Scale-up Optimization and Characterization of High-nickel Cathodes

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OVERVIEW

Timeline

- Project start date: October 2016
- Project end date: September 2021
- 90 % complete

Budget

- Total project funding
  - DOE share: $50M
- Funding received in FY 2020
  - $10M
- Funding for FY 2021
  - $10M

Barriers

- Barriers
  - Energy density
  - Cycle life
  - Cost
- Targets
  - High-energy-density high-nickel cathodes with long cycle life and reduced materials cost

Partners

- PNNL, BNL, INL, SLAC, BU, UCSD, UW

RELEVANCE

Relevance

- Lithium-ion cells with high-energy density and long cycle life at an affordable cost can accelerate vehicle electrification

Objectives

- Develop high-energy, long-life, stable high-nickel layered cathodes
  - High-nickel layered oxides with a specific capacity of > 220 mA h g^{-1}
  - Coprecipitation and testing of novel dopants and compositions
  - Understanding the relationship between nickel content, lithium extraction, and cycle life

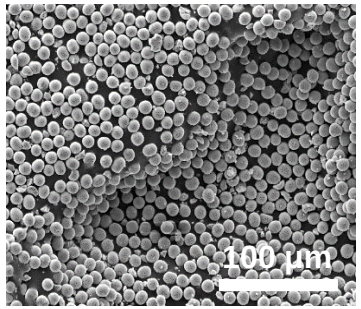
- Validation and characterization of high-nickel cathodes in advanced electrolytes
  - Demonstration of long cycle life without reducing capacity
  - Assessment of degradation mechanisms with advanced characterization
  - Assessment of lithium-metal anode paired with high-nickel cathodes

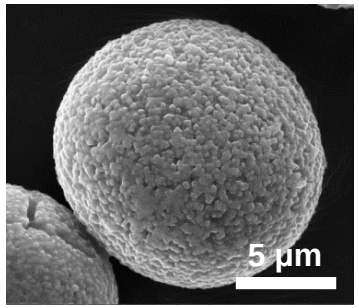
MILESTONES

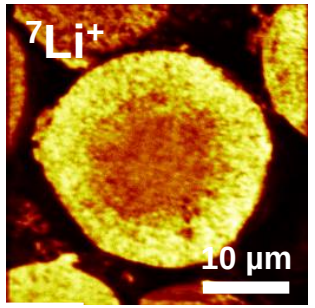
Month/Year	Milestone	Status
December 2020	Investigation of the effect of cathode reactivity on the severity of anode-to-cathode crossover in lithium-metal batteries	Completed
March 2021	Supply high Ni (Ni > 0.8, 220 mAh/g at 4.4 V) cathode for coin cell evaluation with standard protocols and benchmarking with 622 and 811 cathodes	Completed
June 2021	Optimize the N/P ratio, matrix/lithium ratio, and mass loadings in lithiophilic matrices for stable lithium plating on pairing with high-nickel (Ni > 0.8) cathodes	Ongoing
September 2021	Synthesis of high-nickel (Ni content >80%) single-crystal layered-oxide cathodes and their evaluation in long-life graphite and lithium-metal pouch cells	Ongoing

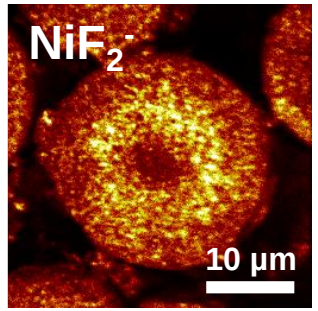
APPROACH

- **Increase energy density and reduce cost:** Increase nickel content in layered-oxide cathodes
- **Novel dopants and compositions**: Coprecipitation of hydroxide precursors with a tank reactor by controlling pH, temperature, and pumping rate
- **Capacity-limited cycling:** Demonstration of superior cycle life with high-nickel cathodes at the same state-of-charge / extent of delithiation
- **Assessment:** Evaluation in pouch cells and characterization after extended cycling to fully understand the degradation mechanisms





