High-Nickel, Cobalt-Free Cathode Materials for Lithium-Ion Batteries

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The University of Texas at Austin

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Project ID #: bat415

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OVERVIEW

Timeline

- Project start date: January 2019
- Project end date: March 2022
- 70% complete

Budget

- Total project funding
  - DOE: $2,400,000
- Funding received in FY 2019
  - $800,000
- Funding received in FY 2020
  - $800,000
- Funding for FY 2021
  - $800,000

Barriers

- Barriers
  - Cycle and calendar life
  - Abuse tolerance
  - Storage stability
- Targets
  - Affordable, high-performance layered oxide cathodes with low or no cobalt content (≤ 50 mg Co/Wh)

Partners

- NREL
- Tesla, Inc.

RELEVANCE

Relevance

- Elimination of cobalt from lithium-ion cathode materials, while maintaining high-energy density and reducing cost, to improve the sustainability of lithium-ion cells

Objectives

- Develop high-nickel, low-cobalt cathodes with long cycle life and high-energy density
  - deliver a specific energy of ≥ 600 Wh kg^{-1}
  - reduce cobalt content to ≤ 50 mg Wh^{-1}
  - realize ≤ 20% energy fade over 1,000 cycles and calendar life ≥ 15 years at C/3 deep discharge

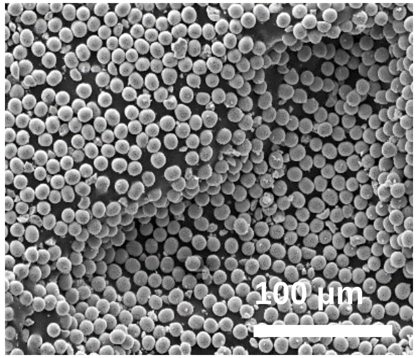
- Characterization of the surface and bulk evolution of electrodes during extended cycling
  - determination of the intricate surface chemistries of high-nickel cathodes and graphite anodes
  - understanding the bulk degradation pathways, particularly under abuse conditions

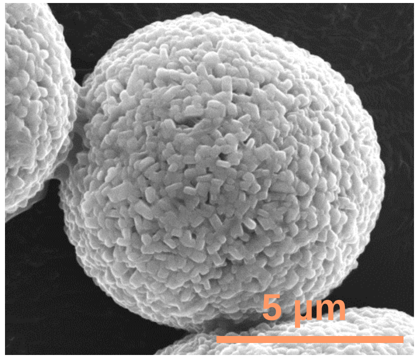
YEAR 2 MILESTONES

Milestone	Type	Description	Status
Dopant Study	Technical	A survey of $LiNi_{1-x-y}Co_yM_xO_2$ ($y \leq 0.05$ and $x \leq 0.15$, M = Mn, Al, Mg, and more) and the effects of dopants on electrochemical performance, air-storage stability, and safety	Completed
Electrode Study	Technical	Effect of electrode loading and calendaring on $LiNi_{1-x-y}Co_yM_xO_2$ ($y \leq 0.05$ and $x \leq 0.15$, M = Mn, Al, Mg, and more)	Completed
ALD Coating Survey	Technical	Further evaluation and validation of ALD coatings on best-performing $LiNi_{1-x-y}Co_yM_xO_2$ ($y \leq 0.05$ and $x \leq 0.15$, M = Mn, Al, Mg, and more)	Completed
Electrolyte Study	Technical	A survey of electrolyte additives on best-performing $LiNi_{1-x-y}Co_yM_xO_2$ ($y \leq 0.05$ and $x \leq 0.15$, M = Mn, Al, Mg, and more) in EC-free electrolytes	Completed
Completion date: 03/31/2021			

APPROACH

- **Compositional Design:** Screening of metal dopants that stabilize high-nickel layered oxides without cobalt
- **Synthesis Scale-up**: Increase the tank reactor size for co-precipitation from 10 L to 30 or 50 L, and the batch size for calcination from 10 – 20 g per batch to 200 – 400 g per batch
- **Surface Stabilization:** Exploration of surface treatments such as chemical coating, atomic layer deposition (ALD) coating, and *in-situ* formed surface layers
- **Electrolyte Modification**: Exploration of functional electrolyte additives in the absence of ethylene carbonate
- **Assessment:** Evaluation in pouch full cells with commercially relevant electrode loading and porosity as well as in-depth characterization to understand the degradation mechanisms





