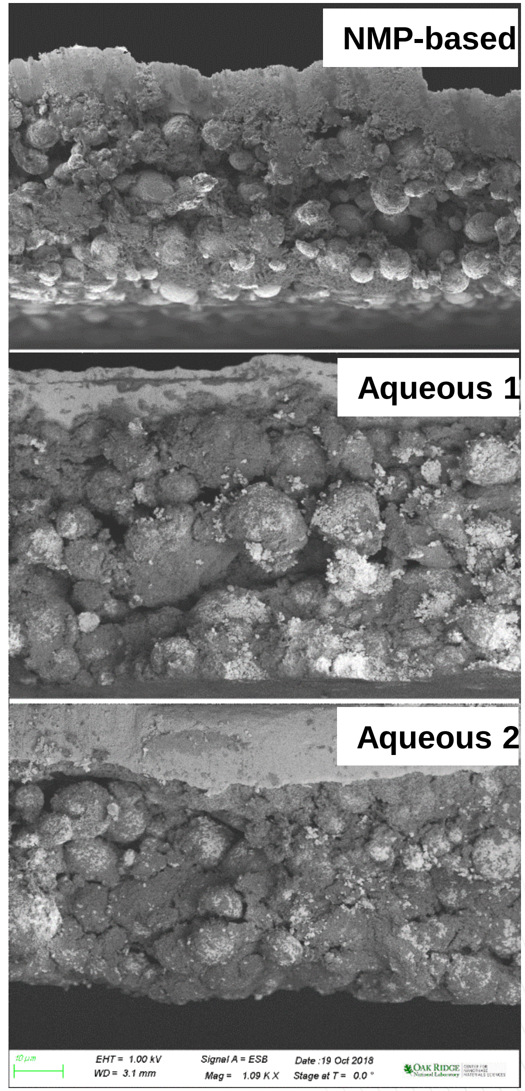
Technical Accomplishments— Understanding Processing-Properties-Performance Relation in NMC811 Cathodes (FY19)

Zeta potential measurement in water



Schematic of dispersion of CB





- Zeta potential of carbon black is < -40 mV at pH ≥ 7, indicating relatively well dispersed in coating conditions.
- SEM images of NMP-based and aqueous-processed coatings show dramatically different dispersion of CB around the NMC particles (see schematic).
  - A CB+PVDF network surrounds the NMC811 particles (left) in NMP-based coating.
  - CB+emulsion binder particles almost fully coat the NMC811 particles leading to a lack of connecting bridges between the NMC particles.
- Studies are ongoing to understand the effect of carbon black+ emulsion binder distribution in the coating on its cohesion, flexibility, and cracking upon drying.
- Preliminary results show a strong dependence of the type of conductive additive used (CB vs. CNTs vs. C nanofibers) on the final distribution of emulsion binder + conductive additive in the coating.

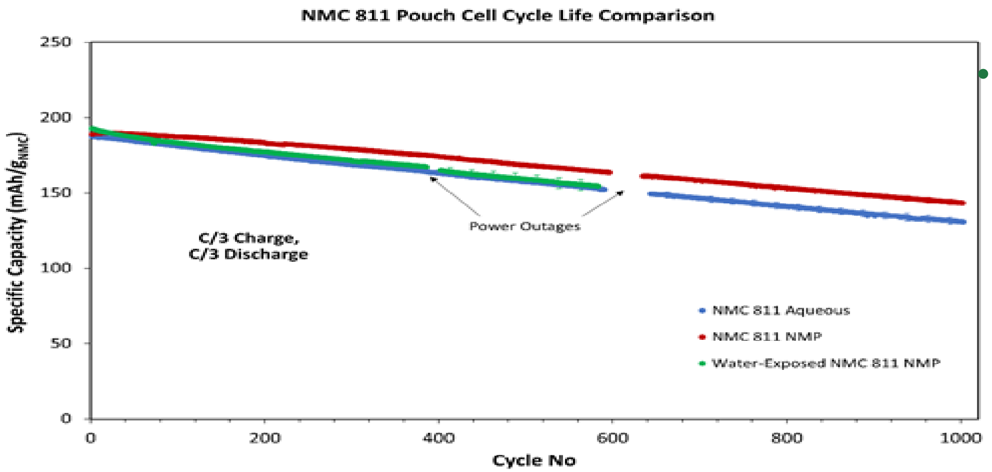
Add binder info

Technical Accomplishments— Excellent Cyclability from Aqueous Processed NMC811 Cathodes (FY18-19)

NMC 811 Cathode Recipes:

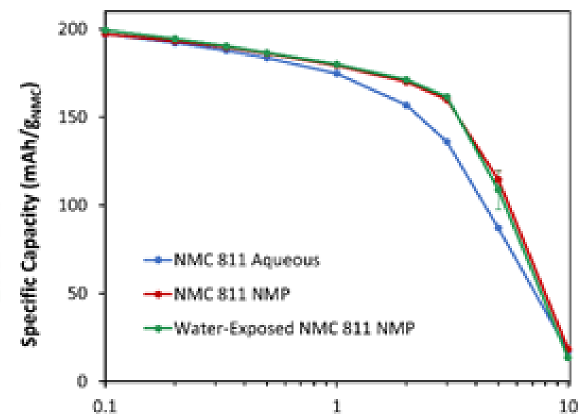
– **Aqueous:** 90 wt% NMC 811 / 5 wt% Carbon Black / 1 wt% CMC Binder / 4 wt% Acrylic Emulsion

