Enhancing Oxygen Stability In Low-Cobalt Layered Oxide Cathode Materials

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Project ID: bat414

Overview

Timeline

- Project start date: 12/01/2018
- Project end date: 12/31/2019
- Percent complete: 10%

Barriers

- Barriers addressed
  - Cost
  - Performance
  - Life

Budget

- Total project funding $3.125 million
  - DOE Share $2.5 million
  - Contractor share $625K
- Funding for FY 2019: $1.15 million

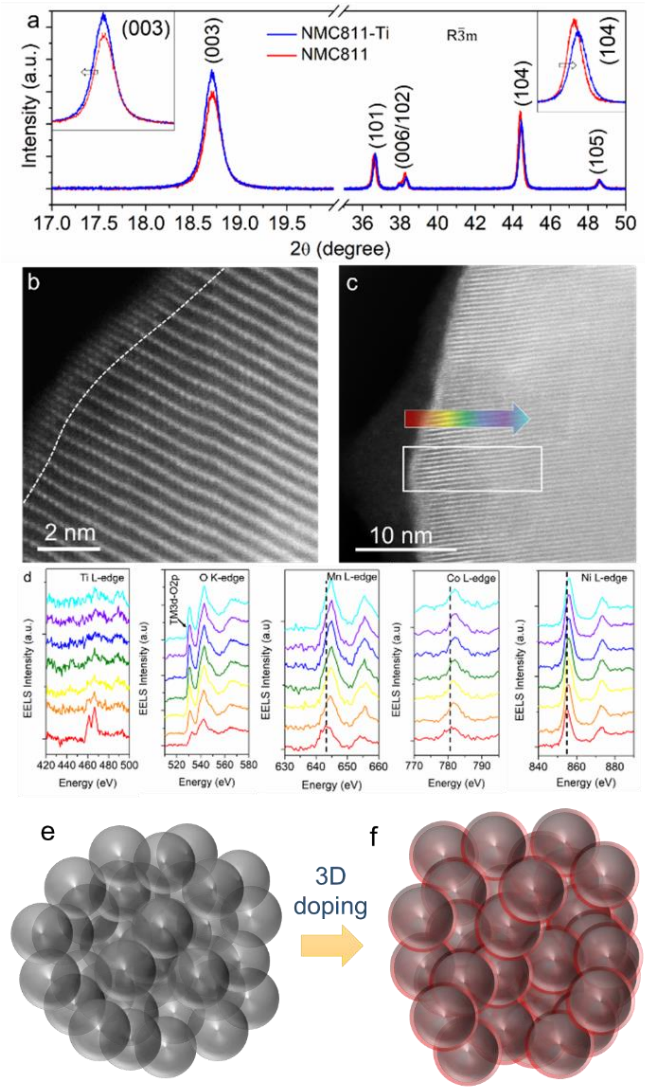
Partners

- UC Irvine: Project Lead Huolin Xin
- Virginia Tech: Feng Lin
- UC Berkeley: Kristin Persson
- PNNL: Xu Wu
- American Lithium Energy: Jiang Fan
- Collaborations: BNL, NSLSII, SSRL

Relevance: Objectives

Overall objectives

- Displace Co while maintaining high-Ni content and high energy density
  - Cobalt concentration < 50 mg/Wh or No-Co
  - Energy density > 750 Wh/kg (C/3, 2.5-4.4 V) at cathode level
  - Cost ≤ $100/kWh
- Improve cycle and calendar life by retaining oxygen through a 3D doping technology
  - Capacity retention > 80% at 1,000 cycles
  - Energy retention > 80% at 1,000 cycles
  - Calendar life: 15 years
- Deliver a theoretical model
  - High-throughput DFT calculations that rationalize the selection of oxygen-retraining surface and bulk dopants
- Formulate new electrolytes
  - New functional additives
  - Understanding of the CEI's influence on high-Ni low-Co cathodes.
- Offer a knowledge base by performing proactive studies of
  - Thermal stability, oxygen loss, and the degradation of the cathode/electrolyte interfaces.



