CATHODE MATERIALS FOR NEXT GENERATION LITHIUM-ION BATTERIES: THEORY AND MODEL SYSTEMS

Project ID: BAT253

HAKIM IDDIR

Argonne National Laboratory
June 21-25, 2021

2021 DOE Vehicle Technologies Office
Annual Merit Review

Overview

Timeline

- Start: October 1, 2018
- End: September 30, 2021
- Percent complete: 85%

Budget

- Total project funding:

  FY20 $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

Geopolitical concerns over critical resources, and in particular cobalt, as well as market demand have instigated new efforts to improve the sustainability of lithium-ion cathode technologies. This project will use first-principles modeling applied to prototypical cobalt free cathode oxides including $LiNiO_2$ (LNO), $LiNi_{0.5}Mn_{0.5}O_2$, and newly developed derivatives thereof in order to advance cathode design in accord with DOE targets for cost, performance, and sustainability

Project Goals

- Identify promising surface and bulk, dopant elements and provide a fundamental understanding of their efficacy in modifying the properties low/no cobalt oxides with respect to cobalt as a counterpart.

- Improve cathode design by understanding and elucidating the mechanisms and tendencies of facet-dependent degradation, stability, and dopant segregation.

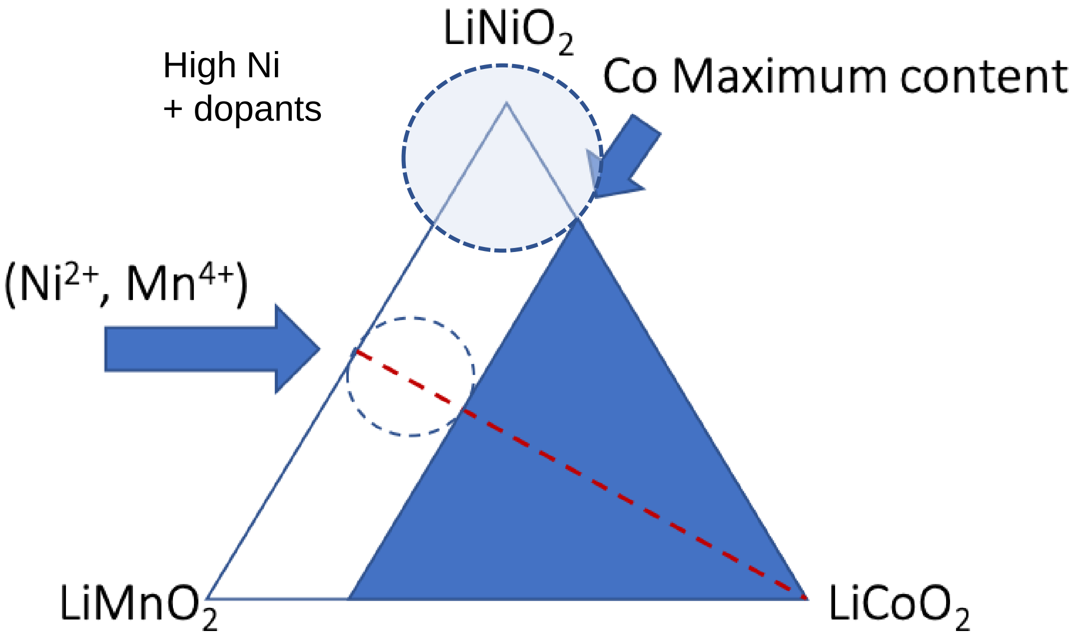
- Narrow the gap in our understanding between structure-property relationships by elucidating the effects that local phenomena (e.g., TM ordering) have on measured, physical and electrochemical data

Milestones

Approach: Understanding the role of Co through modeling and model systems

($LiMn_xNi_xCo_{1-2x}O_2$) model systems have been designed such that Ni resides in a layered structure and exists as only Ni^{2+} in order to investigate:

- Surface composition & stability of (104) & (012) facets and facet reconstruction – accomplished
- Co clustering/next neighbors, domain size, and local configuration effects on structural stability – accomplished
- NMR shifts as a function of local ordering using density functional theory – accomplished
- Surface/electrolyte interaction – accomplished
- Identify dopants (co-dopants) that can mimic the effects of Co – in progress
- Synthesis, characterization and E-Chem testing of model systems (single crystals) - accomplished



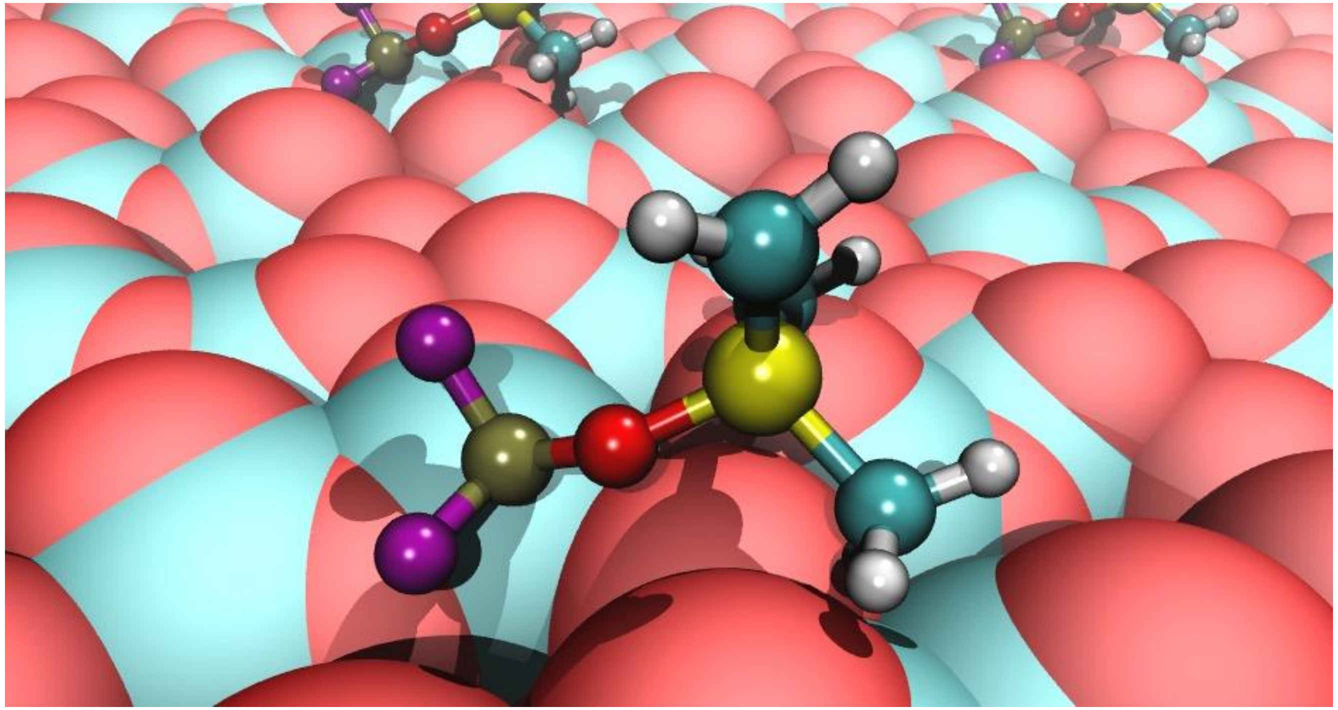
Approach

- Atomistic modeling at the DFT level in order to gain understanding on Li ion batteries at the nanoscopic level and provide physical properties for multi scale modeling.
- **Work in close collaboration with synthesis and characterization for design of new materials.**

