TAILORING INTEGRATED LAYERED- AND SPINEL-ELECTRODE STRUCTURES FOR HIGH-CAPACITY LITHIUM-ION CELLS

Project ID: BAT049

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Argonne National Laboratory
June 1-4, 2020

2020 DOE Vehicle Technologies Office
Annual Merit Review

Overview

Timeline

- Start: October 1, 2018
- End: Sept. 30, 2021
- Percent complete: 50%

Budget

- Total project funding:
  FY19 $900K

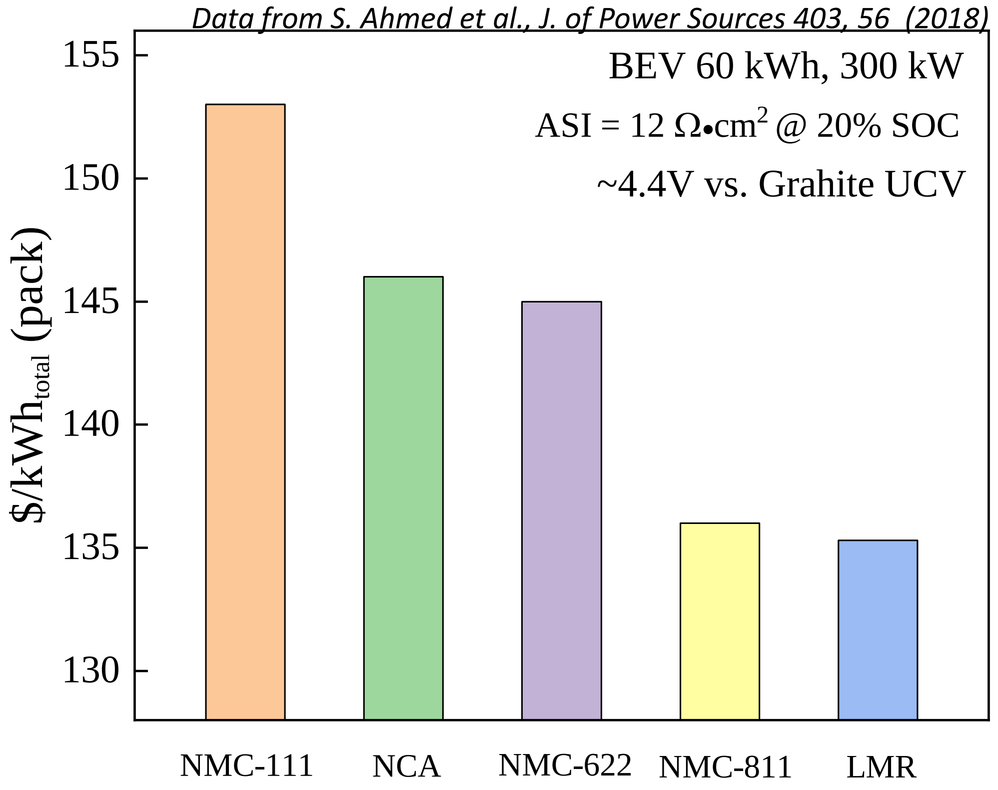
Barriers

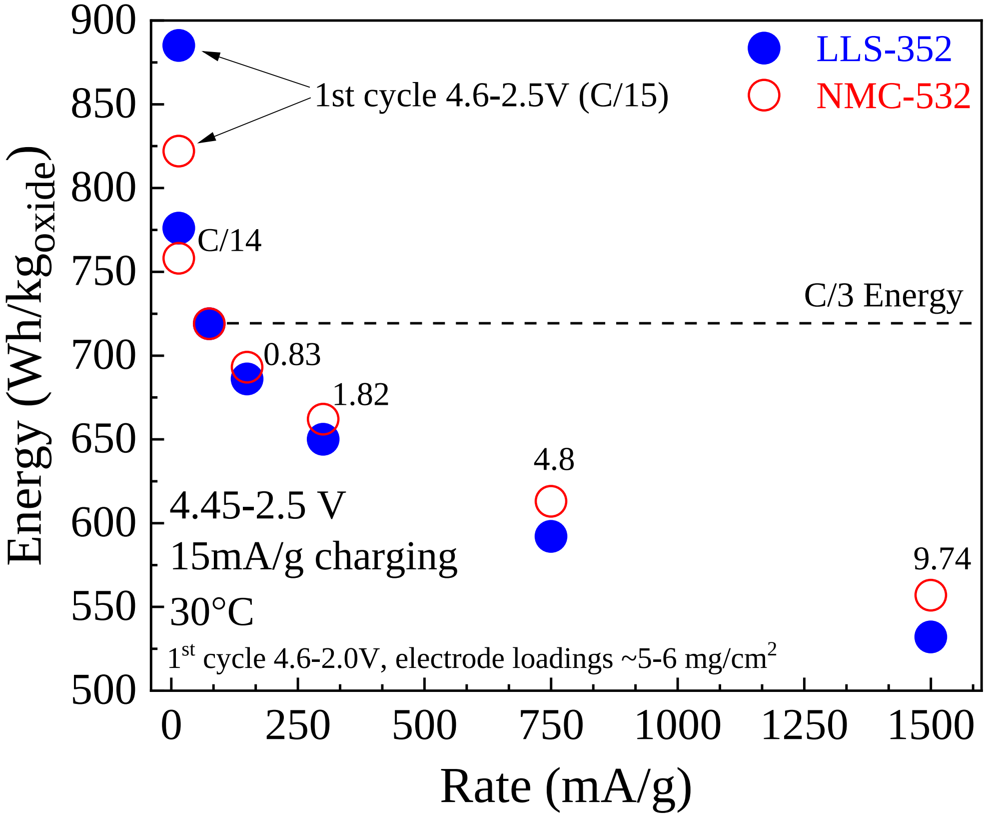
- Development of PHEV and EV batteries that meet or exceed DOE and USABC goals
  - Cost
  - Performance
  - Safety
  - Cobalt content

Partners

- CSE, Argonne: Michael M. Thackeray, Roy Benedek, Eungje Lee, Arturo Gutierrez, Jiajun Chen, Boyu Shi, Jinhyup Han, Venkat Srinivasan, Pallab Barai
- ES, Argonne: Devika Choudhury, Anil Mane, Jeff Elam
- APS, Argonne: Mahalingam Balasubramanian, Yang Ren
- UIC: Soroosh Sharifi-Asl, Reza Shahbazian-Yassar
- Universities – UIC, WPI, UR
- ANL industrial partners

Relevance





- Cost and safety are still the main drivers in the development of EV batteries, Mn-rich oxides offer advantages in both
- Technoeconomic modeling (above, left) shows that Mn-rich electrodes have the potential to reach cost parity with state of the art NMC-811 in terms of pack-level cost
- Work from this project (above, right) has demonstrated that Mn-rich electrodes can achieve similar performance to their NMC counterparts
- Importantly, Mn-rich compositions can be made with little to no cobalt while maintaining performance

Milestones/Approach

This project seeks to make significant advancements toward realizing economically viable manganese-rich cathode oxides by:

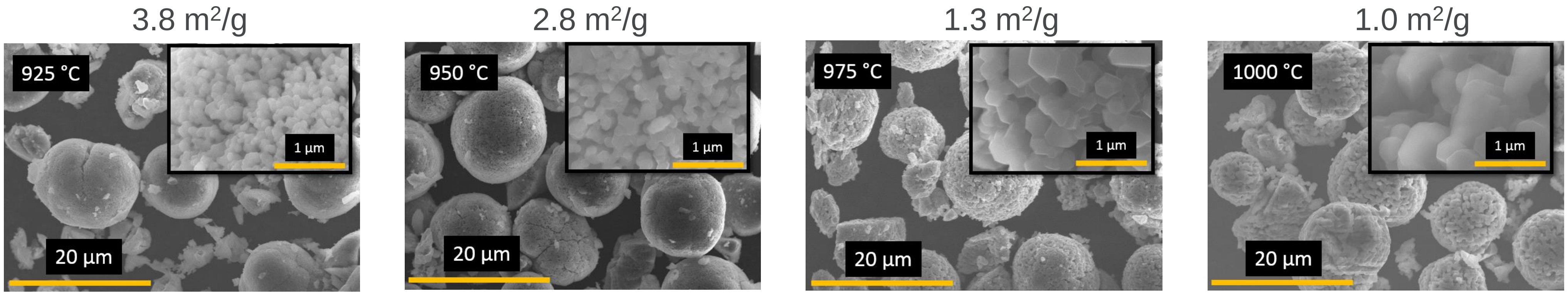
- Exploiting the concept of integrated structures in the form of engineered nanodomains to enhance the stability and performance of Mn-rich oxides
- Exploring how composition dictates local structures and ordering and the associated influence on electrochemical properties – notably, structural stability and impedance at low states of charge
- Understanding the relationships between synthesis parameters and final cathode products with respect to co-precipitation of Mn-rich oxides for practical implementation
- Design and synthesis of robust surfaces that enable low impedance, low impedance rise, high rate capability, and long cycle-life
- Validating promising materials through scale-up and standardized testing procedures
- Strong interactions with industrial partners for information exchange and feedback