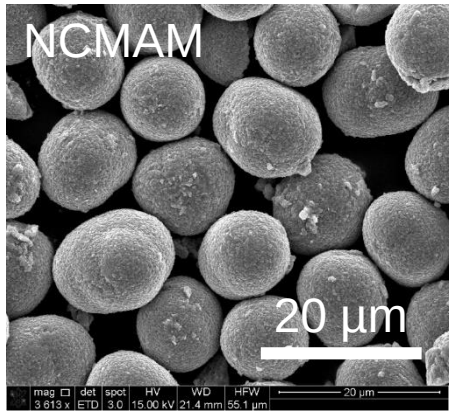


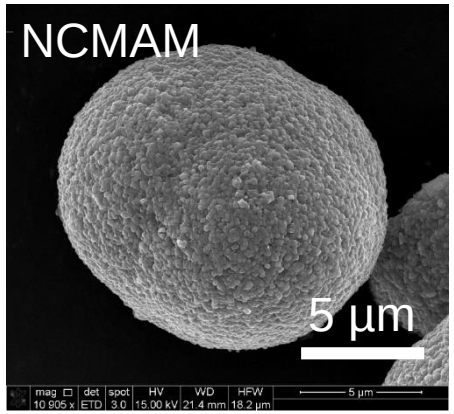


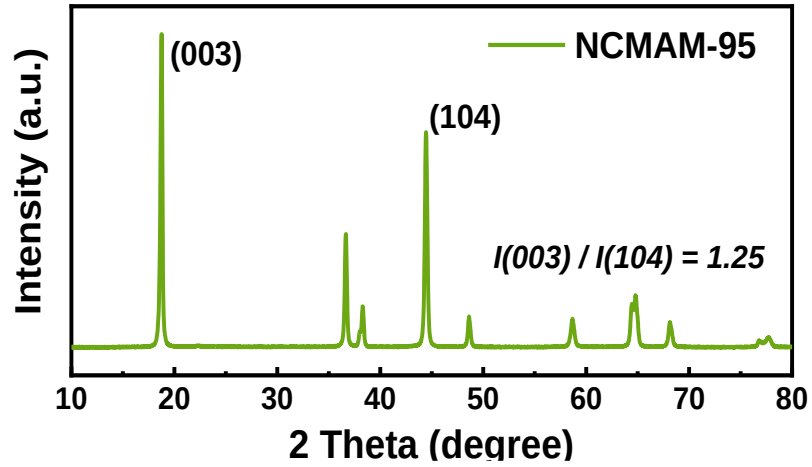
TECHNICAL ACCOMPLISHMENTS AND PROGRESS

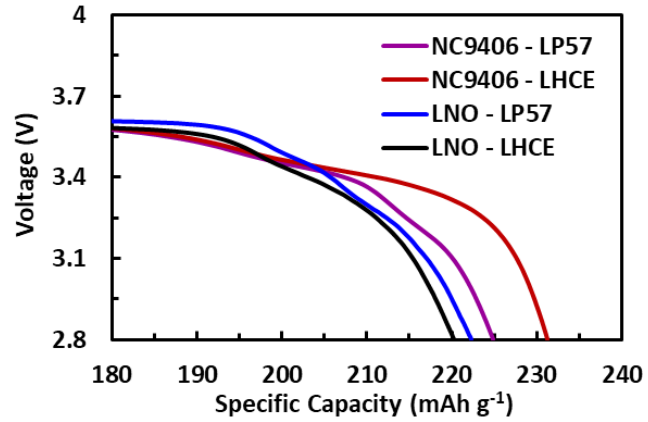
- **Ultra-high capacity:** Several high-nickel cathodes with > 220 mA h g^{-1} at C/3 have been demonstrated; one of them has been delivered to PNNL to benchmark with NMC811
- **$LiNiO_2$ (LNO) vs. NMC 811:** With the same degree of delithiation (charge), $LiNiO_2$ shows better stability/cyclability than NMC 811; degree of Li extraction, not Ni content, determines stability
- **LHCE validation:** Unlike carbonate electrolyte, localized high concentration electrolyte (LHCE) is compatible with Li metal and high-Ni cathodes with good cycle life; but there is a complex two-way crossover

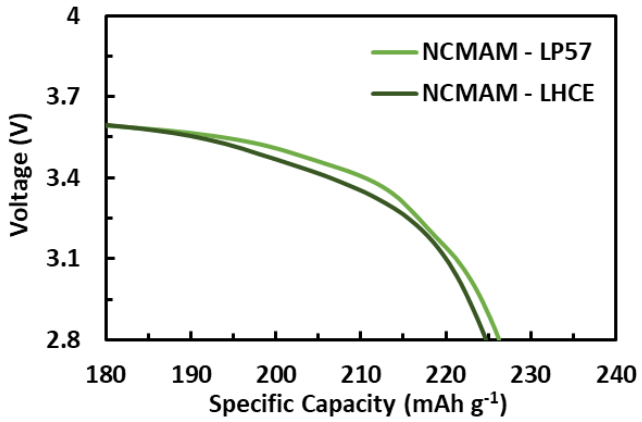
ACHIEVING > 220 mA h g^{-1} AT C/3 WITH HIGH-NICKEL CATHODES IN LHCE

