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

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Overview

Timeline

- Task Start: 10/1/14
- Task End: 9/30/22
- Percent Complete: 85%

Budget

- $350k in FY20
- $400k in FY21

Barriers

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

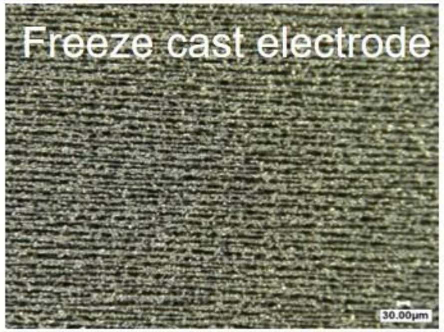
Partners

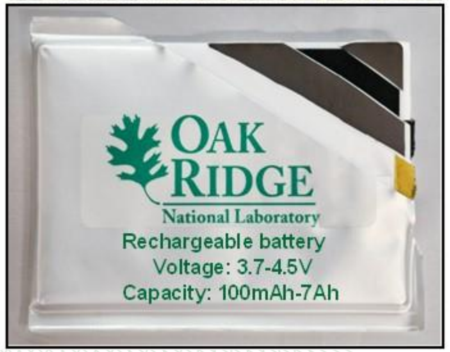
- Interactions/Collaborations
  - National Laboratories: ANL, SNL, INL
  - Universities: KIT, SUNY-Binghamton, University of Picardy Jules Verne, University of Arkansas
  - Battery Manufacturers: XALT Energy, Navitas Systems
  - Material Suppliers: PPG Industries, Targray, Superior Graphite, IMERYS, JSR Micro, Solvay Specialty Polymers, Ashland, Forge Nano
  - Equipment Manufacturer: Frontier Industrial Technology, B&W MEGTEC
- Project Lead: ORNL

Relevance & Objectives

- **<u>Main Objective</u>:** To improve cell energy and power density and reduce battery pack cost by manufacturing thick electrodes with tailored electrode architecture via advanced processing and high-energy, high-voltage cathode materials.

- **Objectives in this period**
  - Apply aqueous processing to Ni-rich layer oxides (NMC811 and NCA)
  - Fabricate thick (6-8 mAh/cm^2), crack-free composite NMC811 cathode via aqueous processing
  - Develop tailored electrode architecture via freeze tape cast
  - Develop composite cathode via co-sintering of cathode and solid-state electrolyte
  - Characterize electrolyte imbibition rate in separator and simulate the electrolyte imbibition in lithium-ion cells
  - Assemble pouch cells with NMC811 and thick, tailored electrode architecture
  - Demonstrate a solid-state battery with an energy density ≥350 Wh/kg





Project Milestones

Status	SMART Milestones	Description
11/30/20 ✓	Quarterly	Installation and commission of the freeze tape caster (delayed to May 2021 due to COVID pandemic and rebuild in the electric circuit to meet NRTL standard)
3/31/21 Delayed by 3 months due to limited lab access during COVID-19 pandemic.	Annual Milestone (stretch)	Fabrication of thick multilayer electrode NMC811/graphite coating with high energy and power density at 8 mAh/cm^2. Quantify impedance (via AC impedance technique) of Gen 3 structured, multilayer anode and cathode coatings (multi-pass, dual slot-die coated, etc. at 8 mAh/cm2) with different individual layer thicknesses and different total thicknesses 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.
9/30/21 On track	Annual Milestone Go/No Go	Demonstration of a working solid-state battery with an areal loading with 3 mAh/cm^2, demonstrating 30 cycles under C/2 with 100% excess Li and >350 Wh/kg.

Project Approach

- **Problems:**
  - Corrosion of aluminum foil from aqueous NMC slurry
  - Cost effective methods of producing thick electrode architectures
  - Cracking of thick coatings with water as solvent
  - Lithium-ion mass-transport limitations thick electrodes
  - Low performance of cathodes for solid-state batteries

- **Technical approach and strategy:**
  - Evaluate stability of high-energy and high-voltage cathodes (NMC811, LMO, NCA) during aqueous processing
  - Incorporate aqueous processing to fabricate NMC811 and NCA cathodes
  - Fabricate crack-free NMC811 cathodes with high areal loading (6-8 mAh/cm^2) via aqueous processing
  - Freeze cast electrodes to overcome Li^+ mass transport limitations
  - Evaluate and simulate electrolyte imbibition in porous electrodes and separator
  - Characterize advanced electrode microstructures
  - Co-sinter cathode and solid-state electrolyte and evaluate cathode electrolyte compatibility

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

Planetary Mixer (≤2 L)

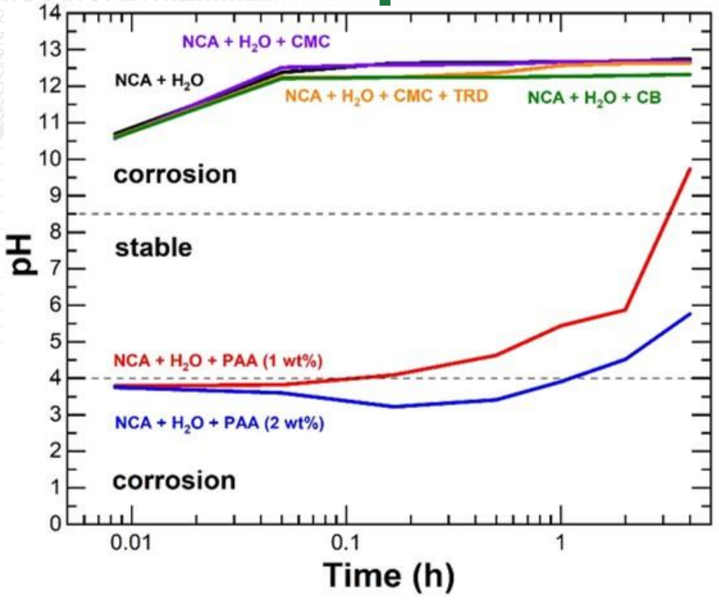
Dual slot-die coater

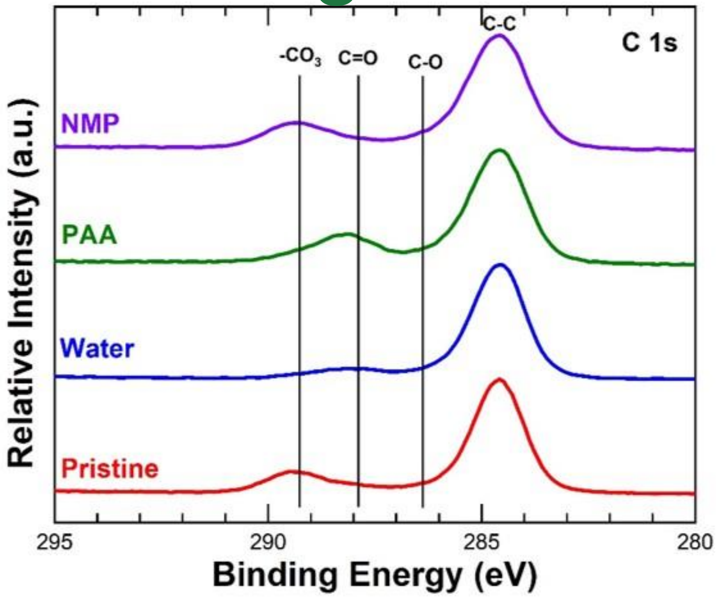
Calender

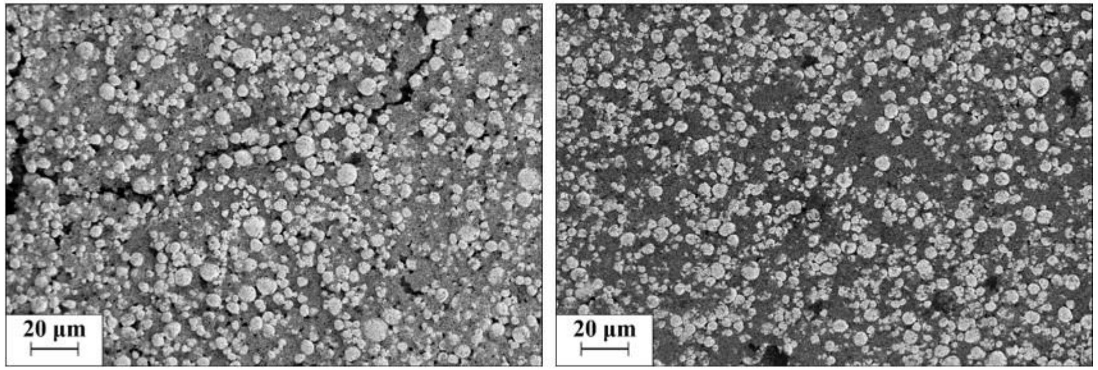
<u>Dry room for pouch cell assembly</u>

- 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 50-100 cells.