Correlated milestones aimed at the development and demonstration of economically viable Mn-rich electrodes

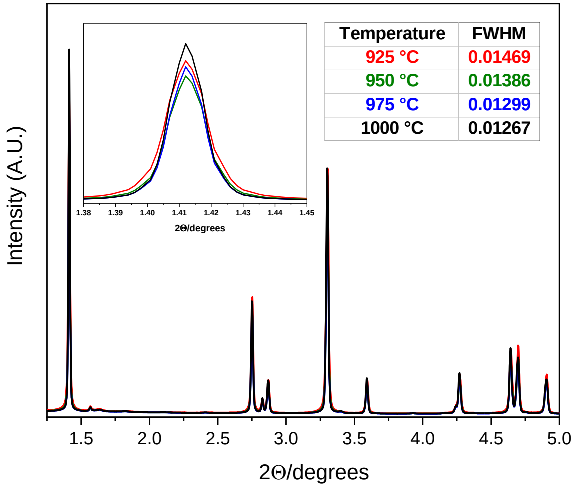
Technical Accomplishments

Synthesis and Morphology

Decreasing surface area



Increasing primary particle size (secondary particle size same)



Temperature	FWHM
925 °C	0.01469
950 °C	0.01386
975 °C	0.01299
1000 °C	0.01267

Sample	Co	Mn	Ni	Li/TM
900°C	19.324	53.303	27.373	1.169
925°C	19.497	53.408	27.095	1.179
950°C	19.357	53.501	27.142	1.165
975°C	19.252	53.475	27.272	1.175

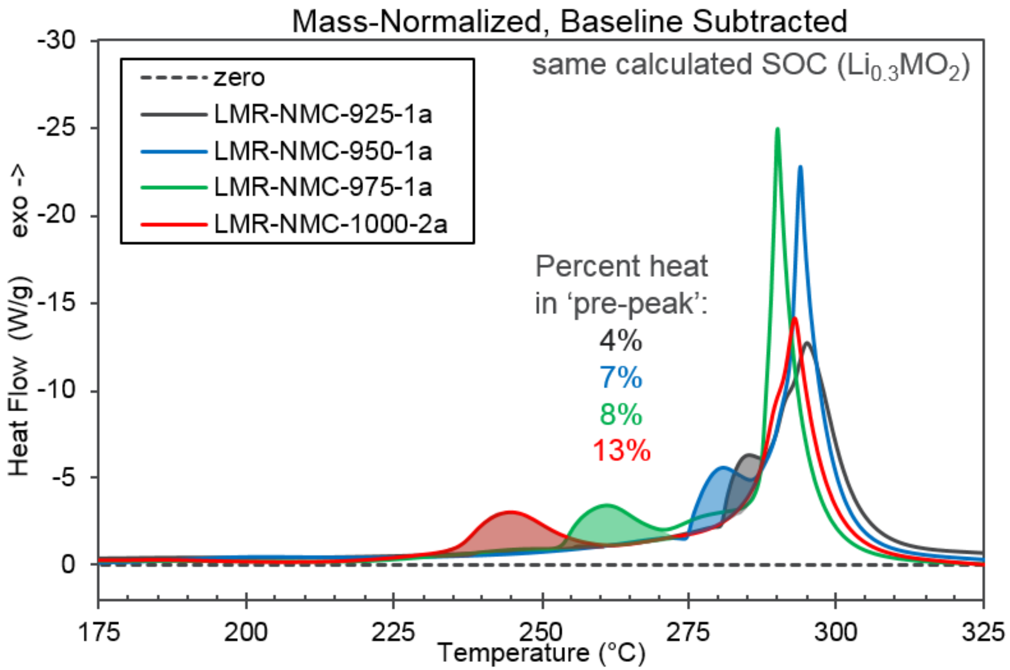
Mn-rich, layered-layered-spinel fired in air at 925°C, 950°C, 975°C and 1000°C

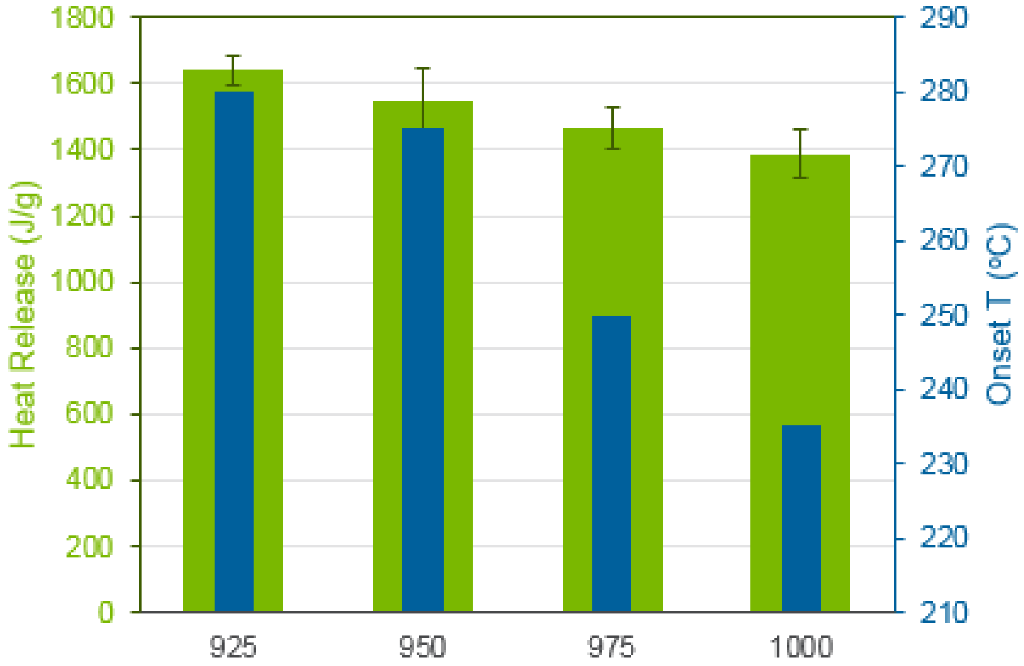
- Precursors were mixed together and split before firing to ensure similar composition was achieved (ICP analysis in table)
- HRXRD analysis confirmed the expected patterns but suggested that samples had different primary particle sizes, confirmed by SEM
- All samples had same the secondary particle sizes
- BET analysis confirmed that the samples exhibited decreasing effective surface areas with increasing processing temperatures

Mn-rich primary particle morphology is extremely sensitive to lithiation conditions