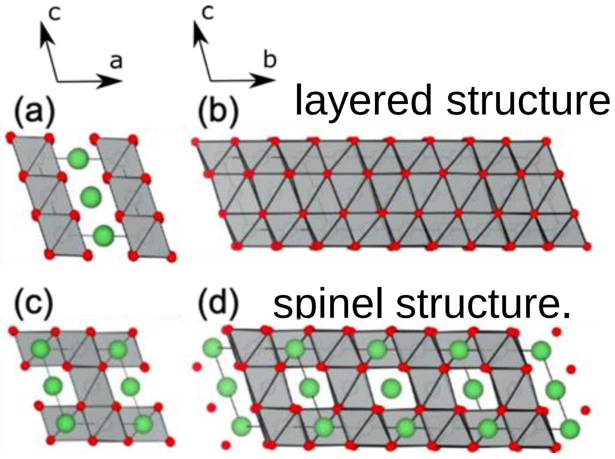
Capabilities

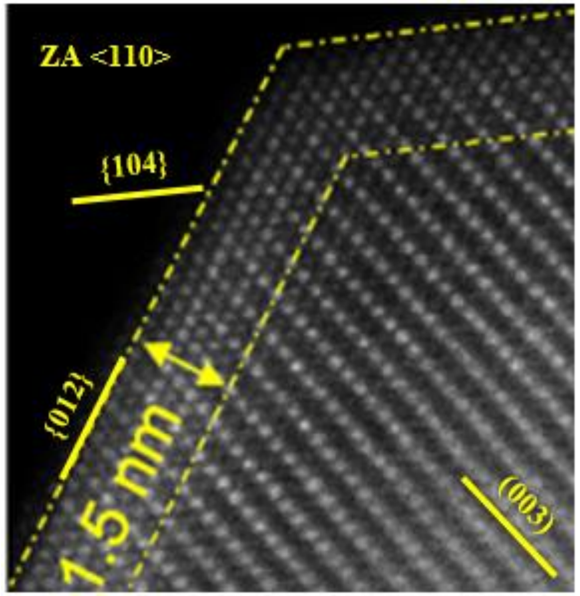
- High performance computing.
- Quantum chemical methods for calculation of electronic structures, reaction energies, ion diffusion barriers, oxidation and reduction potentials.
- Ab-initio molecular dynamics (AIMD) simulations of bulk materials, surfaces, interfaces and electrolytes.
- Ab-initio thermodynamic analysis of surfaces and interfaces.
- Micro-kinetic modeling of complex reaction networks.
- Bulk solvent effects are accounted for by using an implicit solvation (VASPsol).

ANL high performance computing facilities: MIRA 10-petaflops IBM Blue Gene/Q system
Capable of 10 quadrillion calculations per second.



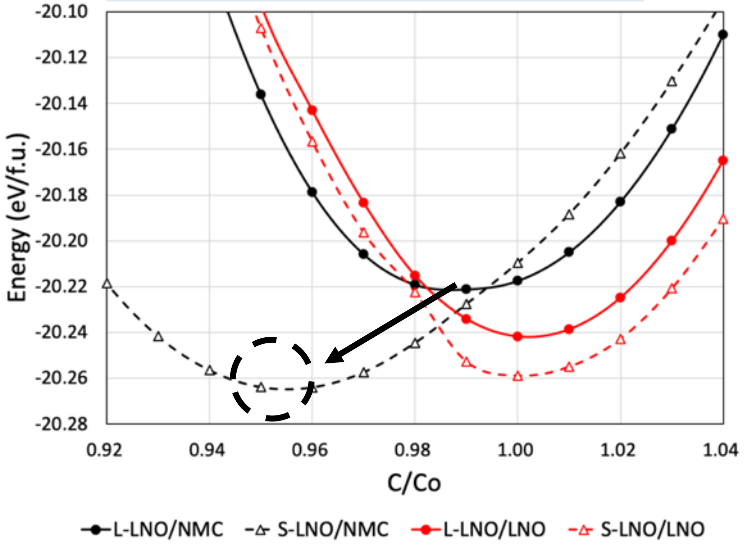
Strain-driven surface reconstruction and cation segregation in layered Li(Ni$_{1-x-y}$Mn$_x$Co$_y$)O$_2$ (NMC) cathode materials





A STEM image shows an area of a primary NMC particle close to a corner between a {012} facet and a {104} facet.

Strain stabilized spinel phase

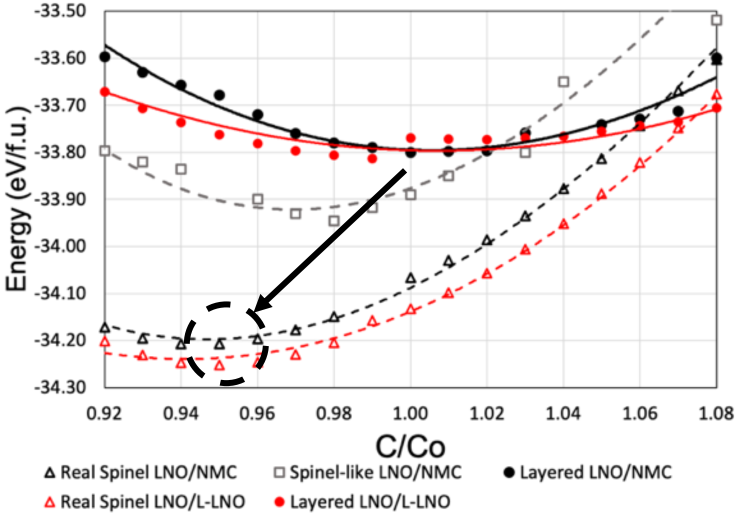


- The reconstructed surface phase is stabilized by the strain.
- Ni prefers the reconstructed surface.

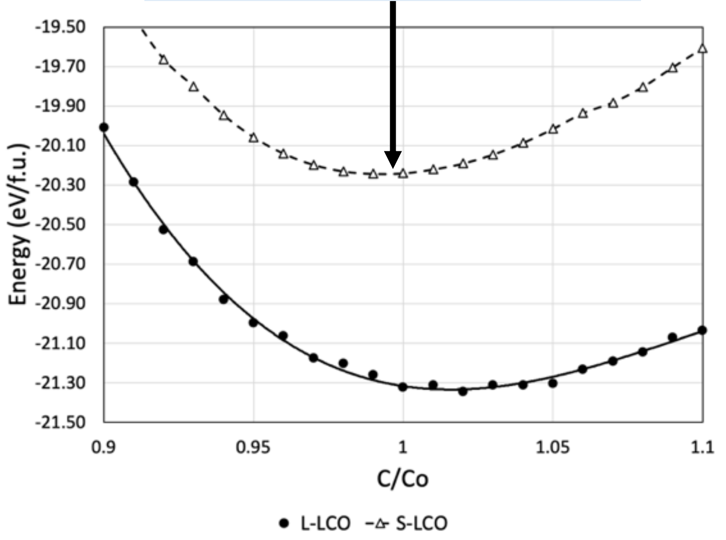
Garcia, J.C.; Bareño, J.; Chen, G.; Croy, J. R.; Iddir, H. Strain-Driven Surface Reconstruction and Cation Segregation in Layered Li(Ni 1−x−y Mn x Co y)O 2 (NMC) Cathode Materials. *Physical Chemistry Chemical Physics* **2020**, *22* (42), 24490–24497.