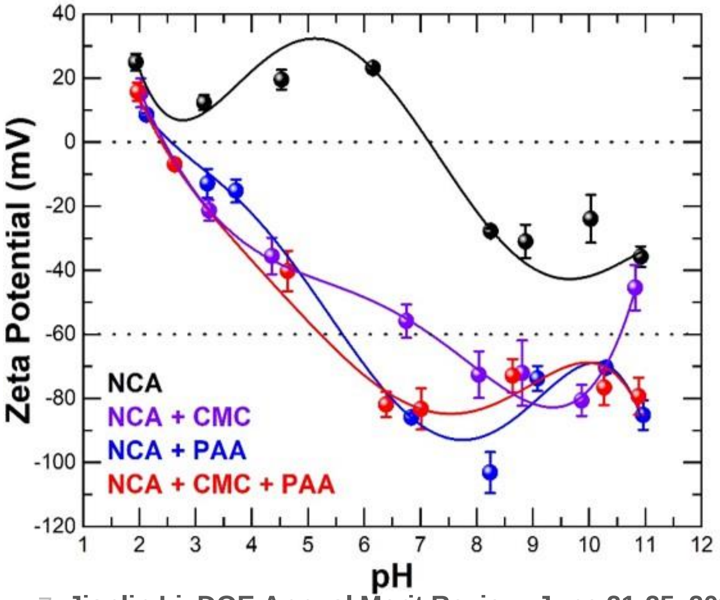
PAA Acts as pH Modifier, Dispersant, and Binder, All-in-One to Enable Aqueous Processing for NCA Cathode

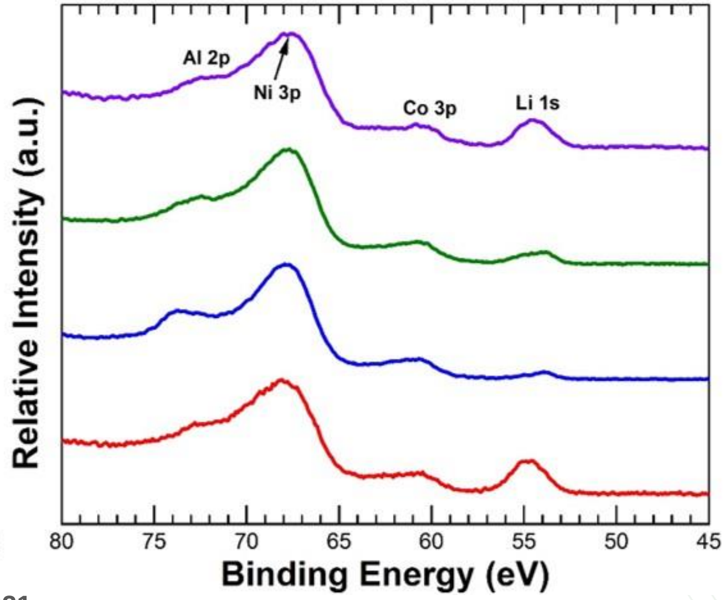






Uncalendered Calendered



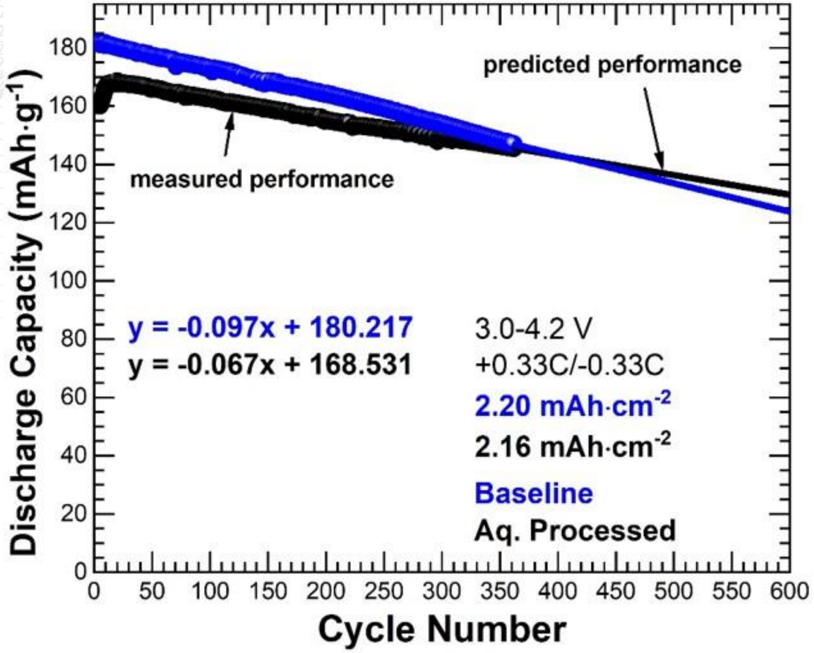


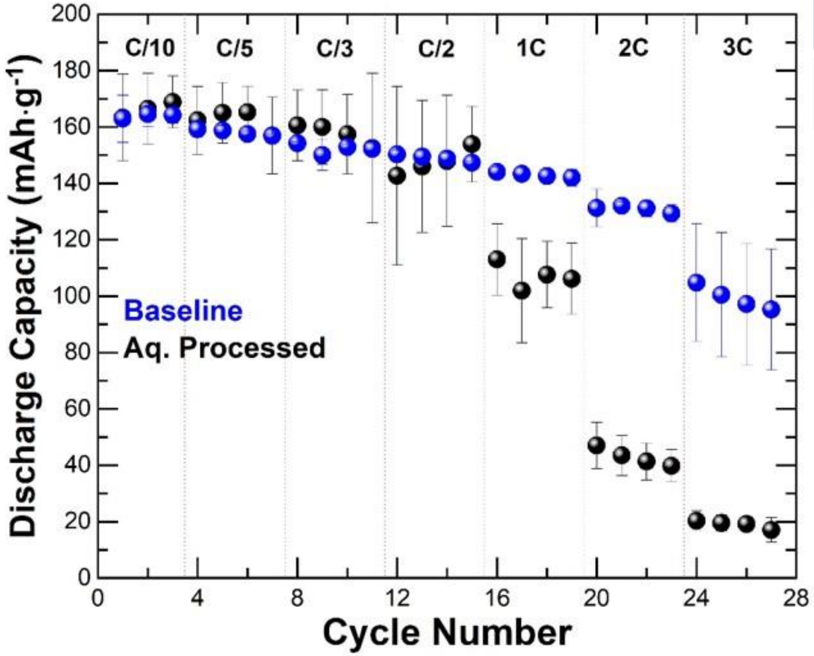
- Slurry components (CMC or TRD 202A binder, carbon black) do not influence slurry pH, though PAA (1 or 2 wt%, MW = 450,000 g·mol^{-1}) makes significant difference
- CMC imparts good electrostatic stability to NCA particles, PAA improves it even further
- PAA adsorbs to NCA particle surface (C=O peak in C 1s scan)
- PAA adsorption prevents detrimental Al dissolution (shift in Al 2p peak) that renders untreated particles incompatible with aqueous processing
- Very minor cracking in uncalendered aqueous-processed NCA cathode, issue is resolved with calendering