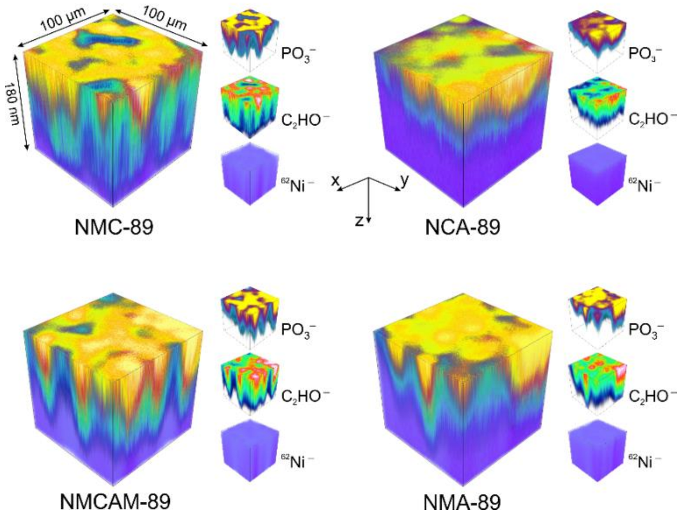
TECHNICAL ACCOMPLISHMENTS AND PROGRESS

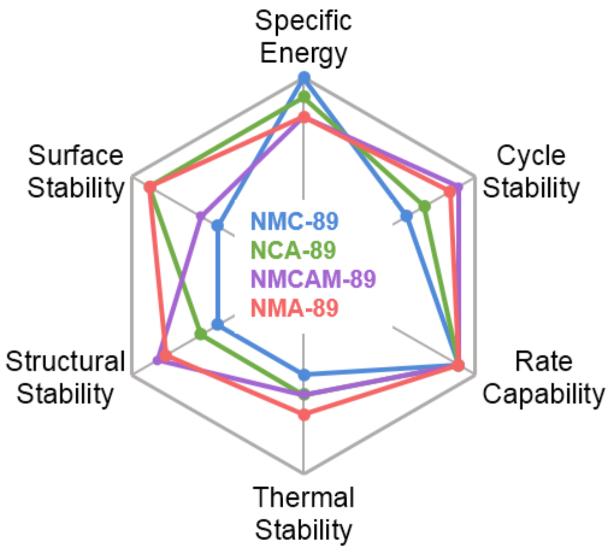
- **Dopant effects on high-Ni cathodes:** Assessment of the effects of various dopant compositions on the performance of high-nickel cathodes with Ni content ≥ 90%

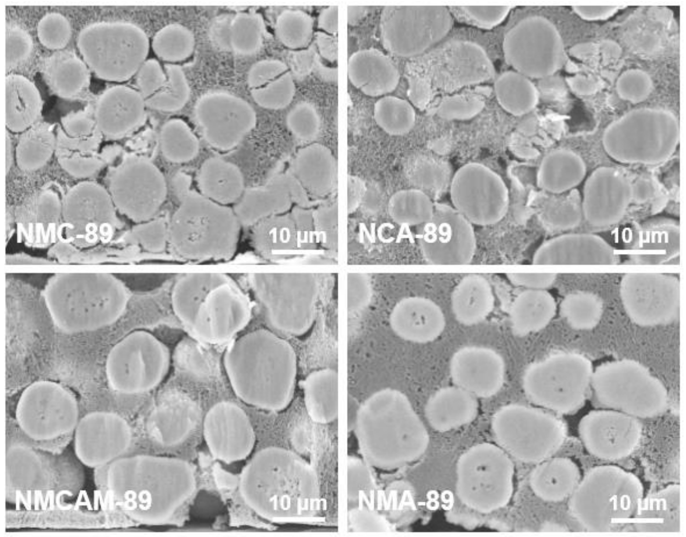
- **Refinement of electrode parameters:** Identification of optimal electrode loading and calendaring parameters to achieve improved performance under industry-relevant conditions

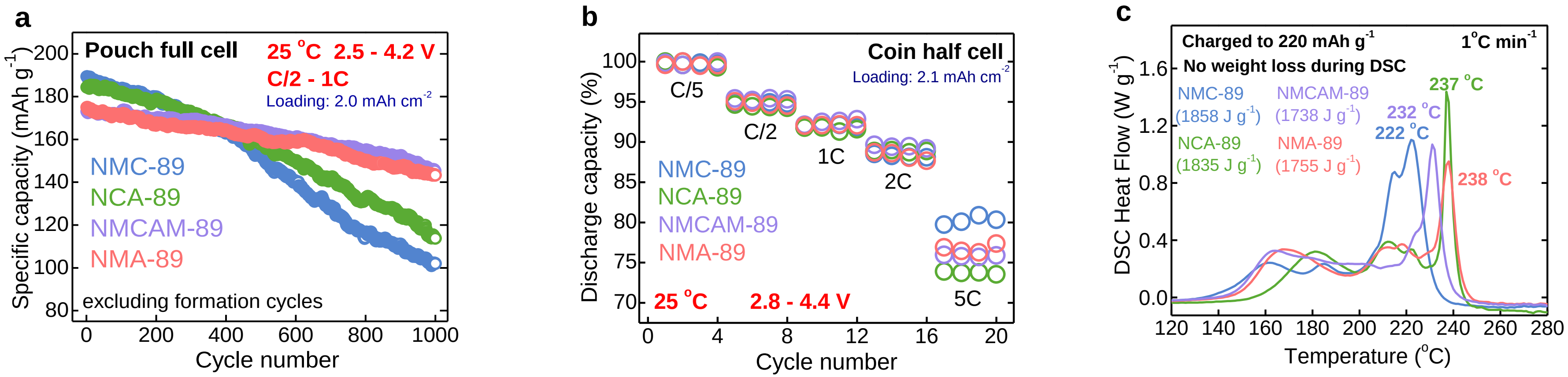
- **Additives for EC-free electrolytes:** Development of EC-free electrolyte systems for enhanced thermal and electrochemical stability in full cells with layered oxide cathode and graphite anode

