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

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The University of Texas at Austin

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OVERVIEW

Timeline

- Project start date: October 2018
- Project end date: December 2021
- 10% complete

Budget

- Total project funding
  - DOE: $2,400,000
- Funding received in FY 2018
  - $0
- Funding for FY 2019
  - $800,000

Barriers

- Barriers
  - Cycle and calendar life
  - Safety under abuse
  - Surface/bulk stability
- Targets
  - Affordable, high-performance layered oxide cathodes with low or no cobalt content (≤ 50 mg Co/Wh)

Partners

- NREL, LG Chem

RELEVANCE

Overall Project Objective

- Develop high-energy, long-life, safe high-nickel, low-cobalt cathodes
  - Affordable, high-performance cathode materials with a specific energy of ≥ 600 Wh kg^{-1} and a cobalt content of ≤ 50 mg Co/Wh
  - Stabilization strategies for long cycle (C/3 deep discharge with ≤ 20% energy fade over 1,000 cycles) and calendar life (≥ 15 years)
  - Stabilization strategies for acceptable safety under abuse

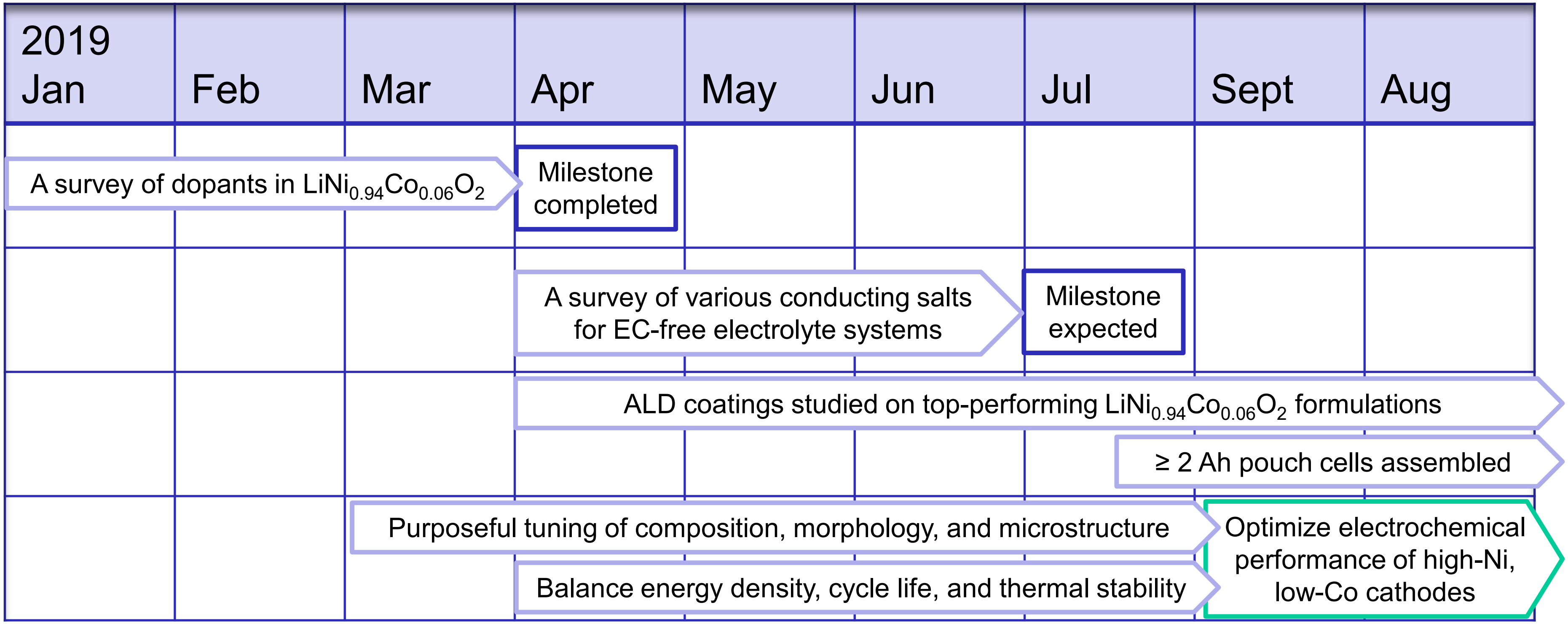
Objectives for Year 1

- Exploration of $LiNi_{0.94}Co_{0.06}O_2$ with surface/bulk stabilization and compatible novel electrolyte systems
  - Understand and suppress bulk and surface degradation during cycling
  - Evaluate long-term cyclability and identify critical barriers
  - Balance energy density, cycle life, and thermal stability
  - Optimize electrochemical performance

MILESTONES

Month/Year	Milestone	Status
March 2019	Technical: A survey of different dopants and electrode formulations of $LiNi_{0.94}Co_{0.06}O_2$ will be performed	Completed
June 2019	Technical: A survey of various conducting salts for EC-free electrolyte systems will be performed, with a selection of top systems for scale-up and further component optimization	Ongoing
September 2019	Technical: ALD coatings studies on top-performing $LiNi_{0.94}Co_{0.06}O_2$ formulations with baseline and EC-free electrolyte systems	Ongoing
December 2019	Technical: ≥ 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	Ongoing

APPROACH



- **Milestones for Year 1 (FY 2019)**
  - The Milestone on the dopant survey of $LiNi_{0.94}Co_{0.06}O_2$ and preliminary structural and chemical evaluation of high-Ni, low-Co cathodes has been completed (marked as *Milestone completed* above)