Milestones

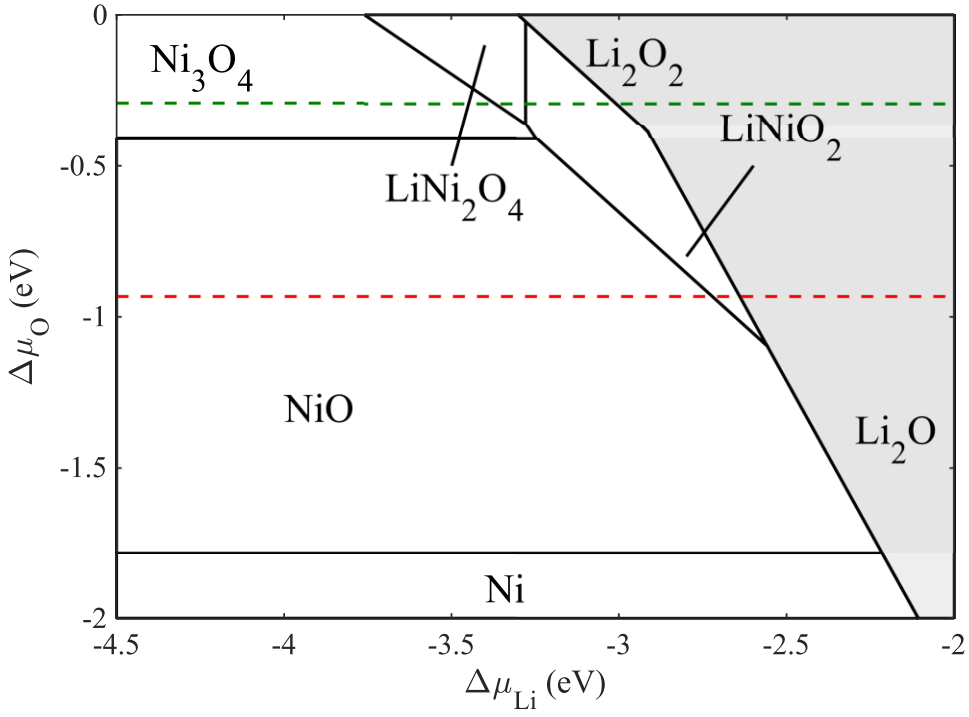
Milestone	Status	Description
Jan 2019 Dopant Selection and Material Synthesis	Completed	Computational down-selection to 2–4 elements for synthesis. Achieve NMC-D electrode materials with Co content <= 3%, Ni >= 90%, Dopant metal (Ti or Al) = 2%
April 2019 Structural Fidelity	Completed	Structural study by synchrotron XRD, and aberration-corrected scanning TEM to confirm that the desired layered structure and 3D composition are achieved.
July 2019 Electrode Performance and Fabrication of PPCs	On track	Evaluate electrochemical performance of BP 1 materials and compare it with the commercial 811 baseline >100 cycles in Li||NMC cells at 4.5 V cutoff and Gr||NMC cells at 4.4 V cutoff. Delivery of PPCs to DOE.
October 2019 Go/No Go	On track	Delivery of a high-Ni and low-Co cathode material with an electrochemical performance comparable to the commercial NMC811 baseline (energy and capacity retention > 90% of NMC811 @ 100 cycles).

Milestone	Status	Description
Jan 2020 Dopant Refinement	N/A	Refine prediction of surface/bulk dopants
April 2020 Synthesis Scale-up	N/A	Scale up synthesis of BP 1 materials to 100 g scale.
July 2020 Performance Evaluation	N/A	Best of BP1 and BP2 materials achieves a comparable performance to the 811 baseline >300 cycles in Gr||NMC pouch cells at 4.4 V cutoff.
Oct 2020 Go/No Go	N/A	Delivery of a high-Ni and low-Co cathode that has a comparable performance to the NMC811 baseline. (Energy target = 650-750 Wh/kg C/3, 2.5-4.4 V at the cathode level; capacity retention: 70%-90% at 500 cycles; cobalt concentration: 50 mg - 70 mg/Wh)

Approach/Strategy

- **We utilize a three-dimensional (3D) doping technology that is a hierarchical combination of surface and bulk doping.**
  - Surface doping stabilizes the interface between the primary particles and the electrolyte
  - Introduction of dopants to the bulk enhances oxygen stability, conductivity and structural stability in low-Co oxides under high voltage and deep discharging operating conditions.
  - A composition controlled and thermodynamics driven synthesis will be used to accurately achieve the desired 3D doping structures.
- **Use high-throughput computational materials design to screen surface and bulk dopants for a low-Co environment.**
- **Formulate new electrolytes that stabilize the cathode/electrolyte interfaces at deep charging conditions.**
- **Advanced computational and characterization techniques are developed to study**
  - Dopant environment and chemistry
  - Thermal stability, oxygen loss, and the degradation of the cathode/electrolyte interfaces.

Technical Accomplishments and Progress
Phase Diagram: Li-Ni-O



Electrochemical testing
30 °C, $p(O_2) = 0.2\ atm$

Synthetic
600 °C, $p(O_2) = 1\ atm$

- A decrease of $\Delta\mu_O$ indicates an increase in temperature and/or a decrease in oxygen partial pressure
- Thermodynamically stable region for $LiNiO_2$ phase:
  $-1.10 < \Delta\mu_O < -0.02\ eV, -3.28 < \Delta\mu_{Li} < -2.56\ eV$
- Higher $\Delta\mu_O$ predicted conversion to spinel Ni_3O_4 / cation-mixed spinel $LiNi_2O_4$
- Synthesis at high lithium chemical potential results in the formation of Li_2O and Li_2O_2