IN-DEPTH CHARACTERIZATION OF HIGH-Ni CATHODES AFTER EXTENDED CYCLING





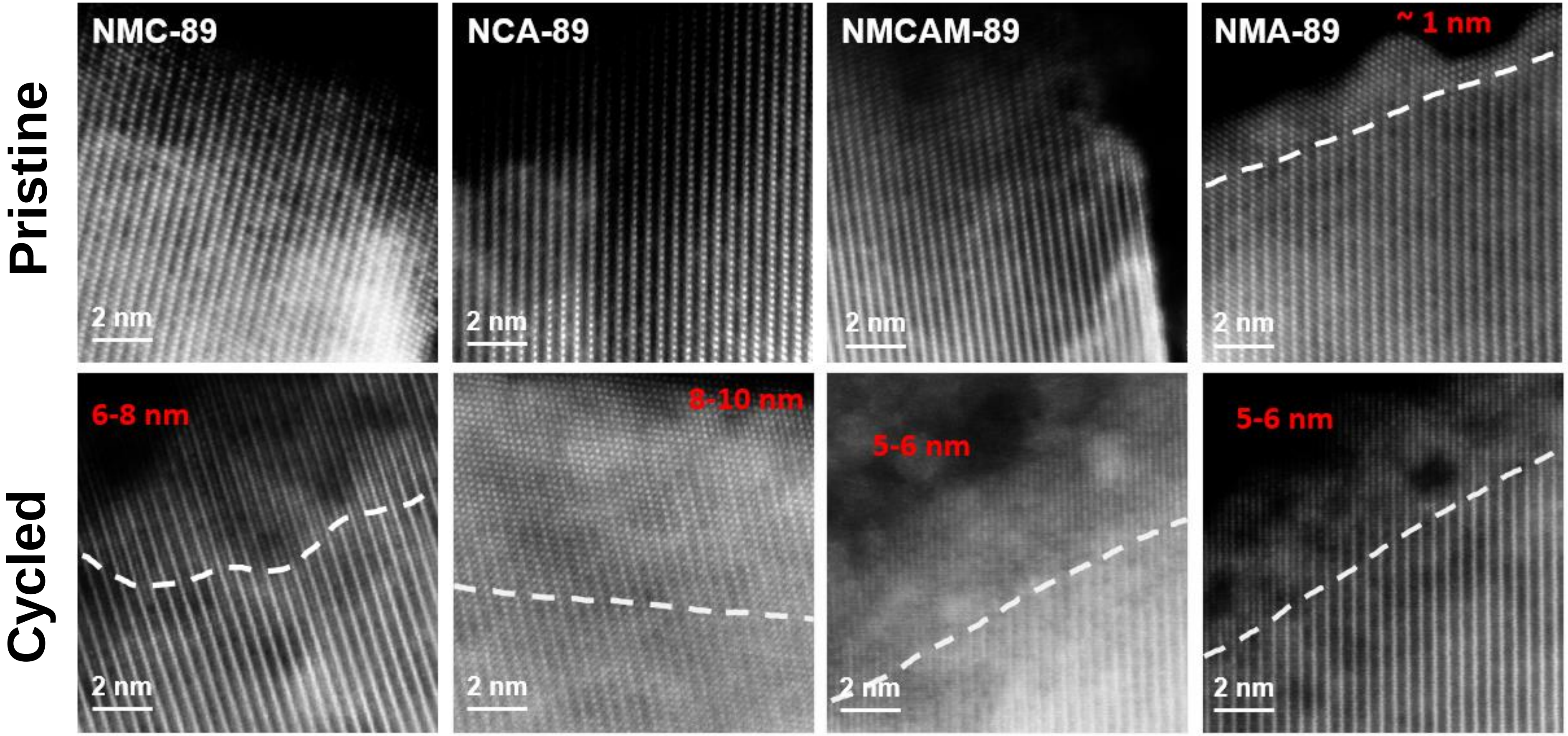




- High-nickel $LiNi_{0.9}Mn_{0.05}Al_{0.05}O_2$ (NMA) shows well-rounded properties compared to cobalt-containing analogs
- Aluminum doping is crucial for reducing surface reactivity
- Mn and Al co-doping in NMA with ~ 90% Ni alleviates internal stress and reduces particle cracking

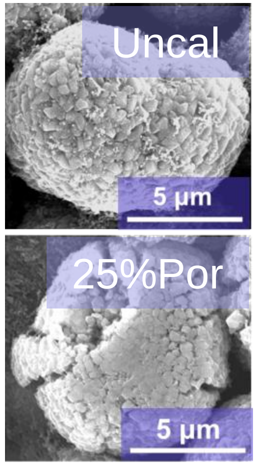
TEM ANALYSIS OF ROCK SALT PHASE FORMATION IN HIGH-NICKEL CATHODES

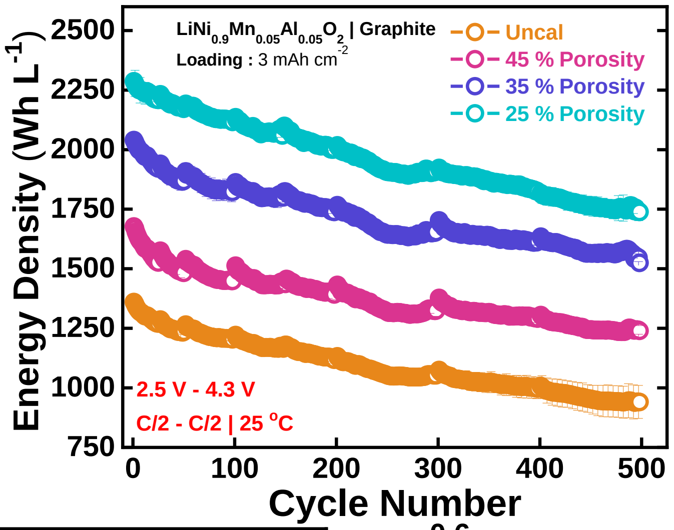
TEM of 90% nickel cathodes before and after 1,000 cycles at 2.8 – 4.2 V in graphite full cells

