CATHODE MATERIALS FOR NEXT GENERATION LITHIUM-ION BATTERIES: DESIGN, SYNTHESIS, AND CHARACTERIZATION OF LOW-COBALT CATHODES

Project ID: BAT251

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Argonne National Laboratory
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2020 DOE Vehicle Technologies Office
Annual Merit Review

Overview

Timeline

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

Budget

- Total project funding:

  FY19 $4.0M
- ANL, NREL, ORNL, LBNL, PNNL

Barriers

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

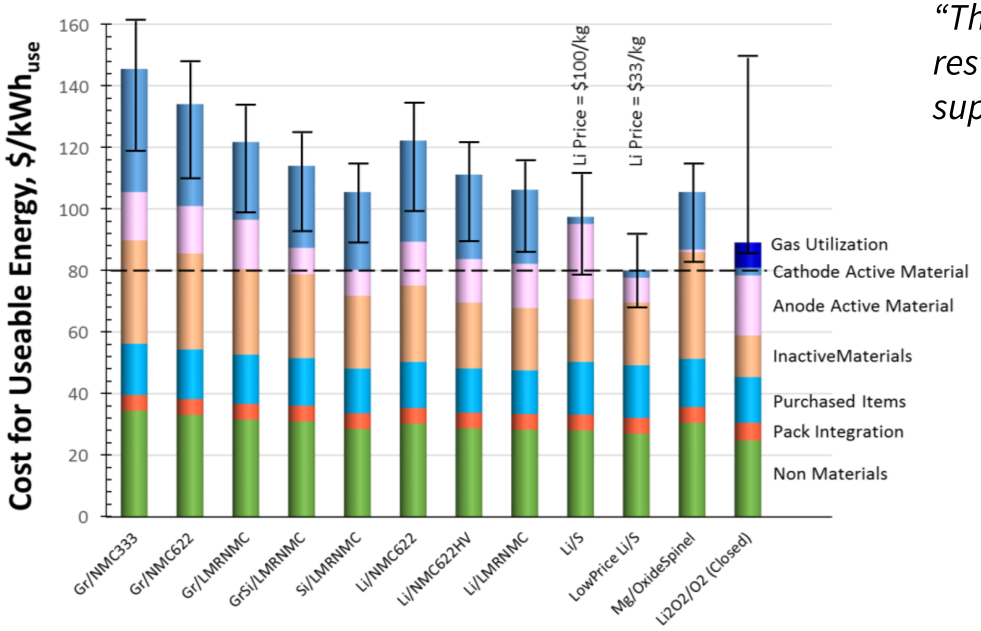
Partners

- ANL, NREL, ORNL, LBNL, PNNL

Students supported from:

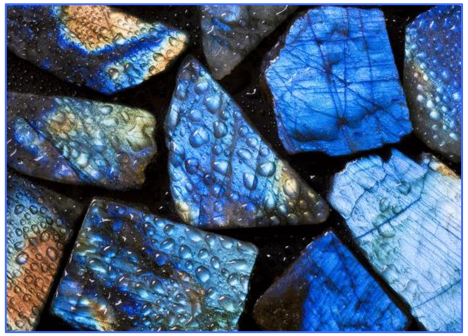
- University of Illinois at Chicago
- University of Rochester
- Oregon State University

Relevance



BatPaC Projected Cost for a $100kWh_{Total}$, 80kW Battery Pack

"The battery industry uses 42 percent of global cobalt production, while the rest is used in industrial and military applications, and all are competing for supply." – supplychainbrain.com



Cost, sustainability, and lack of mature alternatives are the major drivers for continued work in layered transition metal oxides

- Layered transition-metal (TM) oxides represent the best option for near-term advancements for EV batteries
- Li-ion continues to grow and is likely to dominate the market for several decades to come – no guarantees with other technologies (Li-S, "Li-air", multivalent, solid state…)
- Major drivers (safety, energy, power, lifetime, cost) still have room to improve
- ***However, sustainability is a critical factor to the success of the predicted, massive future Li-ion market***

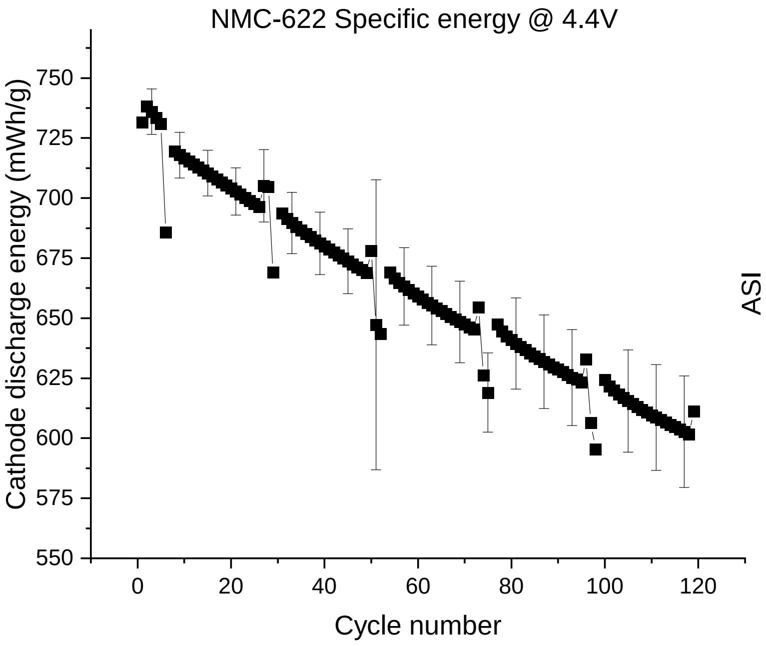
Milestones

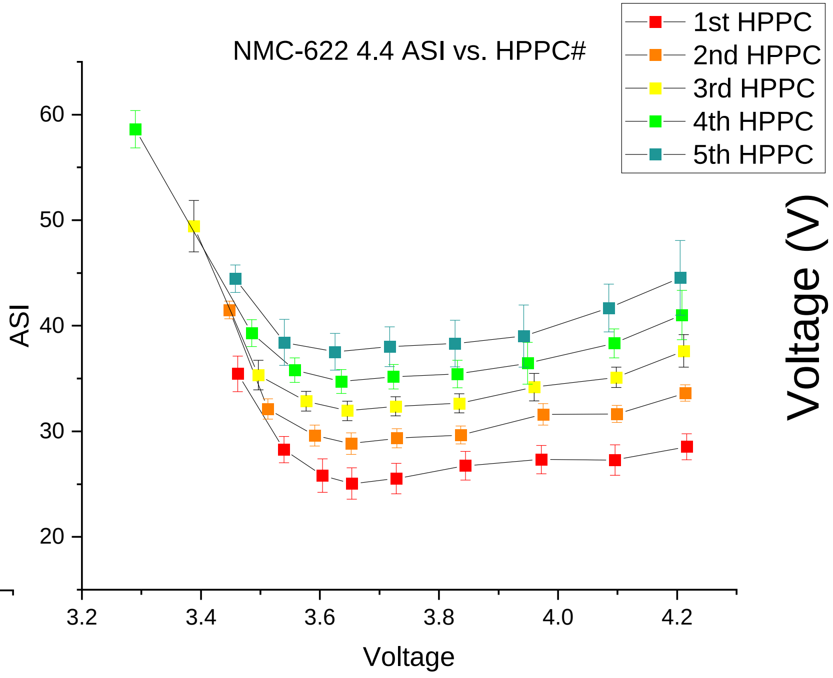
See also BAT252, 253

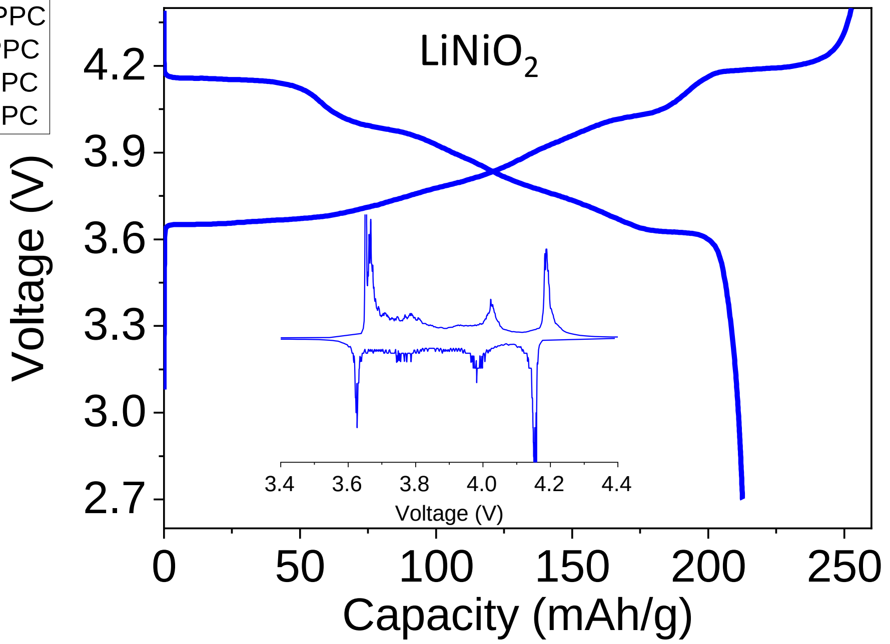
- *This project seeks to make significant progress towards the realization of cobalt-free, TM-oxide cathodes for next-generation, Li-ion batteries*
- *The goals of cathode design are represented by two prototypical materials*

NMC-622 serves as a baseline for minimum performance metrics (energy, power, impedance, retention) under project protocols for new low/no cobalt cathodes

LNO serves as a physiochemical baseline for high nickel, low cobalt cathodes based on LNO (gassing, thermal stability, surface reactivity)