Delithiation

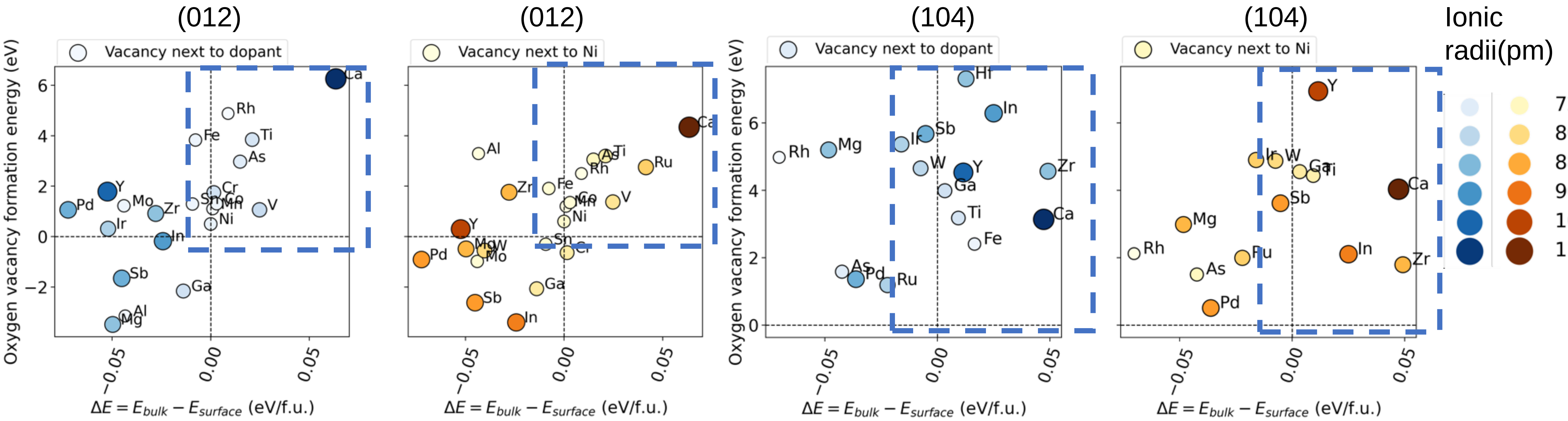
Increased driving force for the stabilization spinel phase