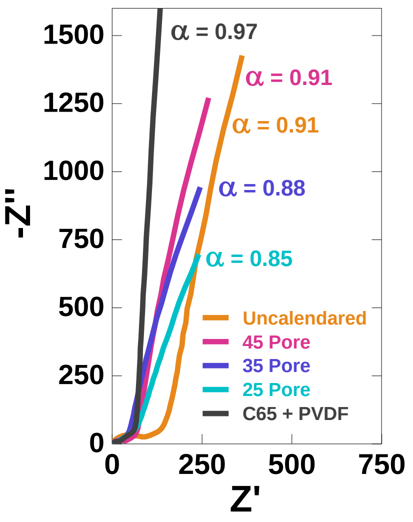


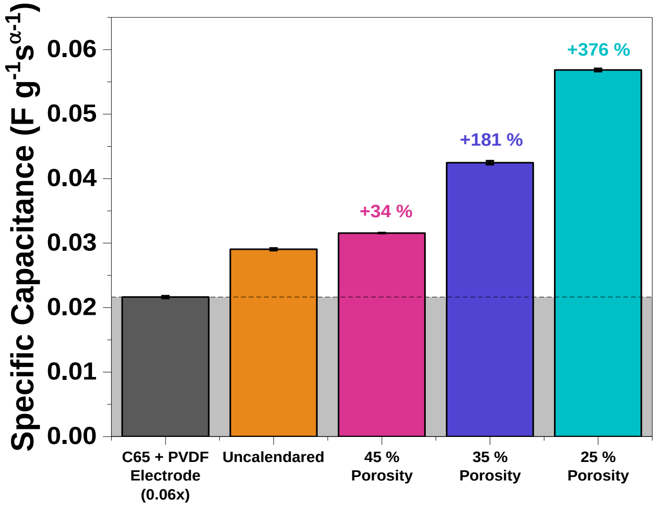
- Cobalt-containing cathodes show no rock salt phase in the pristine state
- Moderate surface reconstruction occurs across all compositions after cycling
- Bulk reordering and mechanical degradation appear to be the main source of capacity fade, not rock salt phase

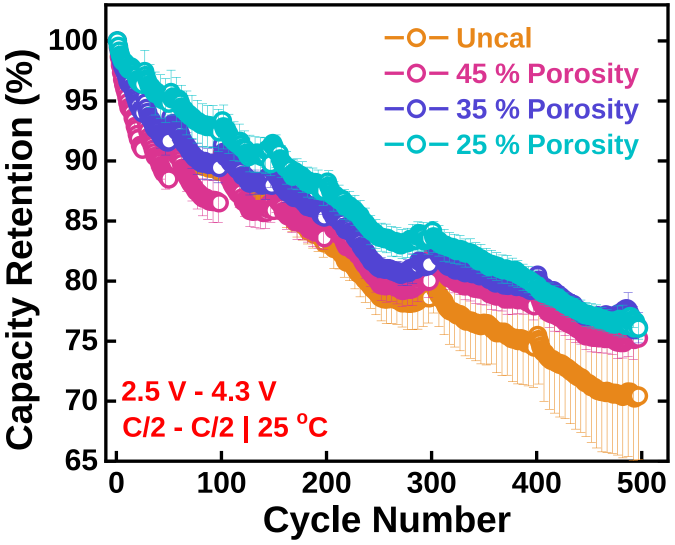
CALENDARING EFFECT ON COBALT-FREE $LiNi_{0.9}Mn_{0.05}Al_{0.05}O_2$