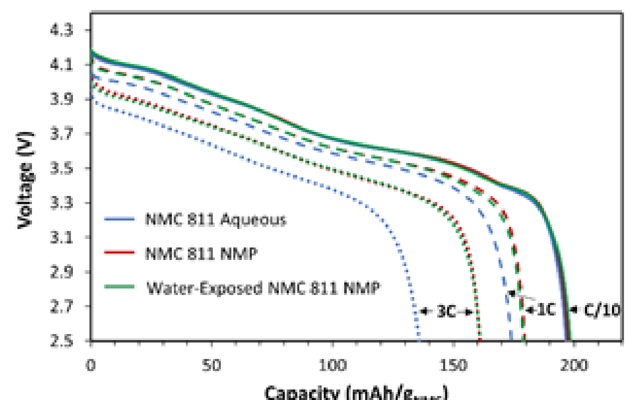
– **NMP**: 90 wt% NMC 811 / 5 wt% Carbon Black / 5 wt% PVDF



- Incorporating aqueous processing with high energy and high voltage cathode for high energy density
- Excellent cycle life in 1000 USABC 0.33C/-0.33C cycles
  – Capacity retention 76% (NMP-processed) vs 70% (aqueous processed)
  – Slightly faster capacity fade could be due to electrode formulation, slurry preparation, and water exposure
  – Rate performance: NMP= water-exposed> aqueous →ascribed to various electrode formulations.

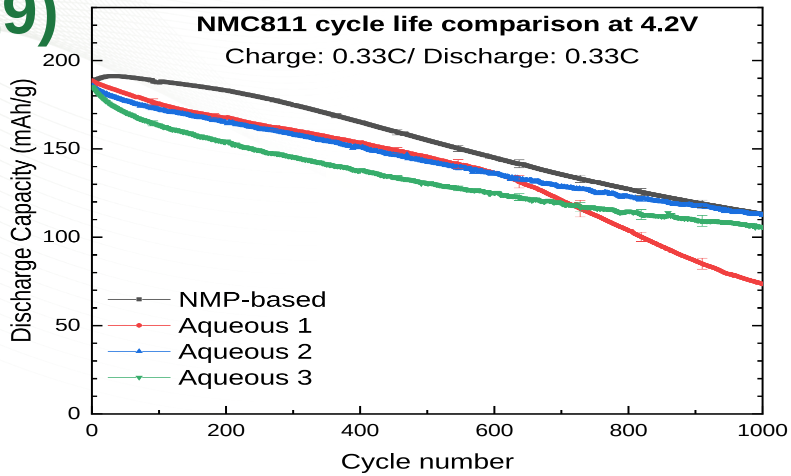
- Single-layer pouch cells with **aqueous**- and **NMP**-processed NMC 811 cathodes and Superior SLC 1520T graphite anodes
  – NMC 811 Loading: 11.6 mg/cm^2 (aqueous) and 11.3 mg/cm^2 (NMP)
- Water-exposed NMP: NMC811 powder was saturated in water for 4 h, dried, and then fabricated into electrodes with NMP-based processing

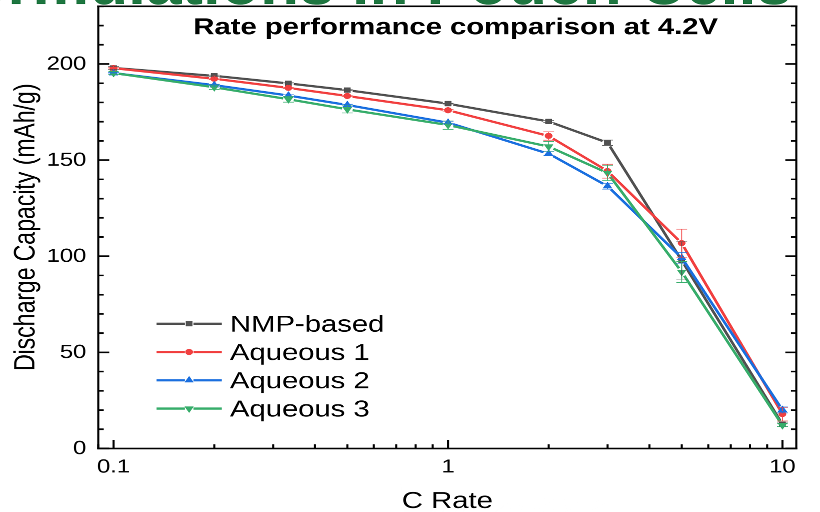


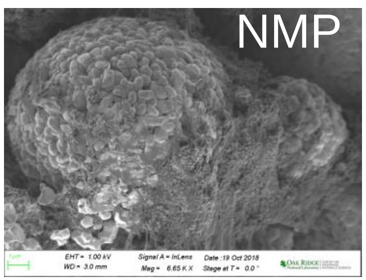


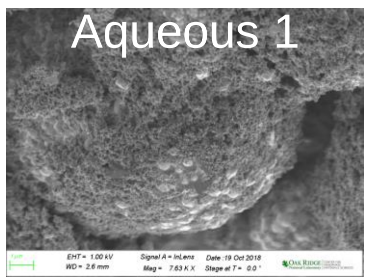
Wood et al., *ChemSusChem*, Under review

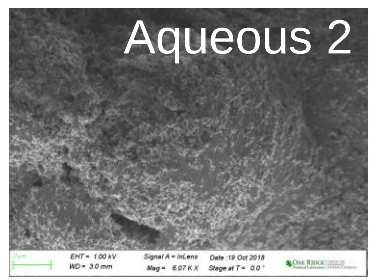
Technical Accomplishments—Demonstrated Rate Performance and 1000 USABC 0.33C/-0.33C Cycles Of NMC811 with Various Aqueous Formulations in Pouch Cells (FY19)