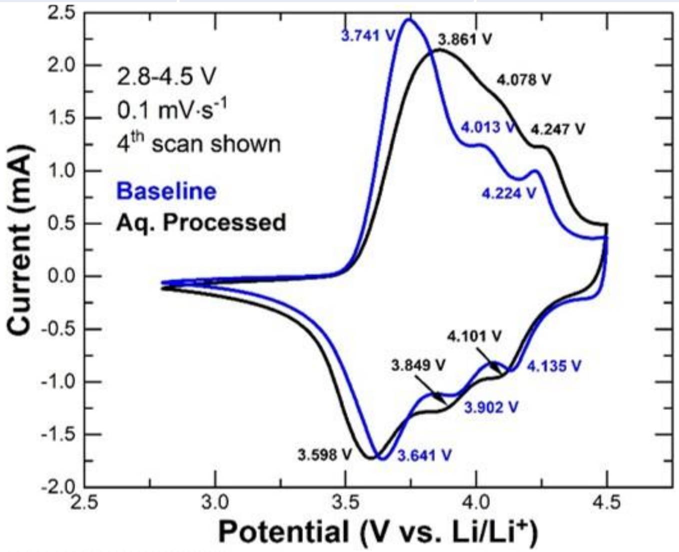
Hawley et al., Electrochimica Acta 380 (2021), 138203

Aqueous Processed NCA Cathodes Demonstrated Good Cycle Life but Lower Rate Performance

Cathode	Initial R_{ct}	R_{ct} After 100 Cycles
Baseline	11.2	8.7
Water	72.4	70.6





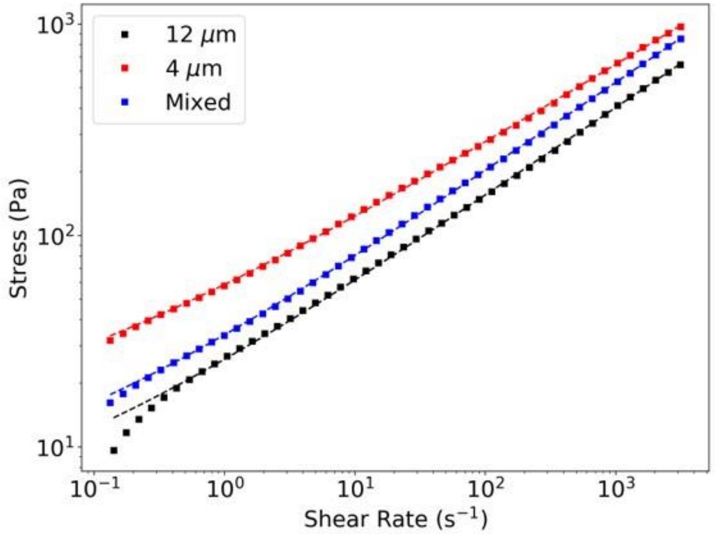


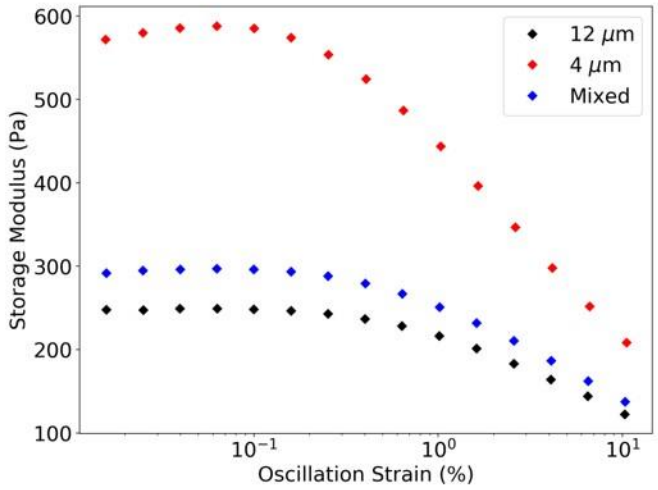
Hawley et al., Electrochimica Acta 380 (2021), 138203

- Realistic cell conditions considered (graphite anode, N:P ratio = 1.1, capacity = 2.2 $mAh\cdot cm^{-2}$, ~34% porosity)
- Initial discharge capacity lower for aqueous-processed cathode compared to NMP-processed baseline (160.4 vs. 181.5 $mAh\cdot g^{-1}$) due to cation exchange
- Water-processed cathode reaches max capacity at Cycle 20 (168.5 $mAh\cdot g^{-1}$) due to reverse cation exchange
- Aqueous-processed cell reaches 80% of initial discharge capacity at Cycle 600, baseline reaches 80% initial discharge capacity at Cycle 360 (predicted), crossover occurs at Cycle 388 (predicted)
- EIS, CV, and rate capability show higher charge transfer resistance (R_{ct}) in water-processed cathode than baseline
- Could optimize performance by reducing PAA amount or improving adhesion with current collector (corona treatment, chemical etching of current collector, etc.)

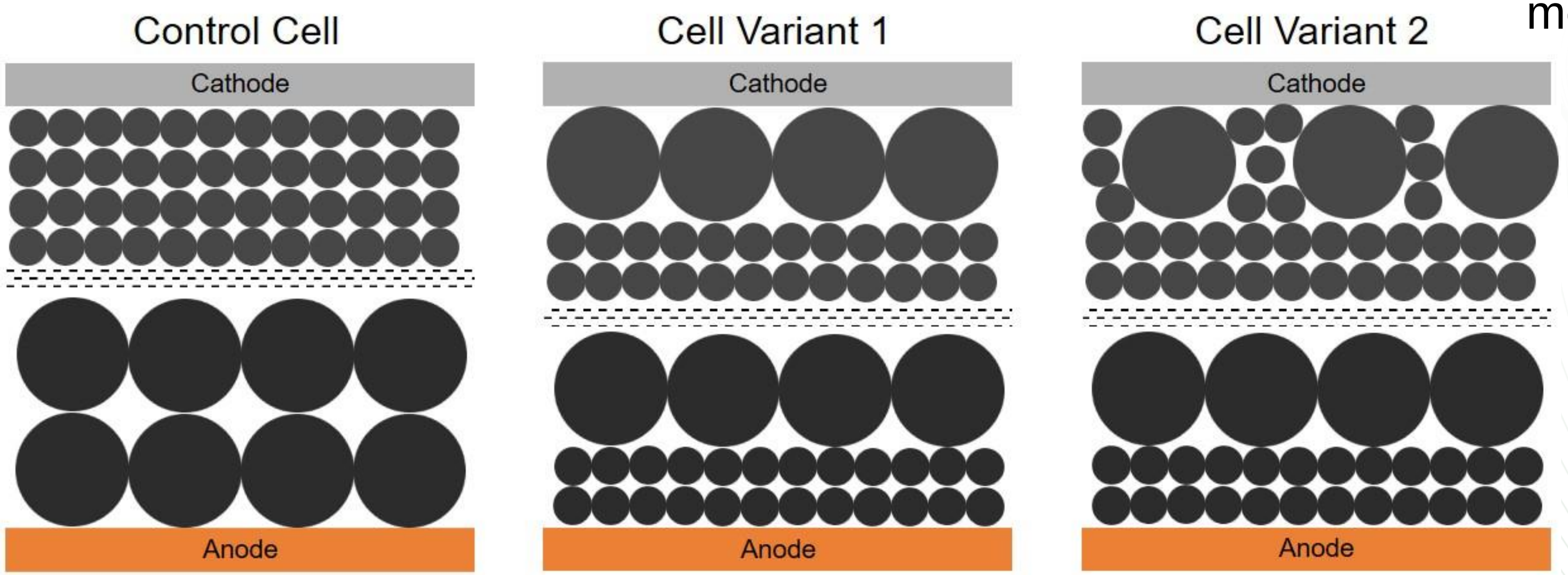
Developed Layer-Structured Cathodes to Improve Rate Performance

- Create layered structure with various particle size: 12 μm and 4 μm NMC 811, 1520 T and 1506 T graphite
- Double pass slot die coating
- 4 mAh/cm^2 per pass for a total of 8 mAh/cm^2
- 30% porosity





- Smaller particle size➔Increased storage modulus➔ stronger binding network



Particle Size	Power – Law Index	Yield Stress (Pa)
12 μm	0.42	4.17
4 μm	0.38	11.40
Mixed	0.42	5.62