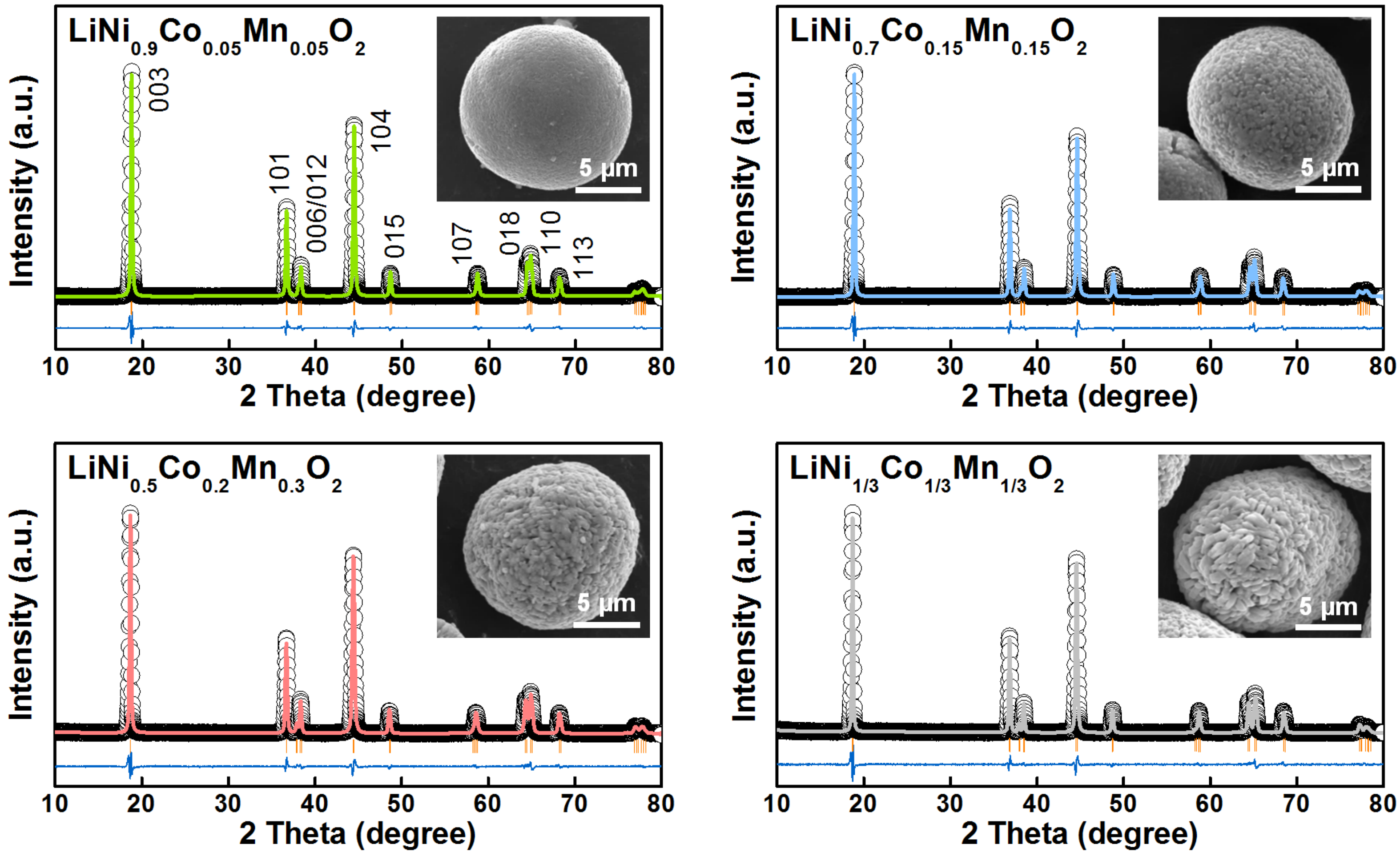
TECHNICAL ACCOMPLISHMENTS AND PROGRESS

- (Prior to project start) The materials chemistry database developed through previously funded DOE projects (*e.g.,* DE-EE0007762) provides a guideline for (i) essential synthetic parameters for successful upscaling of the transition-metal co-precipitation of high-nickel, low-cobalt layered oxide cathodes, (ii) in-depth characterization of chemical/structural evolution of high-nickel, low-cobalt cathodes after battery operation, and (iii) purposeful design of high-nickel, low-cobalt cathodes with balanced performance metrics (specific energy, cycle life, thermal stability, *etc.*).

- (Y1Q1) Optimization of the transition-metal co-precipitation synthesis of high-nickel, low-cobalt layered oxide cathodes (> 1.0 kg product yield per batch) with good electrochemical properties (sample sent to NREL); substantially enhanced cyclability and thermal stability of high-nickel, low-cobalt cathodes through proper elemental doping with suppressed structural degradation visualized.