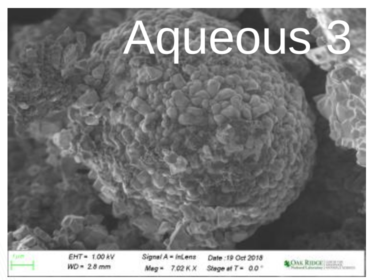








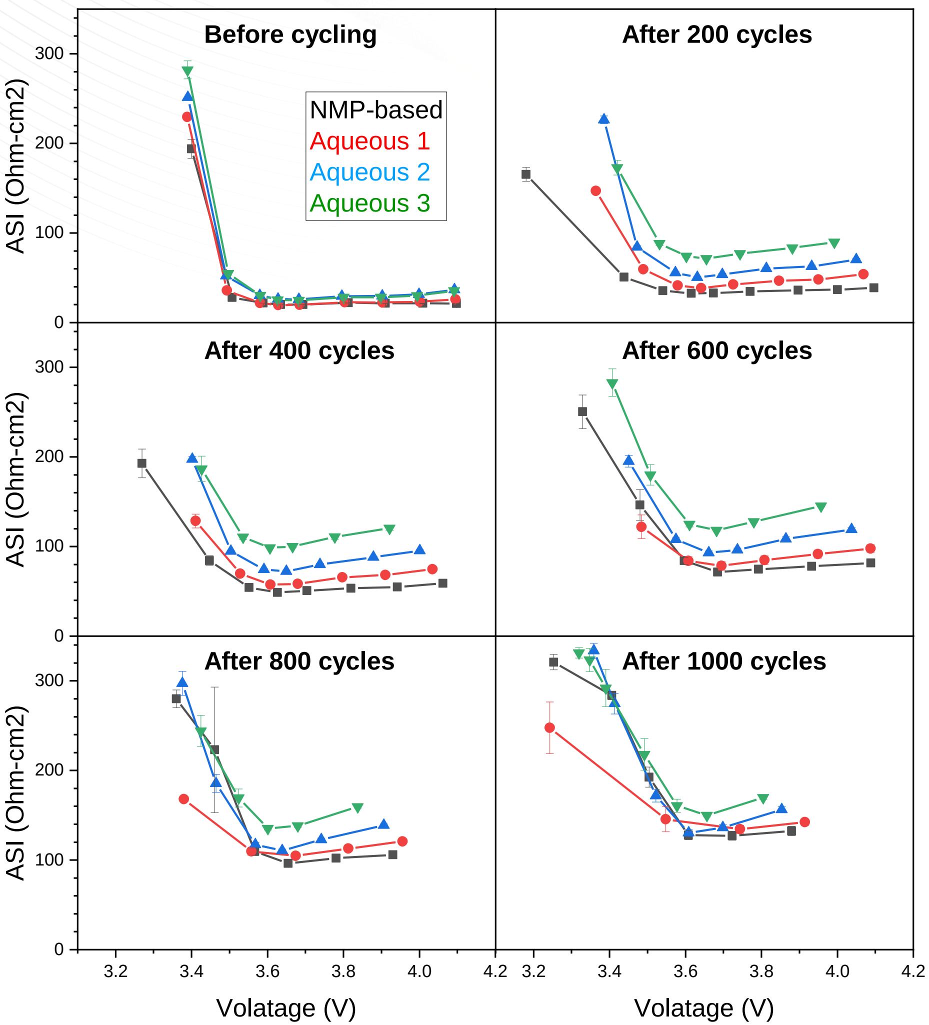




- NMC811 cathodes parameters:
  - **NMP**: 90 wt.% NMC811/ 5 wt.% Carbon Black/ 5 wt.% PVDF Binder; 11.5 mg/cm^2
  - **Aqueous 1**: 90 wt.% NMC811/ 5 wt.% Carbon Black/ 1 wt.% CMC Binder/ 4 wt.% Solvay Latex Emulsion Binder; 11.4 mg/cm^2
  - **Aqueous 2**: 90 wt.% NMC811/ 5 wt.% Carbon Black/ 1 wt.% CMC binder/ 4 wt.% JSR TRD202A Emulsion Binder; 11.4 mg/cm^2
  - **Aqueous 3**: 90 wt.% NMC811/ 5 wt.% Carbon Black/ 5 wt.% LiPAA Binder; 11.6 mg/cm^2
- Single-layer pouch cells with aqueous- and NMP-based NMC811 cathodes with Superior SLC 1520T graphite anodes
- Excellent cycle life, especially aqueous 2 matches the NMP-based one in capacity retention
- Slightly lower rate performance at high rates for the aqueous-based ones is probably due to the higher coverage of binder network on the NMC811.

Technical Accomplishments—Characterized ASI in NMC811 Pouch Cells with Various Aqueous Formulations throughout 1000 Cycles (FY19)

HPPC of full-cells made with NMP- and aqueous-processed cathodes



- Area specific impedance (ASI) of cells with **NMP-based** cathode is the *least* throughout the course of cycling.
- Before cycling, ASI of all the cells is very close; however at the end of 200 cycles, differences in ASI emerges which is maintained through the rest of the 800 cycles.
- ASI of cells with **Aqueous 3** (LiPAA-containing) is the *highest* throughout the course of cycling.
- Interestingly, cells with Aqueous 1 cathode have the lowest ASI among the three aqueous cathodes, but it shows the worst long-term cycling performance.