Layer Structured Electrodes Improved Rate Performance

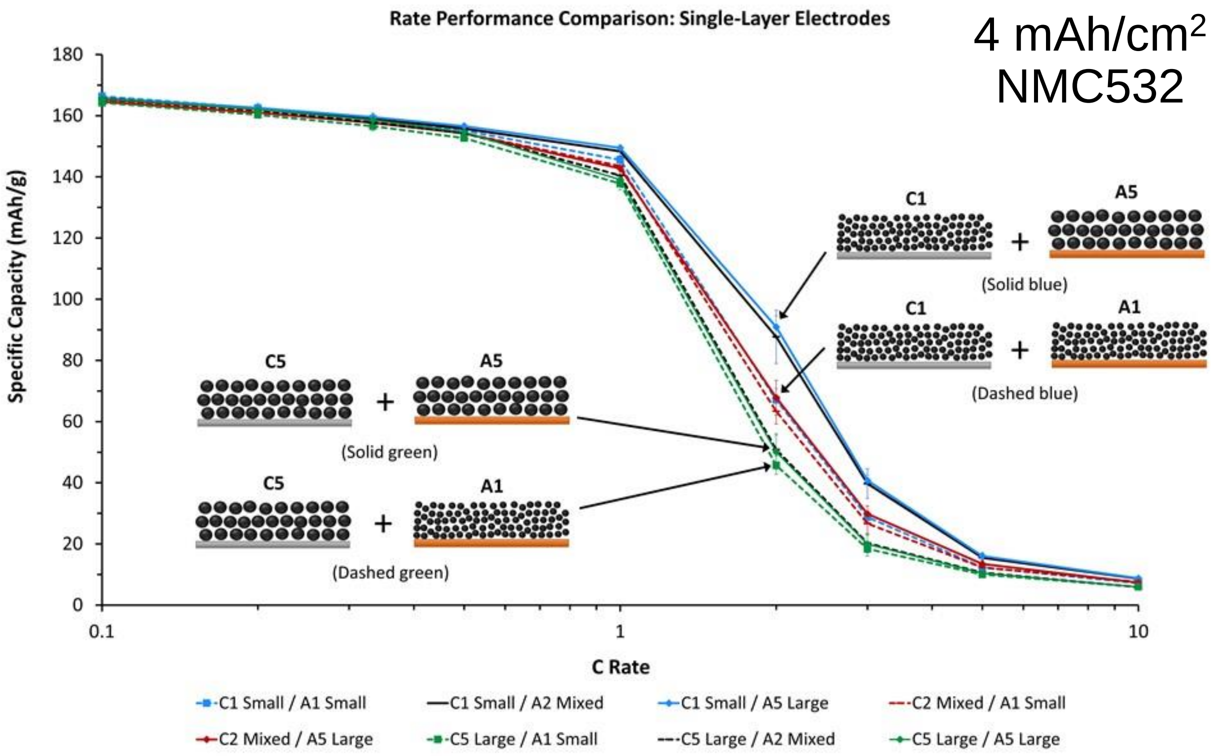
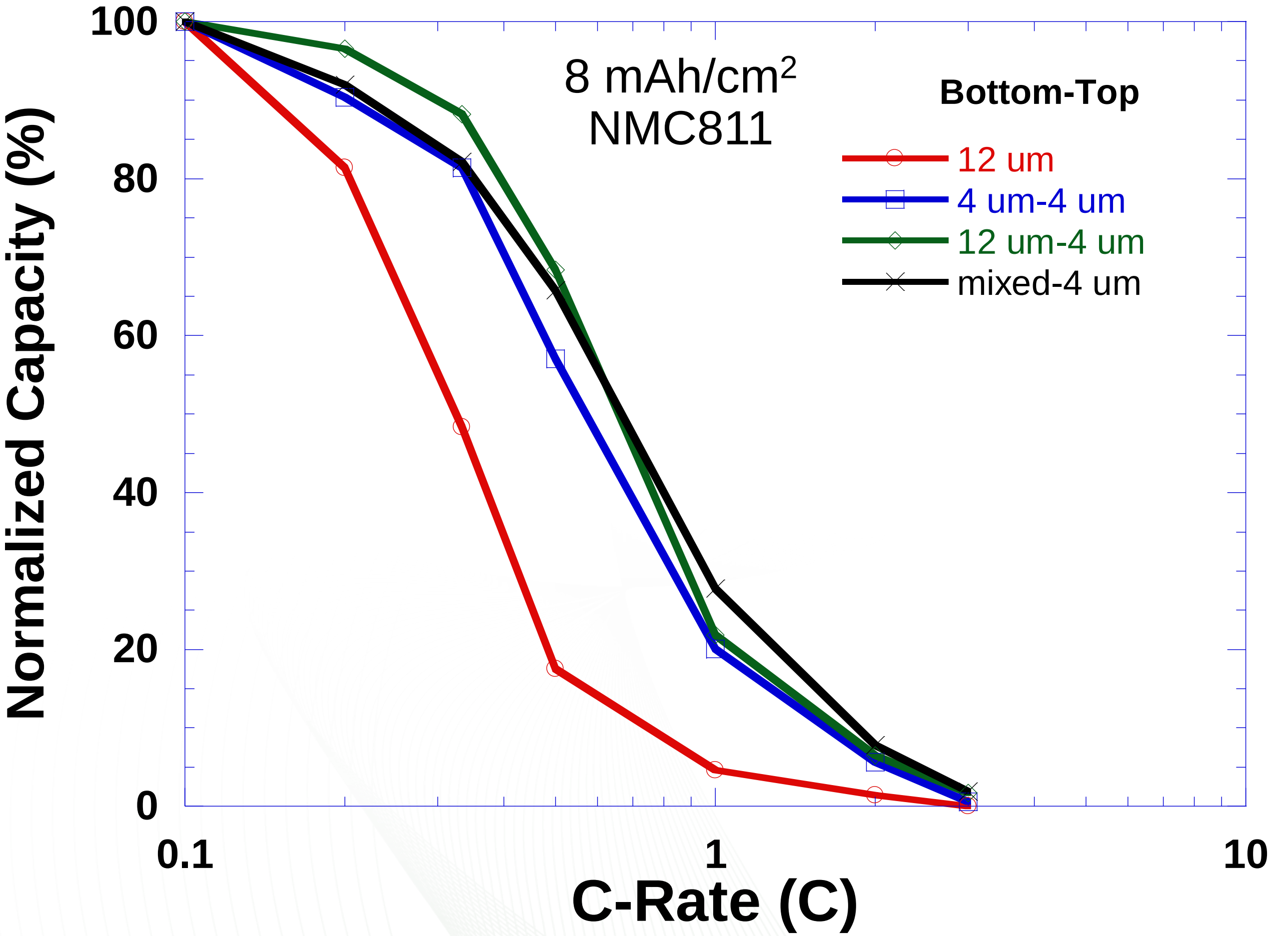


Figure 3. Rate performance comparison for single-layer pouch cells assembled with different *single-layer* cathode/anode combinations. The charge rate was held constant at C/5 while the discharge rate was varied. Each point is an average of 3 cells, and error bars represent the standard deviation of these 3 cells. (Wood, et al., Journal of Power Sources, under review)

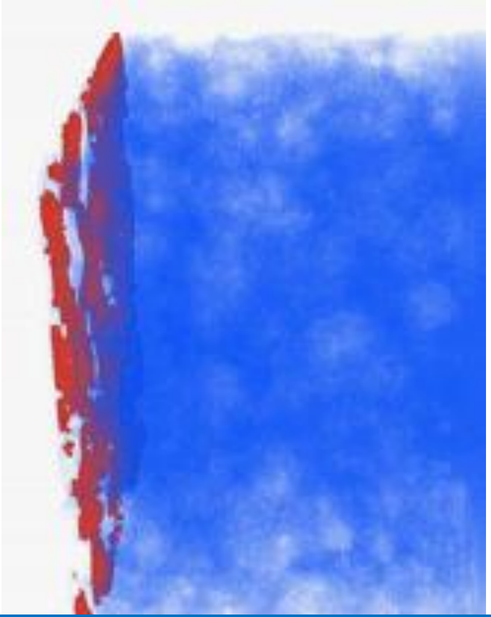


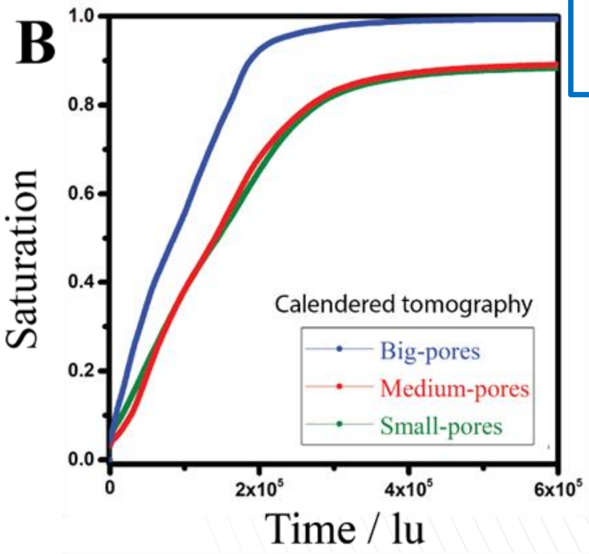
- The three configurations with 2-layer structured electrodes demonstrated improved rate performance compared to the baseline (1-layer structure).
- Having a large particle in the bottom layer for the cathodes seems favorable to rate performance.