BACKGROUND: CATHODE SYNTHESIS CAPABILITY

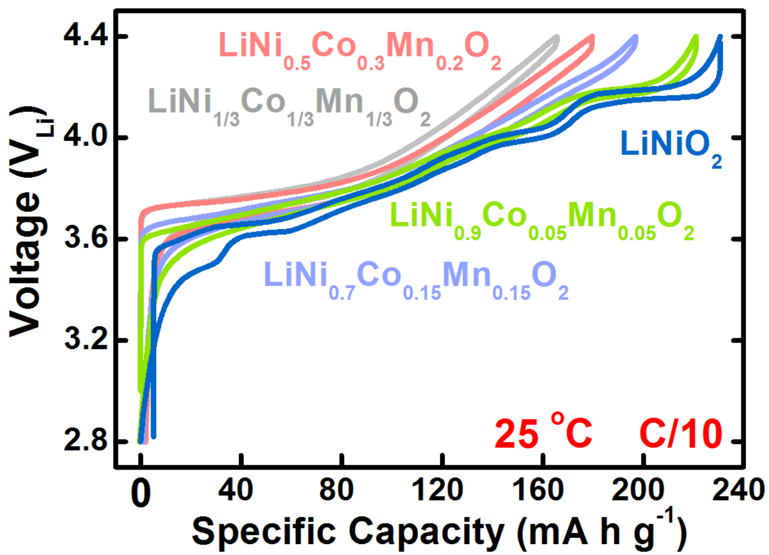
- Synthesis of $LiNi_{1-x}M_xO_2$ cathodes with various Ni contents

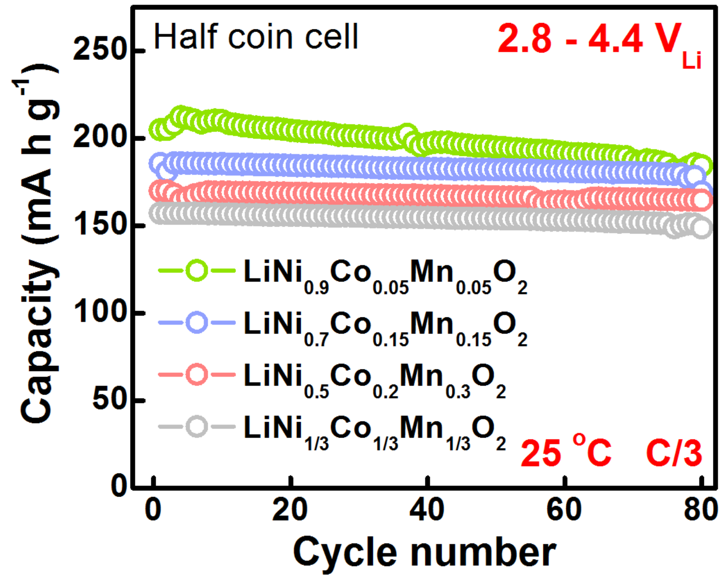


- Consistent structural and morphology of NCMs of varying Ni contents

W. Li, H. Yaghoobnejad Asl, Q. Xie, and A. Manthiram, *Journal of the American Chemical Society*, **2019**,*141*, 5097-5101

CELL PERFORMANCE WITH VARIOUS Ni CONTENTS (0.33 – 1.0)





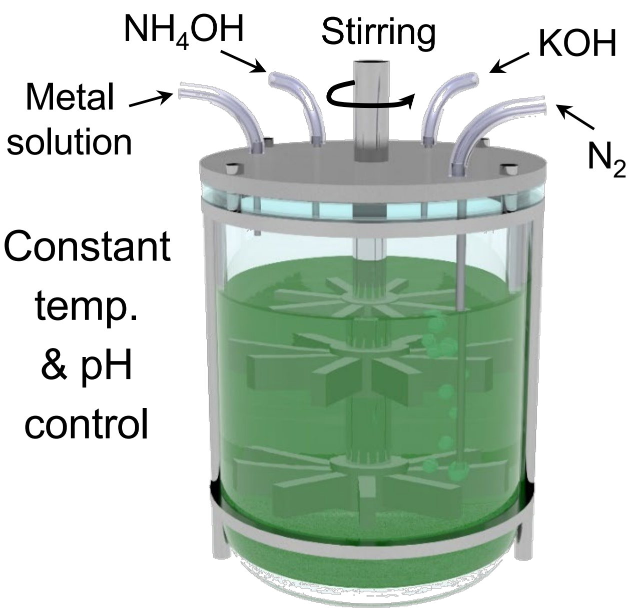
- Benefits with high-Ni, low-Co cathodes:
  - High energy density
  - Superior rate capability