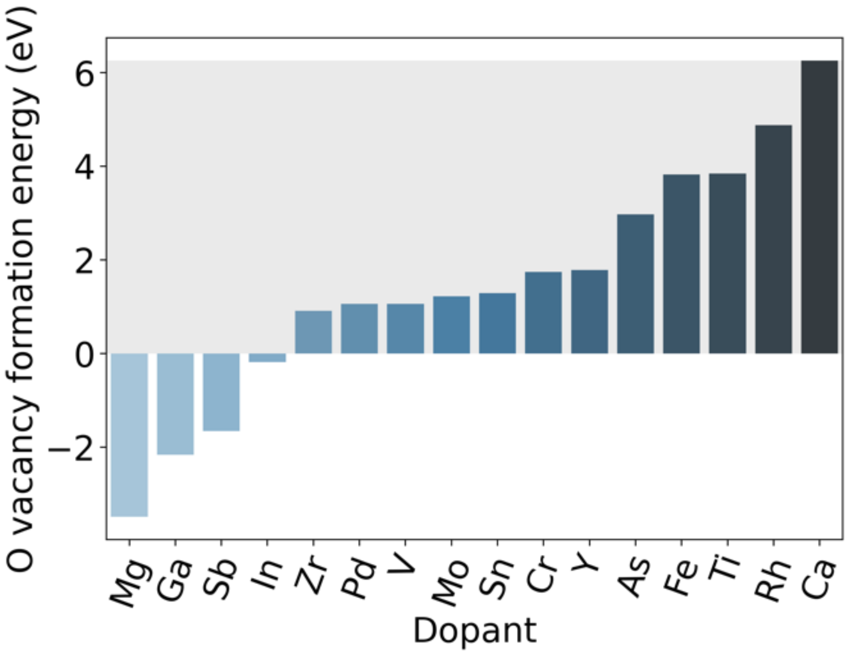


Co rich spinel is not stable



Screening for dopants in Ni-rich materials



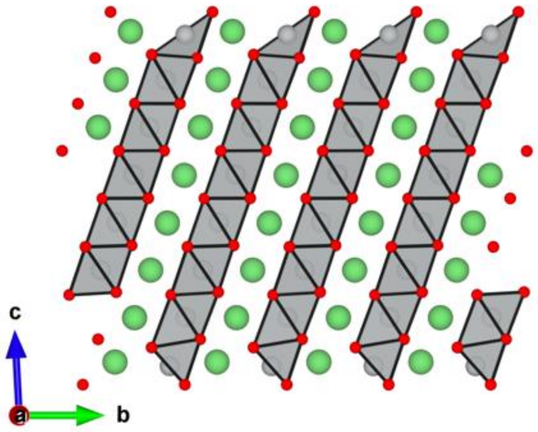


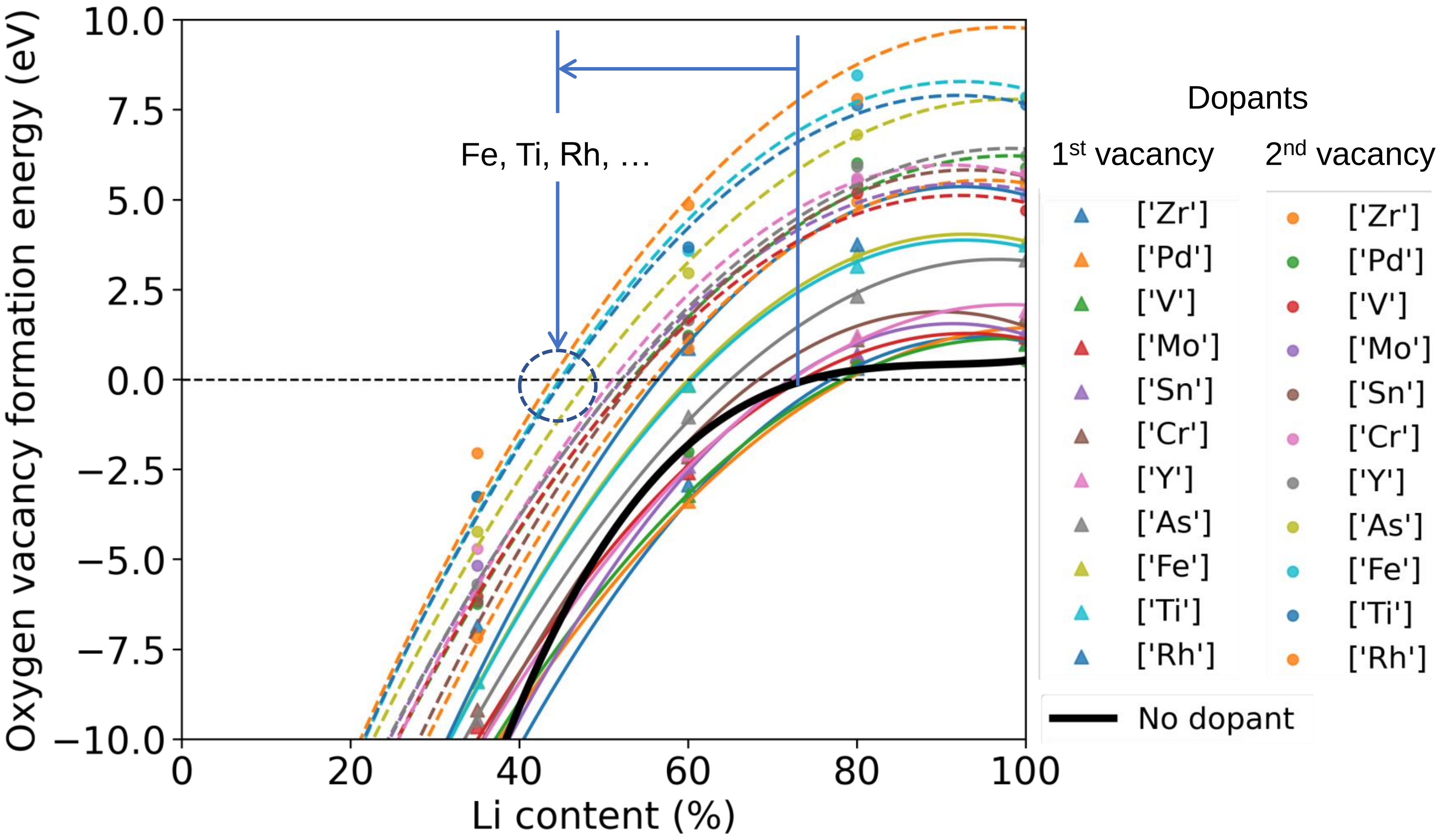
- The ideal dopant prefers to be at the surface and decreases reactivity (blue box).
- The reactivity of the (012) facet, usually the most abundant, decreases for all species with a positive oxygen vacancy formation energy, for instance: Ca, Fe, Ti, Cr, V, Sn, Ru, Rh, As.
- The (104) facet is less reactive than the (012), and all the tested dopants decrease the reactivity even more.

Doped (012) surface $LiNiO_2$ reactivity

Oxygen vacancy formation energy as a proxy for reactivity:

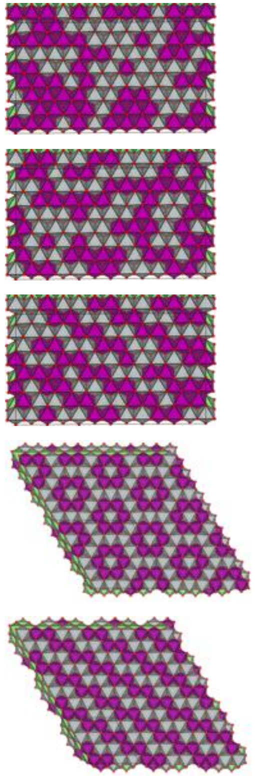
$$\mathrm{E}^{\mathrm{f}}_{\mathrm{ov}} = \mathrm{E}_{\mathrm{pristine}} - \mathrm{E}_{\mathrm{ov}} - \mu(O_2)$$



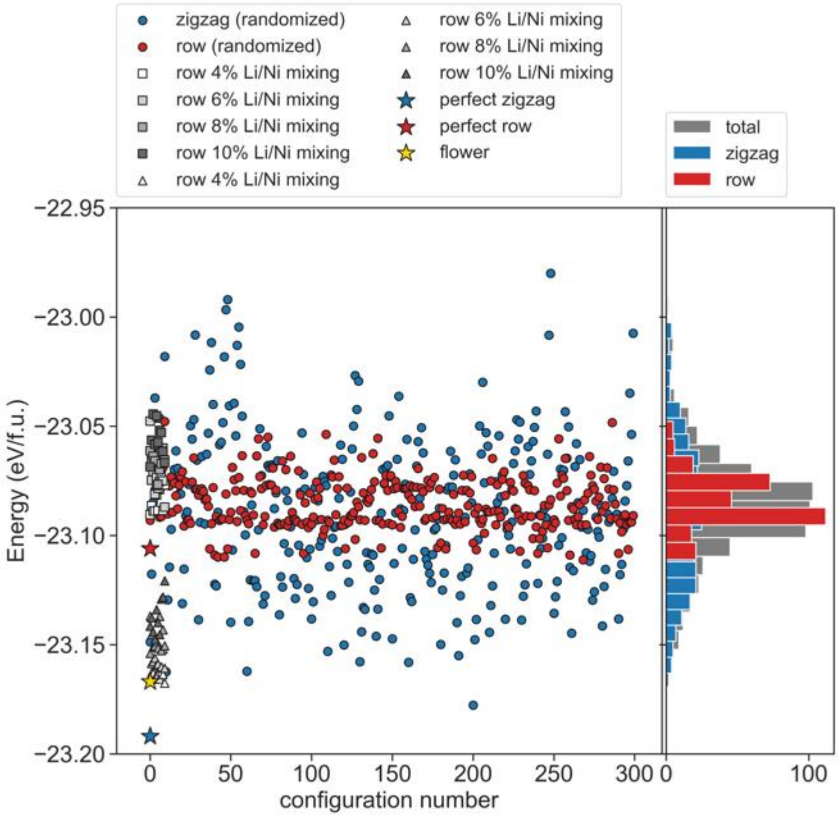


- The surface reactivity increases upon delithiation.
- There is a threshold for spontaneous oxygen evolution (Ef < 0).
- A second oxygen vacancy is harder to make than the first (it is harder to reduce the surface).