Characterized and Simulated Electrolyte Wetting

Separator/Electrode Sample	Porosity	$D_{th}\ (m^2/s \cdot 1e-9)$	$D_{in}\ (m^2/s \cdot 1e-9)$
Celgard 2325	39%	1.13 ± 0.06	—
Celgard 2400	41%	1.48 ± 0.06	—
Celgard 2500	55%	6.68 ± 0.59	—
Uncoated Entek EPX	54%	2.11 ± 0.18	0.32 ± 0.06
Coated Entek EPX	54%	1.62 ± 0.23	4.75 ± 0.46
NMC532-NMP	55%	55.4 ± 3.70 [22]	55.4 ± 3.70 [22]
A12-NMP	55%	115.3 ± 4.30 [22]	115.3 ± 4.30 [22]

- Electrolyte wetting:
  - graphite anode > NMC cathode > separator
- Created lattice Boltzmann model to simulate electrolyte wetting in batteries
- Able to determine correlation between saturation degree and electrode/electrolyte properties



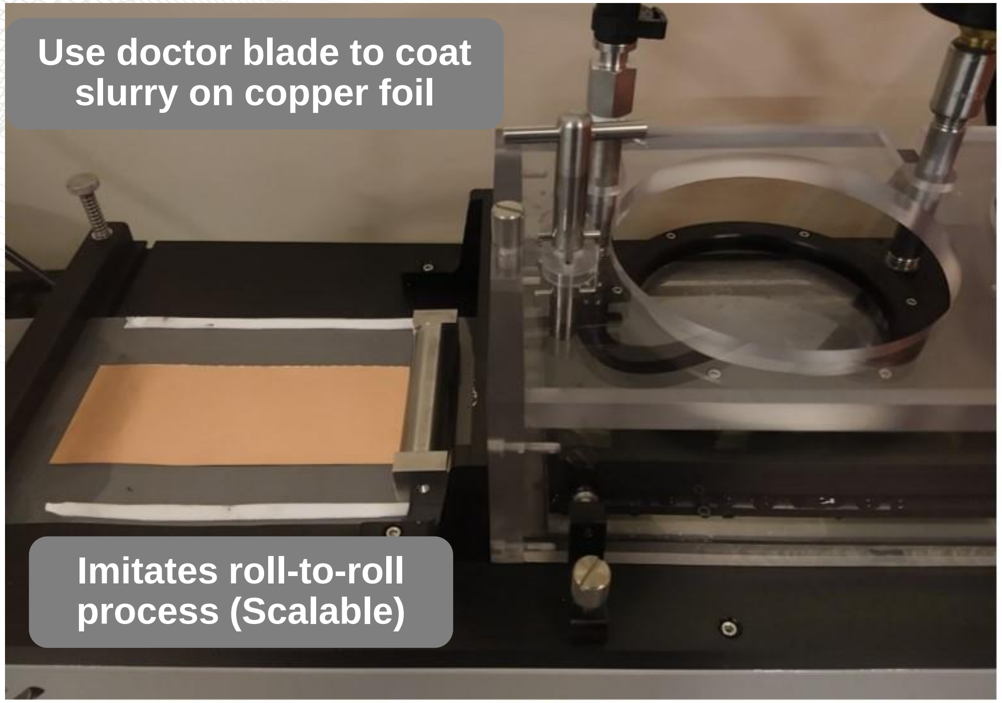


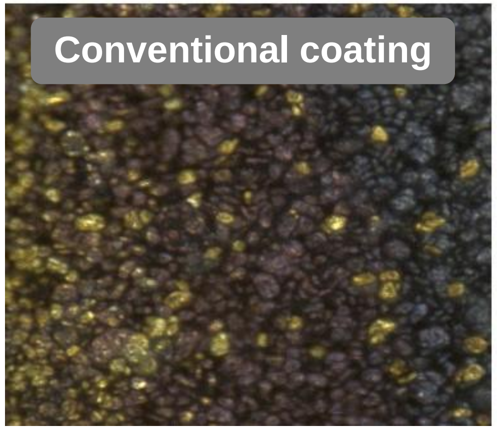
Davoodabadi et al., Extreme Mechanics Letters 40 (2021) 100960

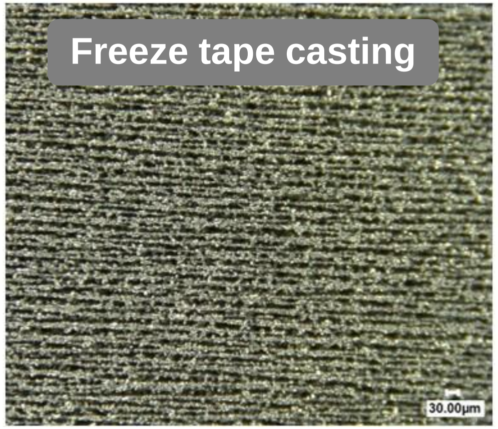
Shodiev et al., Energy Storage Materials 38 (2021) 80-92

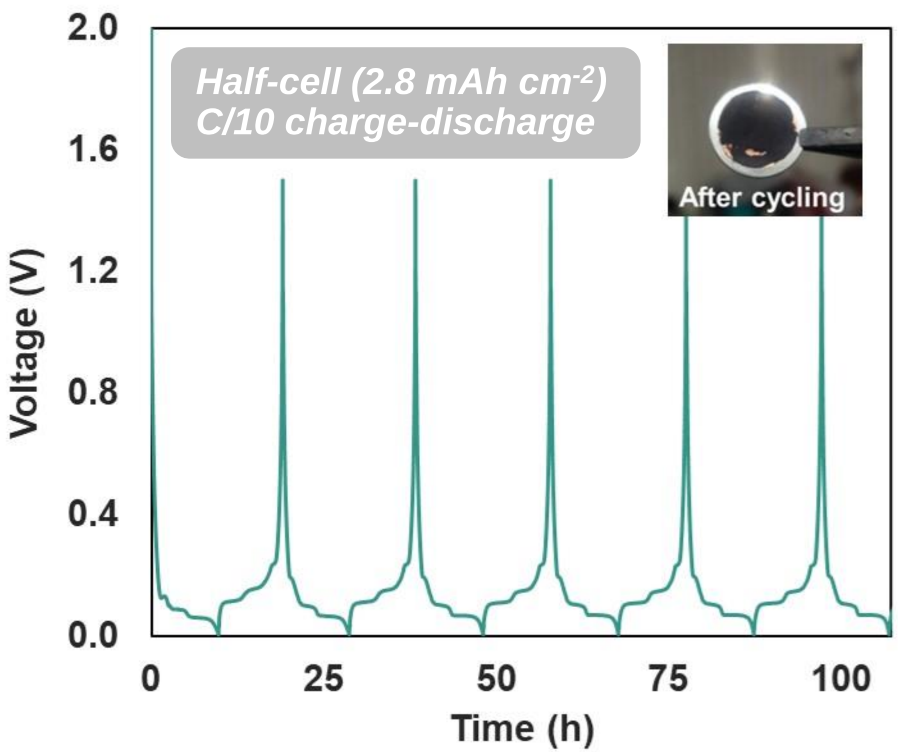
Electrolyte impregnation on 3D within NMC electrode (Geometry of electrode from Tomography)