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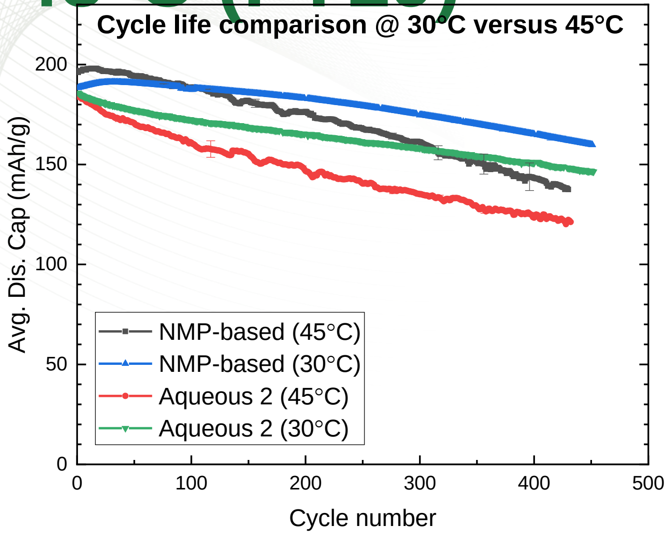
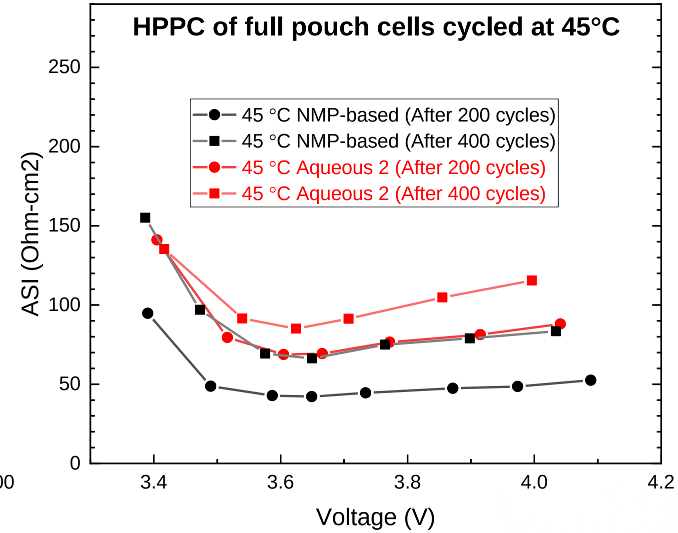
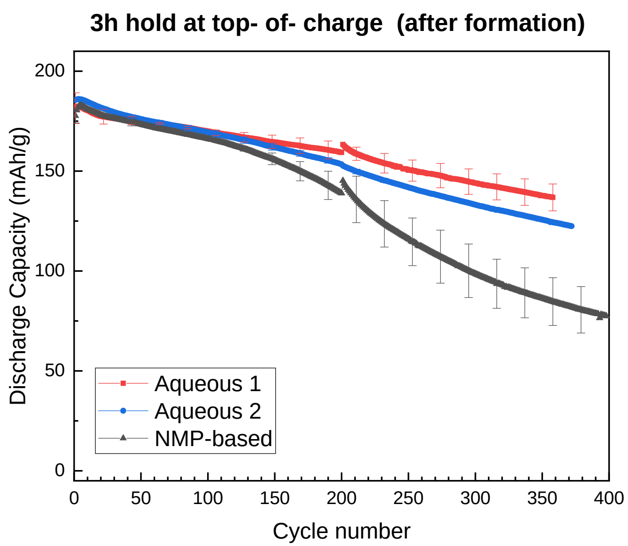
Technical Accomplishments—Higher ASI in the Aqueous Processed NMC811 at 30ºC and 45ºC (FY19)





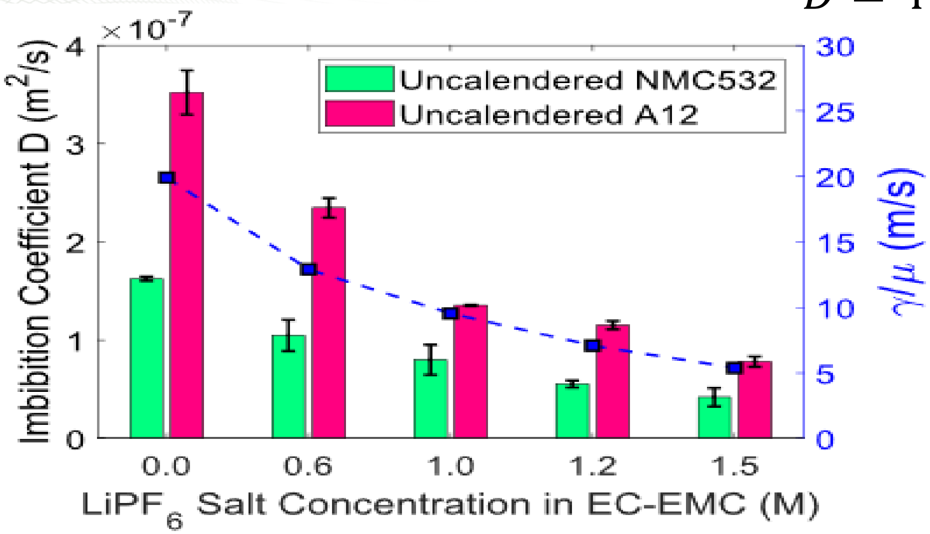
Electrode	% Capacity after 400 cycles
NMP-based @ 30°C	87.7
Aqueous 2 (with CMC+JSR) @ 30°C	81.1
NMP-based @45°C	73.0
Aqueous 2 (with CMC+JSR) @45°C	67.1

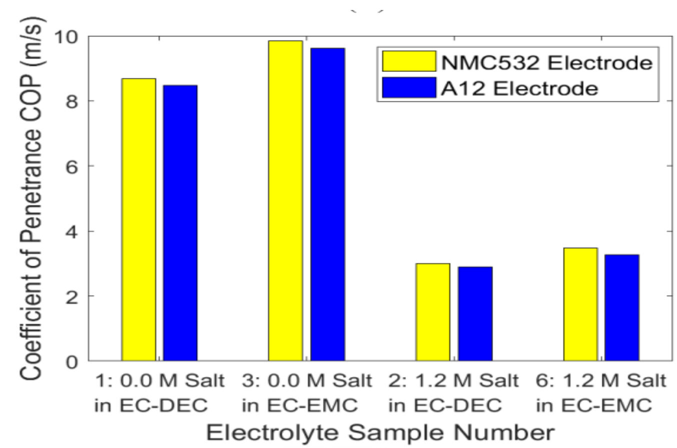


- Cycling performance of cells with both NMP-based and aqueous-based cathodes decline when cycled at 45°C.
  - Capacity retention of cells with aqueous-processed cathode is ~6% lower than NMP-based at both 30°C and 45°C.
- ASI of cells with Aqueous 2 cathodes remains higher than NMP-based cathodes even at 45°C.
- With 3h hold at 4.2V, the capacity of the aqueous processed NMC811 is same as the NMP-based ones and demonstrates better cycle life.