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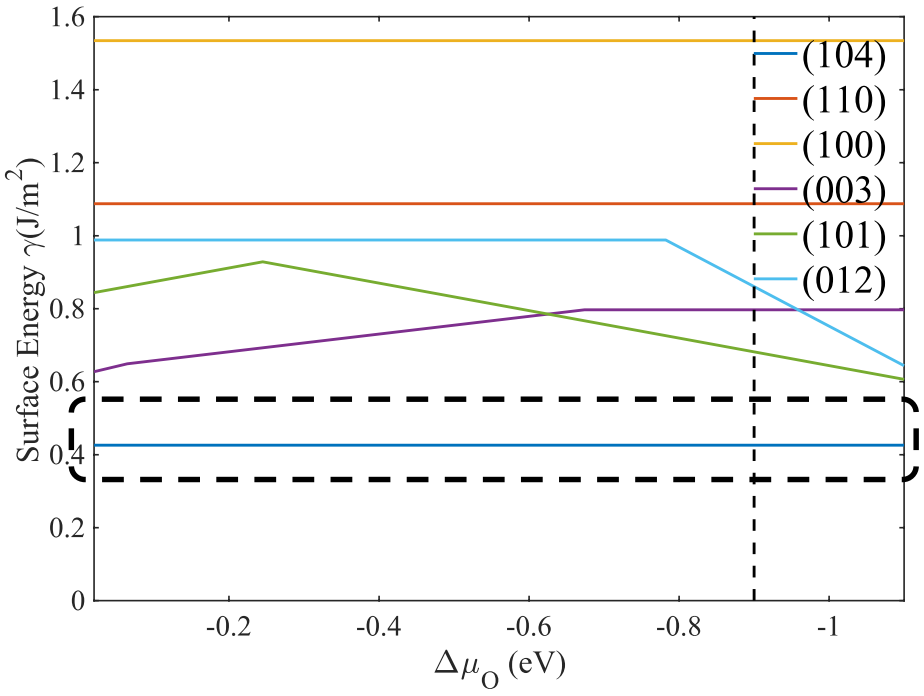
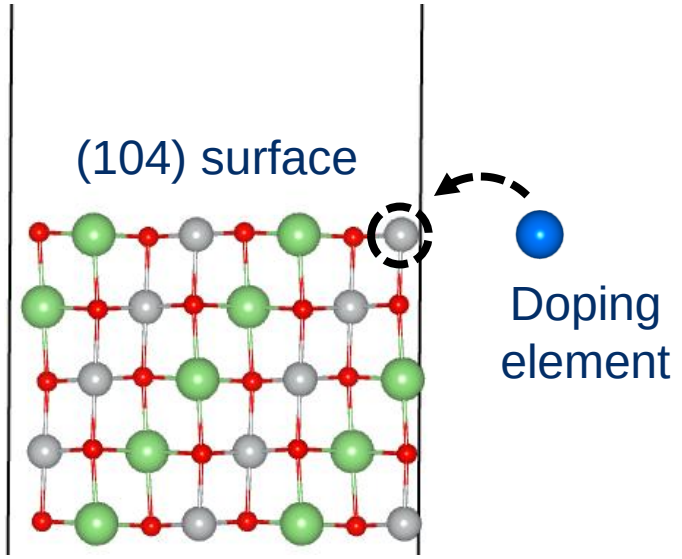
Chem. Mater., 2009, 21 (16), 3799

Technical Accomplishments and Progress
Surface Stability





Green: Li
Grey: Ni
Red: O

- Lowest surface energy: most stable surface: **(104)**
- Investigated doping elements: **Sb^{5+}, Ta^{5+}, Ti^{4+}, Al^{3+}, B^{3+}**
- Dopant effectiveness in surface oxygen retention during delithiaiton of $LiNiO_2$

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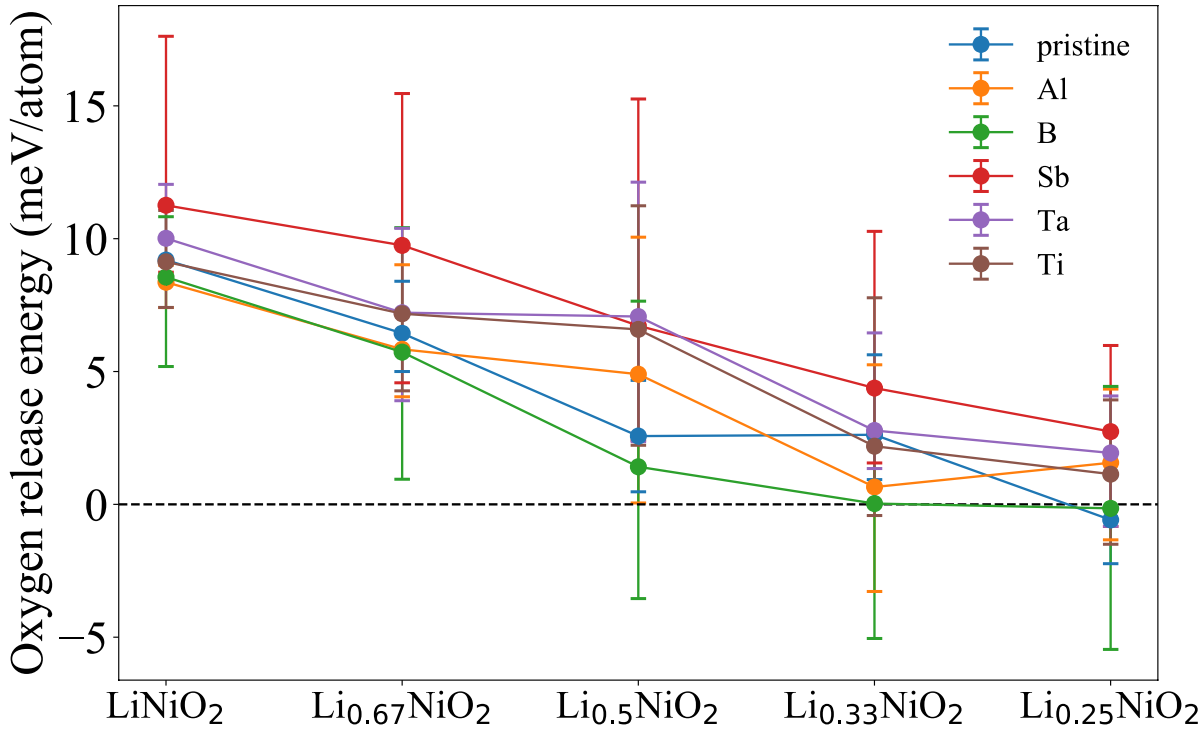
Technical Accomplishments and Progress
Surface Oxygen Retention