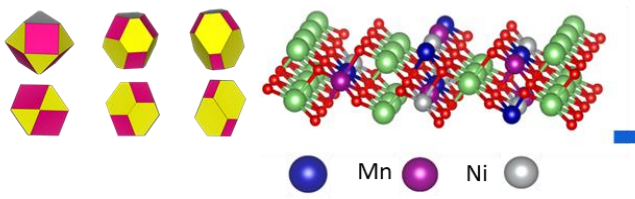




Approach

See also BAT252, 253

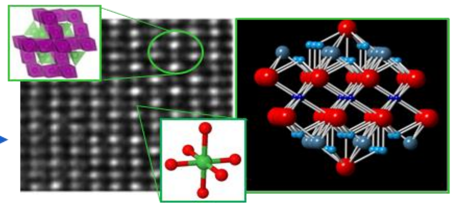
Theory & Models



Atomic-level understanding of the critical roles of cobalt

H. Iddir, G. Chen

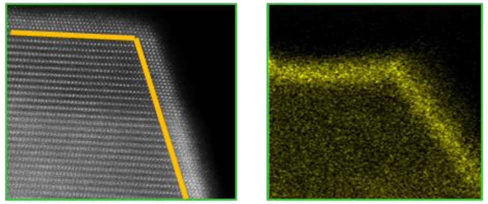
Cathode Design/Synthesis



Implementation of promising cobalt replacement strategies

E. Lee, J. Croy

Surface Stabilization



Design and synthesis of engineered surfaces for high voltage

J. Vaughey, A. Gutierrez

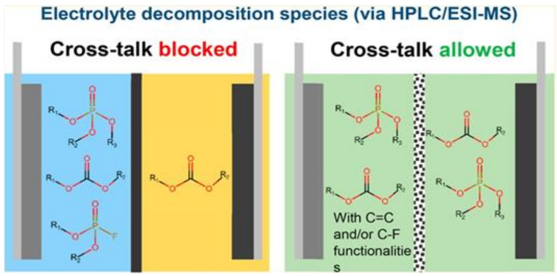
Mechanistic Studies of Critical Issues

Crosstalk, Impedance, Fade…

Coatings, Additives…

Analysis of Modified Cathodes

Full Cell Diagnostics



Understanding mechanisms of cell-level performance & Degradation

D. Abraham, A. Tornheim

Standard Data on all Systems

Electrochemical Analysis

Thermal Properties (DSC)

Gassing Analysis (DEMS)

- The team has developed a multi-thrust approach driven by cathode design and synthesis
- Each thrust has two designated leads and works in parallel, on the same materials, as the other thrusts
- All materials tested and characterized according to program protocols to identify promising strategies

Approach: Two main approaches, broadly categorized as:

LNO-based oxides (e.g. >90% Ni)

Why? Key Advantages
- Clearest path towards low/no cobalt cathodes
- LNO oxides deliver high rate/energy at modest voltages
- Well-layered even with with very low, or no, cobalt
- Long history of work to draw on

Disadvantages
- Thermal instability of LNO-based compositions is high
- Surface impurities – from synthesis and/or storage can lead to poor performance and gassing
- Difficulty with reproducibility due to the sensitivity to synthesis conditions
- Long history of work – very difficult to improve upon or go beyond what is already known

Mn-Rich oxides (e.g. $LiNi_{0.5}Mn_{0.5}O_2$)

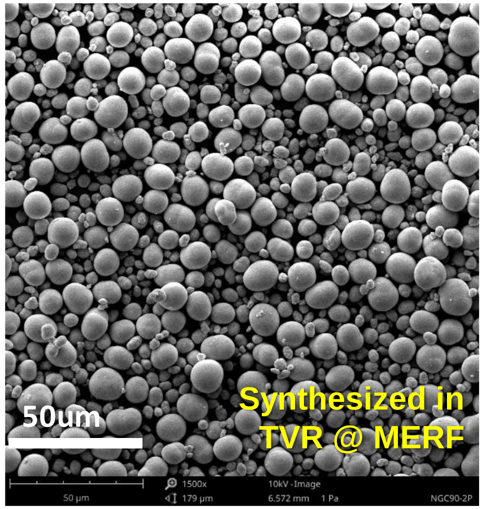
Why? Key Advantages
- Increased Mn improves thermal stability
- Increased Mn decreases cost
- Decreasing Ni allows synthesis at higher temperatures for dense, strong particles and reproducibility
- Less prone to surface impurity issues

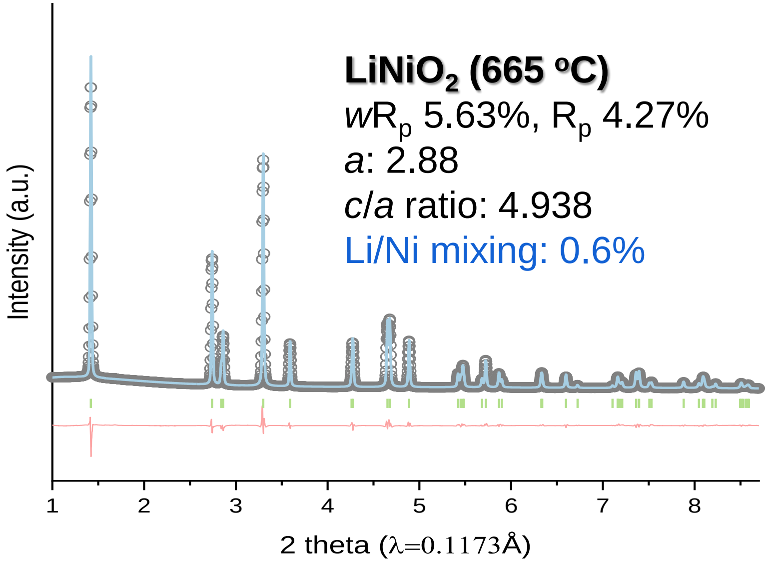
Disadvantages
- Mn^{4+} enhances anti-site exchange between Li^+/Ni^{2+}
- Too much exchange can decrease capacity/rate
- Increasing Mn usually implies increasing upper cutoff to achieve energy
- Mn dissolution can be a problem at graphite anodes

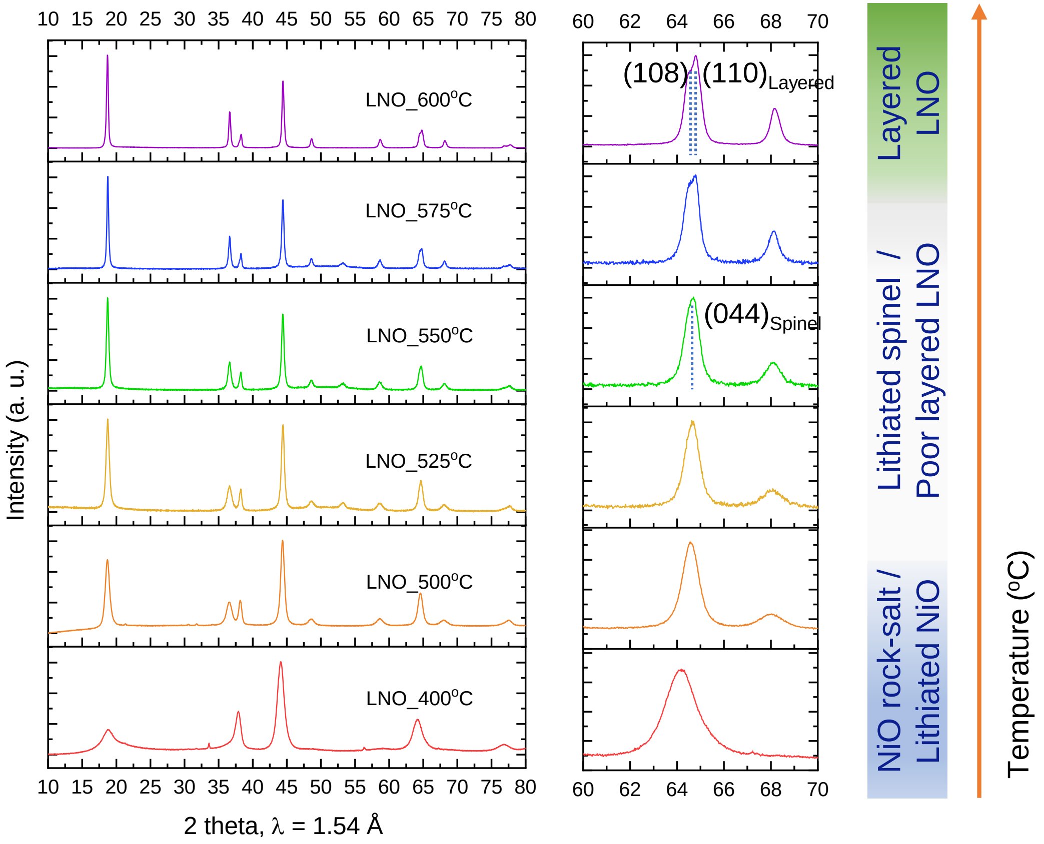
Technical Accomplishments: LNO-based Oxides

Development of optimized, high-performing $LiNiO_2$ as a physicochemical baseline:

- The structural and electrochemical properties of pure $LiNiO_2$ are extremely sensitive to synthesis conditions such as lithium content, oxygen partial pressure, calcination temperature, precursor morphology, and storage
- The behavior of $LiNiO_2$-based, high-energy cathodes can be better understood in light of pure $LiNiO_2$
- Pure $LiNiO_2$ has been re-visited with state-of-the-art co-precipitation and advanced characterization techniques