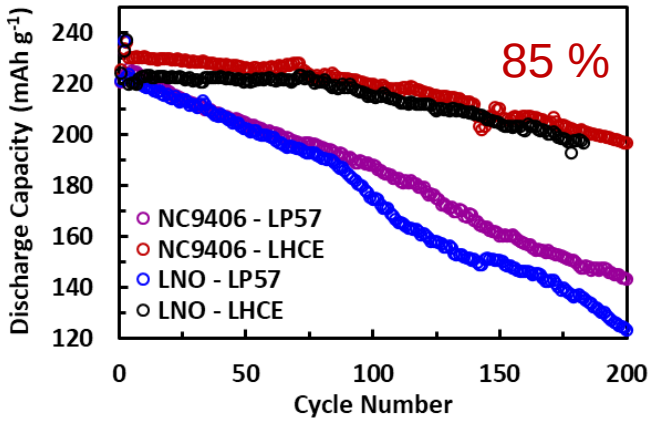


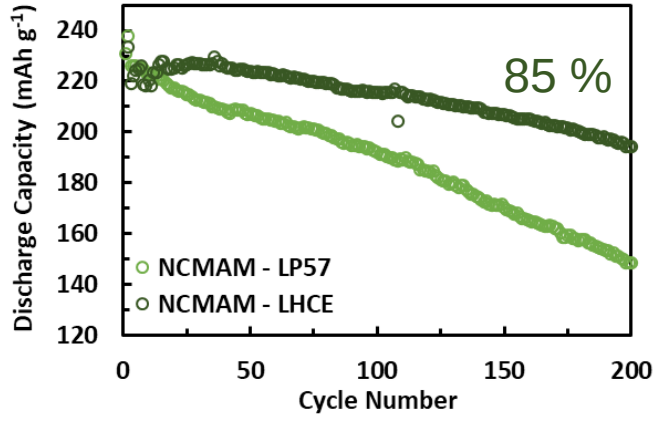












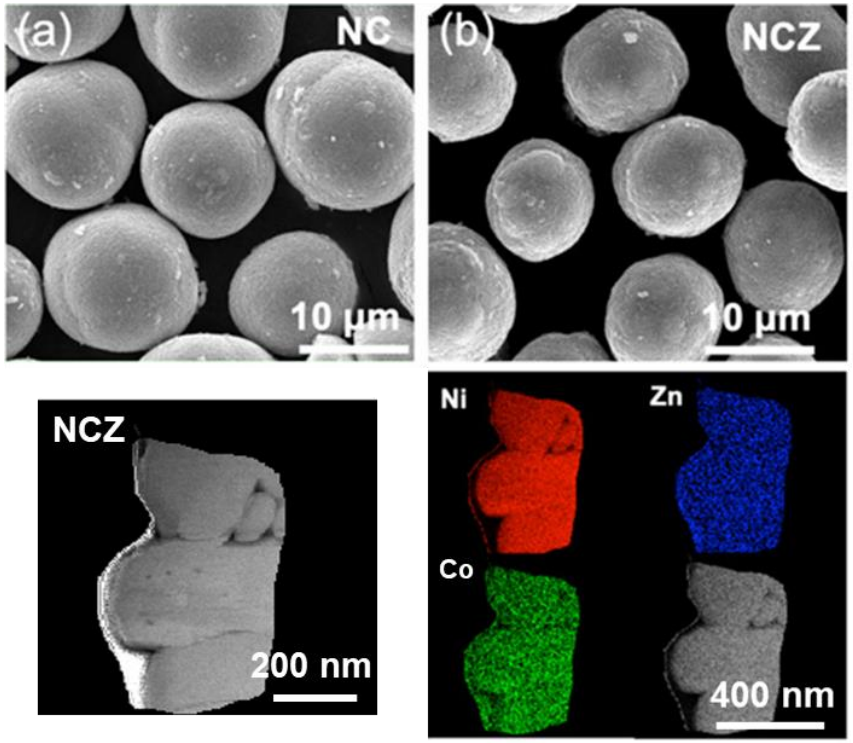
LHCE = LFSI : DME : TTE = 1 : 1.2 : 3

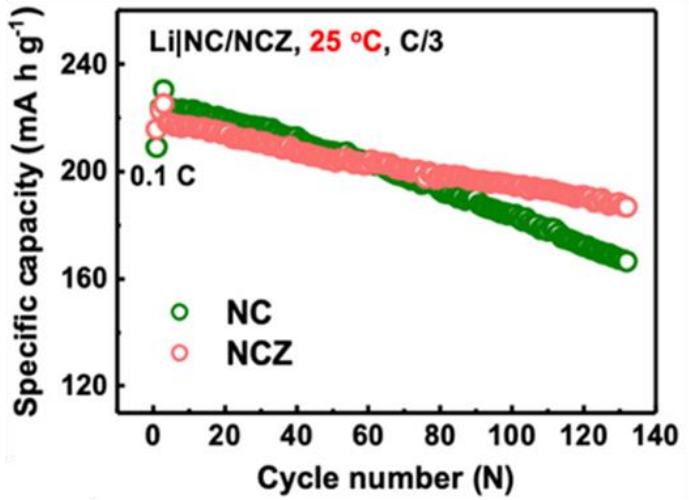
- Several cathodes (*e.g.*, $LiNiO_2$ (LNO), $LiNi_{0.94}Co_{0.06}O_2$ (NC9406), $LiNi_{0.94}Co_{0.04}Zn_{0.02}O_2$ (NCZ)) and $LiNi_{0.95}Co_{0.02}Mn_{0.015}Al_{0.01}Mg_{0.005}O_2$ (NCMAM) exhibit high capacities of > 220 mA h g^{-1} at C/3
- Long cycle life with lithium-metal anode and localized high concentration electrolyte has been achieved