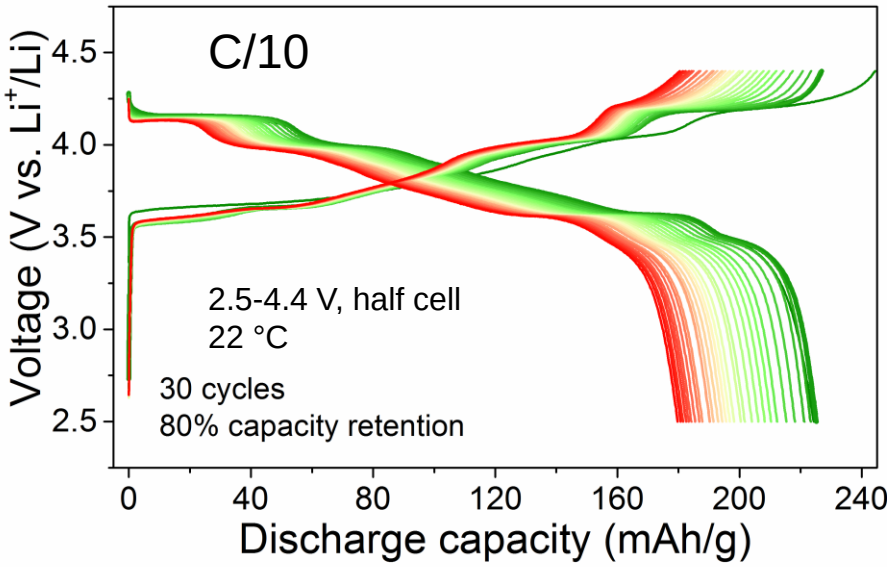


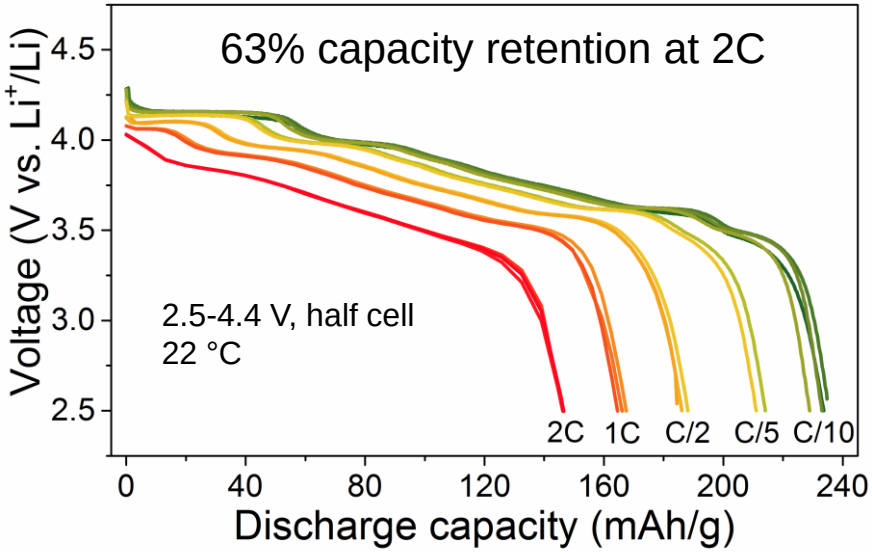
Calculation is based on:
T = 30℃
$p(O_2) = 0.2\ atm$

Surface facet (104)

- Upon delithiation, the thermodynamic oxygen release energy decreases rapidly
- At high charge state, e.g. 75% of Li extraction, oxygen is predicted to spontaneously release from the surface for pristine $LiNiO_2$
- **Sb^{5+}, Ta^{5+}, Ti^{4+}** are found here to enhance surface oxygen retention of $LiNiO_2$