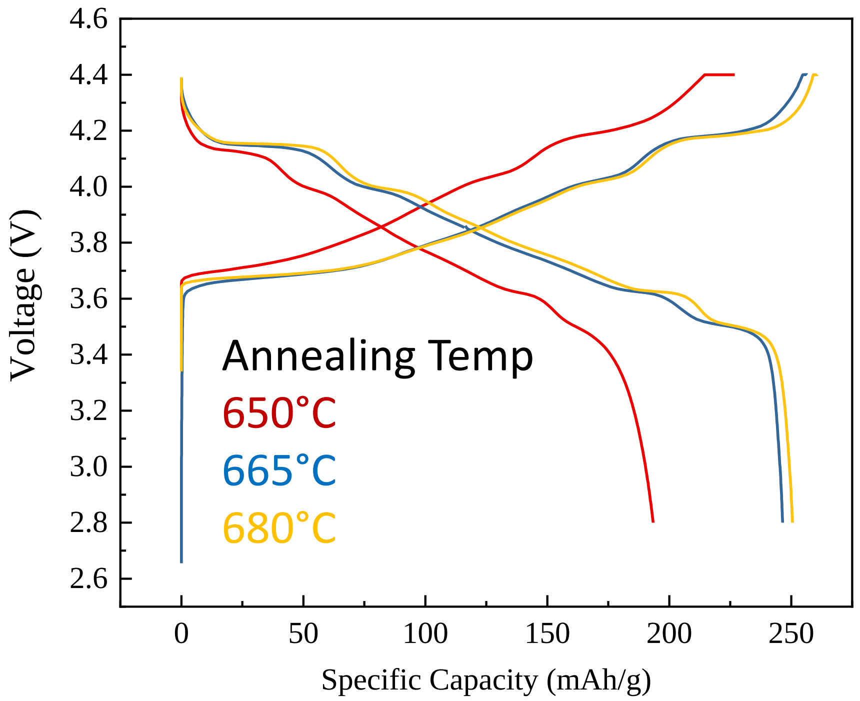


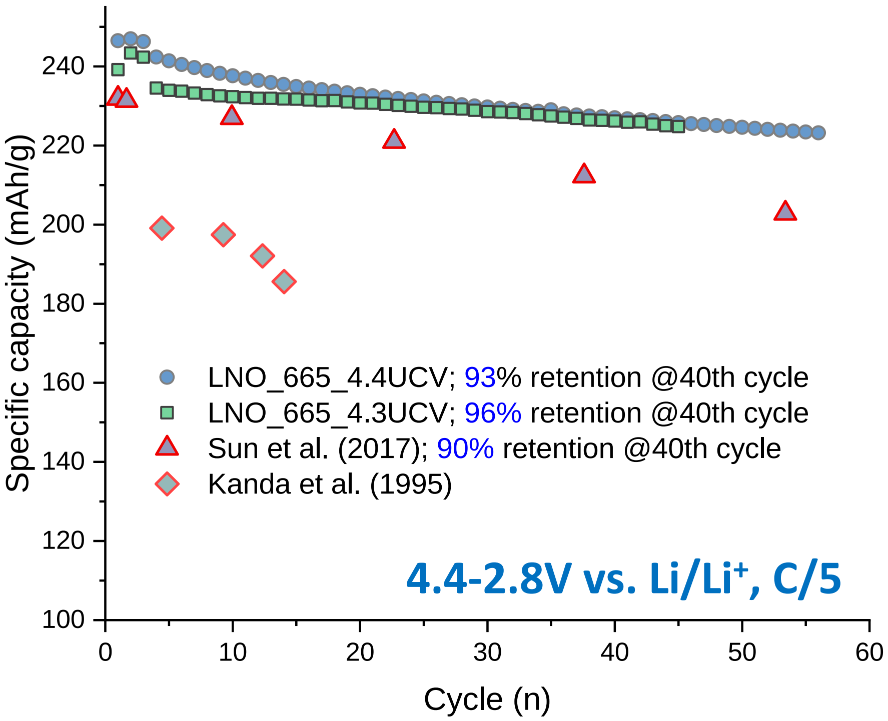
(Left) particle morphology of $Ni(OH)_2$ precursor powder, (middle) Rietveld refinement result of the optimized $LiNiO_2$ material, (right) evolution of the layered $LiNiO_2$ structure via a NiO rock salt and a lithiated spinel structure at low temperatures.

Technical Accomplishments: LNO-based Oxides

$LiNiO_2$: Optimization

Much of the literature either shows poor performance for pure LNO or does not use pure LNO to benchmark LNO-based materials – hinders conclusions and usefulness of the data





- ~1% Li/Ni exchange from X-ray refinements
- >90% retention after 60 cycles at ~245 mAh/g

This is the best performance yet reported for pure LNO!

- As is known, LNO is extremely sensitive to all synthesis parameters and systematic studies must be undertaken if optimal performance is to be obtained – also true for LNO-based derivatives (e.g., doping)
- Pure LNO can be made very well-layered with little Li/Ni exchange, achieve high-capacity and energy, and good cycling performance if synthesized in the correct manner

This LNO serves as a benchmark for the physiochemical properties of all other LNO-based oxides in the program in order to reveal any true differences/advantages over pure LNO

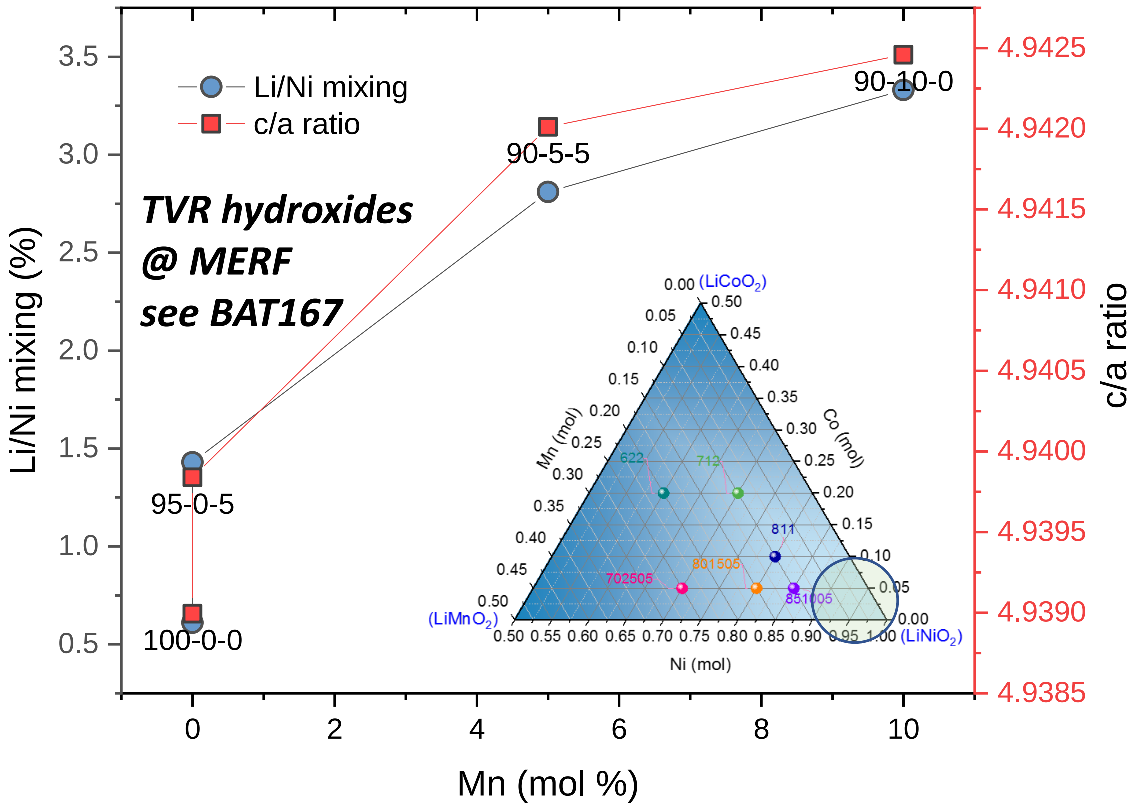
Technical Accomplishments: LNO-based Oxides

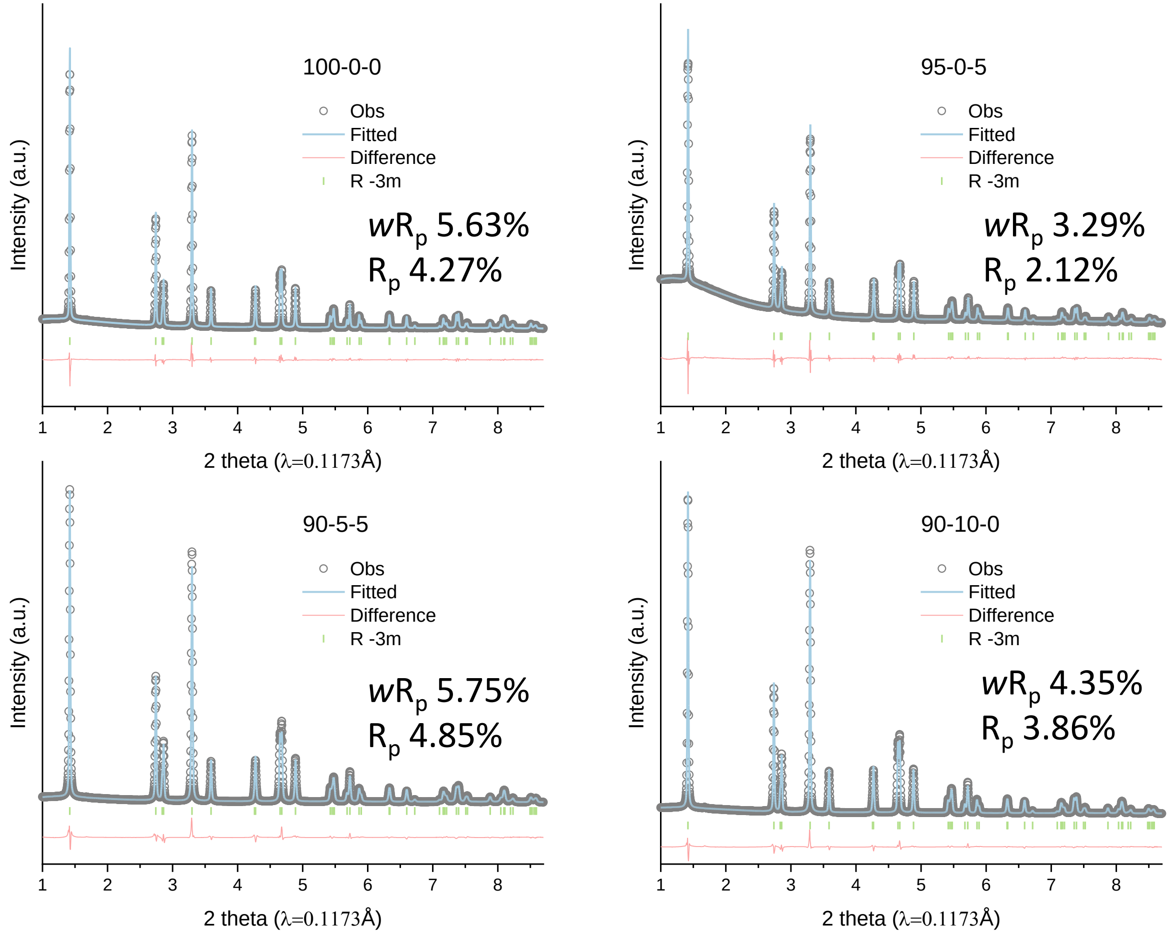
$LiNiO_2$: Impact of Mn and Co

See also BAT252

Impact of Mn and Co substitution:

- The calcination conditions for each $LiNi_{1-x-y}Mn_xCo_yO_2$ sample (x, y ≤ 0.1) were optimized
- $LiNi_{0.95}Co_{0.05}O_2$ (95-0-5), $LiNi_{0.9}Mn_{0.05}Co_{0.05}O_2$ (90-5-5), $LiNi_{0.9}Mn_{0.1}O_2$ (90-10-0) were scaled up for full-cell fabrication





Rietveld refinement results of the optimized NMC100-0-0, 95-0-5, 90-5-5, and 90-10-0 cathode samples show that the degree of Li/Ni anti-site exchange and c/a ratios increase with transition-metal substitution

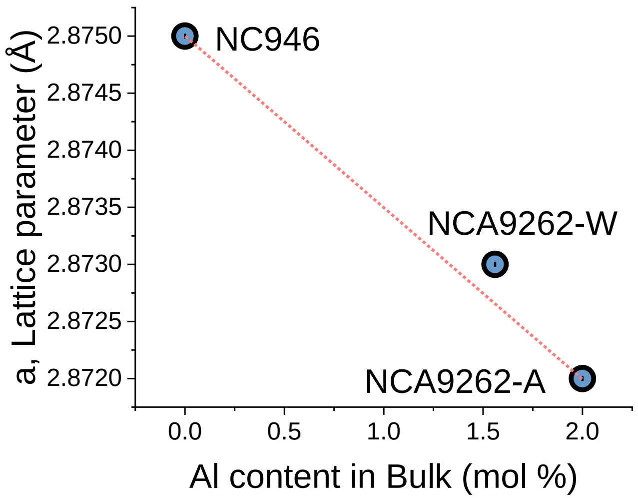
Technical Accomplishments: LNO-based Oxides

$LiNi_{0.94}Co_{0.06}O_2$: Al-doping

Synthesis of $LiNi_{0.92}Co_{0.06}Al_{0.02}O_2$ via ALD method

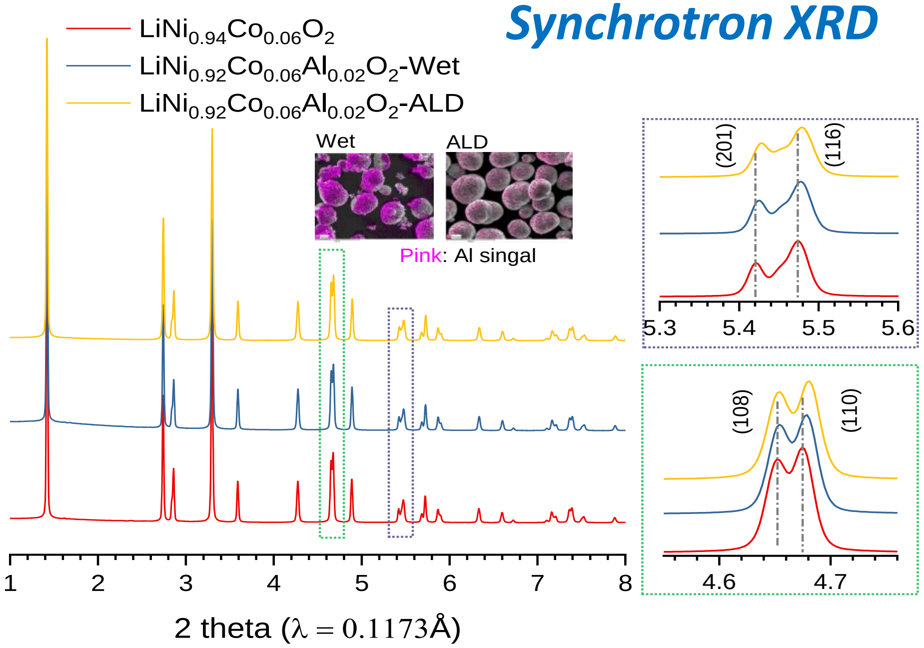
- Al surface layer is introduced on the surface of $(Ni,Co)(OH)_2$ precursors by (1) ALD and (2) wet-chemistry coating methods before high temperature calcination
- Synchrotron XRD and ^{27}Al-MAS-NMR confirms that all of the Al on the precursor surface is incorporated in to the bulk lattice of $LiNi_{0.92}Co_{0.06}Al_{0.02}O_2$-ALD whereas only ¾ of the Al is doped into the structure of the $LiNi_{0.92}Co_{0.06}Al_{0.02}O_2$-Wet sample

Sample	Al overall, ICP [mol%]	Al in bulk, NMR [mol%]
2% Al – Wet	2	1.56
2% Al – ALD	2	2

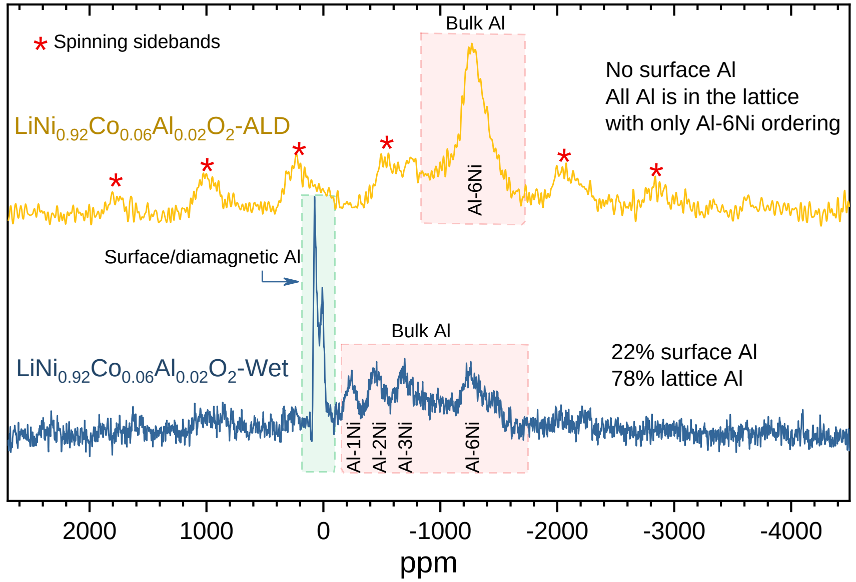


The linear correlation between the lattice parameter (XRD) and bulk Al content (Al MAS NMR) data of the $LiNi_{0.94-x}Co_{0.06}Al_xO_2$ samples highlights the effective Al bulk doping by the ALD method