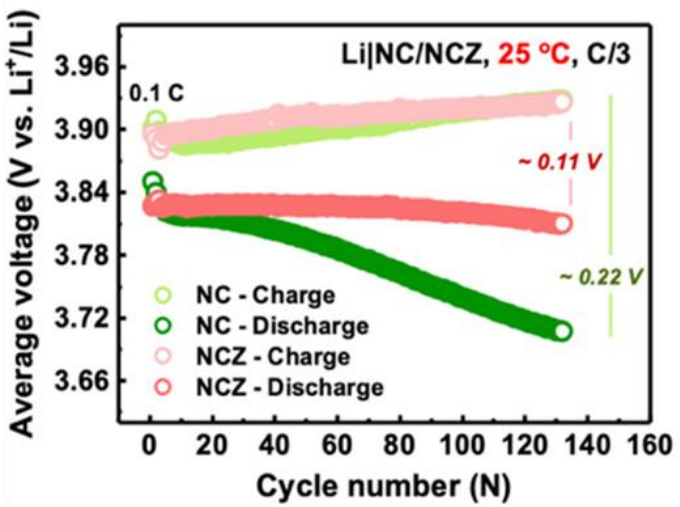
ZINC-DOPED $LiNi_{0.94}Co_{0.04}Zn_{0.02}O_2$ (NCZ)

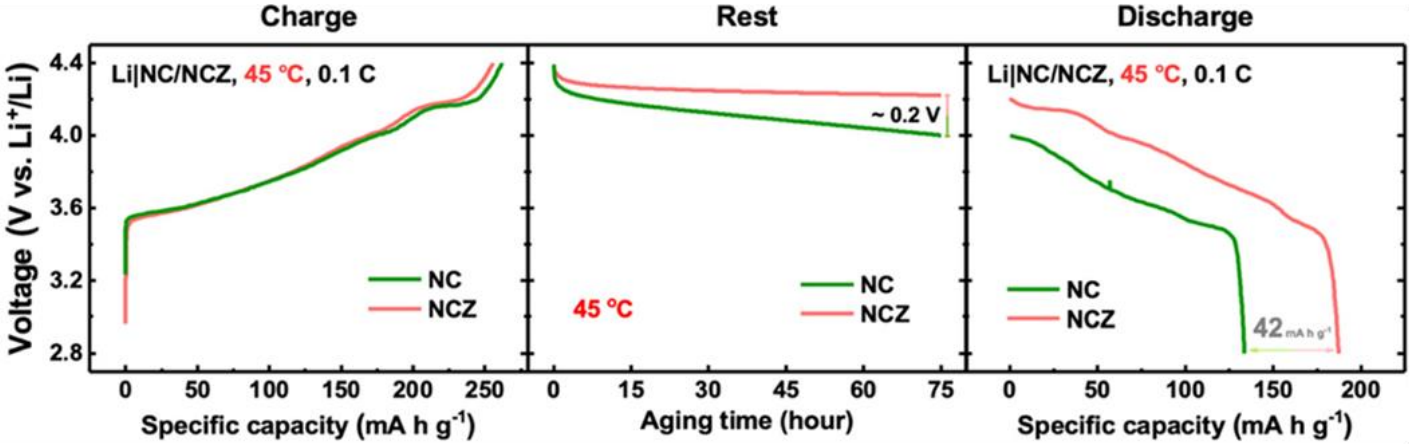
Metal ion	Ni^{2+}	Co^{2+}	Zn^{2+}
K_{sp} of $M(OH)_2$	2.0×10^{-15}	1.6×10^{-16}	1.2×10^{-17}