Technical Accomplishments and Progress
Baseline material: $LiNiO_2$

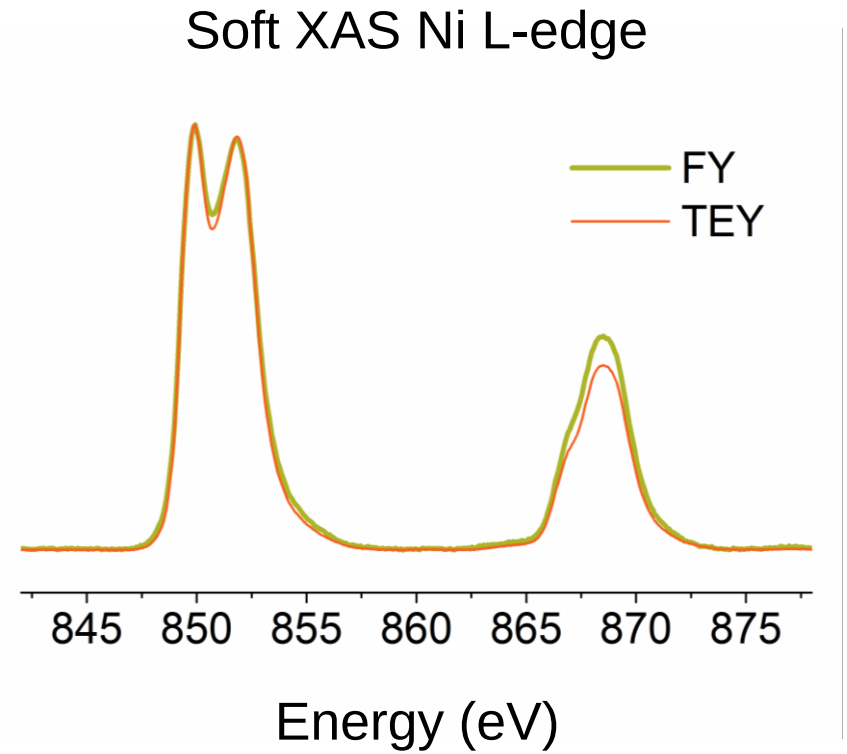




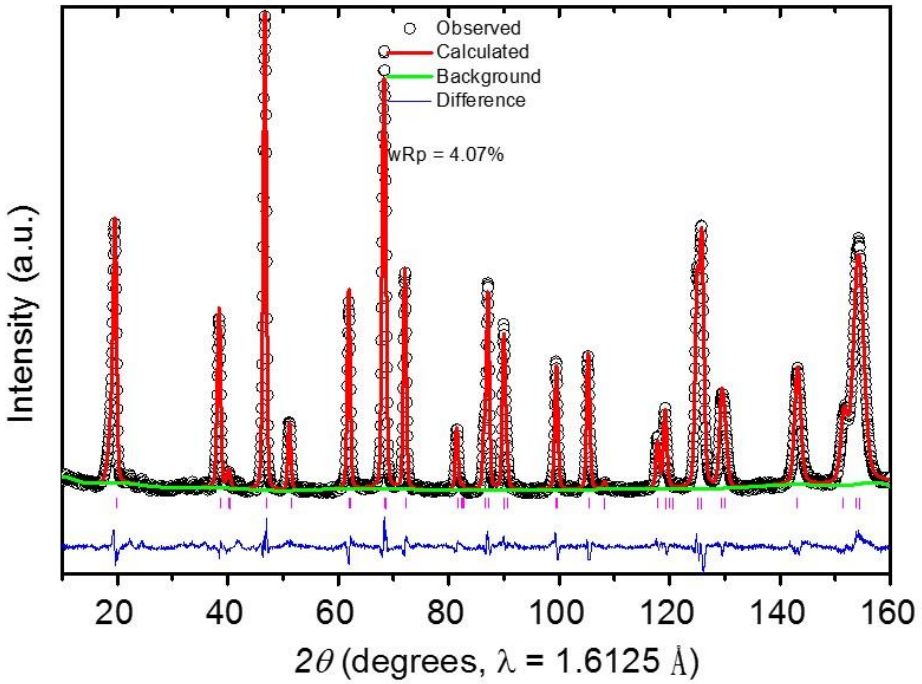
65% capacity retention after 100 cycles

- Can we use the 3D doping approach to improve $LiNiO_2$?
- How much can we improve it?

Technical Accomplishments and Progress
Gen-2: 3D doped $LiNiO_2$ (Co-free, Ni>94%)