Technical Accomplishments—Characterization of Electrolyte Imbibition Coefficient in NMC532 and A12 Graphite Electrodes (FY19)

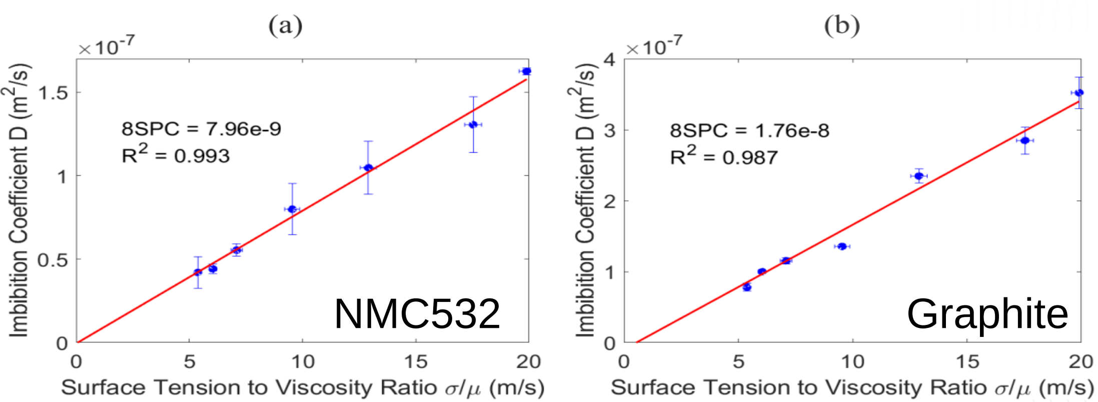
$$D = 4\left(\frac{\gamma}{\mu}\right)\left(\frac{kB}{\epsilon r_e}\right)\cos\theta$$





Coefficient of permeation (COP)= $\gamma \cos\theta /(2\mu)$

Solid permeability coefficient (SPC) $= kB\cos\theta/(2\epsilon r_e)$



- First time characterization of electrolyte imbibition rate via 2D image processing.
- Electrolyte imbibition is faster in graphite anode.
- First time defining SPC and COP to predict electrolyte imbibition of new electrolyte or electrodes without direct experiment, which provides guidance in electrolyte formulation and electrode engineering.

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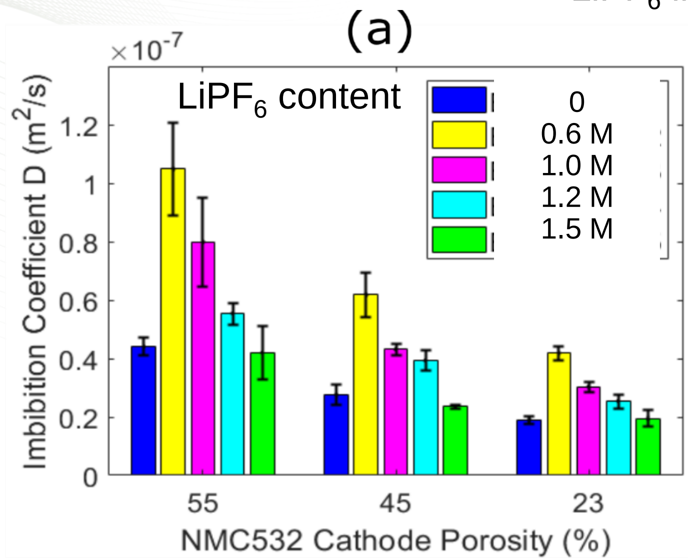
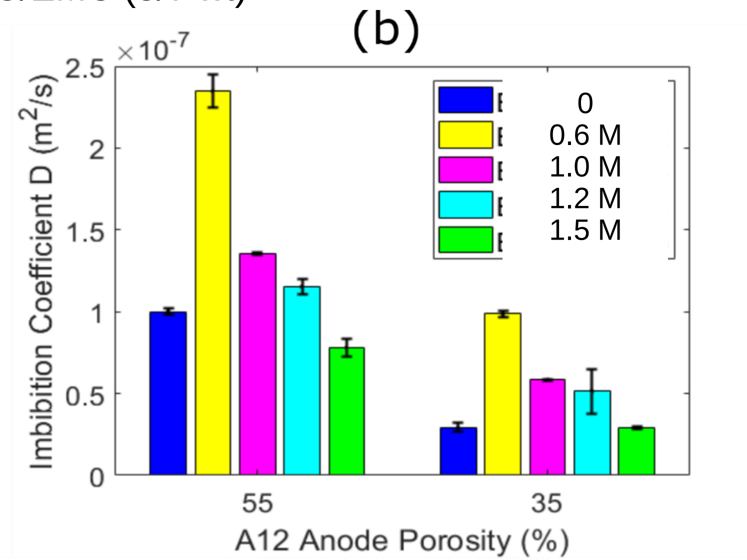
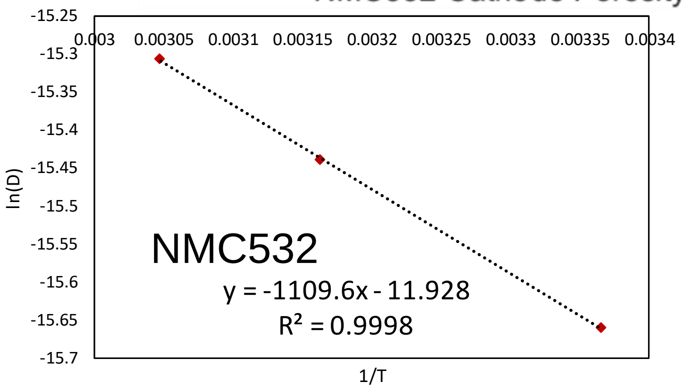
Davoodabadi et al., *Journal of Power Sources*, 424 (2019) 193-203