Metal ion	Ni^{2+}	Co^{2+}	Li^{+}	Zn^{2+}
Ionic radius (pm)	69	65	76	74



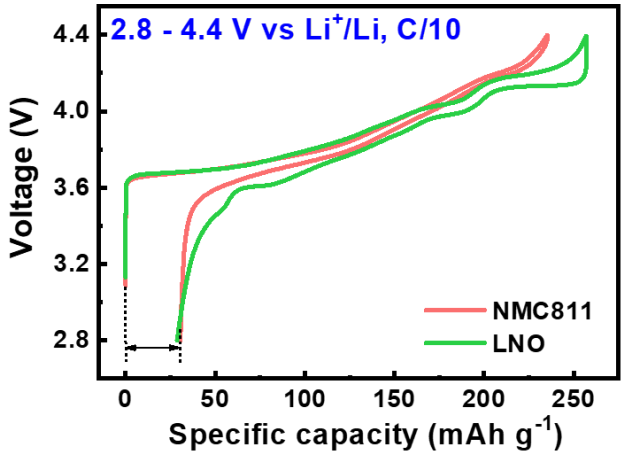


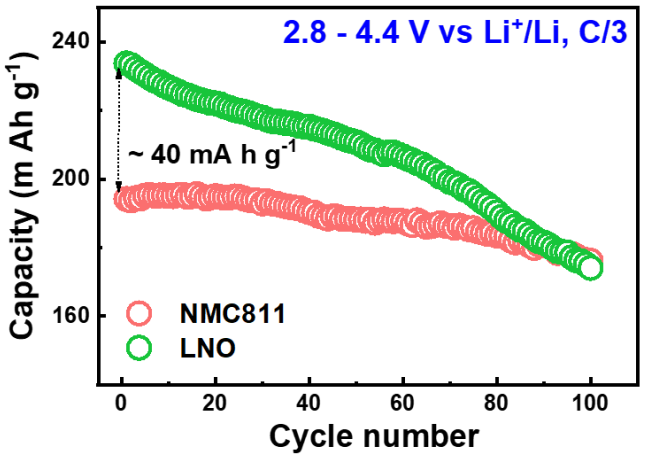


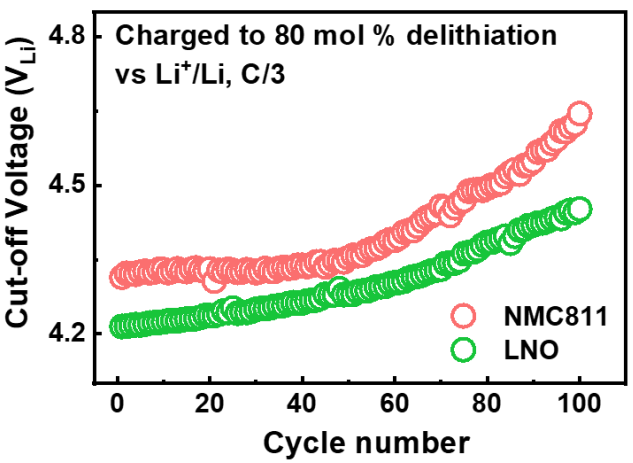


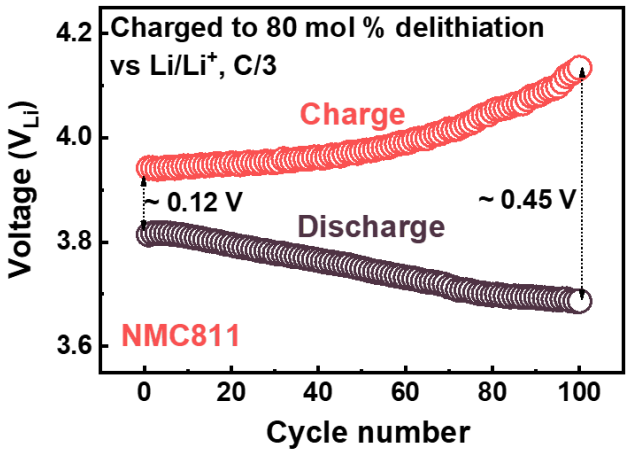
- Zinc can be directly and uniformly incorporated into the coprecipitated hydroxide precursor
- Reduced surface reactivity in NCZ leads to both improved cycle life and storage life at 45 °C

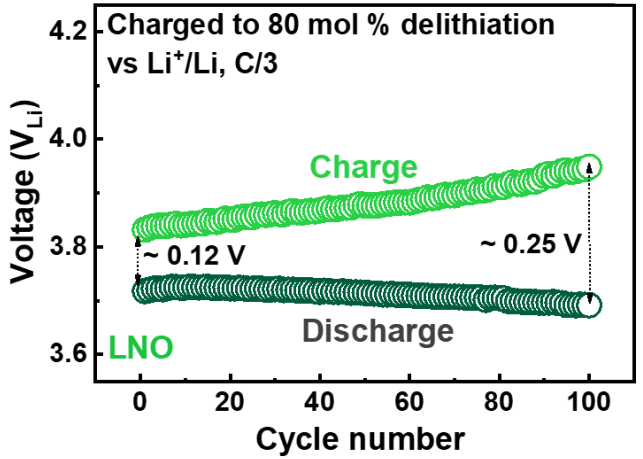
STABILITY OF $LiNiO_2$ (LNO) vs. NMC811 WITH THE SAME STATE OF CHARGE