$LiMn_{0.5}Ni_{0.5}O_2$ NMR modeling



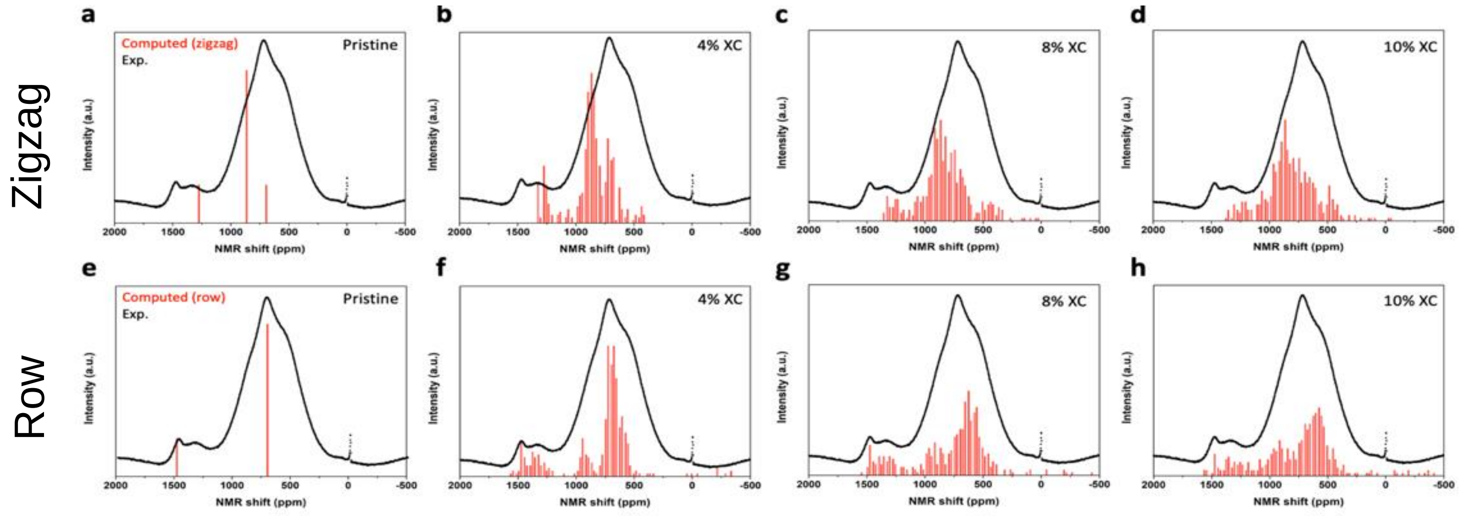
Increased Li-Ni exchange



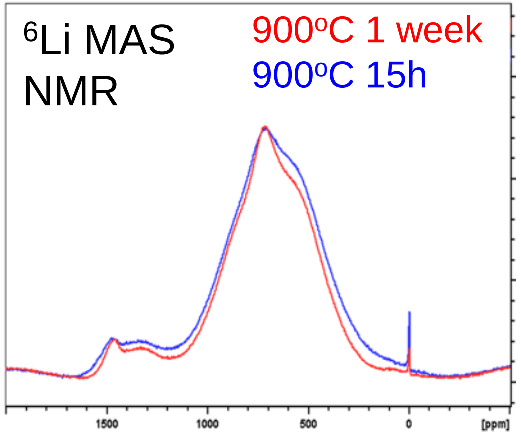
Configurations reached during synthesis at high T

These configurations are mostly locked-in during annealing and cooling,

- The distribution shows that most configurations contain some amount of disorder and Li-Ni exchange.
- The center of the distribution is closer to the row model, hence its higher overall contribution to the overall spectra.
- Inclusion of zigzag configuration increases NMR shifts at ~800 ppm.
- Inclusion of more Li-Ni exchange enhances the intensity of shifts near 500 ppm as well as near 800 ppm.
- Li/Ni exchange is slightly reduced by longer temperature annealing times.

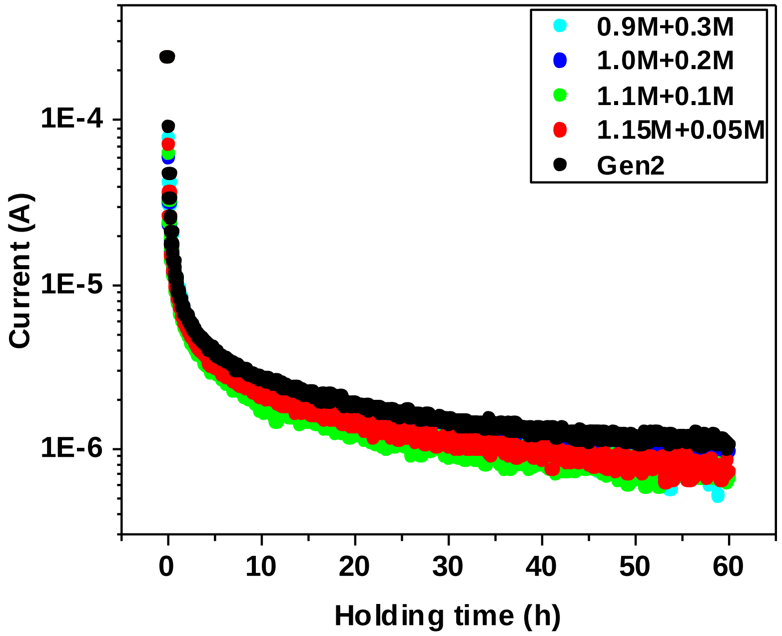


$LiMn_{0.5}Ni_{0.5}O_2$ NMR new experimental spectra



Dual-Salts Electrolyte to Effectively Reduce Impedance Rise of High-Nickel Lithium-Ion Batteries

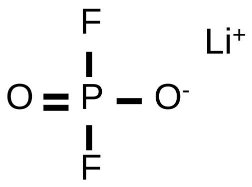
Leakage currents of cells with electrolytes having varied dual-salts ratios and with baseline electrolyte



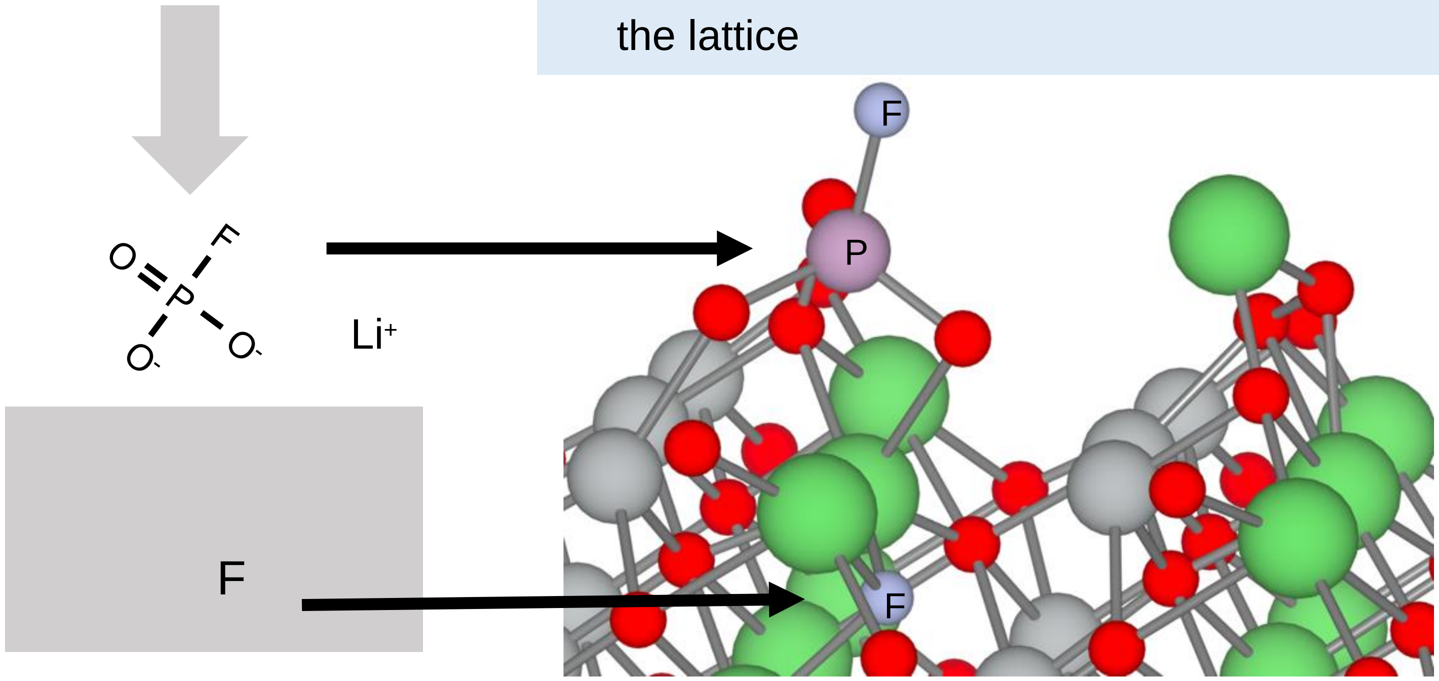
The surface is passivated by the dual salt system