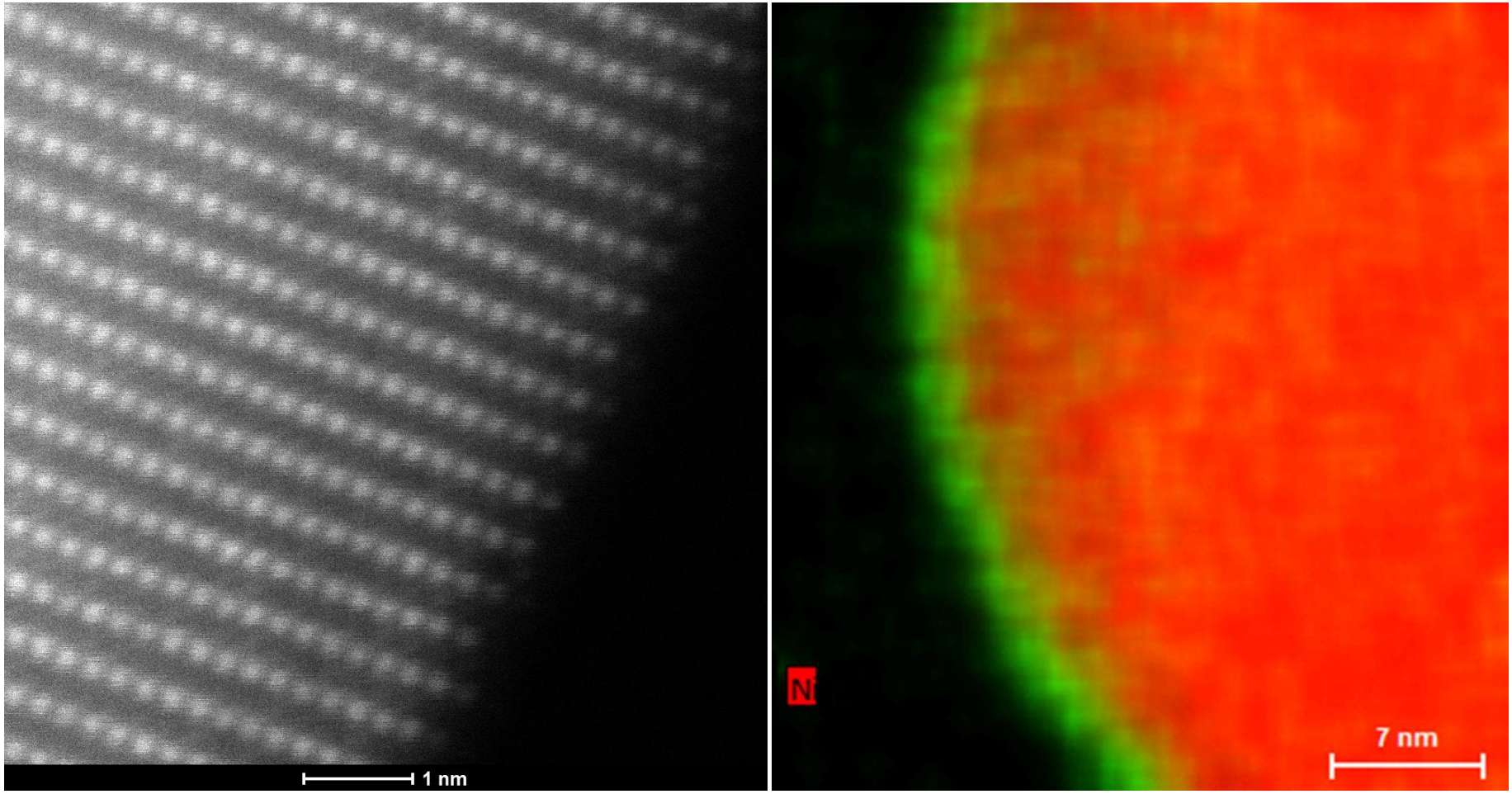
Ni L-edge show that Ni oxidation state is uniform from the surface to the bulk



Neutron diffraction and Rietveld refinement show that the VT Gen-2 material is a O3 phase layered oxide

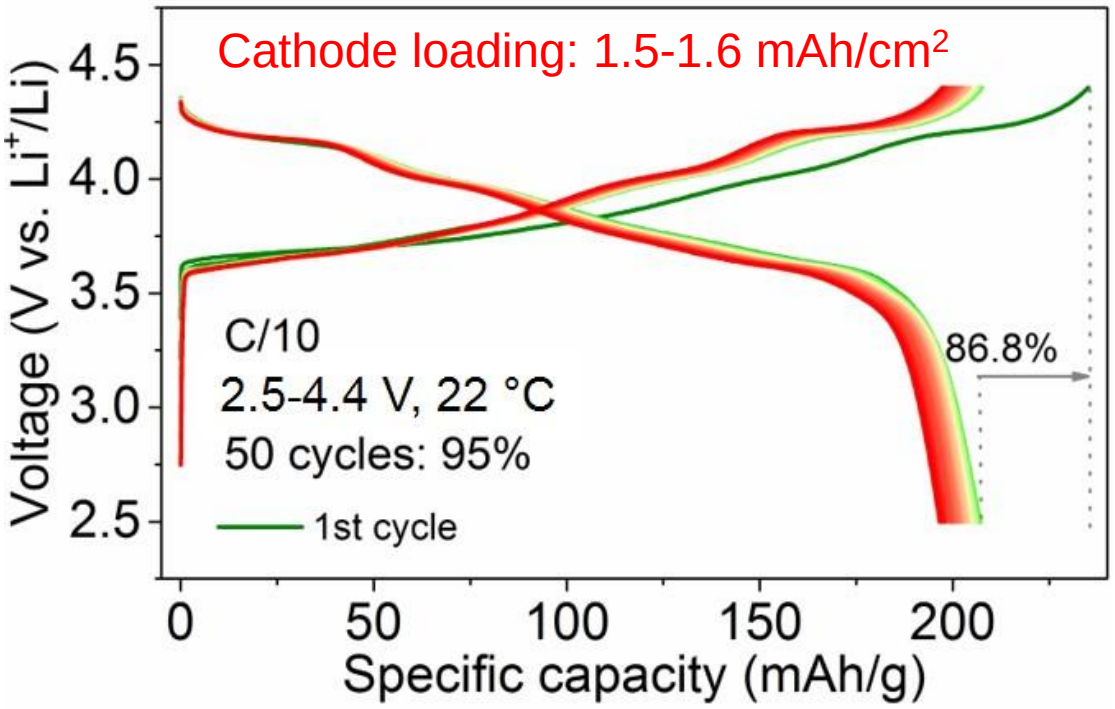
Technical Accomplishments and Progress
Gen-2: 3D doped $LiNiO_2$ (Co-free, Ni>94%)