Synchrotron XRD



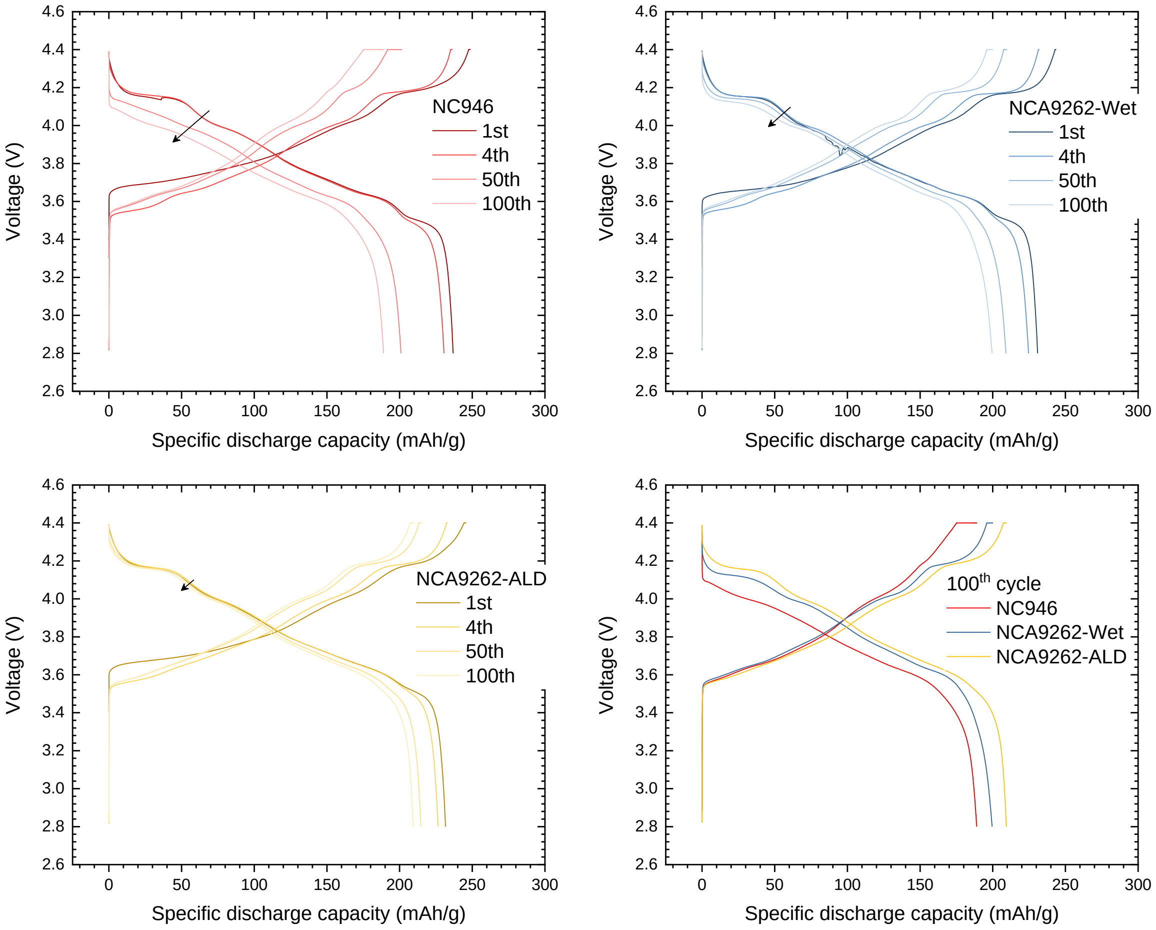
^{27}Al MAS NMR



Technical Accomplishments: LNO-based Oxides

$LiNi_{0.94}Co_{0.06}O_2$: Al-doping

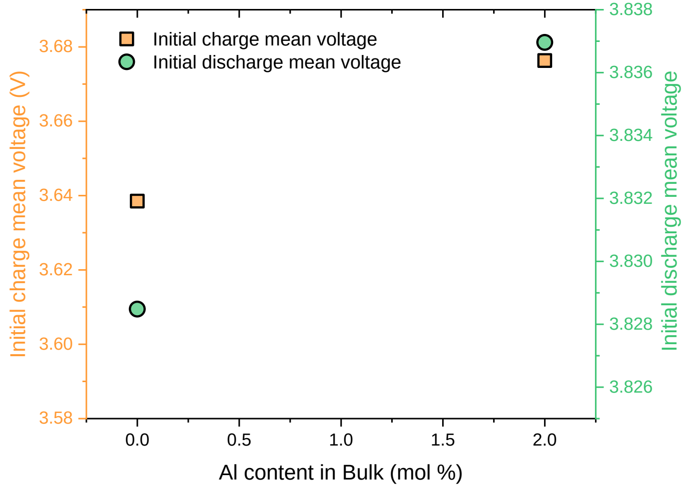
✓ Voltage profile



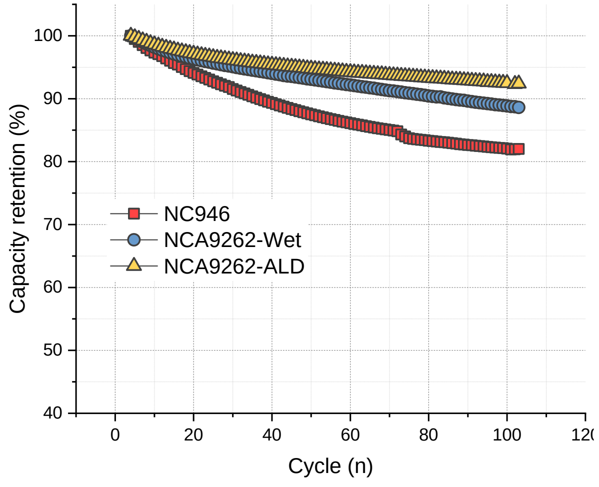
NC946: $LiNi_{0.94}Co_{0.06}O_2$
NCA9262-W: $LiNi_{0.92}Co_{0.06}Al_{0.02}O_2$-Wet
NCA9262-A: $LiNi_{0.92}Co_{0.06}Al_{0.02}O_2$-ALD

Half-cell; V = 4.4 - 2.8 V vs. Li; 3 formation cycles @C/10 followed by 100 cycles @C/5 (1C=180mA/g)

✓ Mean voltage



✓ Capacity retention



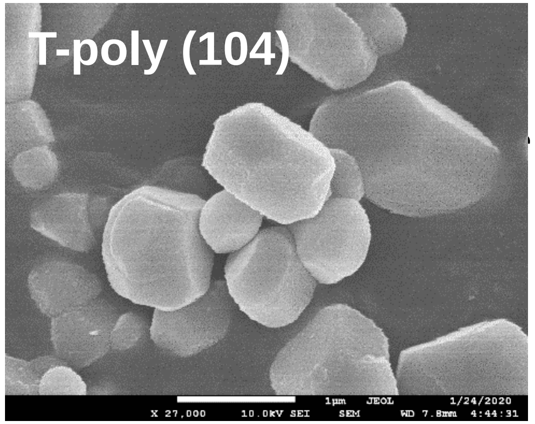
Electrochemical properties of $LiNi_{0.92}Co_{0.06}Al_{0.02}O_2$ prepared via ALD doping method

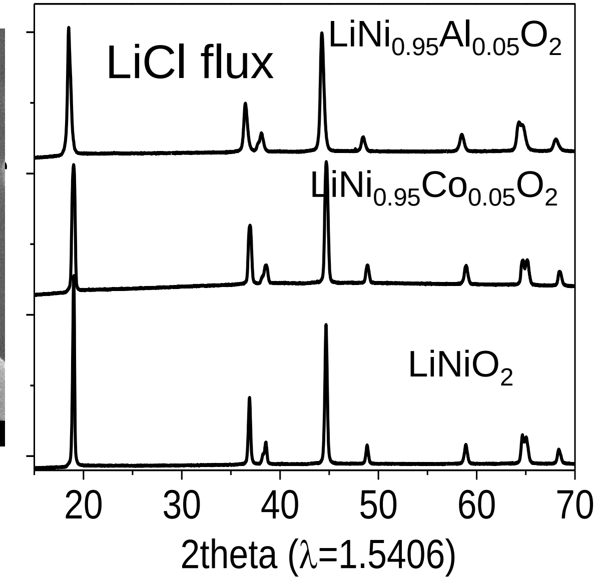
- Al incorporation into the bulk lattice modifies the electrochemical properties of $LiNi_{0.94-x}Co_{0.06}Al_xO_2$: (1) increased charge/discharge voltage, (2) better cycling stability

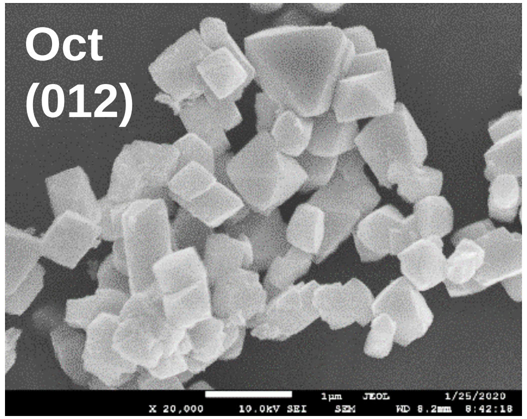
The ALD doping method results in more effective Al bulk doping and hence the highest performance enhancement

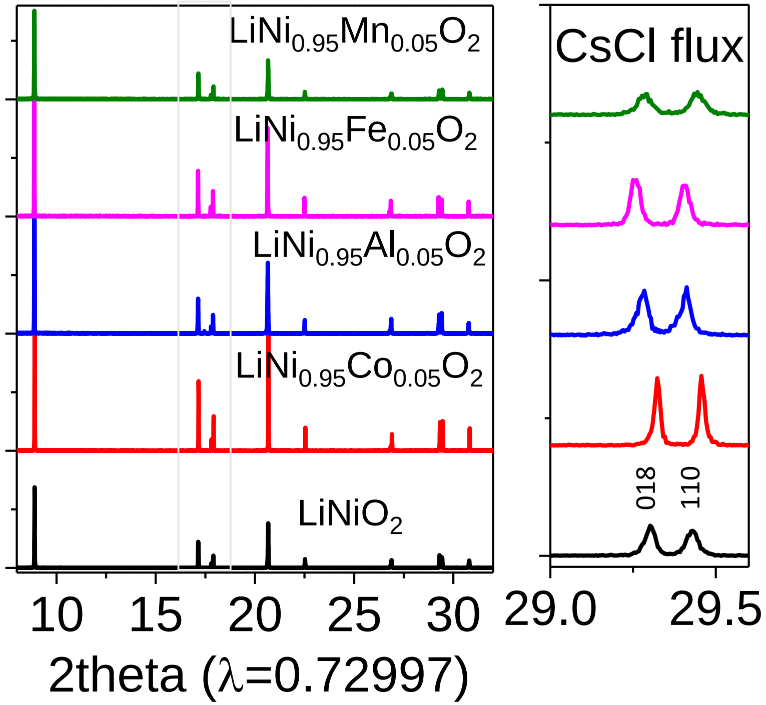
Technical Accomplishments: LNO-based Oxides