Yang, Jianzhong; Rodrigues, Marco; Son, Seoung-Bum; Garcia, Juan; Liu, Kewei; Gim, Jihyeon; Iddir, Hakim; Abraham, Daniel; Zhang, Zhengcheng; Liao, Chen. *Dual-Salts Electrolyte to Effectively Reduce Impedance Rise of High-Nickel Lithium-Ion Batteries.* (submitted)

lithium difluorophosphate (LiDFP)



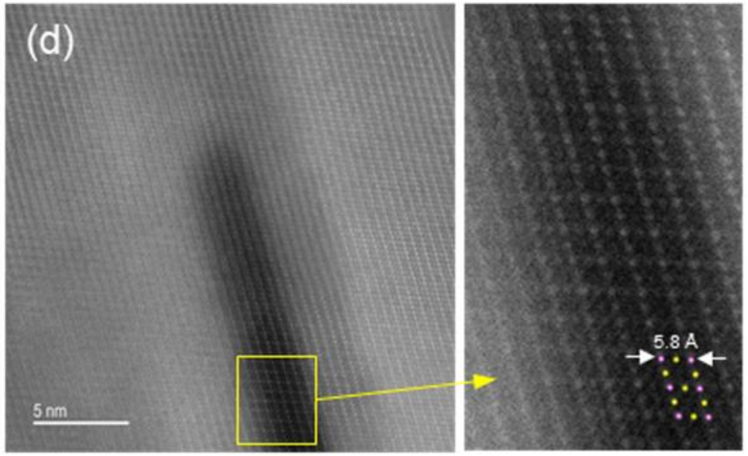
ΔE = -0.11eV~10kJ/mol



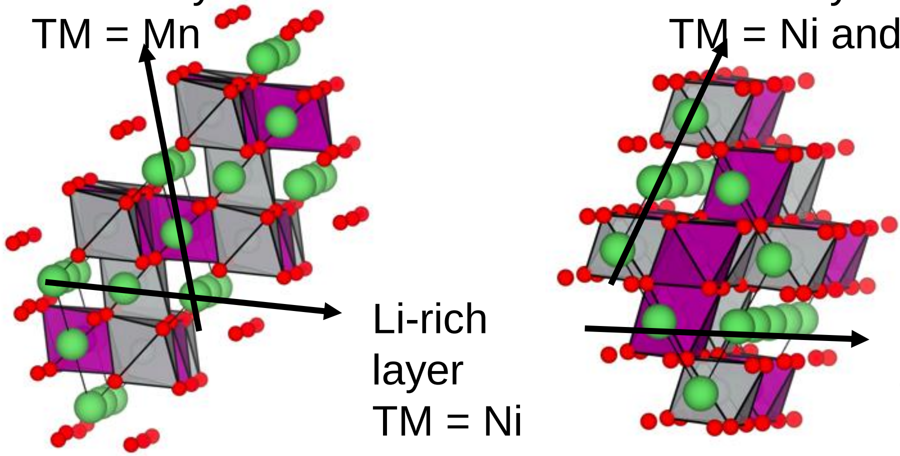
- The salt became lithium monofluorophosphate (MFP) at the surface with a favorable thermodynamic driving force.
- The reaction seems to have a negligible activation barrier (it occurred spontaneously during our simulation).
- One F from LiDPF substituted one O from the lattice

Lithiated-Spinel phases in Li_2MnNiO_4

See also **BAT049**



atomic resolution HAADF-STEM images seen from [110] zone axis,



Li-rich layer
TM = Mn

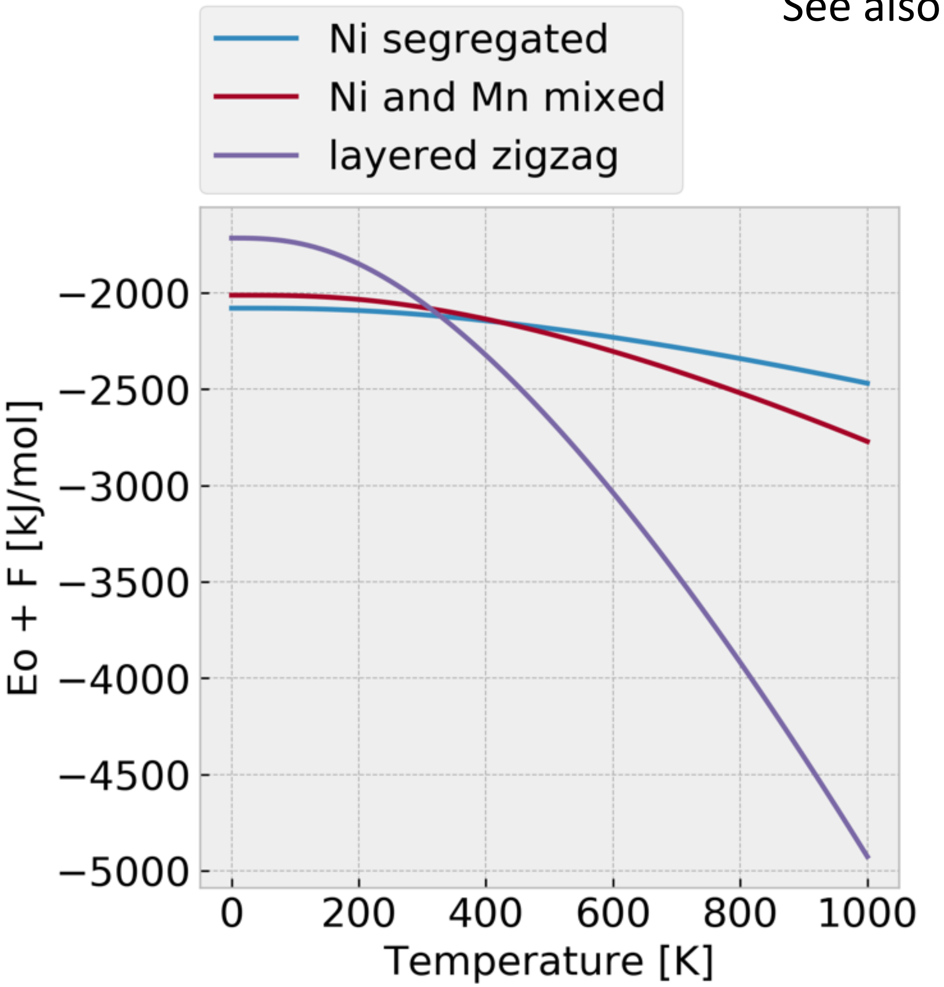
Li-rich layer
TM = Ni

Li-rich layer
TM = Ni and Mn

Li-rich layer
TM = Ni and Mn

-22.52 eV/f.u. - - - - → **-22.82 eV/f.u.**

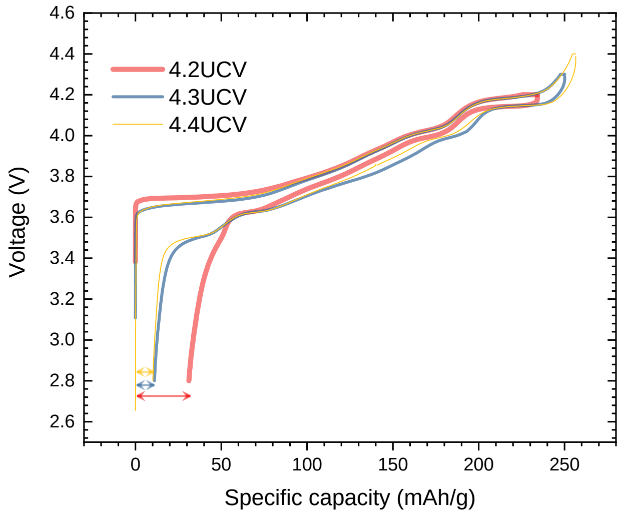
Perfect zigzag layered: -23.24 eV/f.u.