Developed Graphite Anode via Freeze Tape Cast



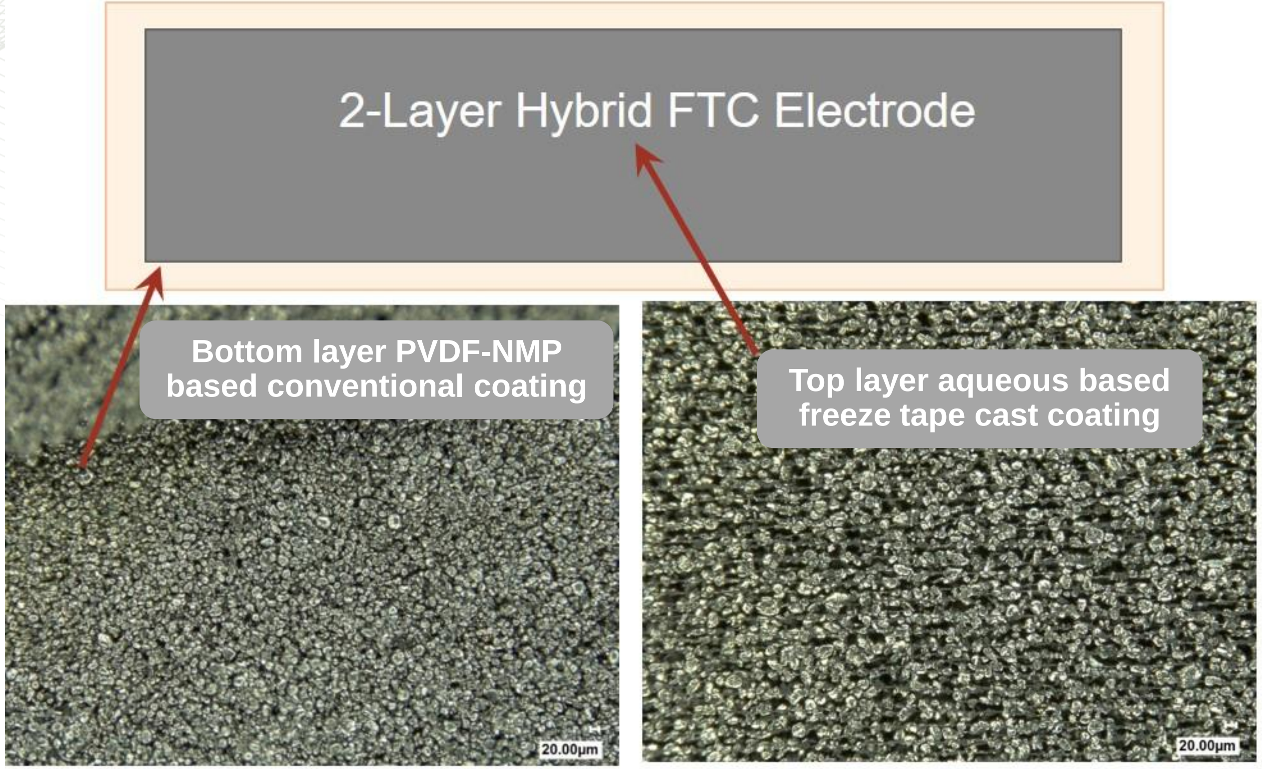


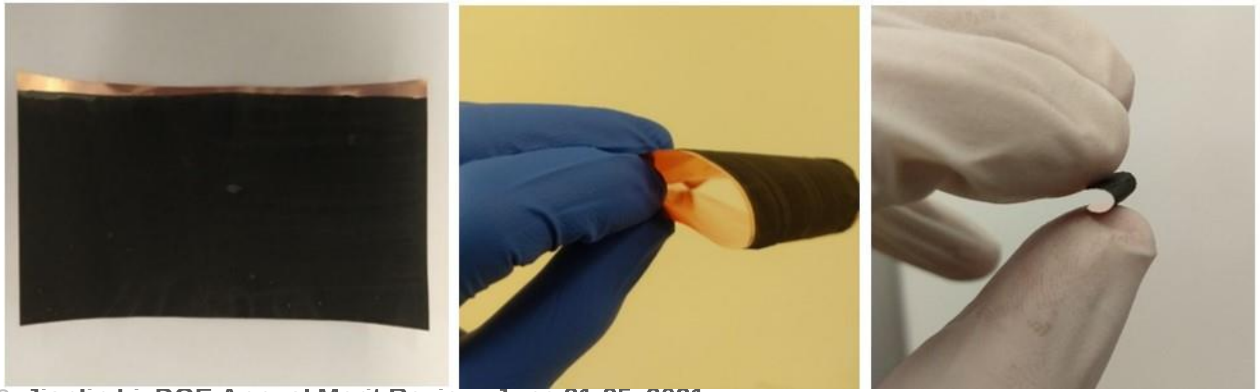


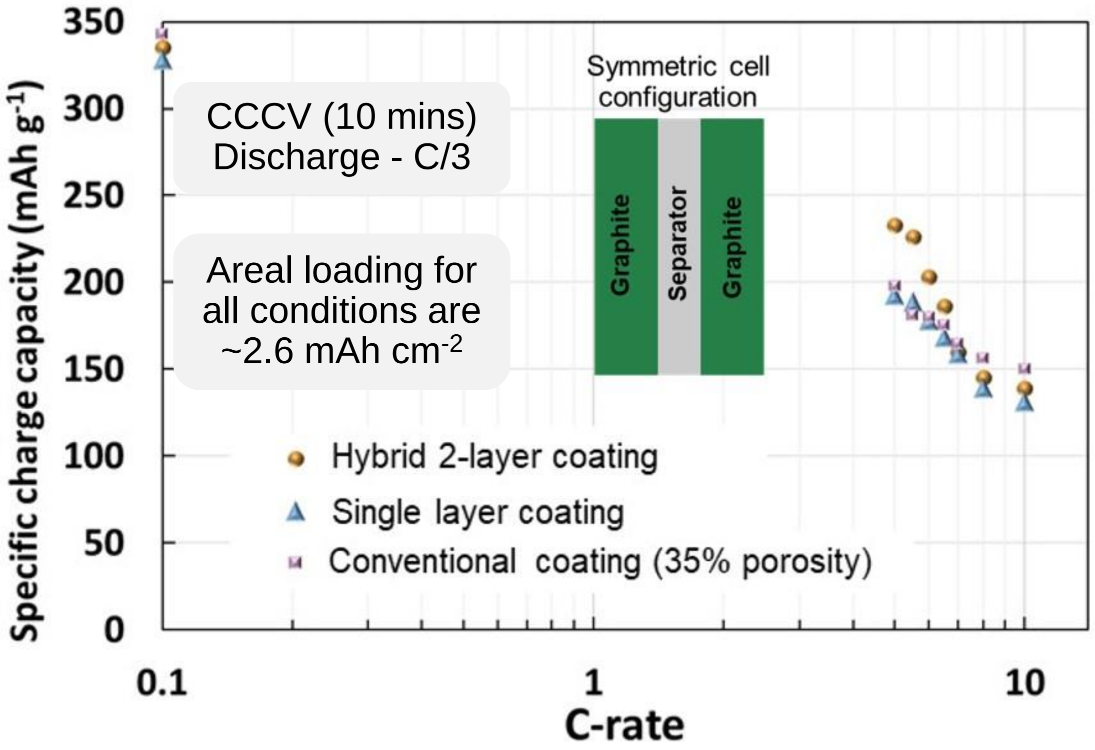


- Aligned structure with freeze tape cast
- Good cycling with half cell configuration at C/10 charge-discharge rate
- Show poor structural integrity after disassembling the half cell

Developed 2-Layer Structured Anodes Via Freeze Tape Casting and Demonstrated Improved Rate Performance