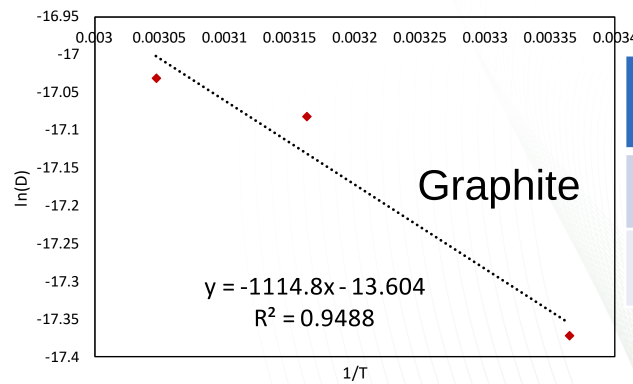
Technical Accomplishments—Understanding of Electrolyte Imbibition-Processing Relation (FY19)

$LiPF_6$ in EC/EMC (3/7 wt)









	Activation Energy (kJ/mol)
NMC532	9.2
A12 graphite	9.3

1.2 M $LiPF_6$ in EC/EMC (3/7 wt)

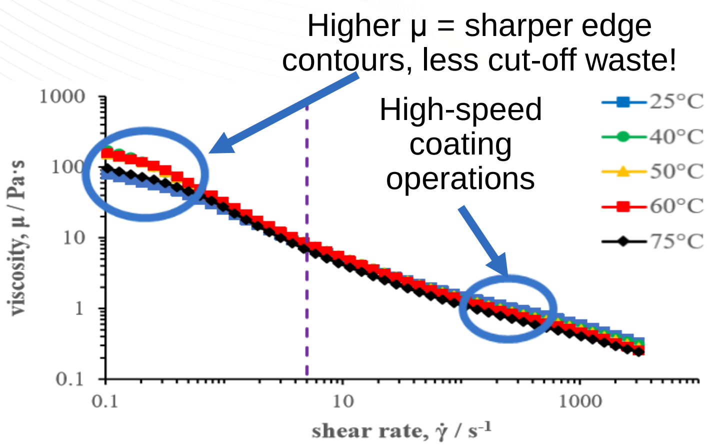
- Electrolyte imbibition reduces with lower porosity and higher salt concentration.
- First time determining activation energy in electrolyte imbibition.

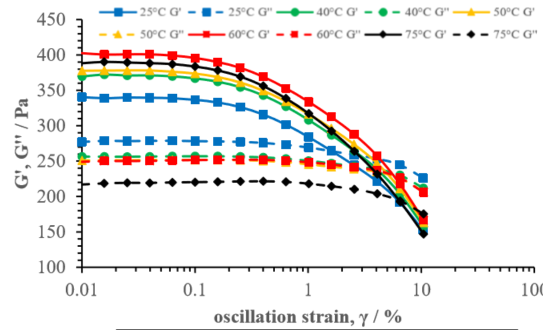
Davoodabadi et al., *Journal of Power Sources*, under review.

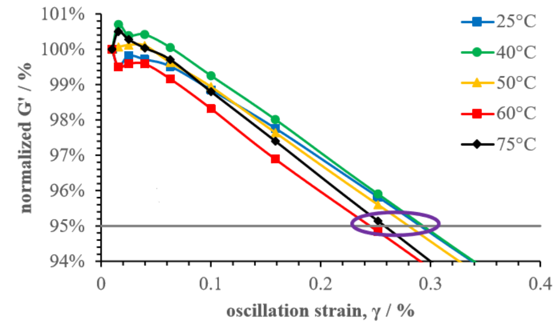
Technical Accomplishments—Slurry Mixed at Elevated Temperature Reduces Viscosity and Increases Coating Speed without Compromising Electrochemical Performance(FY19)