Technical Accomplishments

Morphology & Stability



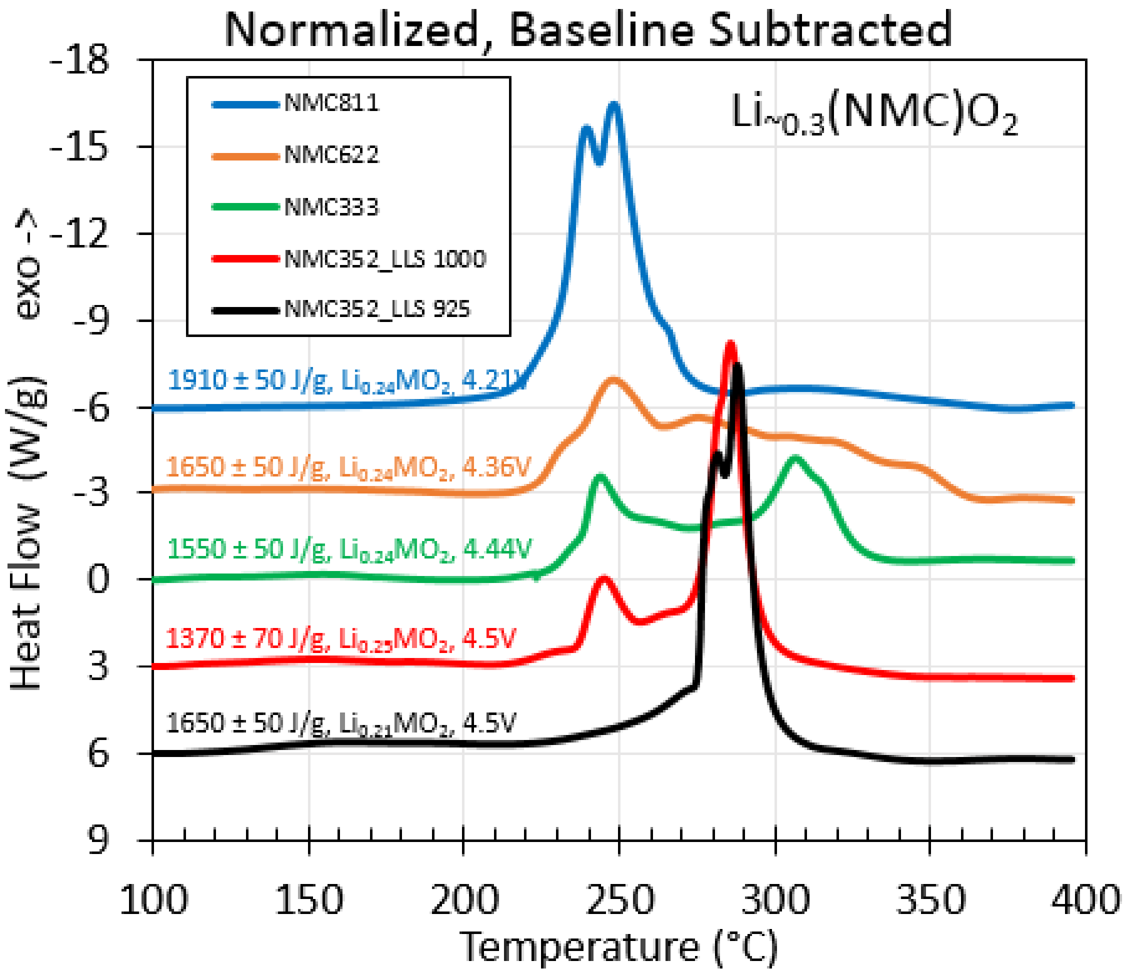


- Main exothermic peaks for all electrodes occurs at ~295°C
- With increasing oxide annealing temperature:
  - 'Pre-peak' shifts to lower temperature
  - The percentage of overall heat released in the pre-peak increase
    - ❖ *These observations are opposite of the expectation that the highest surface area (lowest anneal T) would have the lowest thermal stability.*
- Total heat release decreases slightly with surface area - *This is consistent with the expected surface-area trend*

Sensitivity of particle morphology to synthesis conditions plays an important role in thermal stability

Technical Accomplishments

Morphology & Stability



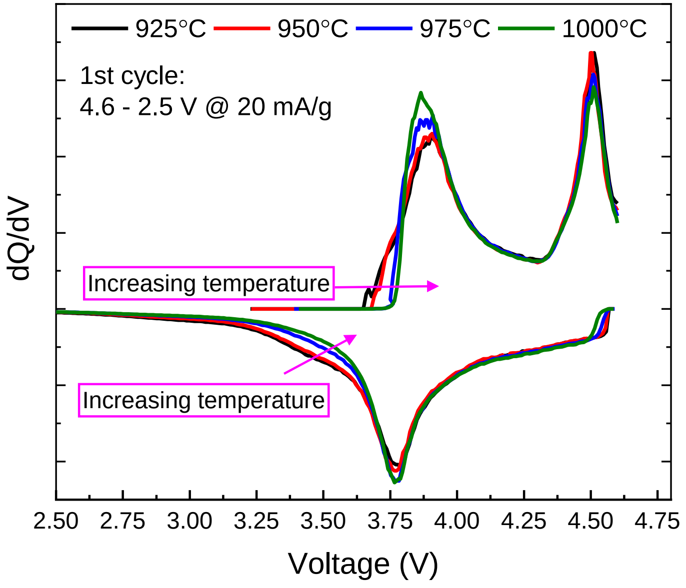
Comparing layered cathode chemistries at similar SOCs:

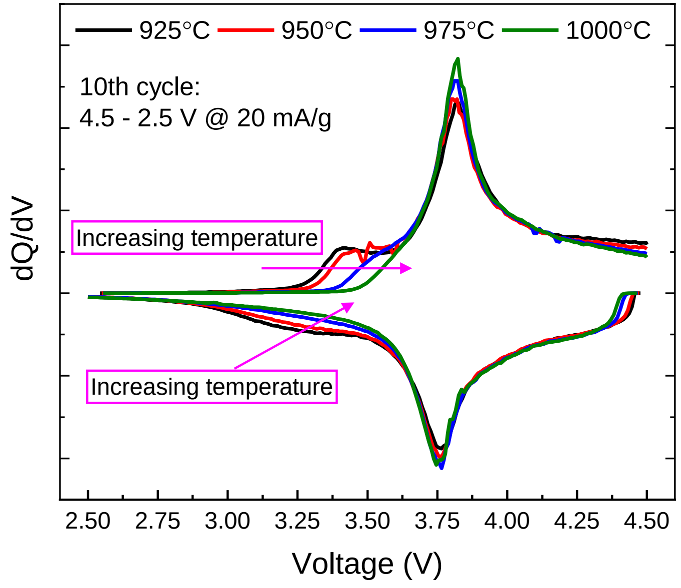
- NMC-333, 622, 811 at ~75% SOC all show onset at ~225°C
- LLS prepared at 1000°C (red) also shows a similar onset temperature of ~230°C
- LLS prepared at 925°C (black) show a noticeably higher onset temperature of ~275°C

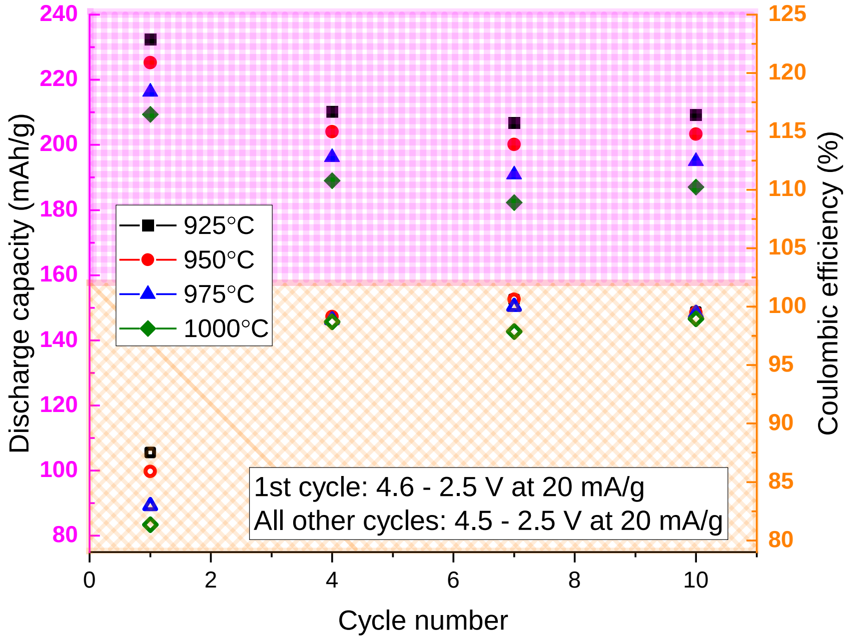
Mn-rich layered-layered-spinel cathode electrodes exhibit good thermal stability (DSC) with respect to standard, commercial NMC electrode materials