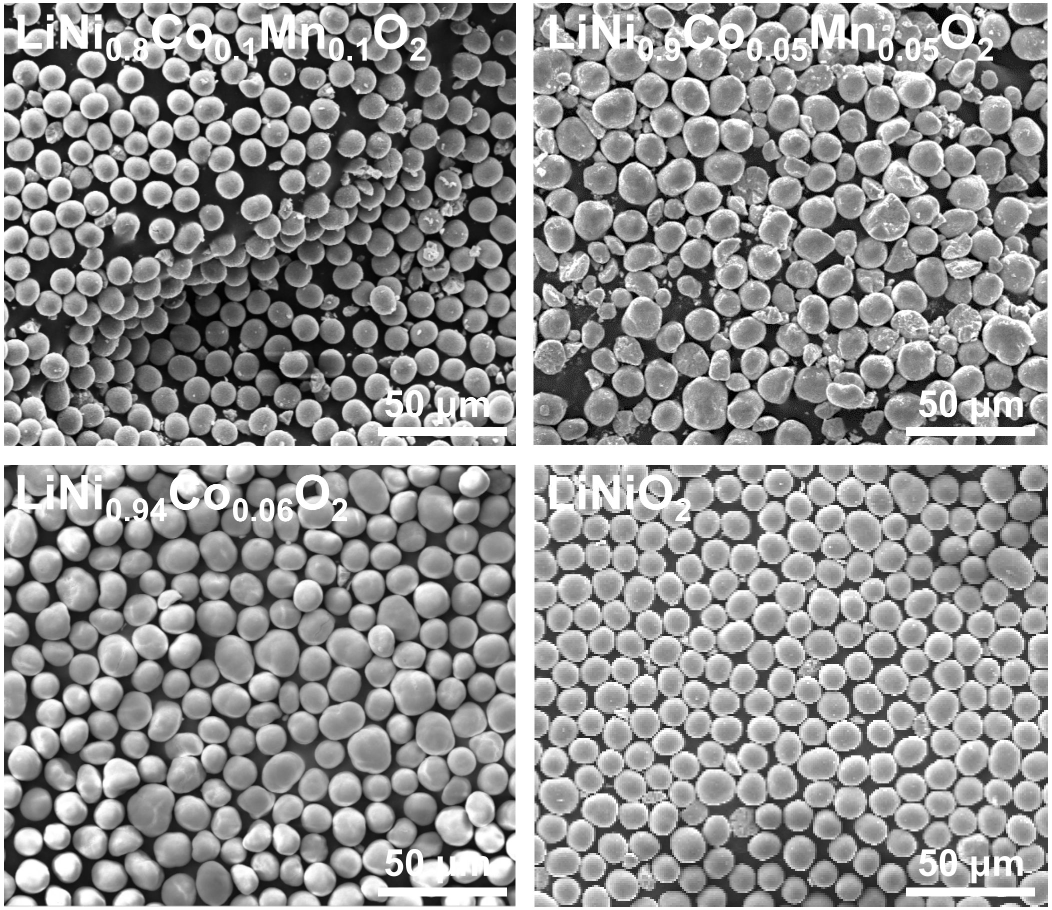
- Issues with high-Ni, low-Co cathodes:
  - high reactivity with ambient air
  - limited electrochemical durability
  - poor safety under abuse

- In-house $LiNi_{1-x-y}Co_xMn_yO_2$ (NCMs) as well as $LiNi_{0.94}Co_{0.06}O_2$ (NC-9406) and $LiNiO_2$ (LNO) demonstrate good electrochemical properties, serving as baseline samples

SYNTHESIS OF LOW-COBALT CATHODE PRECURSORS

- Composition: $LiNi_{1-x-y}Co_xM_yO_2$ (Ni contents ≥ 0.8; M = Mn, Al, Mg, Zr, etc.)

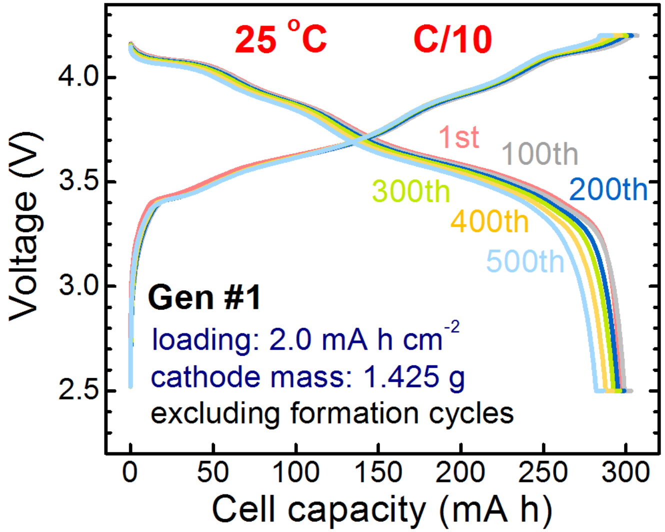


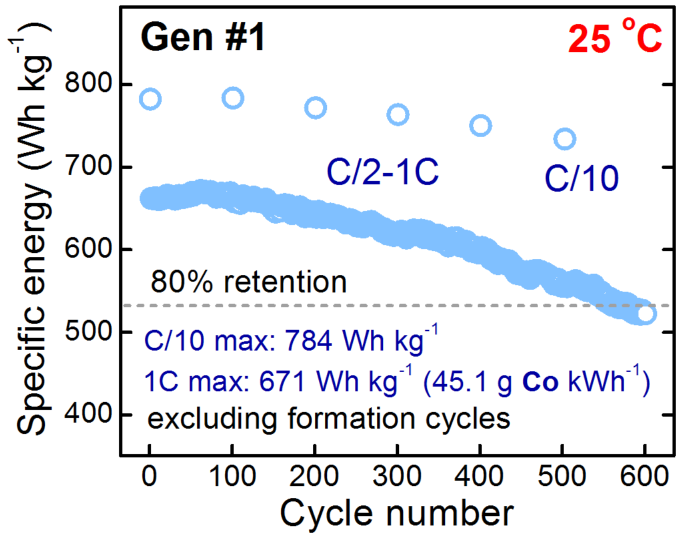


- A series of high-Ni, low-Co layered hydroxide precursors have been prepared through transition-metal co-precipitation with a large yield per batch (> 1.0 kg), which will be continuously enhanced through the current project

