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

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Annual Merit Review

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Overview

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

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

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.

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
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 mA/cm²) 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

<table>
<thead>
<tr>
<th>Status</th>
<th>SMART Milestones</th>
<th>Description</th>
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<tbody>
<tr>
<td>12/31/18</td>
<td>Quarterly Progress Measure (Regular)</td>
<td>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.</td>
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<tr>
<td>3/31/18</td>
<td>Annual Milestone (stretch)</td>
<td>Quantify impedance (via AC impedance technique) of Gen 3 structured, multilayer anode and cathode coatings (6 mAh/cm²) with different individual layer thickness and different total thickness to achieve 225-250 Wh/kg improvement in cell energy density.</td>
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<tr>
<td>To be completed by June</td>
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<tr>
<td>6/30/19</td>
<td>Annual Milestone (stretch)</td>
<td>Quantify impedance of (via AC impedance technique) of Gen 3 structured, multilayer anode and cathode coatings (8 mAh/cm²) with different total thickness to achieve &gt; 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.</td>
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<tr>
<td>9/30/19</td>
<td>Go/No-Go Decision</td>
<td>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 &gt; 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.</td>
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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/cm²) 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 ft² (two 700 ft² 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/cm²) through aqueous processing.
• Discovered variation in binder coverage on NMC811 between NMP-based and aqueous processing.
• Created laser structured NMC811 cathodes (6 mAh/cm²) 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.
Zeta potential measurement in water

- Zeta potential of carbon black is $<-40$ mV at pH $\geq 7$, 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.
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

- Single-layer pouch cells with aqueous- and NMP-processed NMC 811 cathodes and Superior SLC 1520T graphite anodes
  - NMC 811 Loading: 11.6 mg/cm² (aqueous) and 11.3 mg/cm² (NMP)
- Water-exposed NMP: NMC811 powder was saturated in water for 4 h, dried, and then fabricated into electrodes with NMP-based processing

- 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 \(\rightarrow\) ascribed to various electrode formulations.

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/cm²
  - **Aqueous 1:** 90 wt.% NMC811/ 5 wt.% Carbon Black/ 1 wt.% CMC Binder/ 4 wt.% Solvay Latex Emulsion Binder; 11.4 mg/cm²
  - **Aqueous 2:** 90 wt.% NMC811/ 5 wt.% Carbon Black/ 1 wt.% CMC binder/ 4 wt.% JSR TRD202A Emulsion Binder; 11.4 mg/cm²
  - **Aqueous 3:** 90 wt.% NMC811/ 5 wt.% Carbon Black/ 5 wt.% LiPAA Binder; 11.6 mg/cm²

- 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)

- 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.
Technical Accomplishments—Higher ASI in the Aqueous Processed NMC811 at 30°C and 45°C (FY19)

- 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)

\[ D = 4 \left( \frac{\gamma}{\mu} \right) \left( \frac{kB}{2\epsilon r_e} \right) \cos \theta \]

- 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.

**Coefficient of permeation (COP)**

\[ \text{COP} = \frac{\gamma \cos \theta}{2\mu} \]

**Solid permeability coefficient (SPC)**

\[ \text{SPC} = \frac{kB \cos \theta}{2\epsilon r_e} \]
Technical Accomplishments—Understanding of Electrolyte Imbibition-Processing Relation (FY19)

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)

$G' \rightarrow \text{storage modulus}$

$G'' \rightarrow \text{loss modulus}$

- 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., *Electrochimica Acta*, under review.
Technical Accomplishments—Successful Fabrication of Thick NMC811 Cathode (7 mAh/cm²) via Aqueous Processing (FY19)

- 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/H₂O 2/8).
- Flexibility of the thick electrodes needs to be improved.
- The thick electrodes suffer from mass transport limitation.

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<th>NMC811</th>
<th>Conductive Additive</th>
<th>Binder</th>
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<tr>
<td>Mass Fraction (%)</td>
<td>90</td>
<td>5</td>
<td>5</td>
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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/cm²).
  – 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/cm²) 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.

• One reviewer commented during the poster section that high temperature performance needed to be evaluated.
  – HPPC and cycle life at 45°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

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• ORNL Contributors:
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  • 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**


  6. Rong Xu, Luize Scalco de Vasconcelos, Junzhe Shi, Jianlin Li, and Kejie Zhao, “Disintegration of meatball electrodes for LiNi_{x}Mn_{y}Co_{2}O_{2} cathode materials”, *Experimental Mechanics*, 58 (2018), 549-559.

- **Selected Presentations**