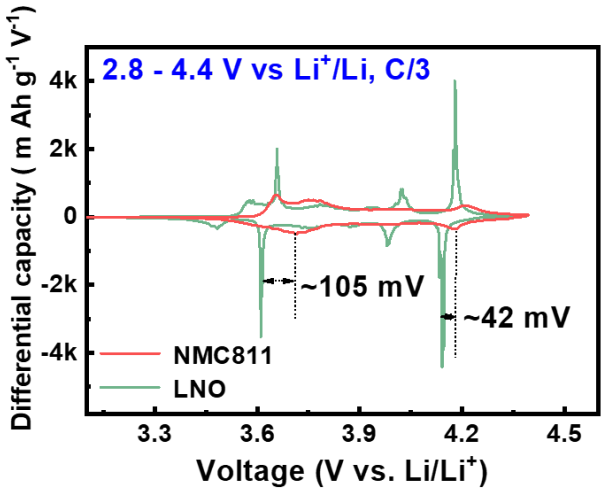






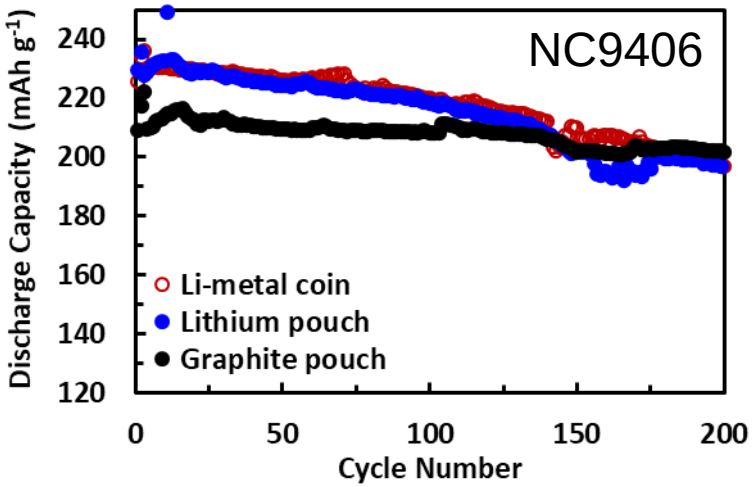


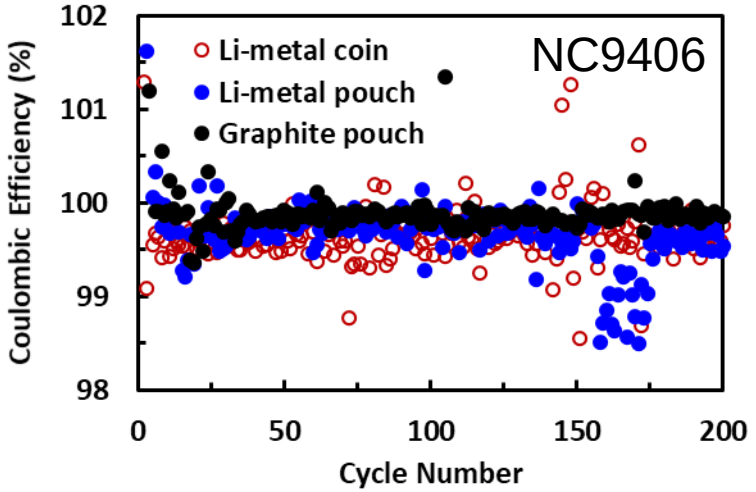


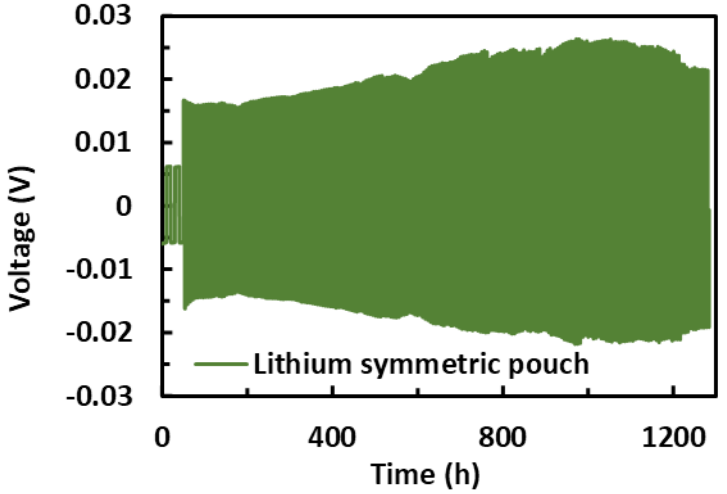


- With the same voltage range, NMC811 shows better cyclability than LNO due to a lower degree of Li extraction
- With the same delithiation degree, LNO shows better cyclability than NMC811 due to lower charge voltage