CELL PERFORMANCE OF HIGH-NICKEL, LOW-COBALT CATHODES

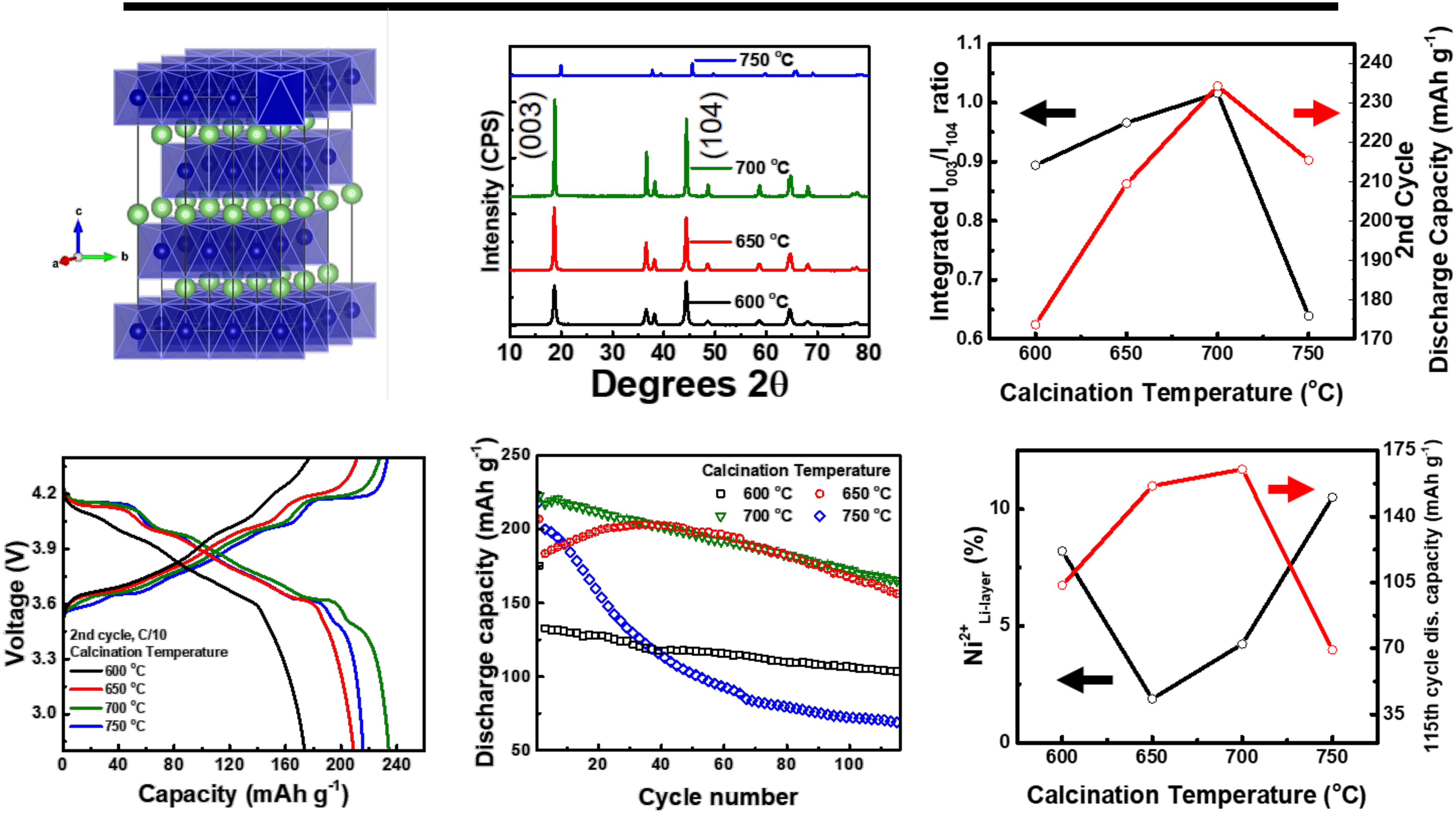
- 300 mA h pouch cell data





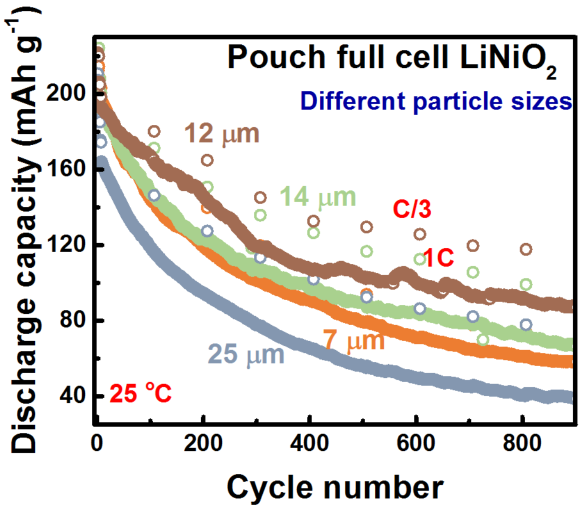
- (Y1Q1) 300 mA h pouch cells consisting of high-Ni, low-Co cathodes and graphite anodes with 2.0 mA h cm^{-2} areal capacity were assembled
- (Y1Q1) The benchmark cathode readily achieves the specific energy and cobalt content targets (≥ 600 Wh kg^{-1} and ≤ 50 g kWh^{-1}) and delivers decent cyclability (80% energy retention at ~ 600 cycles)
- The remaining FY2019 work we will focus on various cathode and electrolyte modifications to prolong cycle life beyond 1,000 cycles, satisfying the end-year milestone (Go/No-Go decision)