$LiNiO_2$: Single Crystals & Dopants

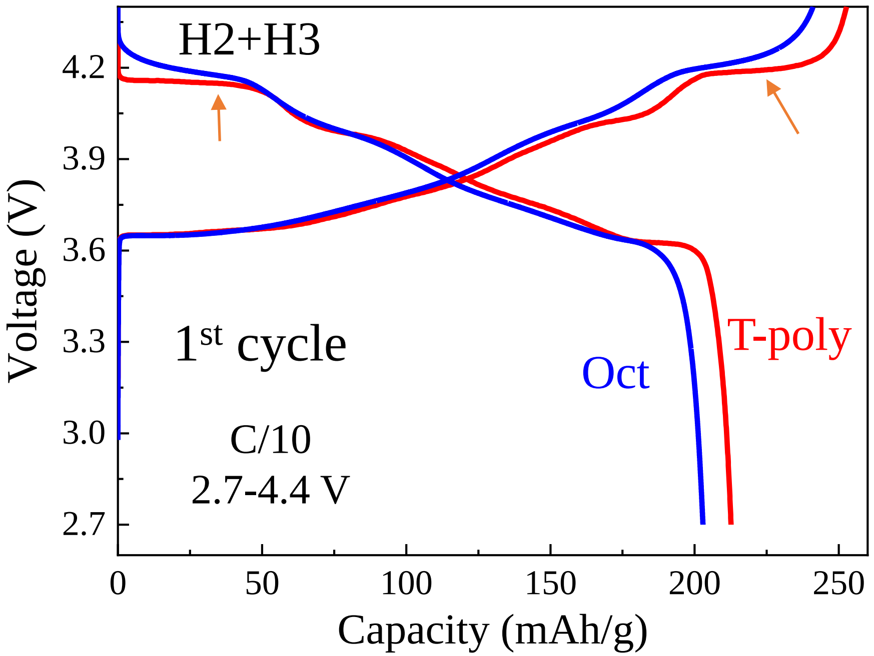








(See also BAT253)

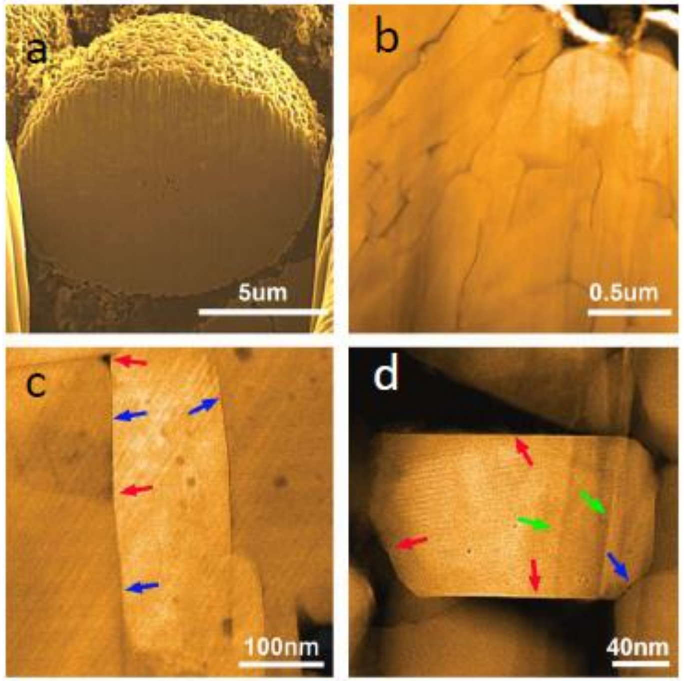


- LNO and 5% TM-substituted LNO samples with truncated polyhedron (T-poly) and octahedron (Oct) morphologies have been prepared
- Dominating surface is (104) for T-poly and (012) for Oct
- Similar performance as shown for co-precipitated samples – added complexity of facet-dependent/morphological influence has important implications for single crystal design for practical application
- Collaboration with Theory Group to understand dopants in terms of facet-dependent synthesis, segregation, and influence on surface and bulk stability

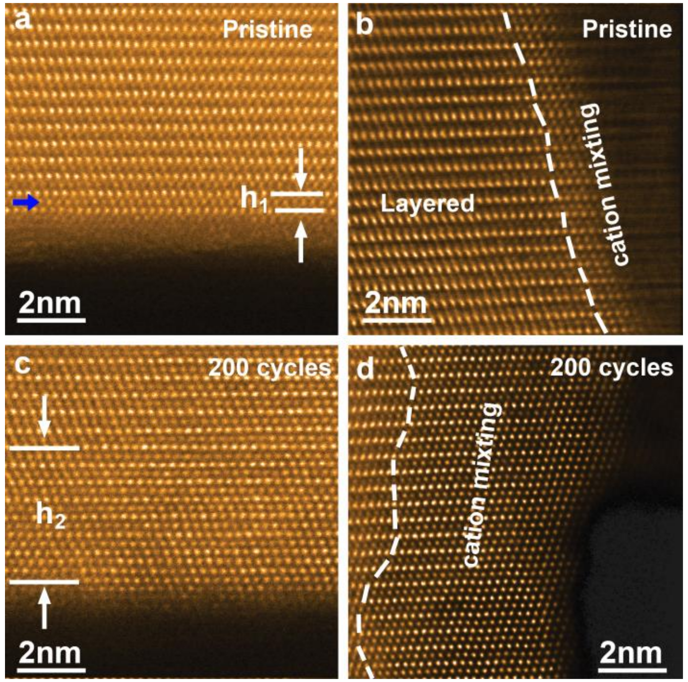
Technical Accomplishments: LNO-based Oxides

Characterization: Particle Structure

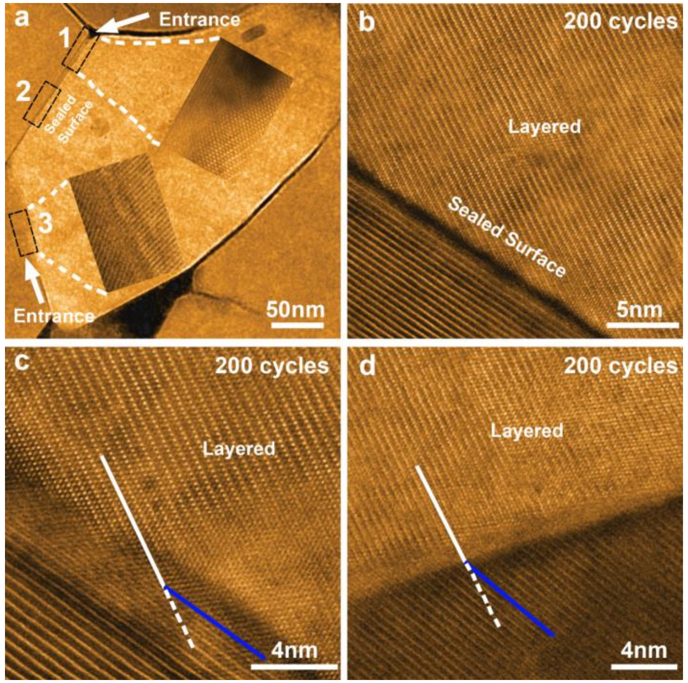
- Within NMC-811 secondary particles, packing of the primary particles leads to different grain boundary structures
- Liquid electrolyte will penetrate the loose or wider opening grain boundaries, but will not penetrate the densely-packed grain boundaries
- Observed that boundary contact with liquid electrolyte leads to a thick surface reconstruction layer – not the case for surfaces that do not contact liquid electrolyte
- Controlling the penetration of liquid electrolyte along the grain boundary will be a critical step for enhancing the stability of secondary, cathode particles



Panel A: Cross sectional SEM and STEM image showing different types of grain boundaries in secondary cathode particles



Panel B: The grain boundary in direct contract with the liquid electrolyte shows a thick surface layer of phase transition upon battery cycling

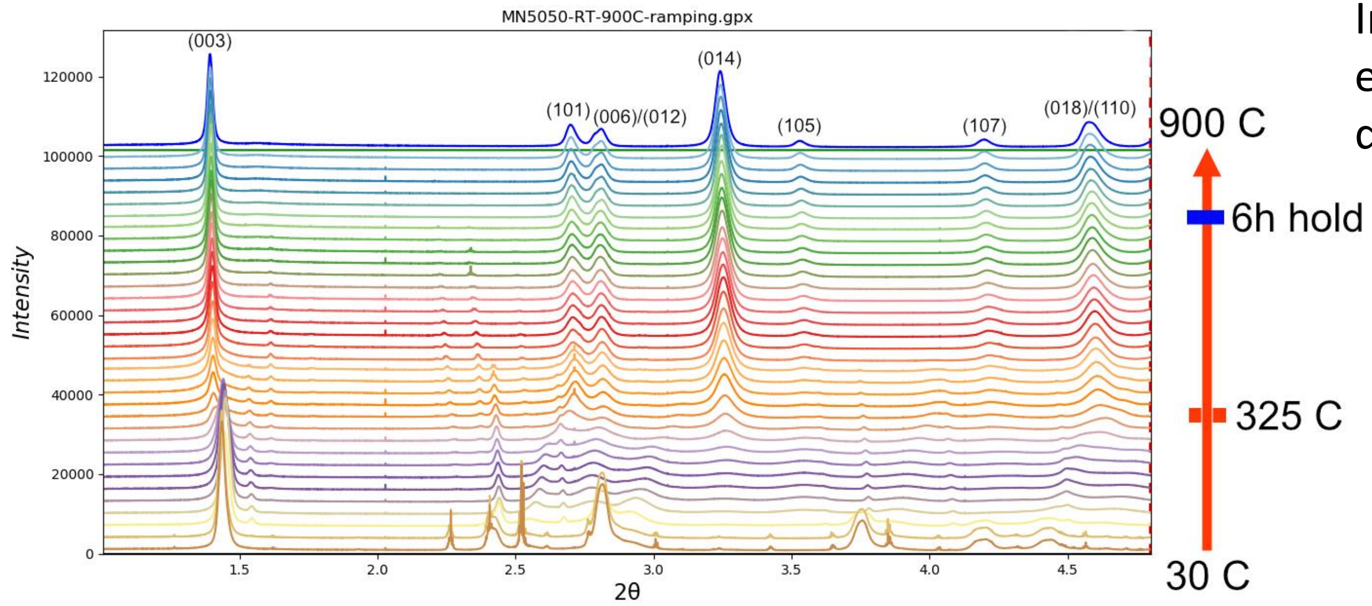


Panel C: The grain boundary does not come in contact with the liquid electrolyte, showing a thin surface reconstruction layer upon battery cycling