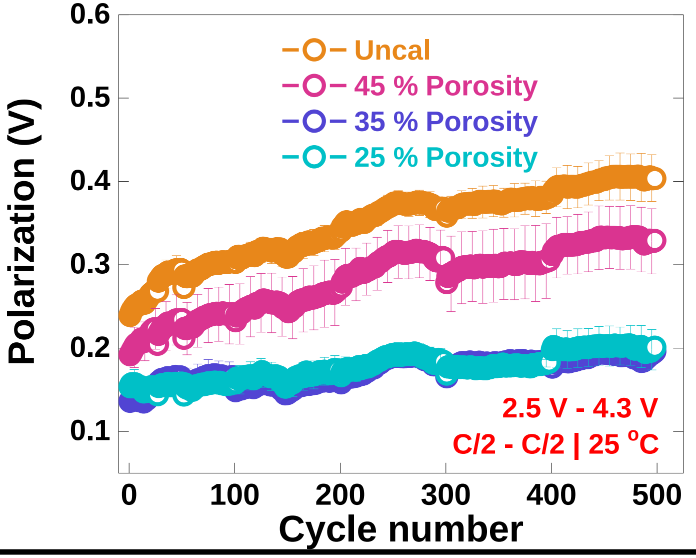


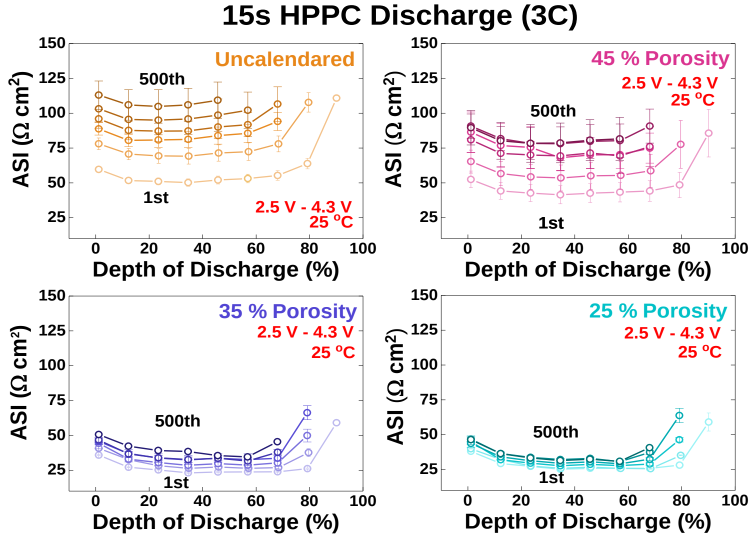






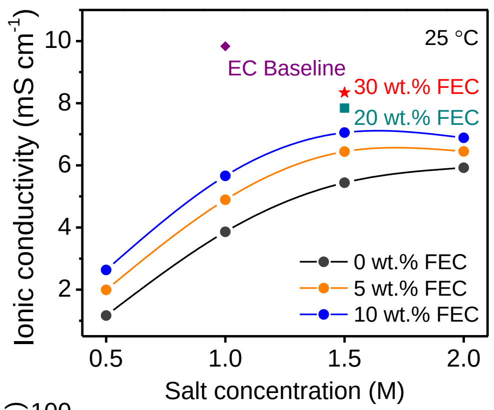


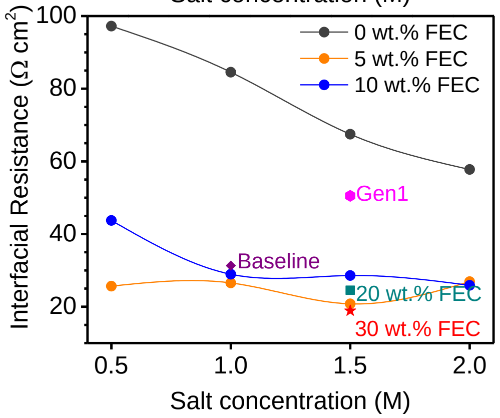


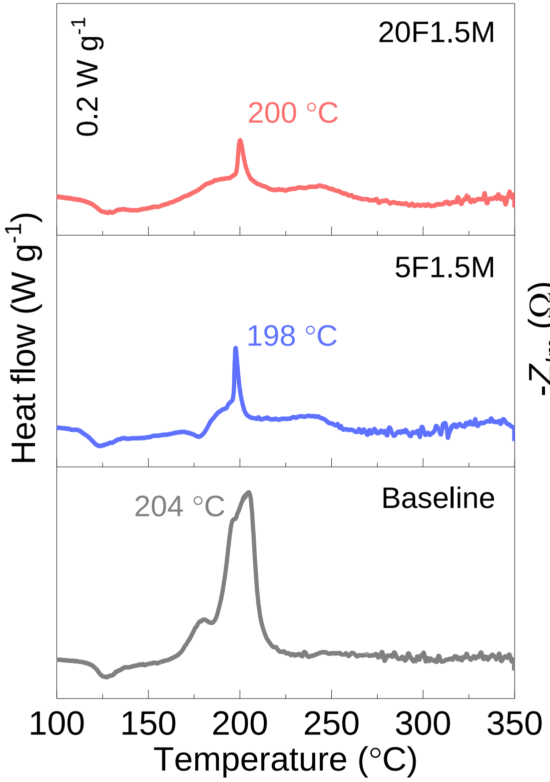


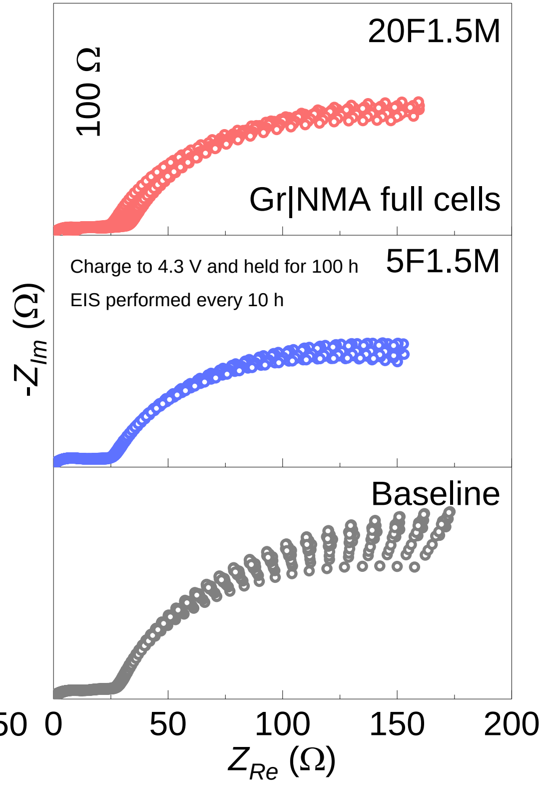
- Effects of calendaring on electrode morphology and electrochemical performance have been evaluated
- Calendaring improves energy density, cycle life, & pulse power performance with reduced polarization