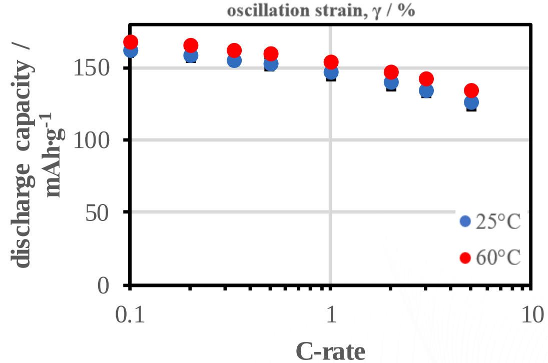
$G' \rightarrow storage\ modulus$

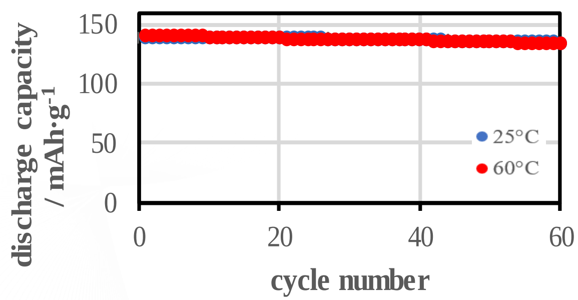
$G'' \rightarrow loss\ modulus$







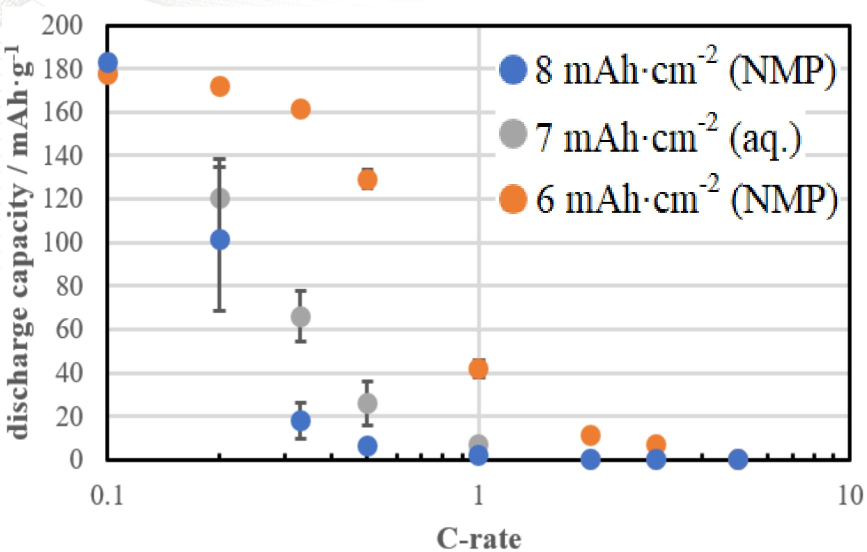


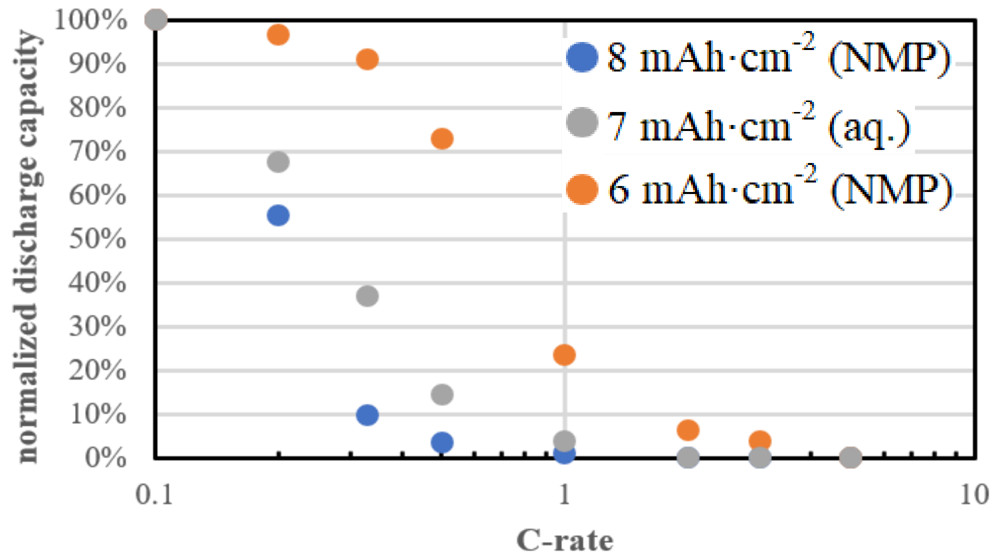


- Slurry at 60°C is 20% less viscous than the 25°C one.
- Storage modulus increases until 60°C due to more binder tangling indicating higher sedimentation resistance.
- Storage modulus reduces when further increasing temperature due to excessive particle motions.
- No negative impact of high temperature on electrochemical performance.
- Coating slurry at elevated temperature would allow to reduce solvent content and increase coating speed.

Hawley et al., *Eletrochimica Acta*, under review.

Technical Accomplishments— Successful Fabrication of Thick NMC811 Cathode (7 mAh/cm²) via Aqueous Processing (FY19)





	NMC811	Conductive Additive	Binder
Mass Fraction (%)	90	5	5

- Successfully fabricated thick NMC811 (6 and 8 mAh/cm²) baseline cathodes via NMP-based processing.
- Successfully fabricated thick NMC811 (7 mAh/cm²) via co-solvent (IPA/H_2O 2/8).
- Flexibility of the thick electrodes needs to be improved.
- The thick electrodes suffer from mass transport limitation.

Collaborations

- Partners
  - National Labs: Argonne National Laboratory, Sandia National Laboratory, Idaho National Laboratory
  - Battery Manufacturers: XALT Energy, Navitas Systems
  - Active Material Suppliers: TODA America, Superior Graphite, ConocoPhillips, PneumatiCoat
  - Inactive Material Suppliers: JSR Micro, Solvay Specialty Polymers, Ashland, IMERYS
  - Equipment/Coating Suppliers: PPG Industries, Frontier Industrial Technology, B&W MEGTEC, DataPhysics
  - Universities: KIT, Binghamton University

- Collaborative Activities
  - Characterization of surface energy and electrolyte wetting with Binghamton University (weekly discussion)
  - Laser structuring of thick electrodes with KIT (monthly discussion)
  - Synthesis of small NMC811 particles with Dr. Ozge Kahvecioglu Ferdun at ANL (Project ID Bat 167)
  - Binder selection and optimization with Solvay, Ashland, and JSR (bi-annual discussion)
  - Sharing of results with strategic battery manufacturers (Navitas Systems and XALT)

Future Work

- Remainder of FY19
  - Fabricate Gen 3 thick NMC811 cathode via Aqueous processing.
  - Characterize rate performance of the laser structured NMC811 cathode.
  - Assemble 1.5 Ah pouch cells with thick NMC811 cathodes (6-8 mAh/cm^2).
  - Evaluate electrochemical performance and energy and power density of pouch cells.
- Into FY20
  - Freeze tape cast Ni-rich NMC cathode.
  - Optimize freeze tape casting conditions for low tortuosity electrode architecture.
  - Densify electrodes.
  - Evaluate energy and power density of the electrodes.
- Commercialization: Highly engaged with potential licensees; high likelihood of technology transfer because of significant cost reduction benefits and equipment compatibility; 2 patents issued.