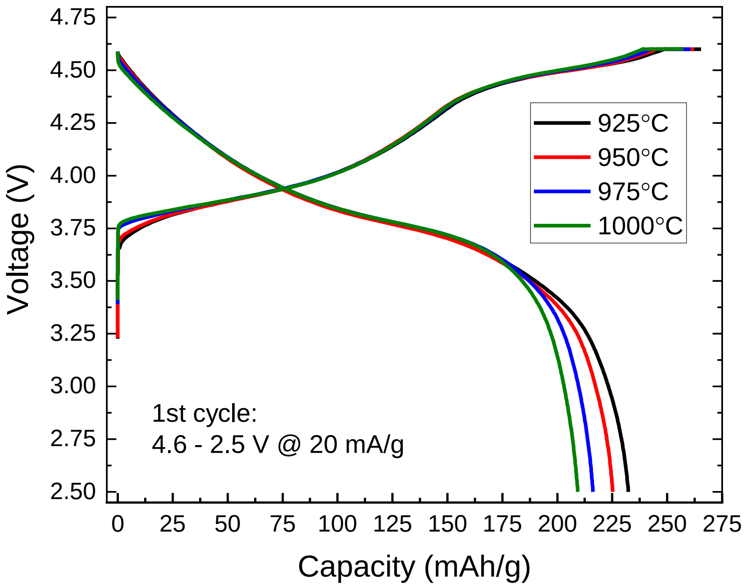
Technical Accomplishments

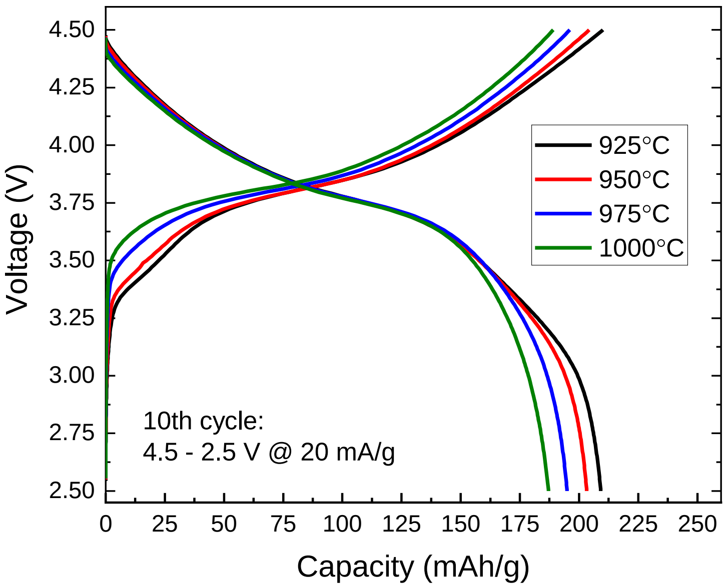
Morphology & Performance











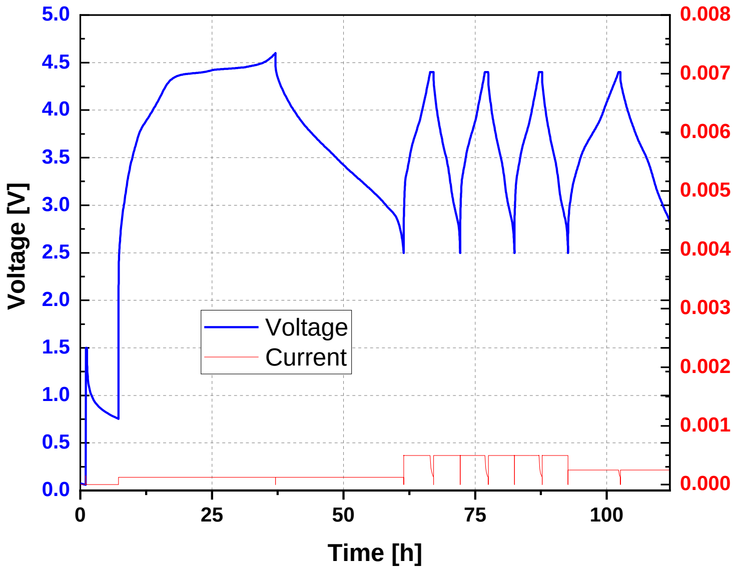
The performance of the four samples followed a trend based off the annealing temperature:

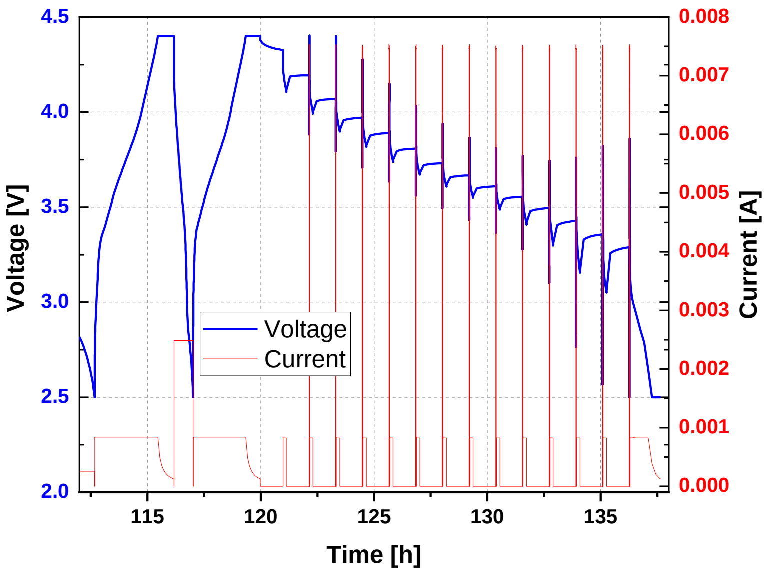
- Lower annealing temperatures exhibited higher discharge capacities and first-cycle efficiencies (FCE)

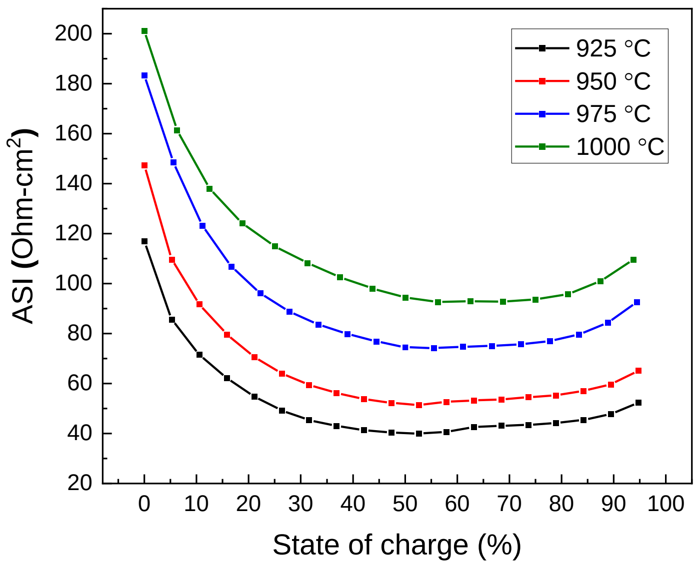
Optimization within a range of just 75°C increased FCE by 6% and cyclable capacity by 20 mAh/g giving ~210 mAh/g @ 4.45V vs Li/Li$^+$

Technical Accomplishments

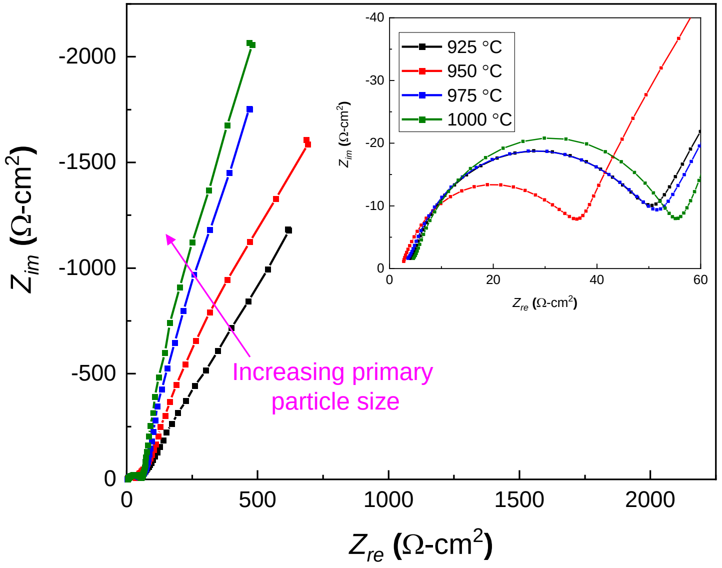
Morphology & Performance







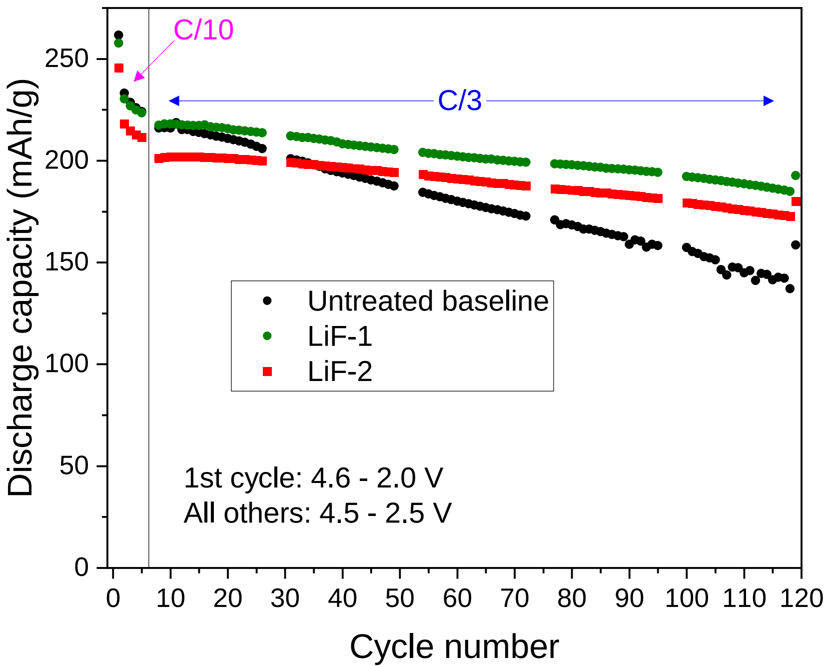
- The initial area-specific-impedance (ASI) was collected in full-cells vs. graphite anodes on the 7th cycle (formation and HPPC protocols above)
- The ASI systematically increased with higher processing temperature (top right)
- AC impedance was collected on each of the samples in symmetric cells (bottom right)
  - No trend observed for interfacial impedance
  - Bulk diffusion decreased with higher processing temperature (larger primary particle size and/or lower effective surface area)