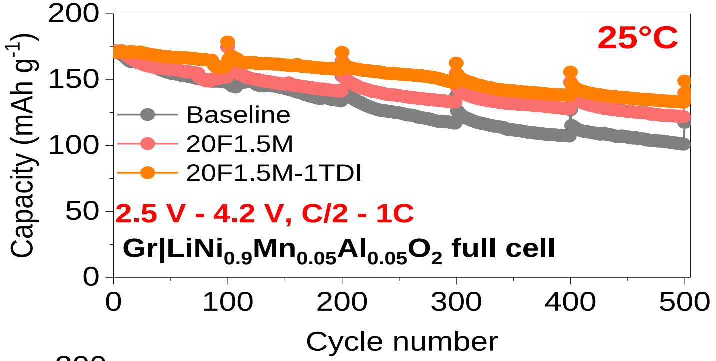
DESIGN OF EC-FREE ELECTROLYTES

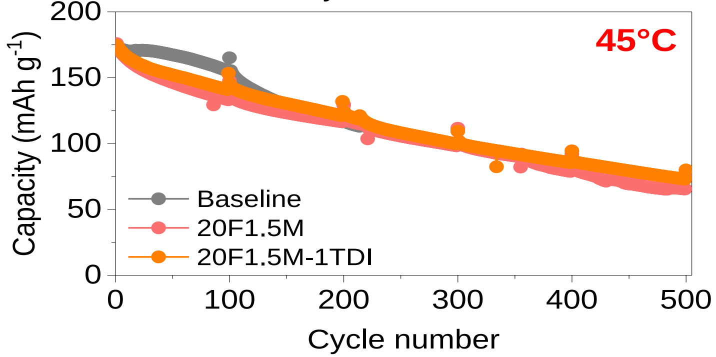






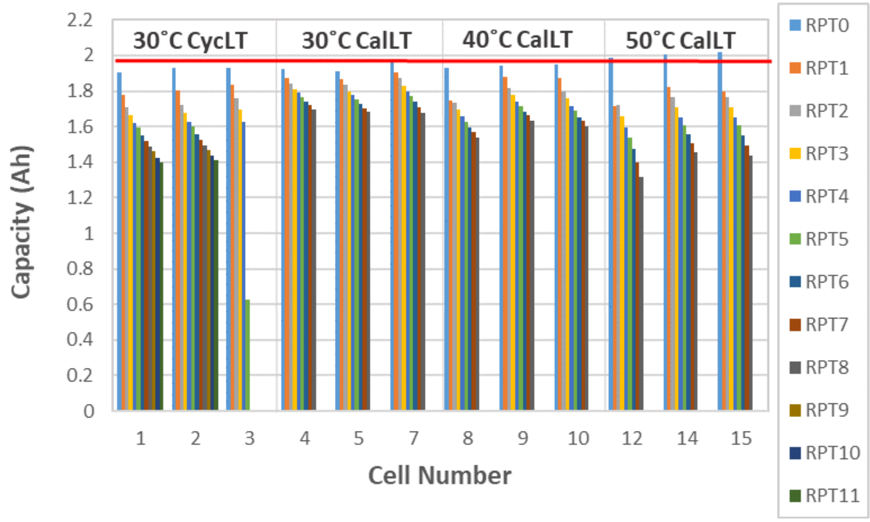


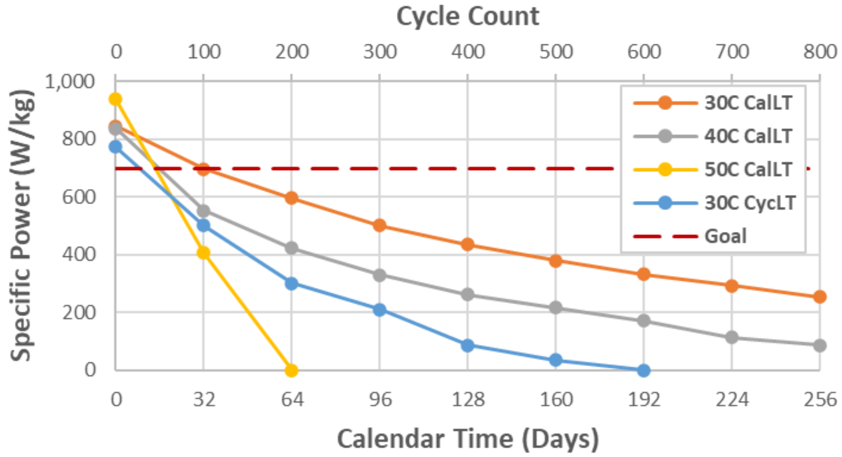




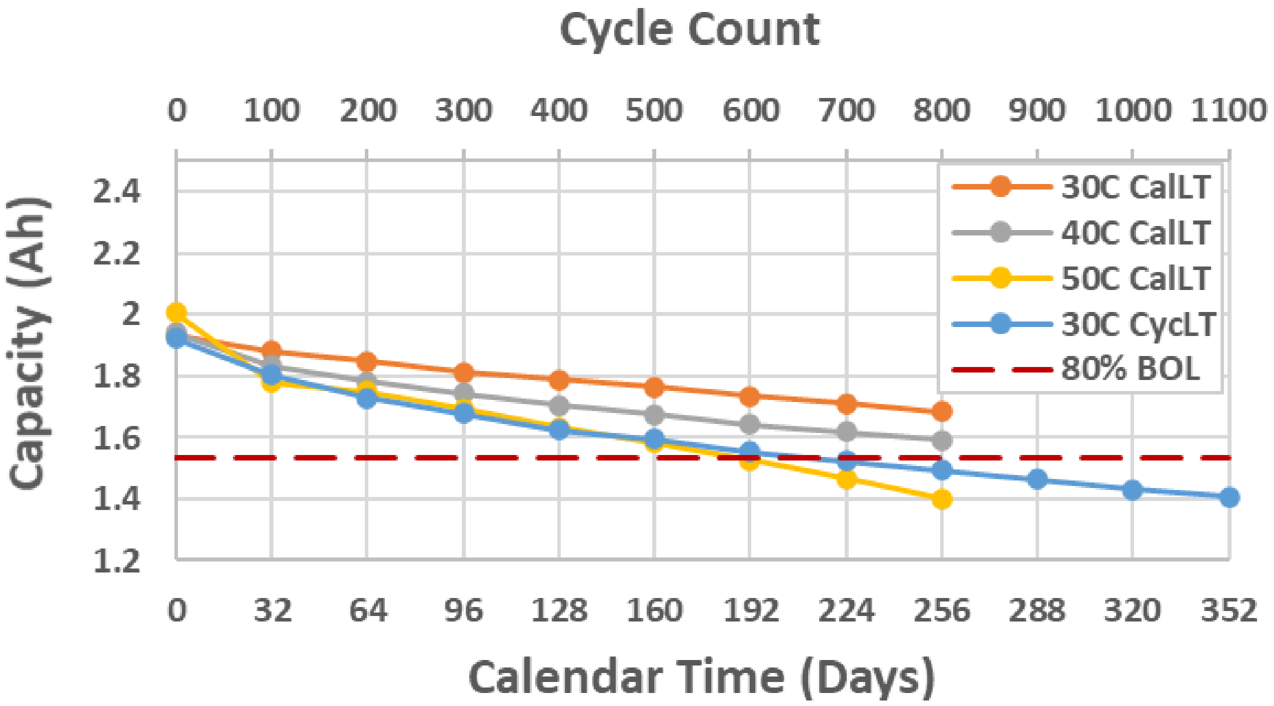
- FEC effectively stabilizes EC-free, EMC-based electrolyte, offering improved conductivity, thermal stability, and electrochemical stability along with reduced interfacial resistance
- Addition of 1 wt.% LiTDI as a moisture-scavenging additive greatly extends the storage life with EC-free electrolyte and provides additional benefits to cycle life, even at elevated temperatures