Any proposed future work is subject to change based on funding levels

Summary

- **Objective:** This project facilitates lowering the unit energy cost by up to 17% by addressing the expensive electrode coating and drying steps while simultaneously increasing electrode thickness.
- **Approach:** Develop green manufacturing with tailored electrode architectures to enable implementation of aqueous processed thick electrodes for high power performance.
  - Understand mass transport limitation in high energy electrodes.
  - Develop electrode formulation and processing to enable thick electrode manufacturing.
  - Develop tailored electrode architecture to overcome mass transport limitation.
  - Integrate aqueous processing with high energy high voltage cathode materials.
  - Demonstrate and validate electrochemical performance in large format pouch cells.
  - Characterize surface energy of electrodes and evaluate electrolyte wetting in thick electrodes.
- **Technical:** Characterized compatibility of NMC811 with aqueous processing;Fabricate thick and crack-free NMC811 cathodes (6 mAh/cm^2) via co-solvent; Demonstrated 225 Wh/kg in pouch cells with NMC811 and graphite electrodes; Demonstrated excellent rate performance and cyclability of aqueous processed NMC811 cathodes; Created laser structured electrodes; Characterized surface energy of electrodes and electrolyte imbibition.
- **Collaborators:** Extensive collaborations with national laboratories, universities, lithium-ion battery manufacturers, raw materials suppliers, and coating producer.
- **Commercialization:** 2 patents issued; high likelihood of technology transfer due to significant cost reduction benefits and equipment compatibility.

Selected Responses to Specific FY17 DOE AMR Reviewer Comments

- Second reviewer commented that the cell level cost reduction with the new manufacturing processing should be quantized. .
  - **A detailed study is done and published in our previous work (Journal of Power Sources, 275 (2015) 234-242; Drying Technology 5(8) (2018) 1311-1321).**

- One reviewer commented during the poster section that high temperature performance needed to be evaluated.
  - **HPPC and cycle life at 45^{o}C has been evaluated and shown in slide 12. The ASI of the aqueous processed NMC811 is higher than the NMP-based one. Similarly, the capacity fade is slightly in the aqueous processed NMC811, ~6% lower after 1000 cycles.**

Acknowledgements

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

- ORNL Contributors:
  - David Wood
  - Claus Daniel
  - Zhijia Du
  - Marissa Wood
  - Ritu Sahore
  - Mengya Li
  - Blake Hawley
  - Kevin Hays
  - Tommiejean Christensen

Technical Collaborators:
- Ozge Kahvecioglu Ferdun
- Robert Wang
- Congrui Jin
- James Banas
- Gregg Lytle

Information Dissemination and Commercialization

- **6 Refereed Journal Papers**

1. Marissa Wood, Jianlin Li, Rose Ruther, Ethan Self, Harry Meyer III, Claus Daniel, Ilias Belharouak, David Wood III, "Chemical stability and long-term cell performance of low-cobalt, Ni-rich layer oxide cathodes prepared by aqueous processing for high-energy lithium-ion batteries", *ChemSusChem*, under reviewed..

2. Seong Jin An, Jianlin Li, Claus Daniel, and David L. Wood, III, "Effect of ultraviolet light treatment in ambient air on lithium-ion battery graphite and PVDF binder", *Journal of the Electrochemical Society*, 166(6) (2019) A1121-A1126.

3. Ali Davoodabadi, Jianlin Li, Yongfeng Liang, David Wood, Timothy J. Singler, Congrui Jin, "Analysis of electrolyte imbibition through lithium-ion battery electrodes", *Journal of Power Sources*, 424 (2019) 193-203.

4. Chengyu Mao, Seong Jin An, Harry Meyer, Jianlin Li, Marissa Wood, Rose Ruther, and David Wood, "Balancing formation time and electrochemical performance of high energy lithium-ion batteries", *Journal of Power Sources*, 402 (2018) 107-115..

5. Ali Davoodabadi, Jianlin Li, Yongfeng Liang, Robert Wang, Hui Zhou, David Wood, Timothy Singler, and Congrui Jin, "Characterization of surface free energy of composite electrodes for lithium-ion batteries", *Journal of the Electrochemical Society*, 165(11) (2018) A2493-A2501.

6. Rong Xu, Luize Scalco de Vasconcelos, Junzhe Shi, Jianlin Li, and Kejie Zhao, "Disintegration of meatball electrodes for $LiNi_xMn_yCo_zO_2$ cathode materials", *Experimental Mechanics*, 58 (2018), 549-559.

- **Selected Presentations**

1. Jianlin Li, Ali Davoodabadi, Congrui Jin, David Wood, "Understanding materials processing effect on surface energy and electrolyte wettability of lithium-ion battery electrodes", 2019 International Battery Seminar, Fort Lauderdale, FL, March 25-28, 2019. (Invited)

2. Jianlin Li, "Advanced Materials Processing and Tailored Electrode Architectures for Low-Cost and High Energy Density Batteries", A123 Systems, Waltham, MA, November 29, 2018. (Invited)