Small changes to lithiation temperatures produced significant differences in baseline impedance characteristics due to primary particle size

Technical Accomplishments

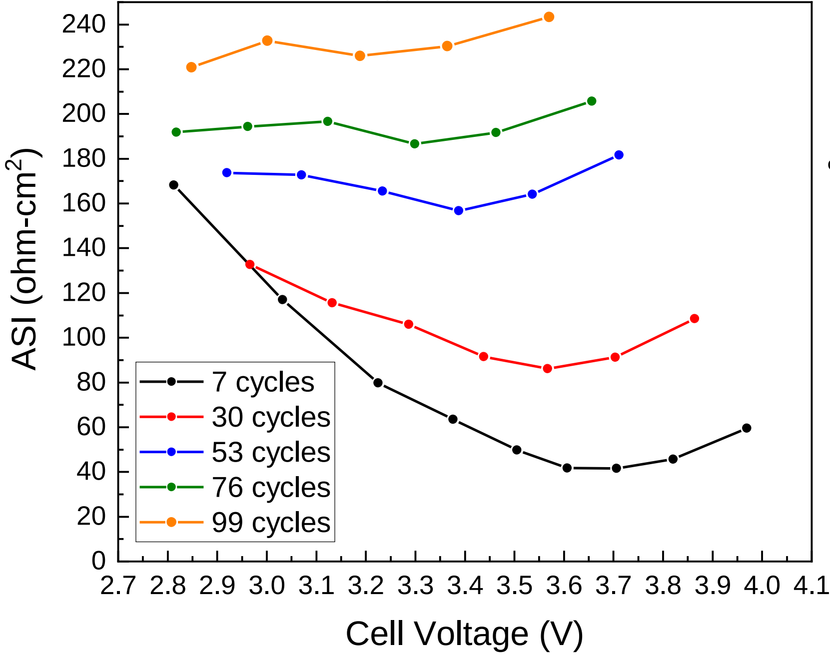
Surface Stabilization

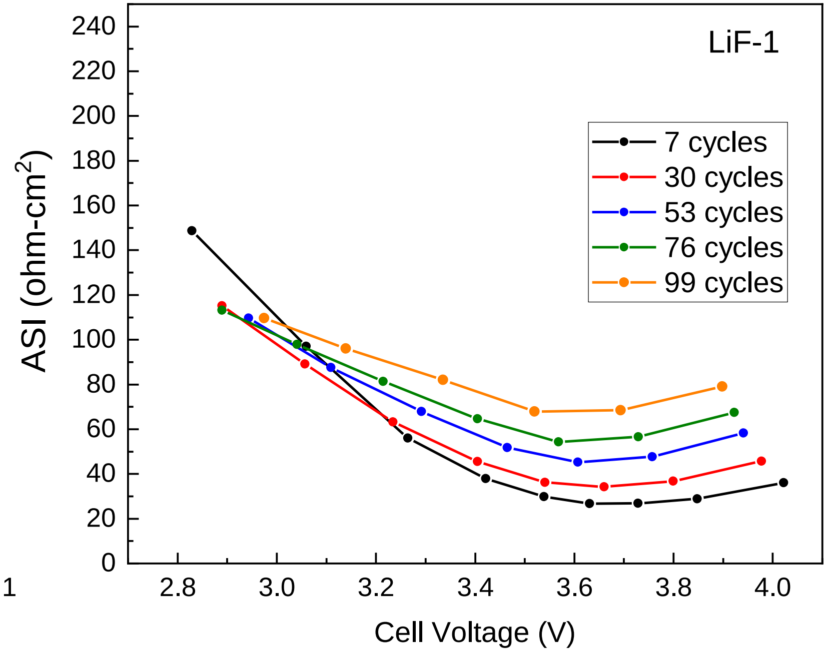


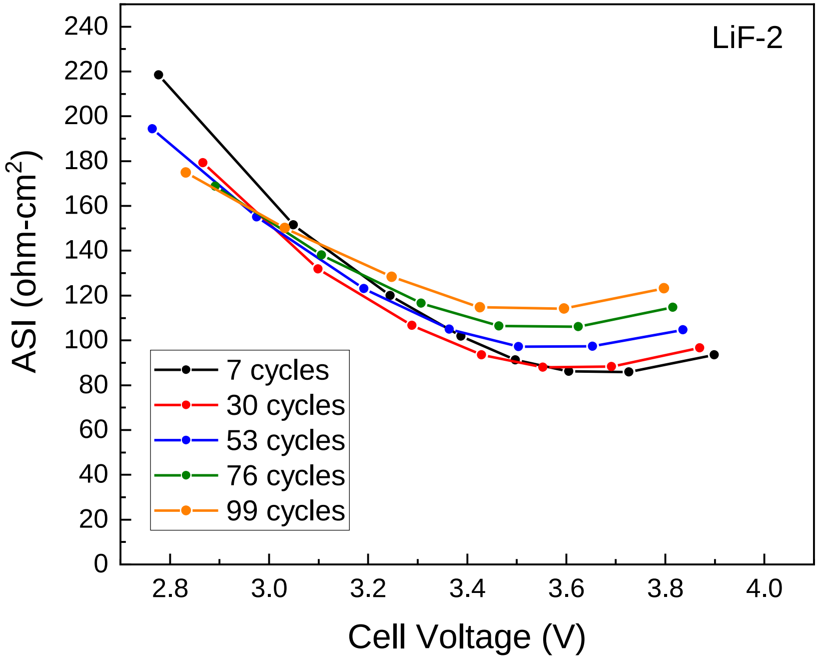
LiF films were applied via ALD on $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.375}Mn_{0.375}Co_{0.25}O_2$ electrodes

- The films were made using WF_6 as a fluorine source instead of the typically-used HF-pyridine
- Conductivity of LiF made with WF_6 (LiF-1) exhibited higher lithium conductivity (data not shown here) than those made with HF-pyridine (LiF-2)
- Both LiF films improved capacity retention
- Electrodes treated using WF_6 (LiF-1) showed lower initial/final impedance

Novel surface treatments show promise for lower cost stabilization of Mn-rich surfaces