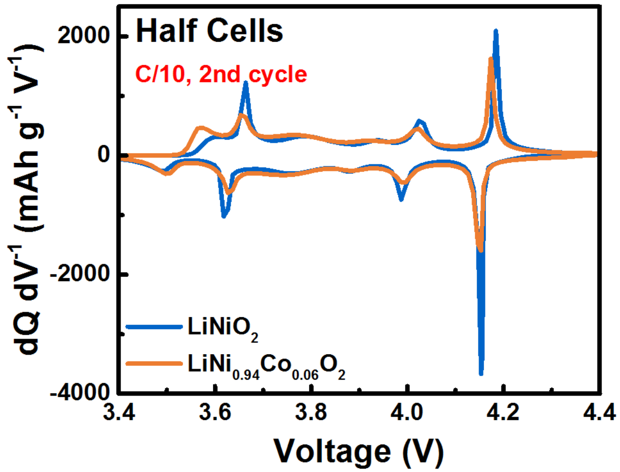
INFLUENCE OF CALCINATION TEMPERATURE ON $LiNiO_2$

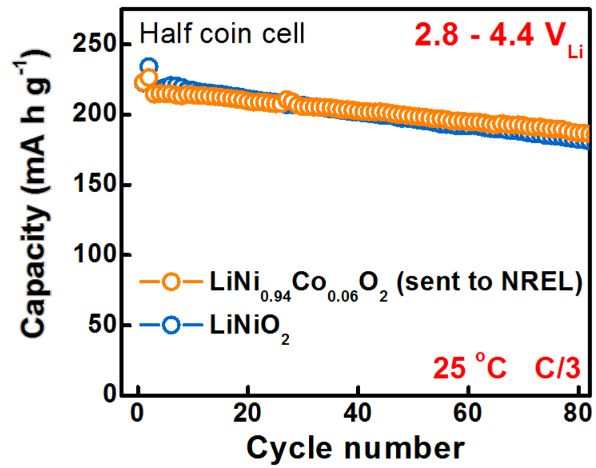


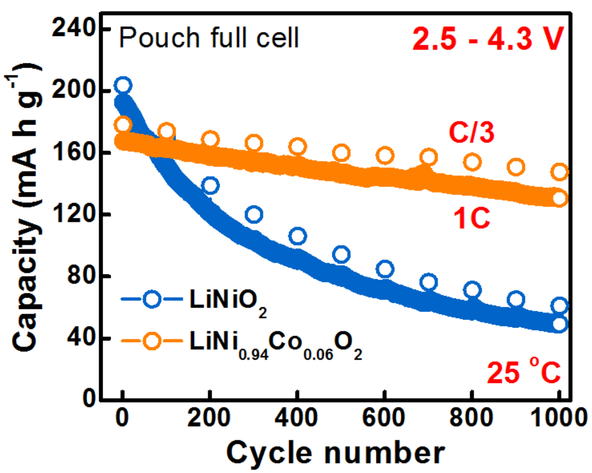
- (Y1Q1) Full lithiation must occur at sufficiently high temperatures during calcination, but extreme high temperatures cause high degree of Li/Ni mixing

CYLABILITY OF HIGH-NICKEL, LOW-COBALT CATHODES



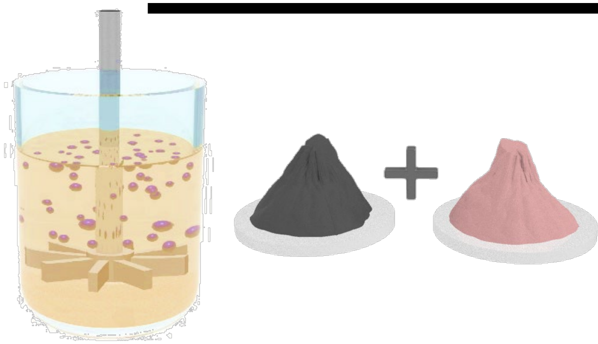




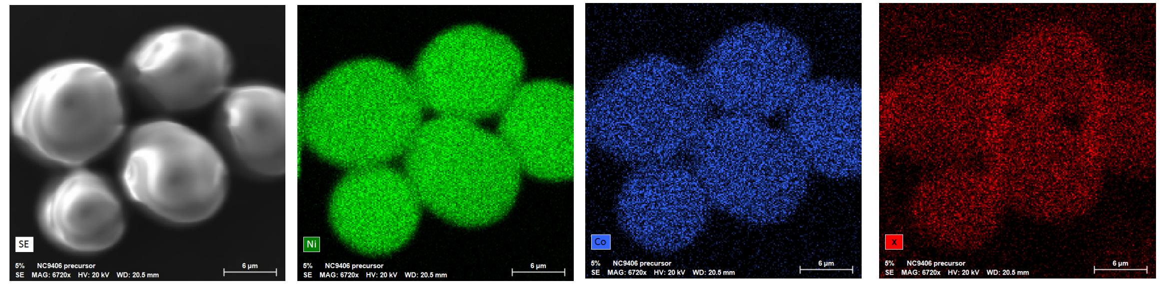


- (Y1Q1) Different particle sizes of $LiNiO_2$ cathode materials were evaluated
- Capacity fading is not caused predominantly by surface phenomena
- (Y1Q1) $LiNiO_2$ and $LiNi_{0.94}Co_{0.06}O_2$ were compared in half cells and full cells
- Full cells show dramatically different results than half cells
- Cobalt broadens and extends voltage ranges for phase transformations, which may be responsible for improved bulk cycle stability in cathode materials
- Other dopants will be explored to find metals with effects similar to cobalt