Compositional Mapping of the **Surface Dopant**



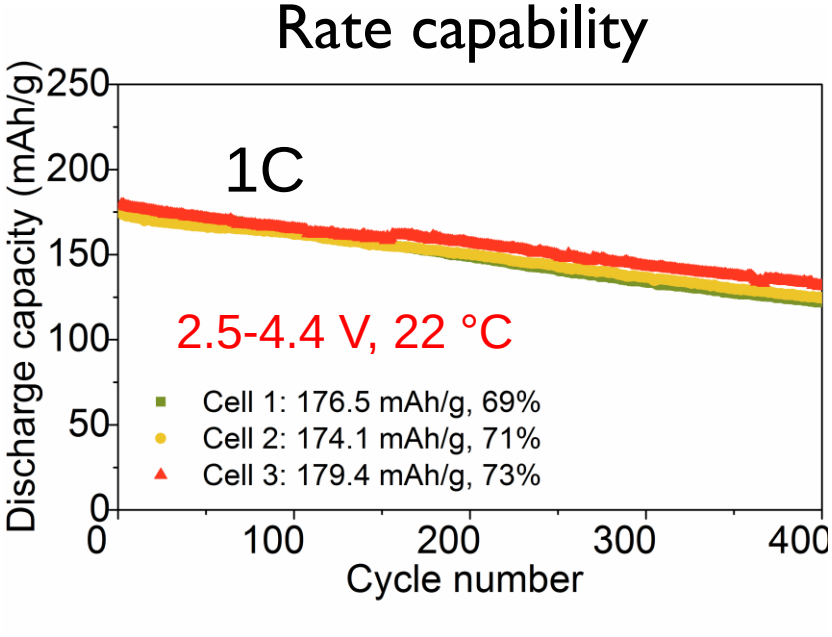
- Layer-layer structure with no surface reconstruction
- Accurate delivery of surface dopant achieved

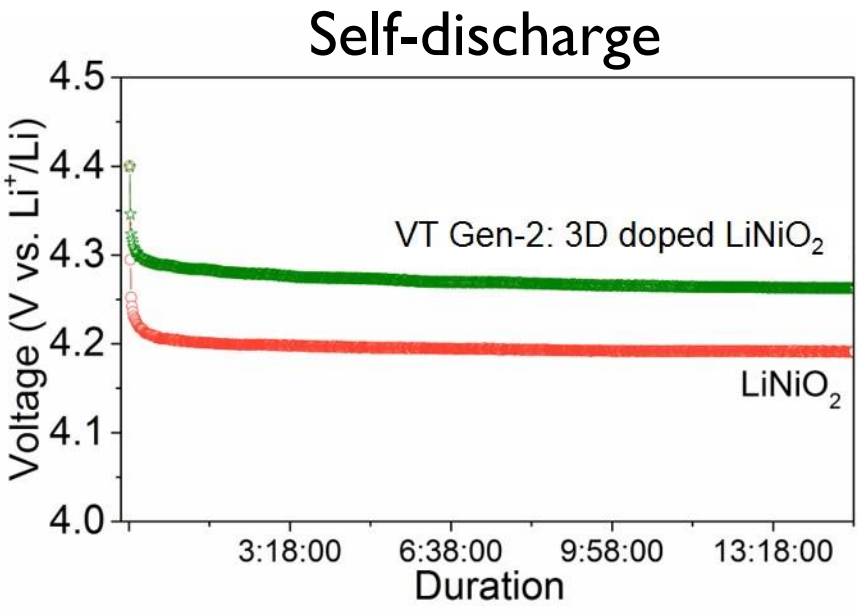
Technical Accomplishments and Progress
Gen-2: 3D doped $LiNiO_2$ (Co-free, Ni>94%)



- Reduced plateaus
- Stable capacity retention, even at a low C rate (C/10)
- Low charge-discharge hysteresis

Technical Accomplishments and Progress
Gen-2: 3D doped $LiNiO_2$ (Co-free, Ni>94%)