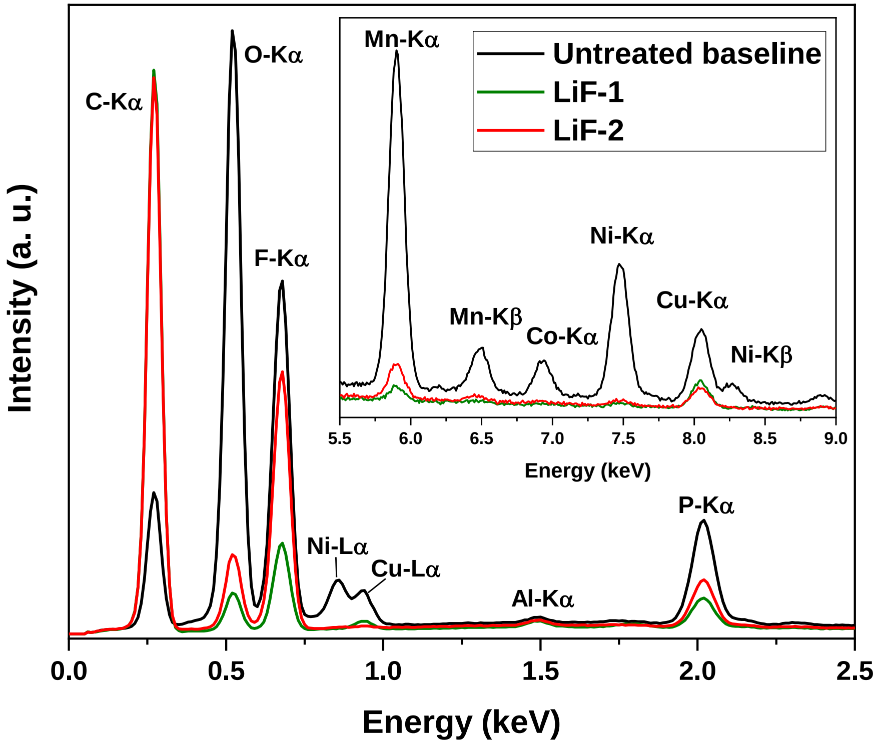


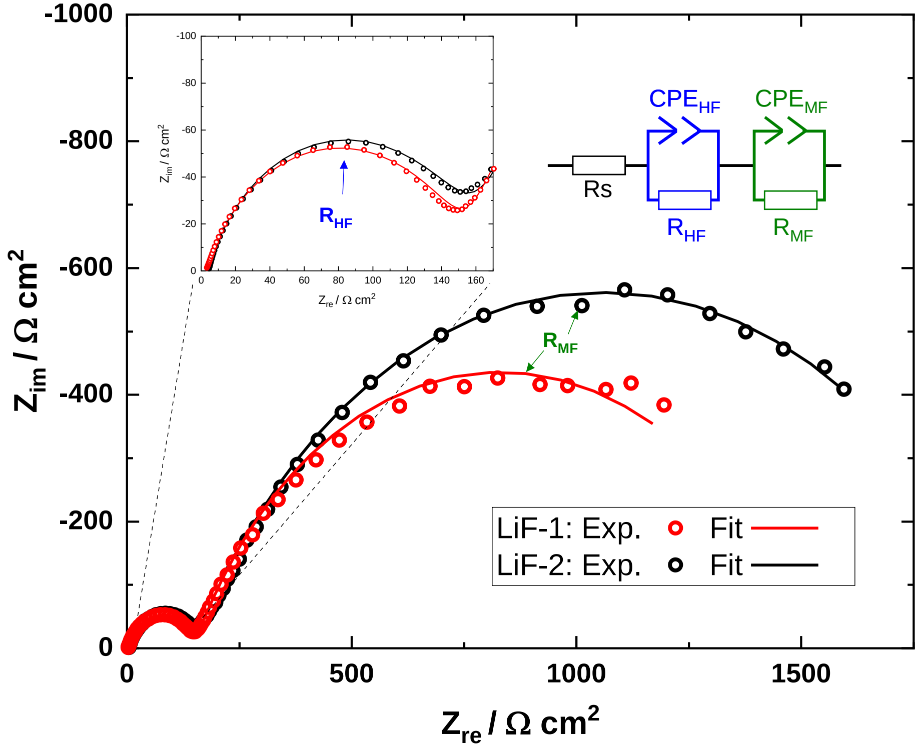




Technical Accomplishments

Surface Stabilization





Post mortem analyses of cathodes and anodes revealed:

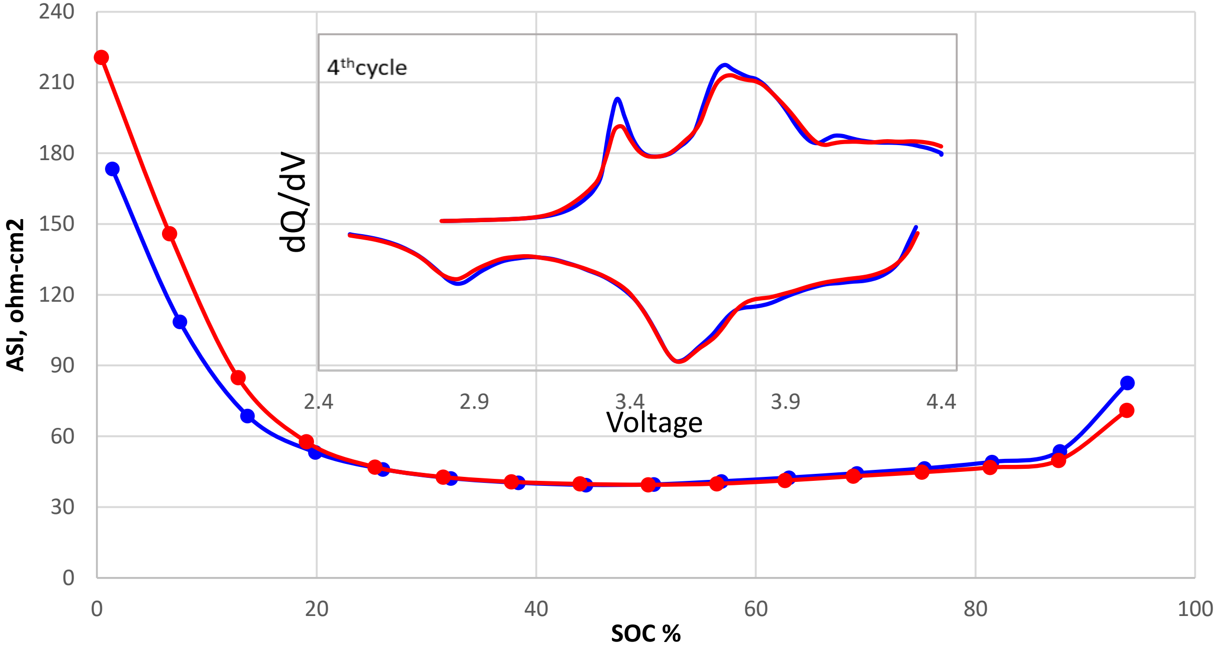
- The anodes from the treated cells showed much less transition metal deposition at the graphite anodes
- The LiF-1 treated cathode, made with the WF_6 precursor, exhibited lower charge transfer impedance compared to the untreated baseline (not shown) as well as the LiF-2 treated cathode after cycling

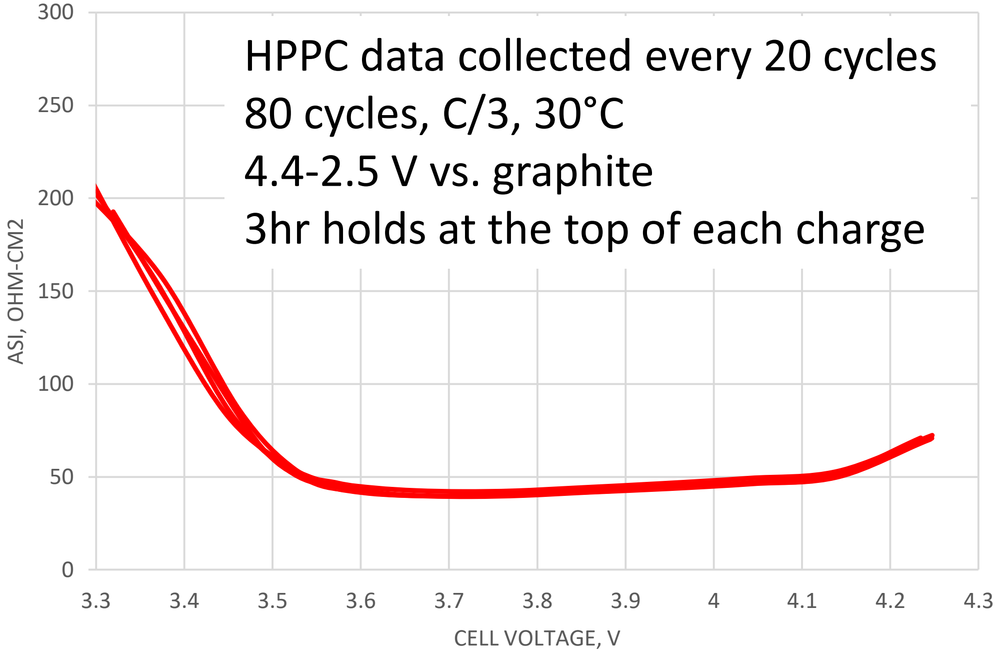
Novel surface treatments show promise for lower cost stabilization of Mn-rich surfaces