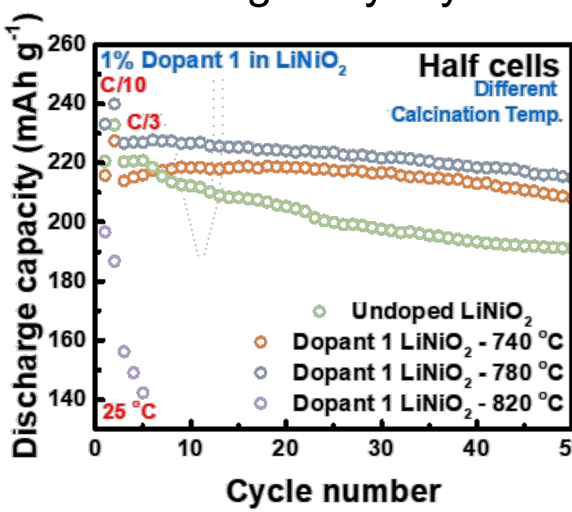
PRELIMINARY ELEMENTAL DOPING RESULTS

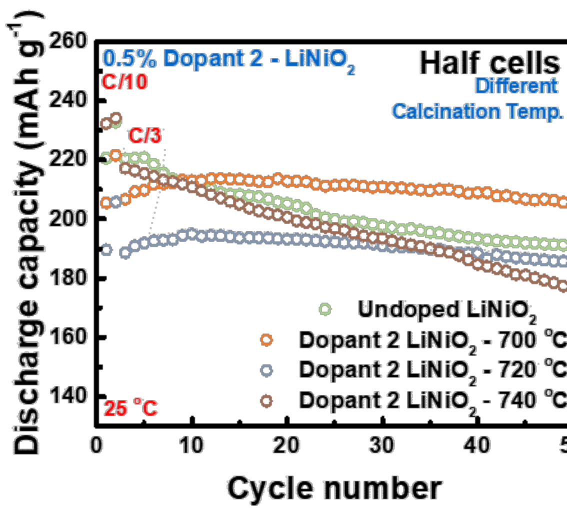


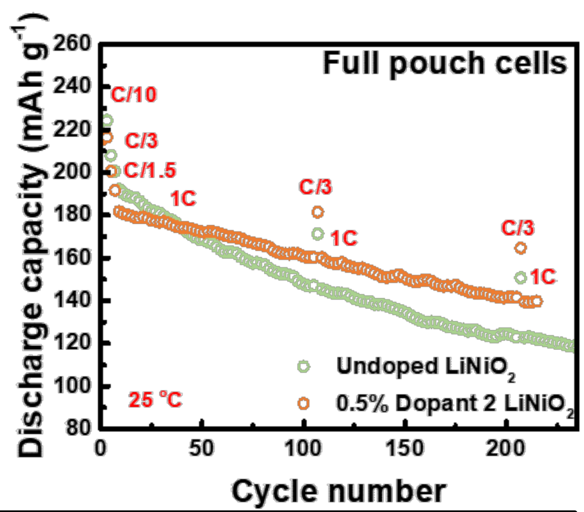
- Doping can be performed during coprecipitation, by wet coating or by dry mixing



- Wet coating and dry mixing before or after lithiation result in segregation that must be heated to dope through the entire particle