PERFORMANCE OF LARGE-FORMAT 2 Ah POUCH CELLS EVALUATED BY INL





- 2 Ah pouch cells fabricated by Tesla Inc. with $LiNi_{0.85}Co_{0.05}Mn_{0.075}Al_{0.02}Mg_{0.005}O_2$ developed at UT Austin



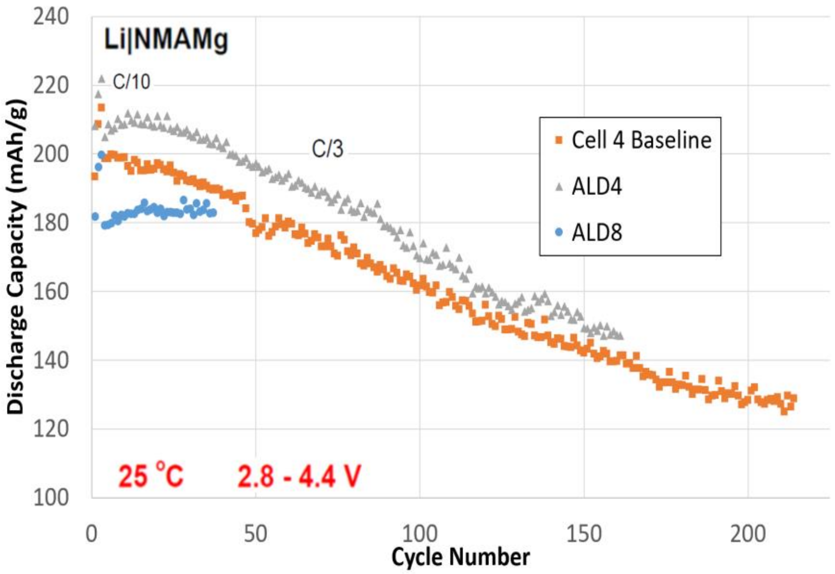
- Pouch cells assembled by Tesla Inc. and evaluated by INL reached 80% capacity after ~ 700 cycles
- Pulse power capability fade dramatically increases with temperature during calendar life aging
- Performance fading is mostly due to increase in pulse resistance (cell impedance)

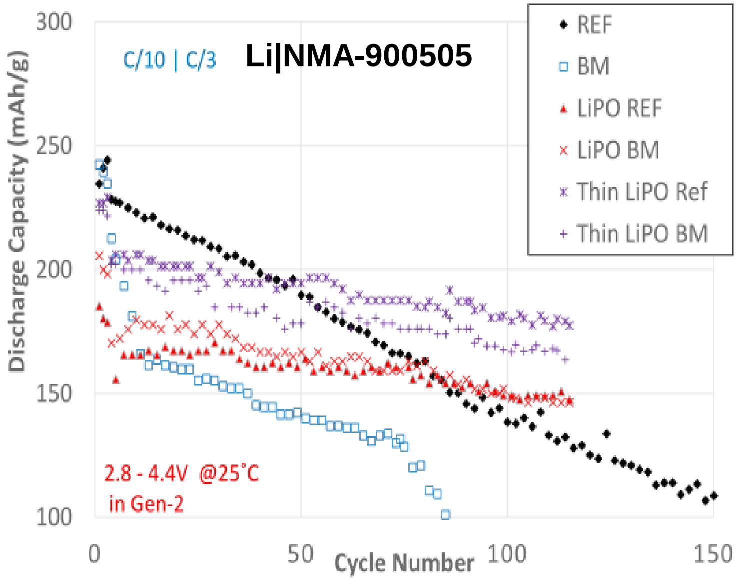
RESPONSE TO PREVIOUS YEAR REVIEWER'S COMMENTS