Technical Accomplishments

Surface Stabilization & Impedance

0.3Li_2MnO_3•0.7$LiMn_{0.5}Ni_{0.5}O_2$/graphite



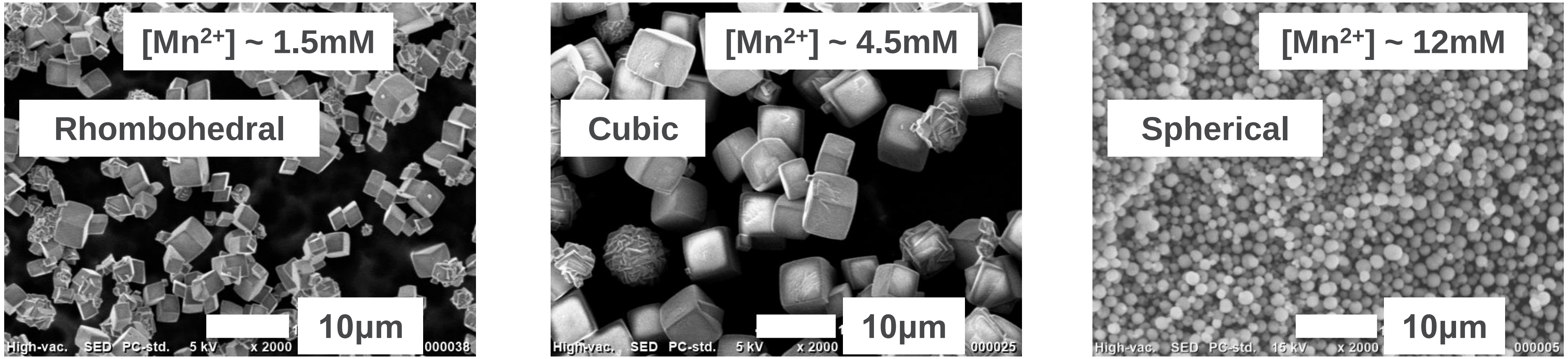

HPPC data collected every 20 cycles
80 cycles, C/3, 30°C
4.4-2.5 V vs. graphite
3hr holds at the top of each charge

- ***Above*** – Treated/untreated samples are similar in all respects during initial cycling as shown by ASI data collected on cycle 7, inset shows dQ/dV of cycle 4
- ***Right*** – 4 HPPC cycled collected every ~20 cycles over ~80 cycles at 4.4 V vs graphite for the treated samples
- This program has a strong record of developing novel surface stabilization approaches and a portfolio of associated patents, exemplified by the data above – see, for example, *A. Gutierrez et al., JES, 166, A3896 (2019).*

Surface stabilization can be achieved for Mn-rich cathodes and eliminate convoluting effects on impedance of surface damage with cycling

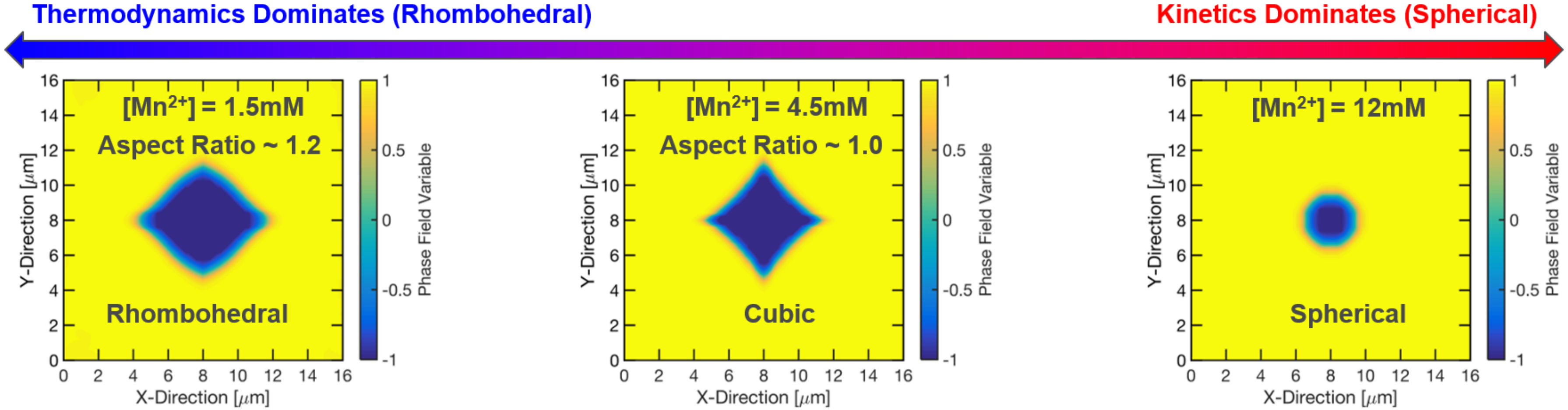
Technical Accomplishments

Understanding Synthesis & Structure



(See also BAT402)

Coprecipitation of $MnCO_3$ in a batch reactor with a solution pH of 7.5 shows that morphology is a function of [Mn^{2+}]

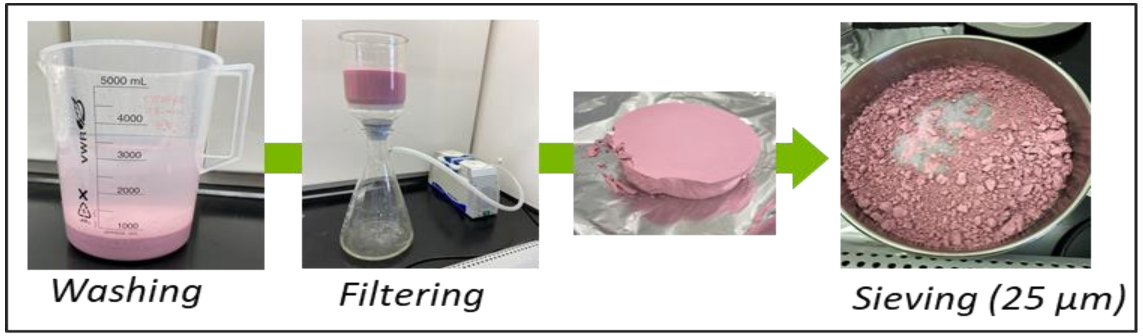


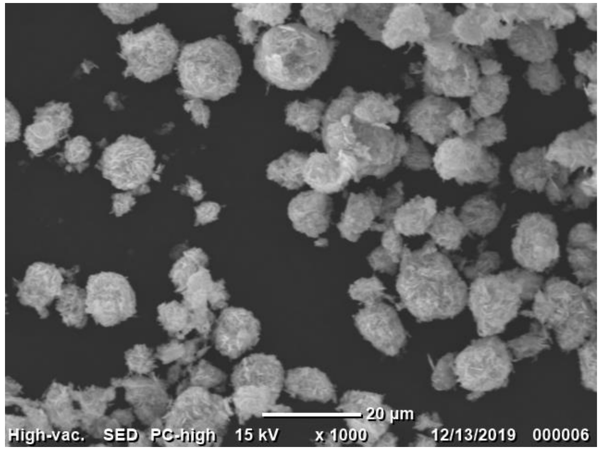
Modeling reveals that the competition between different growth mechanisms dictates particle shape

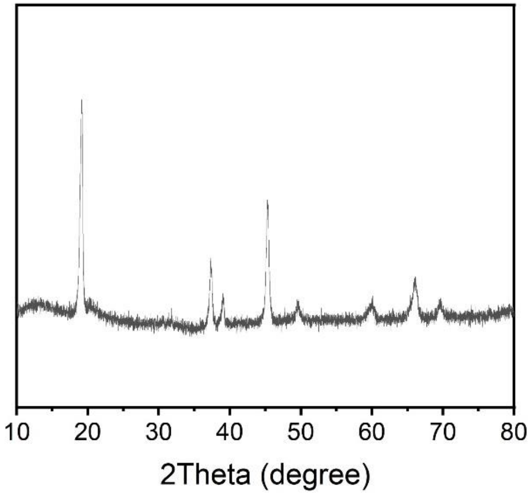
- ***The properties of Mn-rich, cathode-electrodes depend in a significant way on particle morphology***
  – a property that is very sensitive to synthesis conditions, as shown by the work herein
- Detailed investigations have produced single-crystal $MnCO_3$ precursor particles with different morphologies
- Collaboration with computational modeling at ANL is ongoing to enhance our knowledge and control of co-precipitated, Mn-rich oxides to further enhance cathode design and performance