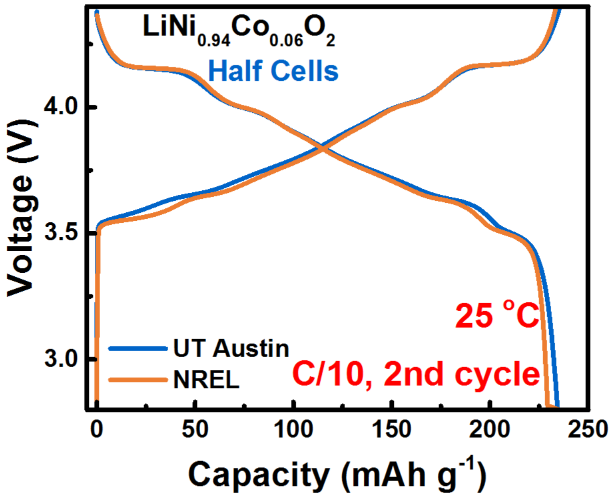


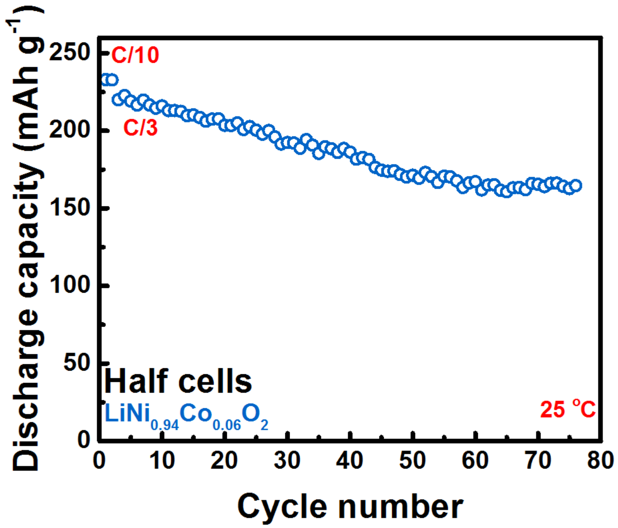


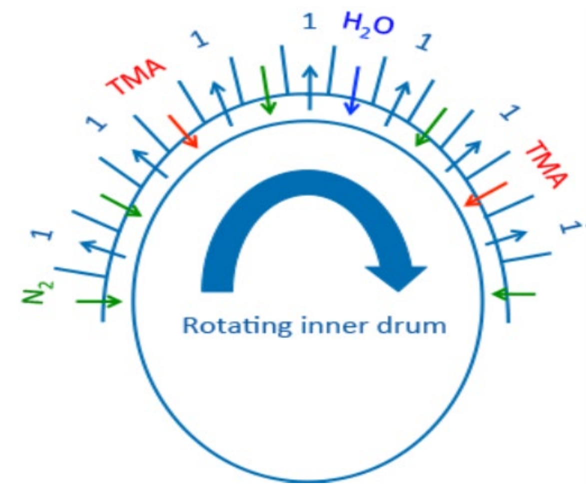


- (Y1Q1) Doping of $LiNiO_2$ and $LiNi_{0.94}Co_{0.06}O_2$ in concentrations up to 5% with lithiation temperatures screened in half cells, with full cells tests ongoing

ALD COATINGS AND FULL CELLS AT NREL







- (Y1Q1) A recent batch of $LiNi_{0.94}Co_{0.06}O_2$ was sent to NREL for coating exploration. Shipment of the material in vacuum-sealed Al-coated mylar bags was successful, with NREL-produced coin cells performing similar to cells produced from fresh material at UT Austin
- Atomic layer deposition (ALD) coatings produced with rotating drum systems offer higher cycle throughput than conventional systems, making them more affordable
- NREL will explore ALD coatings with materials shipped from UT Austin, as well as large format, 1 Ah pouch cells

RESPONSE TO REVIEWERS' COMMENTS

No presentation was given in the previous year as this is a new project

COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- Dr. Shriram Santhanagopalan, Nation Renewable Energy Laboratory (NREL)

  Electrochemical testing and atomic layered deposition (ALD) coating exploration of high-Ni, low-Co cathode samples (e.g. NC-9406) from UT Austin

- Dr. Mohamed Alamgir, LG Chem Michigan Inc.

  Fabrication of 2 Ah cells with the cathode powders supplied by UT Austin

REMAINING CHALLENGES AND BARRIERS

- **Challenge/Barrier 1:** During the scaled up of transition-metal co-precipitation process, we notice sometimes a small fraction of particles appear fragmented in as-prepared hydroxide precursors. In addition, with a newly purchased large tube furnace, we will increase the production volume for lithiation calcination as well. Therefore, we will continue to tune and optimize our synthesis routine.

- **Challenge/Barrier 2:** A trade-off relationship among energy density, cyclability, and thermal stability exists for high-Ni, low-Co layered oxide cathodes. As we push to higher Ni and lower Co contents, cycle/calendar life, particularly at elevated temperatures, and thermal-abuse tolerance need to be improved for practical applications. In addition, residual Li compounds need to be reduced at the surface of as-prepared materials. We will apply a variety of surface/bulk stabilization strategies to address this challenge.

PROPOSED FUTURE WORK – PART I

- FY2019
  - To address Challenge/Barrier 1: We have developed extensive experience in the synthesis of high-Ni, low-Co layered oxide cathodes with relatively small yields. A careful control/tuning of the reaction temperature, pH, precursor feeding rate, stirring rate, and total time will be applied to optimize transition-metal co-precipitation during upscaling. Meanwhile, a careful control/tuning of the reaction temperature, duration, oxygen flow rate, lithium/transition-metal ratio, and cooling rate will be applied to optimize calcination.
  - To address Challenge/Barrier 2: A series of surface/bulk stabilization strategies (coating/doping and electrolyte modification) will be applied to enhance cyclability and thermal stability and reduce surface residual Li on high-Ni, low-Co cathodes.

PROPOSED FUTURE WORK – PART II

- FY2019
  - (Q2 July-19) Technical Milestone II: We will conduct a survey of various conducting salts (*e.g.*, $LiPF_6$, $LiClO_4$, $LiBF_4$, LiTFSI, LiDFOB, and LiFSI) in EC-free nonaqueous electrolytes for long-term operation of pouch full cells consisting of high-Ni, low-Co cathodes and graphite anodes.
  - (Q3 Sep-19) Technical Milestone III: We will continue to supply our collaborator NREL our high-Ni, low-Co cathodes for a survey of ALD coating for improved cycle/calendar life and thermal-abuse tolerance as well as suppressed formation of residual Li compounds.
  - (Q1 Dec-19) Technical Milestone IV: Top-performing cathode materials produced by UT Austin and NREL will be sent to LG Chem for making 21 large-format, ≥ 2 Ah pouch cells using compatible novel electrolyte systems. After 30 days of pre-cycling, 15 of these cells will be sent to Department of Energy for independent testing and analysis.

SUMMARY

- The material chemistry database and characterization methodology developed are facilitating the selection of desired high-Ni, low-Co cathode candidates with balanced performance metrics, including energy density, cycle life, and thermal stability (prior to project start)
- The scaled up high-Ni, low-Co cathodes achieve the following (Y1Q1):
  (i) high tap density (~ 2.5 g cm^{-3}) comparable to commercial products
  (ii) high specific capacities in the range of 190 – 220 mA h g^{-1}
  (iii) decent long-term cyclability for certain compositions (*e.g.*, NC-9406)
- A survey of elemental doping demonstrates that (Y1Q1): cycle/calendar life and thermal stability of high-Ni, low-Co cathode materials can be substantially improved through proper doping by suppressing detrimental phase transitions during (de)lithiation
- Material was successfully shipped to NREL for ALD exploratory studies, using a packaging method that prevents degradation due to air exposure