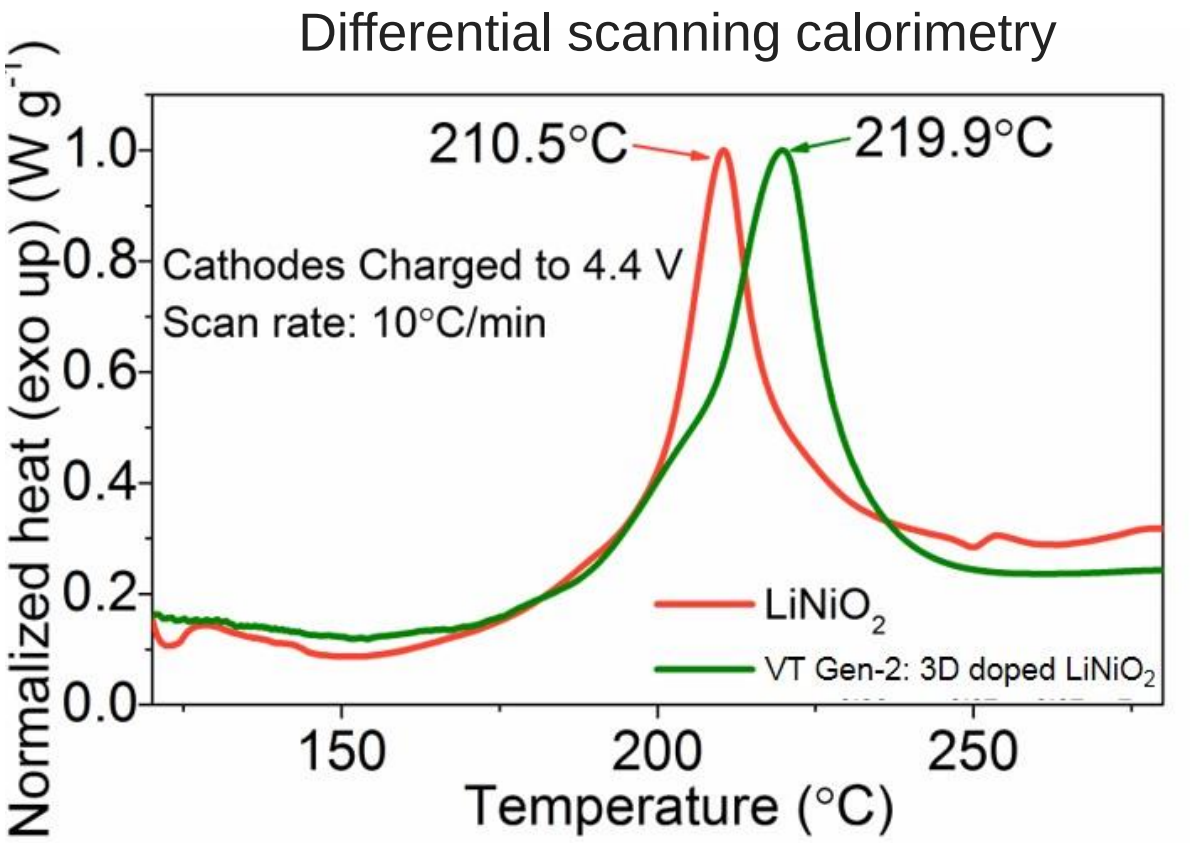




Stronger stability against self-discharge

- Good rate capability
- Reproducible performance
- Reasonable cycle life (initial assessment)

Technical Accomplishments and Progress
Gen-2: 3D doped $LiNiO_2$ (Co-free, Ni>94%)



Initial thermal characterization showed improved thermal stability in the charged state

Responses to Previous Year Reviewers' Comments

- The project started in Dec 2018. There are no reviewers' comments on this project.

Collaboration and Coordination with Other Institutions

Sub-recipients	Institution	Tasks
Feng Lin	Virginia Tech	Synthesis and X-ray Diagnostics
Kristin Persson	UC Berkeley	High-throughput DFT calculation
Wu Xu	PNNL	Synthesis scale-up and electrolyte formulation
Fan Jiang	American Lithium Energy	Electrode and Cell Fabrication

Collaborators	Institution	Nature of Collaboration
Xiao-Qing Yang	Brookhaven National Lab	X-ray Diagnostics/TEM
Kim Kisslinger	Brookhaven National Lab	FIB Sample Prep
Dennis Nordlund	SSRL/SLAC	Soft X-ray Absorption
Jack Kan	Australian Nuclear Science and Technology Organisation. Now at China Spallation Neutron Source.	Neutron Scattering Refinement

Remaining Challenges and Barriers

- A fundamental and atomistic understanding of high-voltage cycling and thermal behavior of the 3D-doped $LiNiO_2$ requires in-operando synchrotron XRD studies. The team is actively procuring XPD beamtime at NSLSII, APS, and SSRL.
- While the 3D-doped $LiNiO_2$ performs better during high voltage cycling, there is still capacity fading. Multiple strategies will need to be pursued to ensure stable cycling to high potentials, including electrolyte formulation, and the use of novel dopants predicted by our theory team.
- Scale-up of calcination precursors for project cell delivery.

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

Proposed Future Research

- Morphology and tap density control of cathode particles.
- Investigation of cathode-anode cross-talk.
- Screening of electrolyte additives and salts.
- Study the cathode electrolyte interface and interphases.
- In-situ investigation of structural stability of Co-free layered oxides particularly under thermal abuse conditions.
- Computational investigation of the cathode surface chemistry.
- Use experimentally observed surface and bulk transformation and degradation pathways to refine the selection of surface/bulk stabilizing elements for Co-free materials.

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

Summary

- We have developed a 3D-doped $LiNiO_2$ layered cathode material (Gen-2 Ni > 94% and Co-free) that meets the energy density target of the project.
- The phase purity, layered structure integrity, and the desired 3D dopant profile have been verified by Neutron and X-ray diffraction, soft-XAS and TEM.
- Initial thermal characterization show 3D-doping improves thermal stability of the material
- First-principle calculations offer predictions of new dopants that stabilizes the $LiNiO_2$ surface.