CROSSOVER EFFECTS IN LITHIUM-METAL BATTERIES WITH LHCE





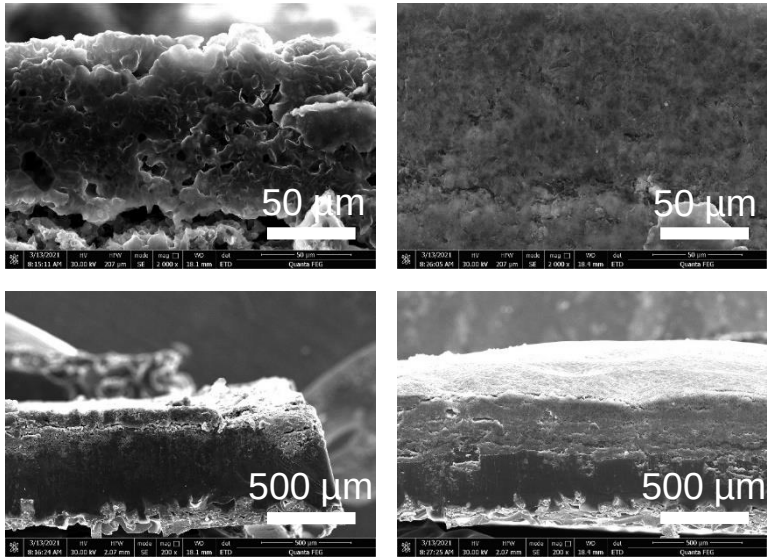


LHCE refers to localized high concentration electrolyte (LHCE)

- SEI on Li metal is dramatically thicker (~ 300 µm) in Li – Li symmetric cell than in Li – NC (~ 100 µm) cell
- Surface morphology of Li is mossy with a higher surface area in Li – Li symmetric cell than that in Li – NC cell