Technical Accomplishments

Scale-up of Novel Cathodes





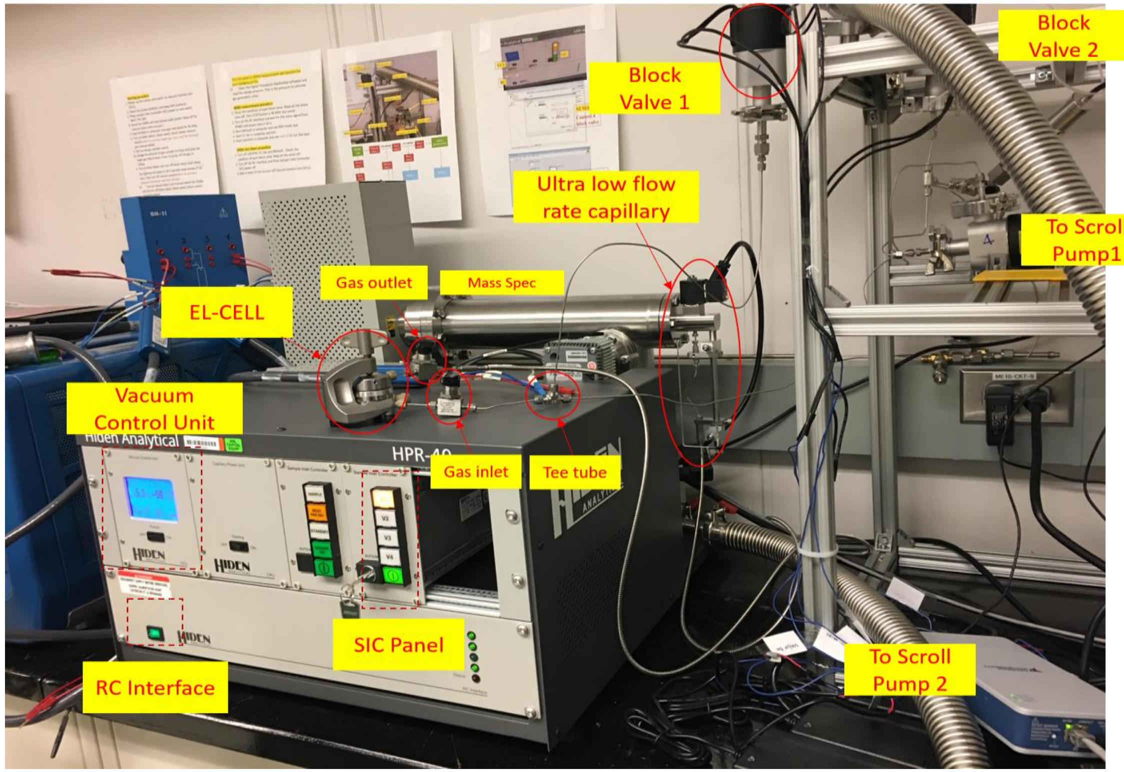


- Last FY this project reported the discovery of a novel LT-$Li_2Co_{2-x}Al_xO_4$, lithiated spinel, ***zero-strain*** cathode as a new class of materials
- This FY the procedures for larger-scale, co-precipitation synthesis of these materials were optimized

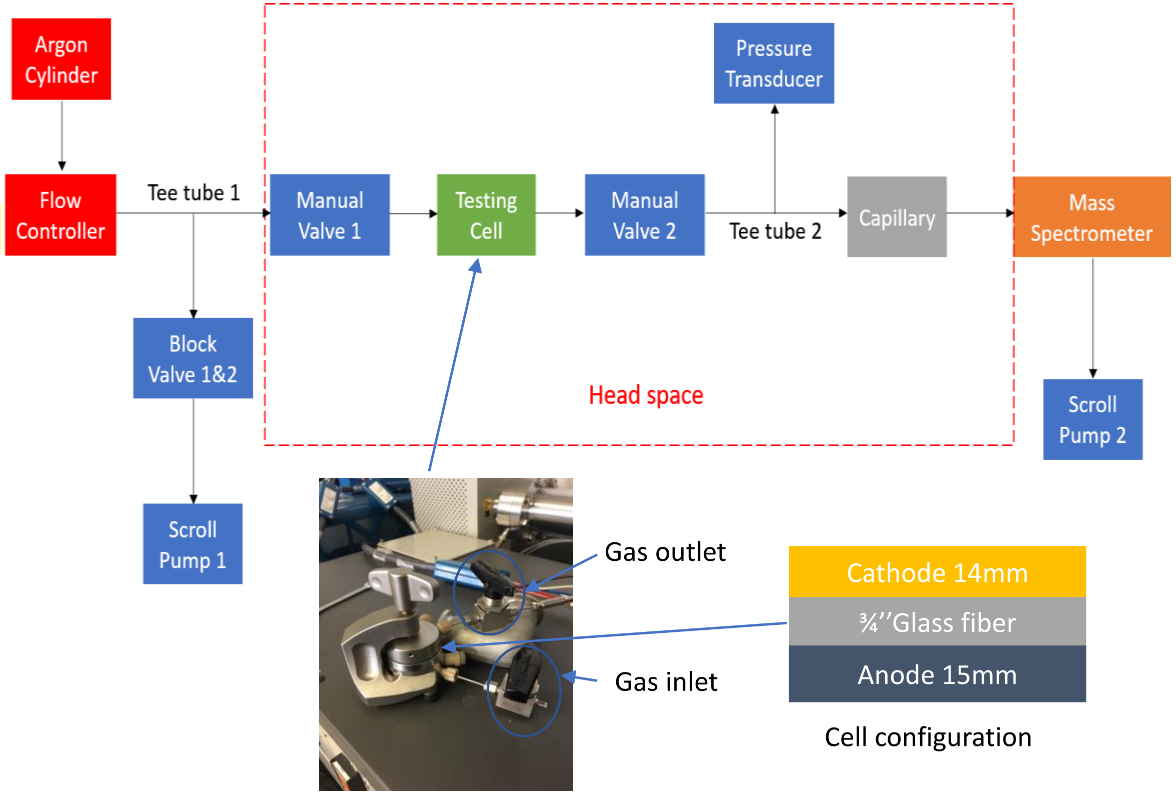
Development of a recently discovered cathode and spinel end-member for LLS materials is continuing with good progress

Technical Accomplishments

Gas Analysis Set Up (OEMS)



Online Electrochemical Mass Spectrometry



Cell configuration

EL-CELL electrochemical cell connected to quadrupole mass spectrometer (Hiden analytic) via a micro flow-rate capillary (Hiden analytic) to monitor gassing behavior of newly developed cathode-electrodes and system modifications in working cells

Summary

Work from this program has produced advancements towards achieving economically-viable, Mn-rich cathodes as alternatives to Ni-rich and LNO-based oxides by:

- Developing novel, integrated structural compositions that contain ~50% or more manganese, have high first-cycle efficiencies, and perform well when compared to NMC-counterparts in terms of energy, rate, and cost
- Developing Mn-rich oxides that show enhanced thermal properties under DSC tests when compared to standard, commercially-available NMCs
- Developing novel surface treatments, including the application of thin films, that reveal viable strategies towards cathode/electrolyte interface stabilization
- Revealing how subtle changes in particle morphology, influenced by synthesis parameters, can be used to enhance the properties of Mn-rich cathode electrodes
- Developing a new class of zero-strain cathodes with implications for stabilization of bulk and surface structures
- Implementation of standardized DOE protocols into the program for confident verification of results including electrochemical performance, gassing, and thermal properties

Proposed Future Research

- Continue exploring the design and synthesis of new integrated structures and the influence on electrochemical properties – notably, detailed investigations of impedance characteristics as a function of particle structure/composition will be carried out
- Continue exploring the design and synthesis of more robust surface structures, thin films, and treatments
- Implement gassing studies using OEMS into the characterization of electrodes that utilize structurally-integrated cathode oxides
- Continue collaborations with computational modeling to gain new insights into the synthesis of Mn-rich precursor materials
- Scale-up and testing of promising systems in larger-format cells, including gassing and thermal studies

Any future work is subject to change depending on funding levels

Collaboration and Coordination

Project Contributors

- CSE, Argonne: Michael M. Thackeray, Roy Benedek, Eungje Lee, Arturo Gutierrez, Jiajun Chen, Boyu Shi, Jinhyup Han, Venkat Srinivasan, Pallab Barai
- ES, Argonne: Devika Choudhury, Anil Mane, Jeff Elam
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- Universities – UIC, WPI, UR
- ANL industrial partners

Major Research Facilities Used

- Post-Test Facility (PTF)
- Cell Analysis, Modeling, and Prototyping (CAMP)
- Spallation Neutron Source (SNS)
- Environmental Molecular Sciences Laboratory (EMSL)
- Advanced Photon Source (APS)
- Argonne Leadership Computing Facility (ALCF)
- Nuclear Magnetic Resonance Spectroscopy Lab (ANL)
- UIC Electron Microscopy Core, Research Resources Center

Support for this work from the ABR Program, Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged – Peter Faguy, David Howell

Response to Previous Year's Reviewer Comments

This project was not reviewed last year