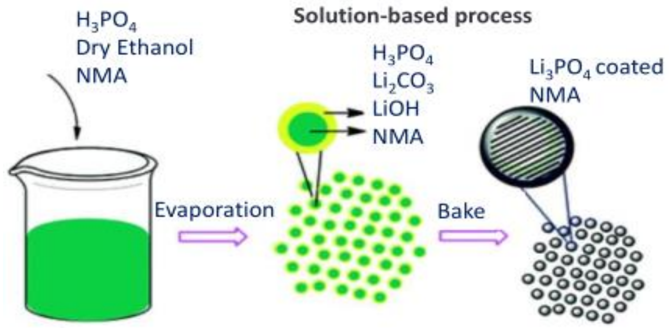
- There were two main comments on the 2020 AMR presentation:
- "Work performed by partner NREL provided a LiNiCoMnAlMg material to Tesla for evaluation. It was not clear to the reviewer why this material was chosen or how it fits into the overall program."
  - Response: The LiNiCoMnAlMg material was developed by UT Austin. The material was designed based on results from doping trials performed earlier towards the project milestones. At the time of selection, the material displayed excellent preliminary results and showed potential to meet the overall project goals of ≥ 600 Wh kg^{-1} energy density with greater than 1,000 cycles above 80% energy retention and less than 50 mg Wh^{-1} cobalt content.
- "The initial doping studies are interesting; however, with a comparison only to the control—pure NiO_2 material—it is a little difficult to assess just how the doped materials compare to known standard material sets.
  - Response: Doping trials were performed on $LiNiO_2$ to remove any confounding interactions with other elements in NMC-based cathodes. This allowed us to evaluate dopants under idealized conditions to better understand the fundamental effects of individual dopants, making us better able to select constituent elements for more complex high-nickel compositions.

COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- Dr. Shriram Santhanagopalan, Nation Renewable Energy Laboratory (NREL): ALD and wet chemical coating exploration of high-nickel, cobalt-free cathode samples (*e.g.*, NMA-900505, NMAMg) supplied by UT Austin
- Dr. Hieu Duong, Tesla Inc.: Fabrication of 2 Ah pouch full cells with a high-nickel, low-cobalt cathode ($LiNi_{0.85}Co_{0.05}Mn_{0.075}Al_{0.02}Mg_{0.005}O_2$) supplied by UT Austin. 2 Ah Cells were shipped to and evaluated by INL for DOE







REF	Uncoated NMA
BM	Uncoated ball milled NMA
LiPO REF	Lithium phosphate coated NMA
LiPO BM	Lithium phosphate coated ball milled NMA
Thin LiPO	Thin phosphate coating

- 4 nm thick Al_2O_3 ALD coating carried out at NREL affords enhanced surface passivation, simultaneously increasing initial discharge capacity and cycling stability
- *In-situ* formed Li_3PO_4 coating produced from conversion of LiOH and Li_2CO_3 surface species with H_3PO_4 enhances cycling stability by scavenging residual lithium species and improves surface Li^+ conduction

REMAINING CHALLENGES AND BARRIERS

- **Main barrier:** Capacity and energy fade have been the main barriers for high-nickel, cobalt-free layered oxides cathodes for commercial Li-ion batteries
- **Technical challenges:** Large scale synthesis of high-nickel cathode materials presents several challenges that must be addressed to enable the end goal of 2 kg of optimized cathode material delivered to Tesla Inc. for large format pouch cell fabrication
    - Oxygen diffusion through precursor powder limits the depth of precursor packing within synthesis crucibles
    - Large furnace sizes required to calcine kilogram-scale quantities of materials can produce uneven temperature distributions
    - If several batches are required to reach desired quantity, storage of the synthesized materials must minimize air/moisture exposure or strategies to improve the air-storage stability of the final material must be employed

PROPOSED FUTURE RESEARCH

- FY2021
  - A survey of $LiNi_{1-x}M_xO_2$ ($x \leq 0.15$, M = Mn, Al, Mg, and more) and the effects of dopants on electrochemical performance, air-storage stability, and safety
  - Continued survey of functional electrolyte additives on best-performing cobalt-free $LiNi_{1-x}M_xO_2$ ($x \leq 0.15$, M = Mn, Al, Mg, and more) in EC-free electrolytes
- FY2022
  - Exploration of methods to improve air-storage stability of $LiNi_{1-x}M_xO_2$ ($x \leq 0.15$, M = Mn, Al, Mg, and more), such as chemical coating, doping, and in-situ formed surface layers
  - Synthesis scale-up and optimization for the best-performing $LiNi_{1-x}M_xO_2$ ($x \leq 0.15$, M = Mn, Al, Mg, and more) and delivery of 2 kg of material to Tesla Inc. for fabrication of 2 Ah pouch cells
  - End of Project Goal: Thirty 2 Ah pouch cells capable of 600 W h kg-1 (cathode level) and ≥ 80 % energy retention after 1,000 cycles with cobalt content below 50 mg Co/Wh, delivered to DOE for independent evaluation

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

SUMMARY

- Calendaring an $LiNi_{0.9}Mn_{0.05}Al_{0.05}O_2$ cathode to a sufficient level of porosity produces overall desirable physical and electrochemical properties, including energy density, impedance growth, cycle life, polarization growth, and pulse power performance in comparison with uncalendared cathodes
- Inclusion of 20 wt.% FEC enables an EMC-based, EC-free electrolyte with broadly improved transport properties, thermal stability, and electrochemical stability. Further incorporation of a moisture-scavenging agent LiTDI improves storage capability and enhances cycling stability of high-nickel cathodes in graphite full cells
- ALD coating of high-nickel cathode material with Al_2O_3 produces a passivated surface layer that reduces irreversible capacity loss and improves cycling stability
- *In-situ* formation of Li_3PO_4 surface coating generated through a reaction of residual LiOH and Li_2CO_3 with H_3PO_4 removes residual lithium species and reduces initial irreversible capacity loss, while the Li_3PO_4 layer improves surface Li^+ conduction