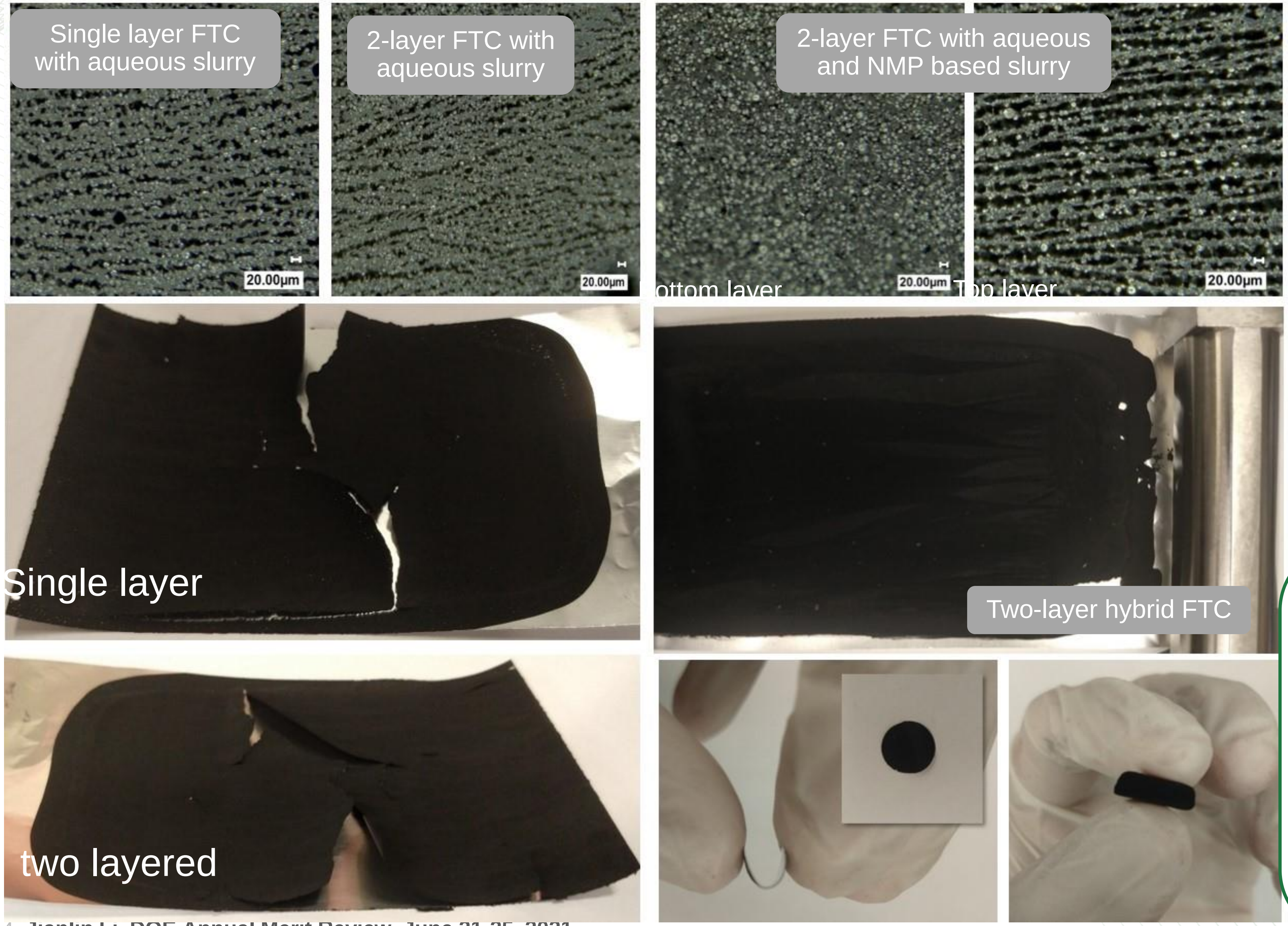


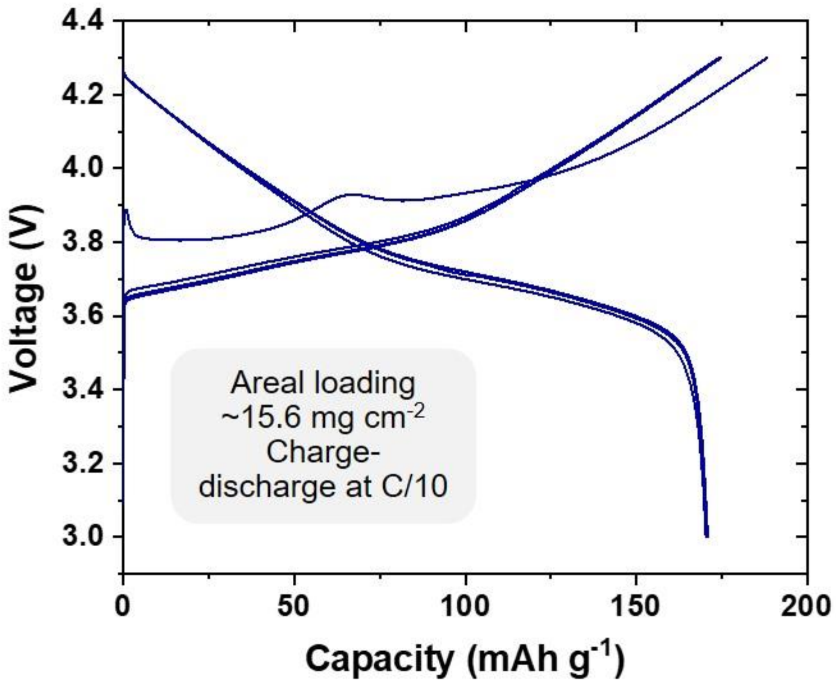




- Symmetric cell configuration with 50% SOC electrodes are used for rate capability studies
- ~20% improvement in charge capacity at 5C charge rate with 2-layer hybrid freeze tape cast anode

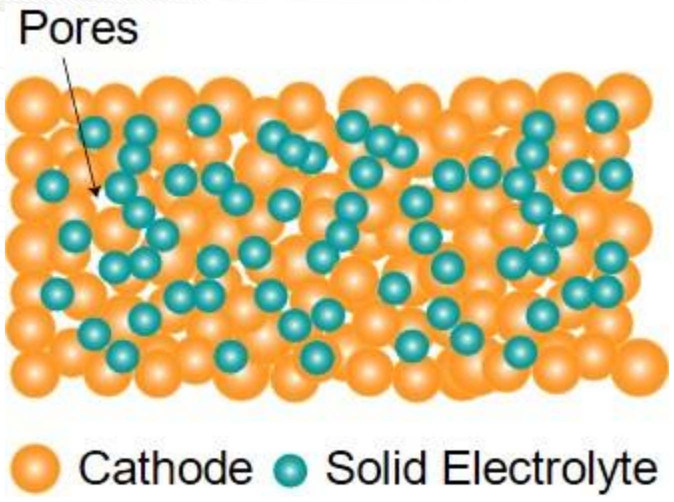
Developed 2-Layer Structured Cathodes to Improve Mechanical Integrity