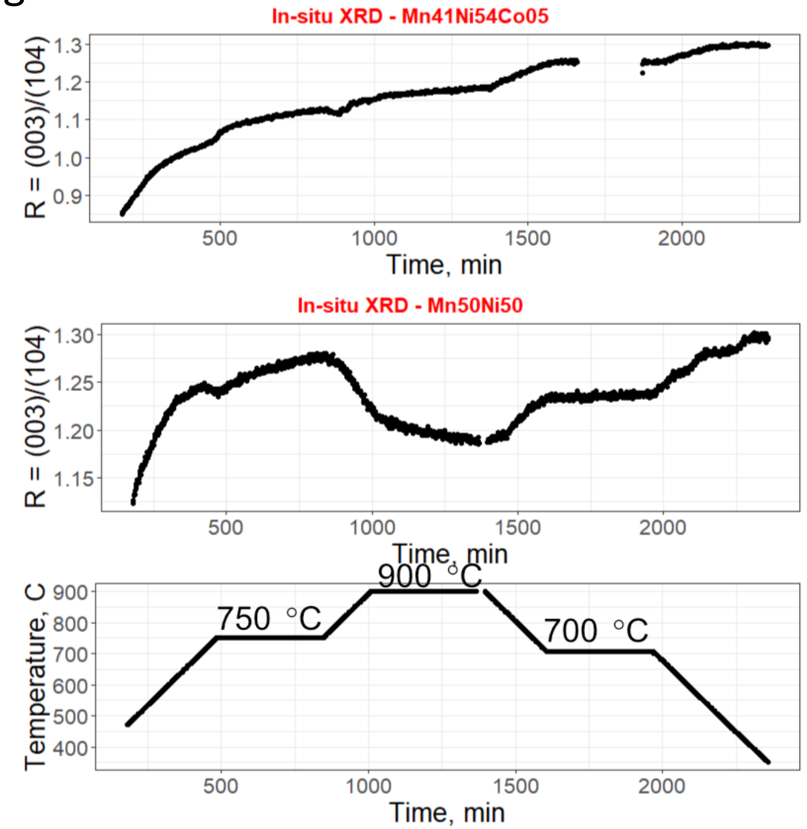
Zou et al., Chem. Mater. 2020, online

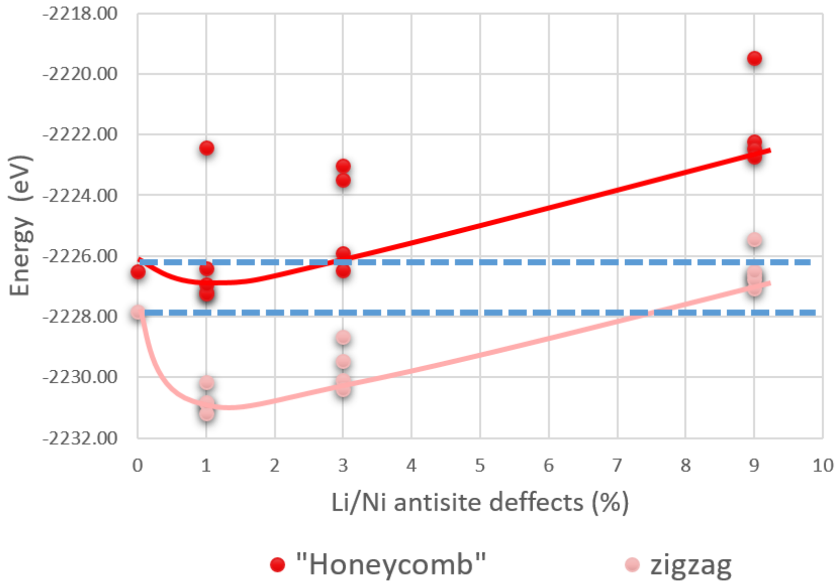
Technical Accomplishments: Mn-Rich oxides

Li/Ni Exchange



In situ synchrotron diffraction (APS) - Phase evolution of a $Mn_{0.5}Ni_{0.5}(OH)_2$+$LiOH·H_2O$ mixture during calcination





~1-3% exchange predicted by calculation for $LiMn_{0.5}Ni_{0.5}O_2$

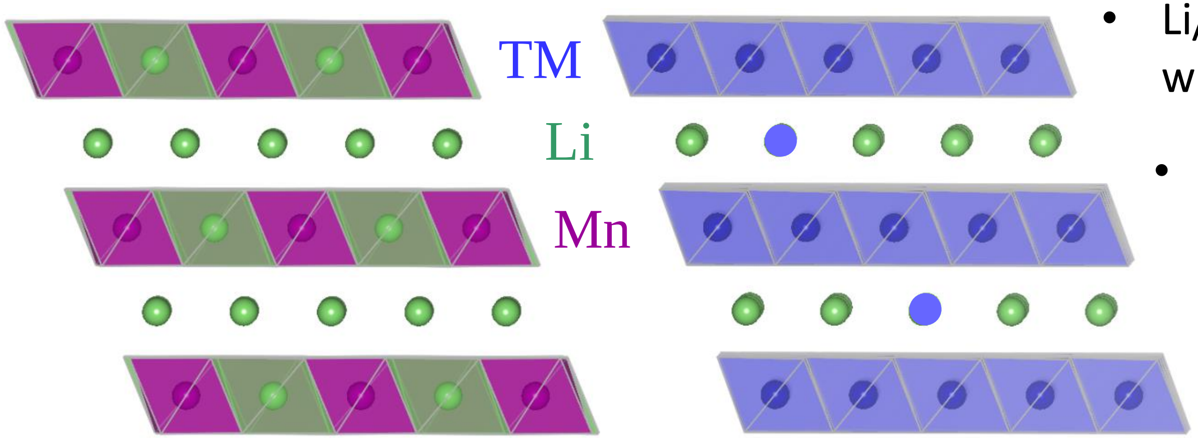
How to achieve in practice?

(See also BAT253)

Detailed theoretical and experimental studies are in progress leading to new insights on Li/Ni exchange in Mn rich, layered oxides

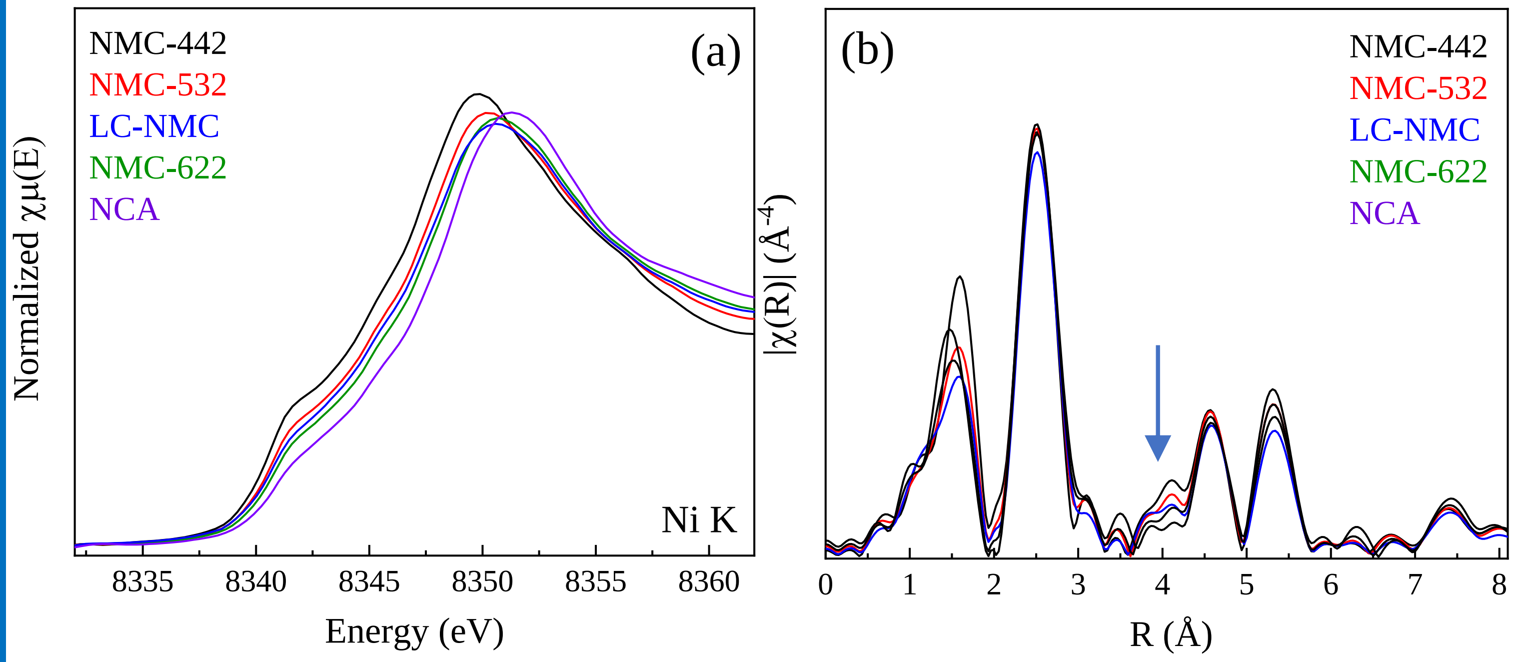
Technical Accomplishments: Mn-Rich oxides

Design for Low Li/Ni Exchange



- Li/Ni anti-site exchange is a critical issue for compositions with significant Mn and Ni
  - Our work has shown that exchange takes place almost exclusively in the TM-rich regions of Li/Mn-rich compositions
    - By careful control of Li:Mn:Ni:Co ratios, the layering effects of Co^{3+} can be 'directed' to regions of interest and alleviate exchange, even at low Co levels