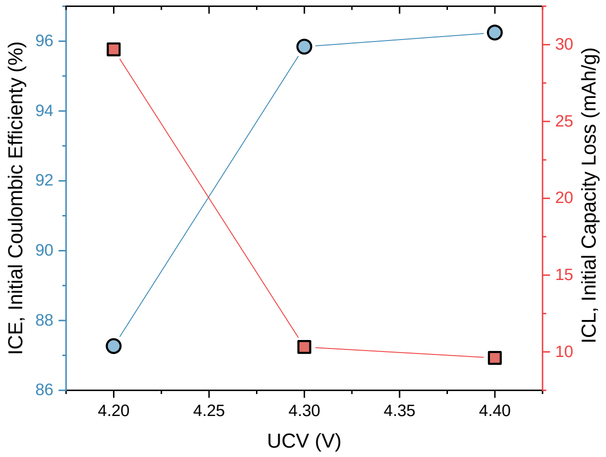


Spinel phase more stable than the layered phase at low temperatures

Shi, Boyu; Gim, Jihyeon; Li, Linze; Wang, Chongmin; Garcia, Juan; Iddir, Hakim; Vu, Anh; Croy, Jason; Thackeray, Michael; Lee, Eungje. Li_2MnNiO_4: A Co-Free Cathode with Lithiated-Spinel Character for High Energy Li-Ion Cells. (submitted)

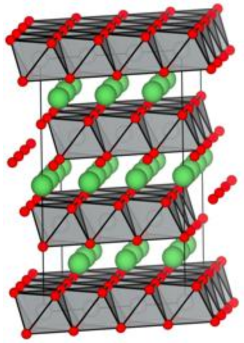
Ni migration across layers at high state of charge



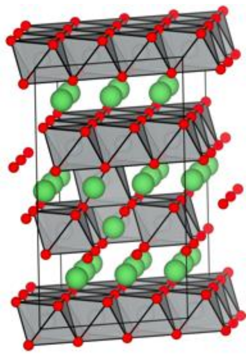


See also **BAT251**

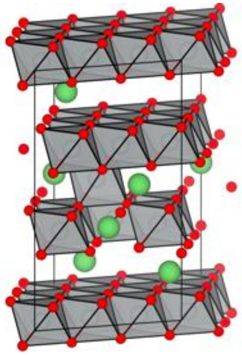
- Capacity lost is reduced when cycled at voltages higher than 4.3V.
- The driving force is larger (thermodynamics) and the activation energy is smaller (kinetics) with increase in SOC.
- Higher states of charge (SOC) promote Ni migration to the TM layer.
- Once Ni is back in the TM layer, Li/Ni defect formation has a positive energy: irreversible process at high SOC.



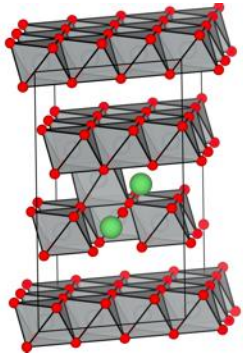
100% Li
Ni^{3+} everywhere



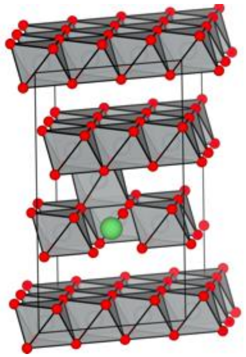
100% Li:
Li/Ni defect
Ni^{2+}, Ni^{3+}
"Hole" is delocalized



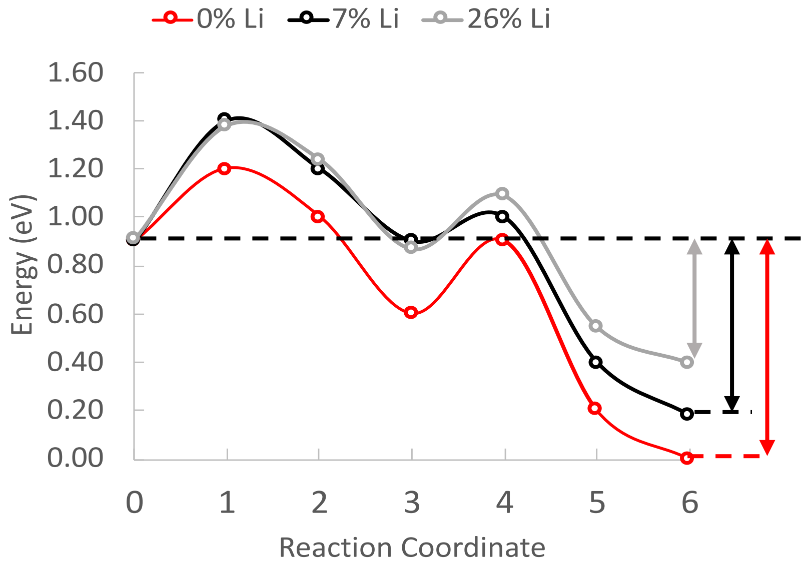
26% Li
Ni^{2+} , Ni^{3+},
Ni^{4+}



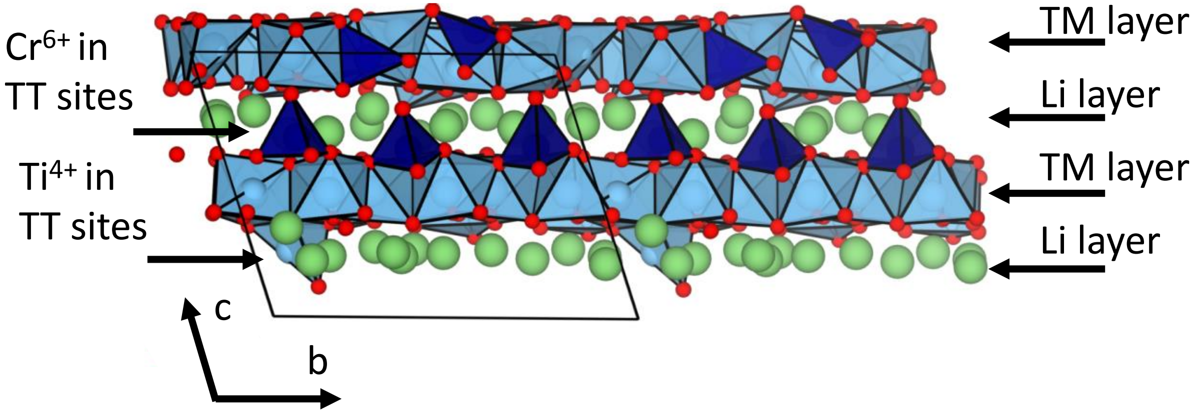
7% Li
Ni^{2+} , Ni^{3+}, Ni^{4+}
Magnetization of
Ni^{2+} has increased.