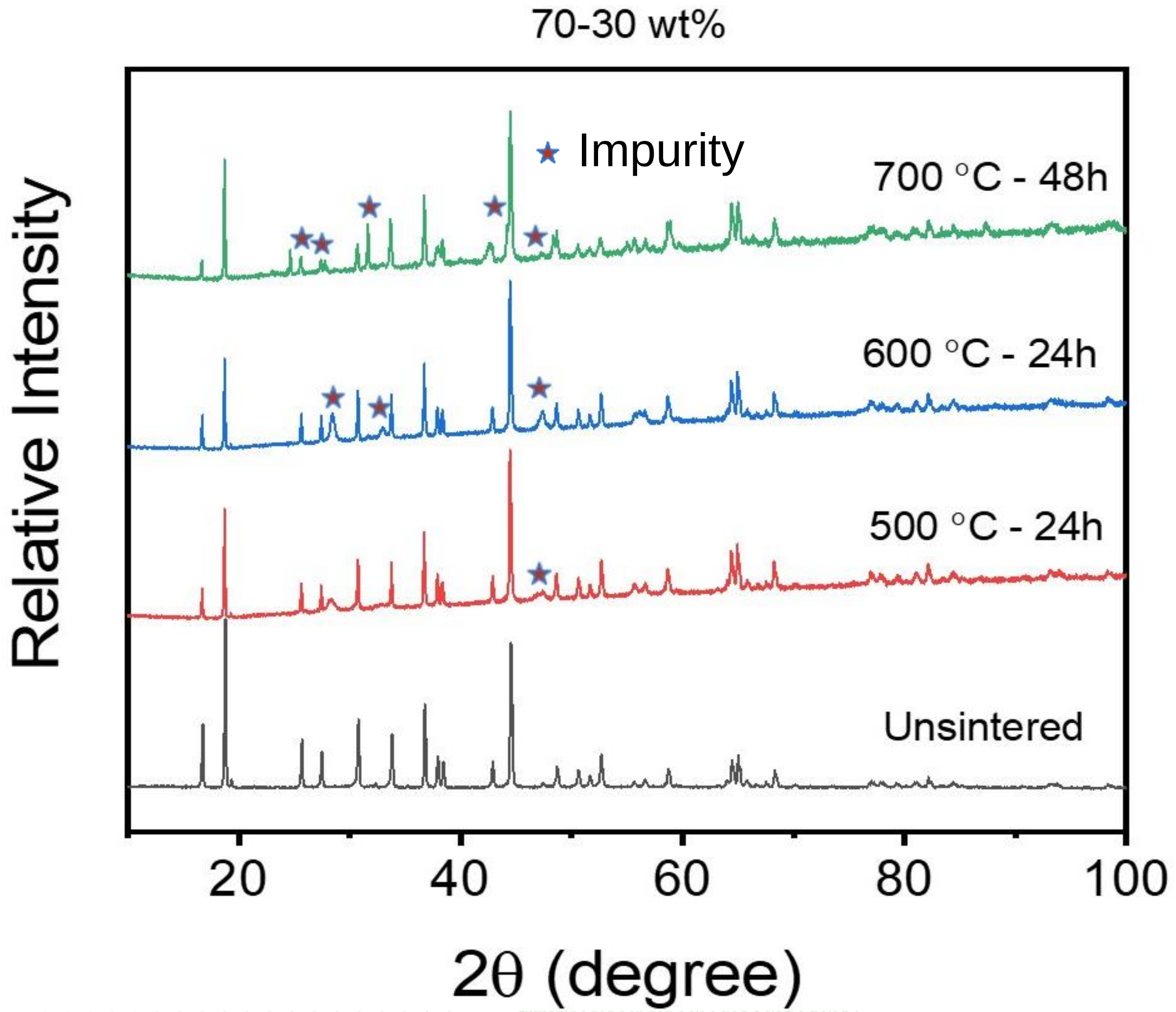




- Cracking of single/two-layer freeze casting using aqueous based slurry
- Hybrid two-layer FTC with PVDF/NMP based coating as bottom layer (conventional method) and aqueous slurry coating on top (freeze tape cast)

Optimization of Composite Cathode by Co-Sintering of LLZO and NMC622



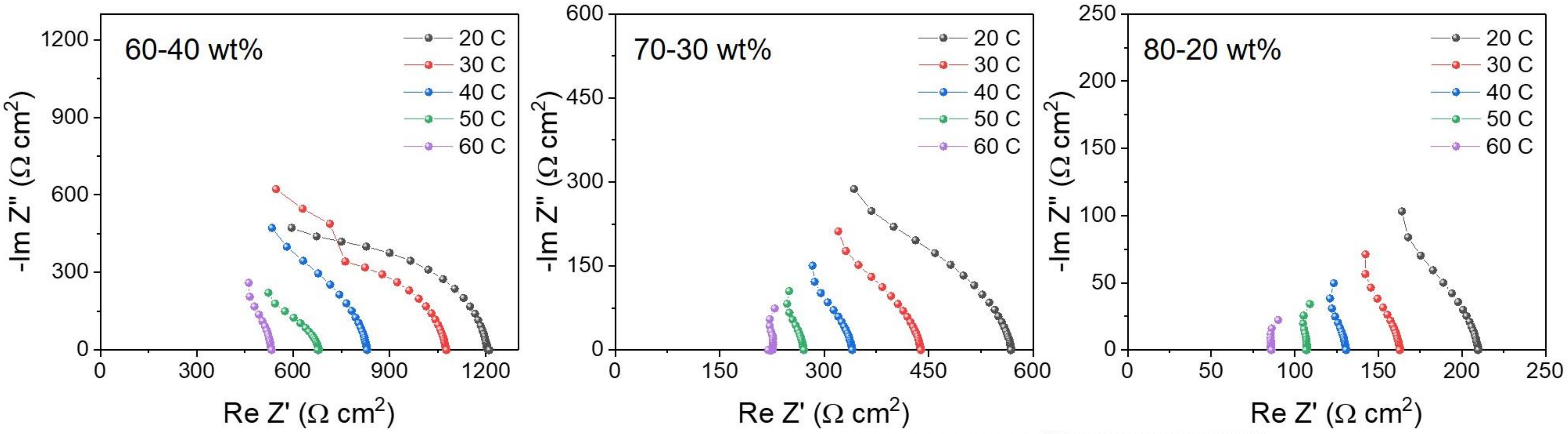


Composite cathode for solid state batteries

- Ion conduction pathway in cathode
- Porosity increases tortuosity of Li-ions
- Sintering can be utilized to reduce the number of pores in composite cathode
- Chemical stability of solid electrolyte and cathode particles at higher temperatures
- Porosity, conductivity and interphase trade-off

Resistance Decreased with Increasing NMC Content

Composite cathode sintered at 600 ^{o}C for 24 h in air



Composite cathode sintered at -
500 ^{o}C for 24 h showed high porosity and high ASR
700 ^{o}C for 24 h showed more resistive interphases and high ASR

Collaborations

- Partners
  - National Labs: Argonne National Laboratory, Sandia National Laboratory, Idaho National Laboratory
  - Battery Manufacturers: XALT Energy, Navitas Systems
  - Active Material Suppliers: Targray, Superior Graphite, Forge Nano
  - 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, University of Picardy Jules Verne, University of Arkansas
- Collaborative Activities
  - Characterization of surface energy and electrolyte wetting with Binghamton University (weekly)
  - Electrolyte wetting simulation with University of Picardy Jules Verne (monthly)
  - Synthesis of small NMC811 particles with Dr. Ozge Kahvecioglu Ferdun at ANL (BAT167)
  - Binder selection and optimization with Solvay, Ashland, and JSR (bi-annual)
  - Sharing of results with strategic battery manufacturers (Navitas Systems and XALT)

Remaining Challenges and Barriers

- **Main Barriers**
  - Sluggish mass transport in thick electrodes
  - Incompatibility between cathode and electrolyte in solid-sate batteries
  - Lack of established processes in fabricating solid-state-batteries
- **Technical Challenges**
  - Development of low temperature densification method for composite cathode
  - Development of processes to fabricate thin solid-state electrolyte with excellent conductivity and processibility
  - Optimization of electrode architecture via freeze tape cast for low tortuosity and improved mass transport

Future Work

- Remainder of FY21
  - Fabricate composite NMC cathode with 3 mAh/cm^2 for solid-state batteries and characterize the cathode properties.
  - Fabricate polymer electrolyte for solid-state batteries.
- Into FY22
  - Optimize co-sintering of cathode and solid-state electrolyte.
  - Freeze tape cast NMC cathodes for solid-state battery application.
  - Optimize freeze tape casting conditions for low tortuosity electrode architecture.
  - Develop methods for densifying freeze-tape-cast electrodes.
  - Evaluate energy and power density of the electrodes.
  - Evaluate cathode and solid-state electrolyte interface.

- Commercialization: Highly engaged with potential licensees; high likelihood of technology transfer because of new processes and equipment compatibility; 3 total patents issued on aqueous processing methodologies.

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 liquid-phase Li^+ mass-transport limitations in high energy electrodes.
  - Develop electrode formulation and processing to enable thick electrode manufacturing.
  - Develop tailored electrode architectures to overcome Li^+ mass-transport limitations.
  - 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 various cathode materials with aqueous processing; Enabled aqueous processing for NCA cathode fabrication; Fabricated thick, crack-free NMC811 cathodes (6-8 mAh/cm^2); demonstrated excellent rate performance and cyclability of aqueous processed NMC811 cathodes; improved rate performance of thick NMC811 cathode via 2-layer and laser structuring, respectively; correlated electrolyte imbibition and processing relationship; Developed hybrid electrode structure via freeze tape cast; investigated co-sintering of composite cathodes for solid-state batteries.
- **Collaborators:** Extensive collaborations with national laboratories, universities, lithium-ion battery manufacturers, raw materials suppliers, and coating equipment manufacturers.
- **Commercialization:** 3 patents issued; high likelihood of technology transfer due to significant cost reduction benefits and equipment compatibility.

Selected Responses to Specific FY20 DOE AMR Reviewer Comments

- Project not reviewed in 2020

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