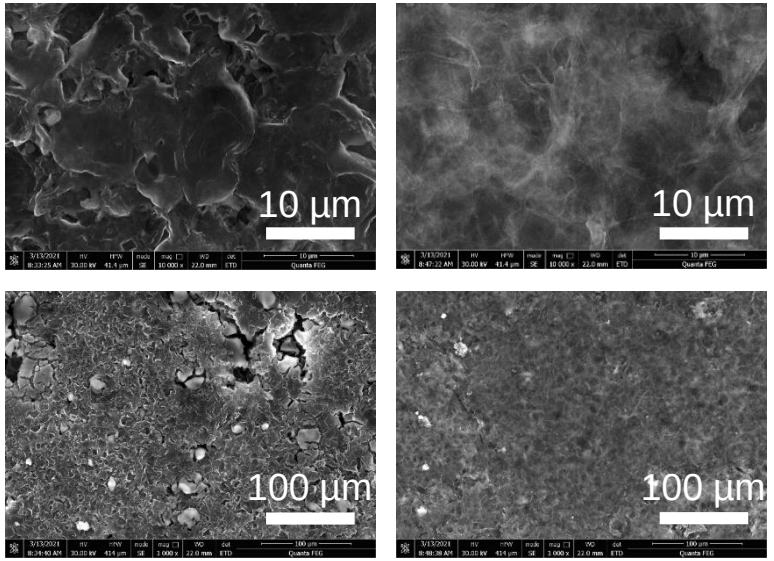
Cross-sectional lithium SEM

Li | NC9406 200 cycles **Li | Li 200 cycles**

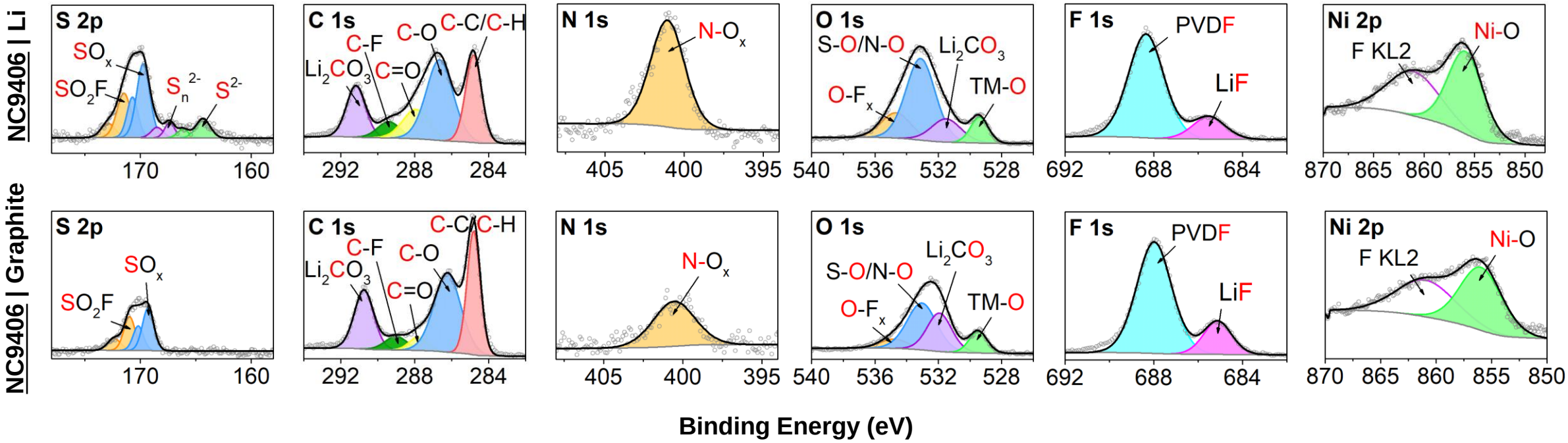


Planar lithium SEM

Li | NC9406 200 cycles **Li | Li 200 cycles**



XPS ANALYSIS OF NC9406 CATHODE AFTER CYCLING IN LHCE



- NC 9406 cathode in the NC – Li cell shows a dramatic increase in sulfur and nitrogen contents compared to that in the NC – Gr cell
  - several of these sulfur species are unique to the NC – Li
- NC 9406 cathode in the NC – Gr cell displays moderately larger LiF peak than in the NC – Li cell

RESPONSE TO REVIEWERS' COMMENTS

"The reviewer would like to see Professor Manthiram's team supply materials and possibly cells to other teams for independent evaluation."

> We appreciate and agree with the reviewer's comment. This year, we synthesized and provided several high-nickel cathodes (NCMAM and NC9406) to PNNL for independent evaluation.

"…scale-up is difficult for an academic laboratory. One possible solution is to utilize the Materials Engineering Research Facility (MERF) at ANL…"

> We thank the reviewer for this suggestion. It has not yet been necessary to contact MERF, as the acquisition of several large furnaces in our lab has enabled large-scale calcination. If additional scale-up is required, we will keep the facilities at ANL in mind.

COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- We have provided the high-nickel, high-capacity cathodes developed in our laboratory to other partner institutions for various complimentary investigations and benchmarking. A few recent examples are given below.

- Bor Yann Liaw, Idaho National Laboratory

  In-depth electrochemical analysis of NMC 811 with different particle sizes

- Wu Xu, Pacific Northwest National Laboratory

  Evaluation of $LiNi_{0.94}Co_{0.06}O_2$ (NC 9406) with different electrolyte compositions

- Jie Xiao, Pacific Northwest National Laboratory

  Benchmarking of cathodes with > 220 mA h g^{-1} with NMC811

BROOKHAVEN NATIONAL LABORATORY

BINGHAMTON UNIVERSITY STATE UNIVERSITY OF NEW YORK

INL Idaho National Laboratory

Pacific Northwest NATIONAL LABORATORY

UC San Diego

UNIVERSITY of WASHINGTON

REMAINING CHALLENGES AND BARRIERS

- **Challenge/Barrier 1:** Although the localized high-concentration electrolyte offers excellent performance, the performance can still be improved at a reduced cost by the identification of new diluents, additives *etc*.
- **Challenge/Barrier 2:** New cathode morphologies (*i.e*., single crystals) can offer significant performance benefits at low nickel content, but it appears to be especially difficult to synthesize single crystals for high-capacity, high-nickel cathodes
- **Challenge/Barrier 3:** While crossover between the high-nickel cathode and the lithium-metal anode in localized high concentration electrolytes (LHCE) has been identified, the chemical and quantitative nature of this phenomena must be determined

PROPOSED FUTURE WORK

- Optimize the practical parameters (N/P ratio, mass loading etc.) in lithiophilic matrices for demonstration in pouch cells
- Develop an understanding of the synthesis of high-nickel single-crystal cathodes
- Continue optimization and analysis of the interplay between lithium-metal anode, high-nickel cathode, and localized high concentration electrolytes (LHCE)
- Expand the design space of LHCE electrolytes through the testing of novel additives, diluents *etc*.

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

SUMMARY

- Several high-nickel (> 94%) cathodes with > 220 mA h g^{-1} capacity at C/3 have been developed
  - one of them (NCMAM) with 95% Ni has been delivered to PNNL to benchmark with NMC 811
  - hard-to-dope ions like Al, Mg, and Zn can be directly coprecipitated with Ni, Mn, and Co
  - zinc-doped NCZ exhibits better cycle life due to reduced surface reactivity and particle cracking

- With the same degree of delithiation, $LiNiO_2$ displays better stability than NMC 811
  - what determines stability is the degree of lithium extraction (extent of charge), not Ni content itself

- Crossover is both ways in Li-metal cells, unlike in graphite cells, especially crossover of nitrogen and sulfur species from Li metal; more detailed investigation is underway