$0.05Li_2MnO_3 \bullet 0.95LiNi_{0.55}Mn_{0.40}Co_{0.05}O_2$

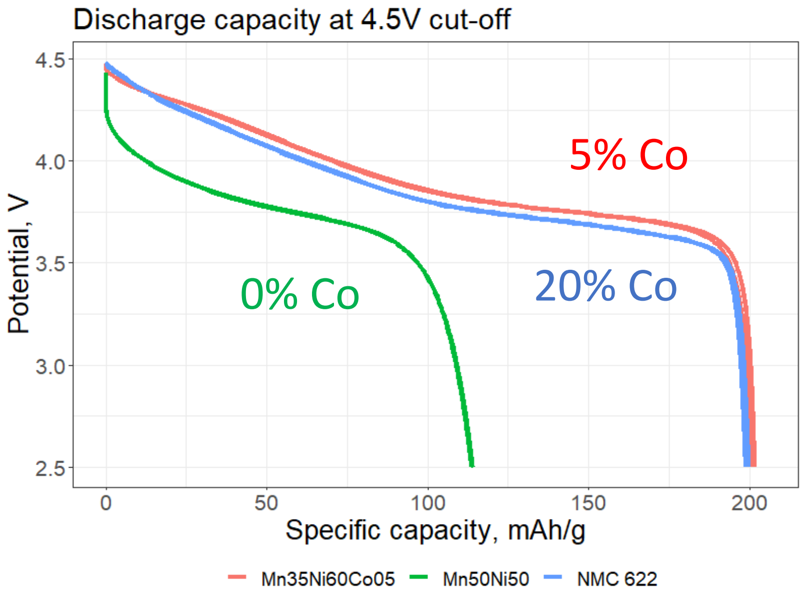


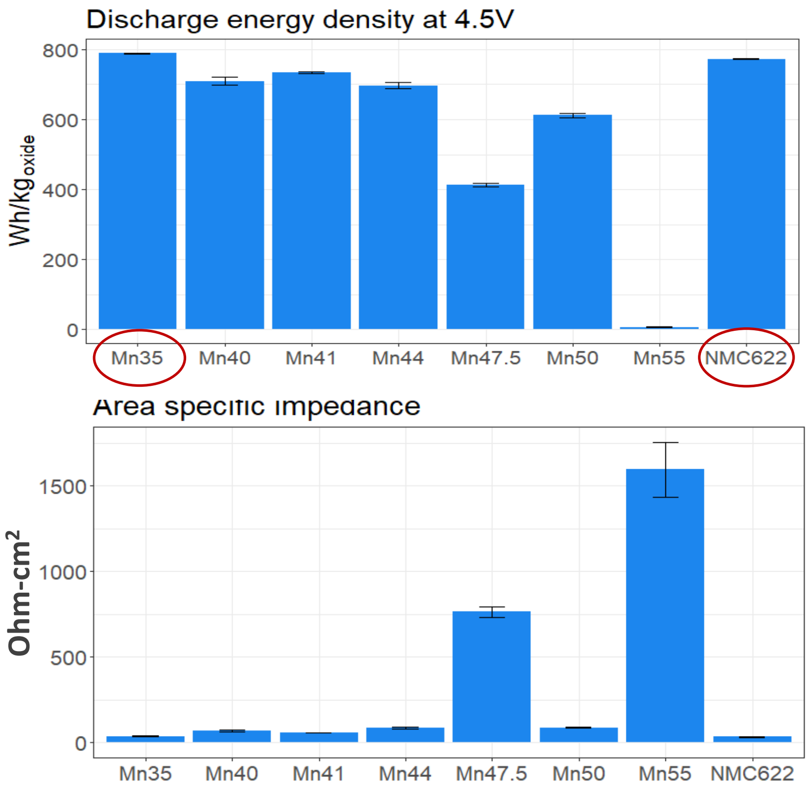
Compositions of just ~3-5% excess Li and Mn:Ni:Co ratios of ~35:60:05 show Li/Ni exchange on par or better than NMC-622, even with ~15% less cobalt and more manganese

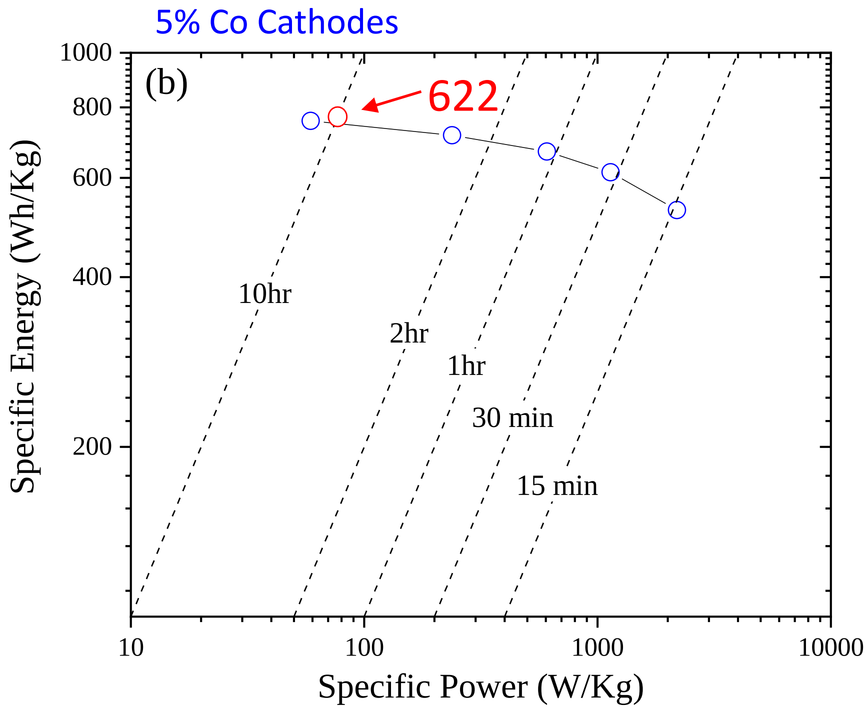
Croy et al., J. Power Sources, 440, 227113 (2019)

Technical Accomplishments: Mn-Rich oxides

Performance







- Substantial improvements over the prototypical Co-free, $LiMn_{0.5}Ni_{0.5}O_2$ have been realized with just 5% Co by understanding the effects of local ordering on composition
- These oxides have energy and impedance characteristics similar to NMC-622
- Preliminary results show that rate/power performance is also high

Cathode design and synthesis efforts have led to the development of cathodes that perform on par with commercial NMC-622 but have 15% less cobalt and 15% more manganese – important implications for cost, safety, and sustainability

Summary

The Cathode Design and Synthesis component of this project has:

- **Re-examined pure $LiNiO_2$** from a synthesis perspective and produced a material that outperforms all $LiNiO_2$ reported in the literature to date – this cathode is serving as a new physiochemical baseline for understanding and modifying the true properties of LNO-based cathode oxides
- **Re-examined Al as a dopant** in LNO-based structures with respect to synthesis and characterization – typical methods were found to give improved performance over untreated samples, however, detailed characterization revealed and non-uniform distribution of Al – A new method of using atomic layer deposition to uniformly dope the bulk of cathode particles was developed and proven to give uniform substitution and further enhancements to cycling performance
- **Developed synthesis procedures** for the fabrication of pure and doped, single-crystal $LiNiO_2$ – collaboration with theory is examining the effect of morphology/faceting and dopant segregation on electrochemical properties
- **Used a detailed understanding** of how composition effects local ordering to develop a cathode consisting of ~35% Mn^{4+} and ~60% Ni while maintaining low Li/Ni exchange with just ~5% Co – these cathodes perform on par with commercially available NMC-622 – this result has important implications for cost, safety, and sustainability
- **Uncovered through advanced microscopy** the important role that grain boundaries play in electrochemical degradation
- **Delivered more than 10 baseline compositions** to the different project thrusts for detailed investigation
- These efforts have been an **intensive collaboration** between cathode PIs across four national labs, the *Materials Research and Engineering Facility* (MERF), the *Cell Modeling and Prototyping Facility* (CAMP), and User facilities such as the *Advanced Photon Source* and the *Environmental and Molecular Sciences Lab*

Future Work

- Development of surface modifications in the form of coatings, treatments, and dopants that can suppress surface and performance degradation in working cells
- Detailed characterization utilizing element-specific spectroscopies, such as NMR and XAS, as well as diffraction techniques to examine the synthesis-structure-property relationships that govern newly developed, low/no-cobalt cathodes – including single crystals and doped derivatives
- Continued collaboration with theory and modeling on the effects of low-level substituents in LNO-based cathodes
- Scale up (~1kg) two promising cathode oxide compositions for larger-format cell builds and evaluation under project protocols including LNO-based and ‘high-Mn’ LNMO-based compositions

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

Collaboration and Coordination

Next-Gen Cathode Project Contributors

- Daniel Abraham
- Khalil Amine
- Mahalingam Balasubramanian
- Ilias Belharouak
- Ira Bloom
- Anthony Burrell
- Guoying Chen
- Jiajun Chen
- Lina Chong
- Devika Choudhury
- Jason Croy
- Dennis Dees
- Fulya Dogan
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- Juan Garcia
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- Jihyeon Gim
- Arturo Gutierrez
- Yeyoung Ha
- Sang-Don Han
- Kevin Hays
- Hakim Iddir
- Andrew Jansen
- Christopher Johnson
- Ozge Kahvecioglu Feridun
- Minkyung Kim
- Joel Kirner
- Eungje Lee
- Linze Li
- Xuemin Li
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- Mei Luo
- Anil Mane
- Jagjit Nanda
- Nate Phillip
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- John Vaughey
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- Chongmin Wang
- Jianzhong Wang
- David Wood
- Zhenzhen Yang
- Junghoon Yang
- Jianzhong Yang
- Haotian Zheng
- Lianfeng Zhou

Major Research Facilities

- Materials Engineering Research Facility
- Post-Test Facility
- Cell Analysis, Modeling, and Prototyping
- Spallation Neutron Source
- Environmental Molecular Sciences Laboratory
- Advanced Light Source
- Battery Manufacturing Facility
- Advanced Photon Source (APS)
- Laboratory Computing Resource Center (ANL)
- NMR Spectroscopy Lab (ANL)
- National Energy Research Scientific Computing Center (LBNL)
- Stanford Synchrotron Radiation Light Source

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Response to Previous Year's Reviewer Comments

This project was not reviewed last year