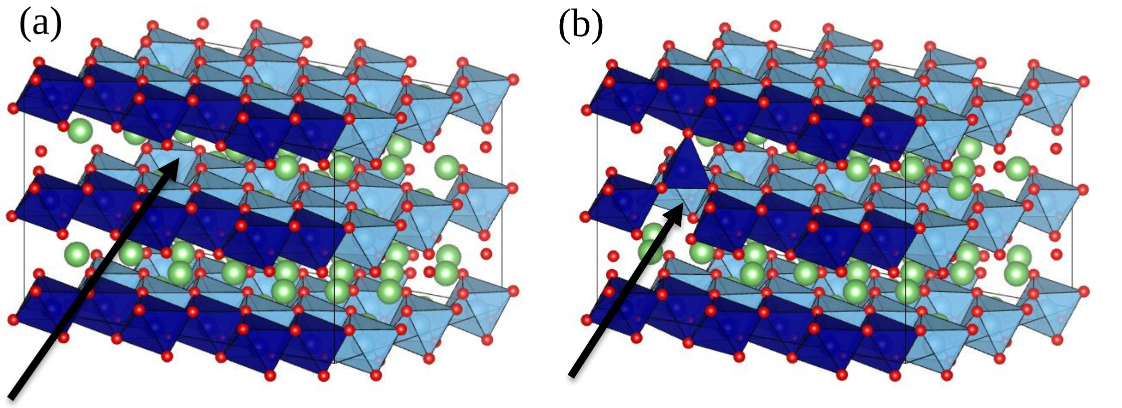
4% Li
Ni^{3+}, Ni^{4+}



Hysteresis in Lithium Rich Oxides: Anionic Activity or Defect Chemistry of Cation Migration



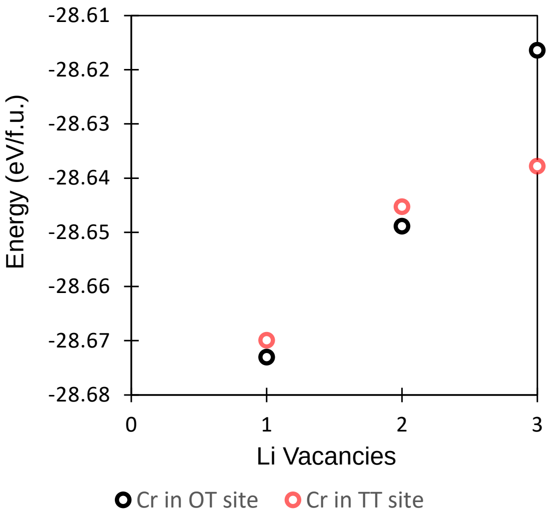
Polyhedral representation of a $Li_{1.2}Ti_{0.4}Cr_{0.4}O_2$, simulation cell after 7ps at 750K AIMD - NVT. Most of the oxidized chromium in the cell migrated to tetrahedral sites —even for this short simulation time.

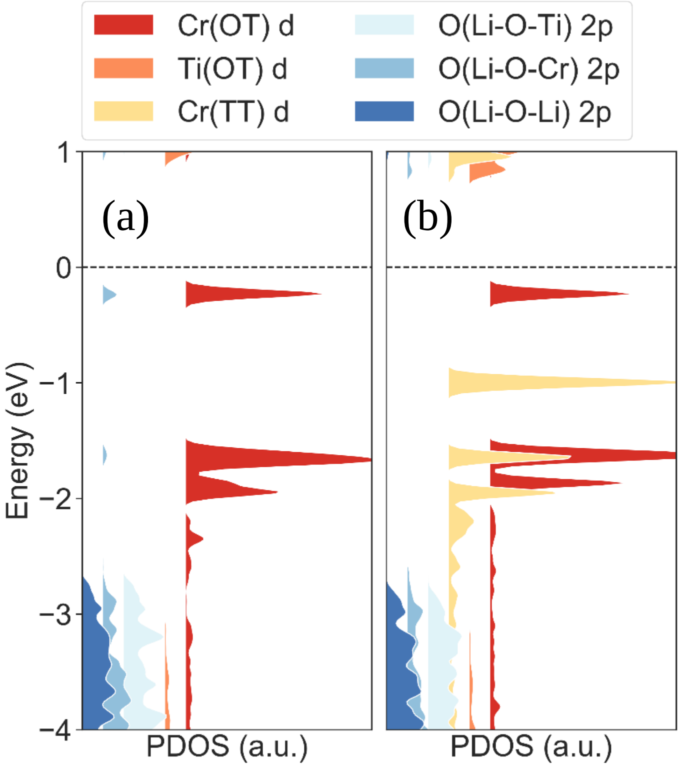


Vacancies around redox active Cr ions

Cr ion in a tetrahedral site

- Calculations show that neither oxygen nor Ti contribute to the electrochemical capacity of this material.
- Oxidation of Cr^{3+} to Cr^{6+} is concomitant with both Cr and Ti migration from octahedral to tetrahedral sites, enhanced by a d^0 configuration.
- Subsequent re-lithiation of the oxide is subject to an energy penalty due to the unfavorable occupation of lithium surrounding the tetrahedral sites.

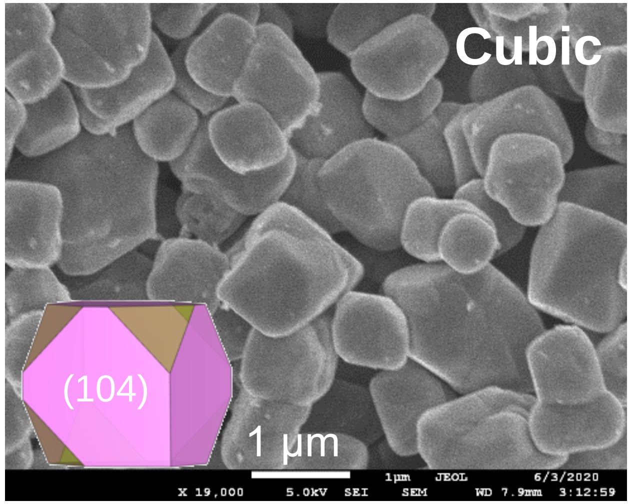


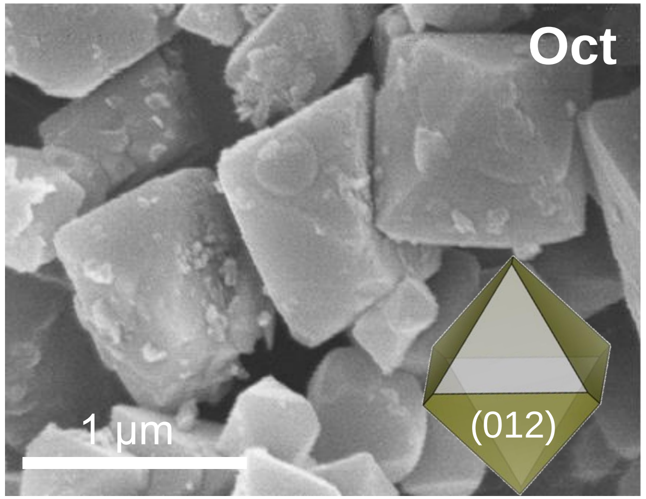


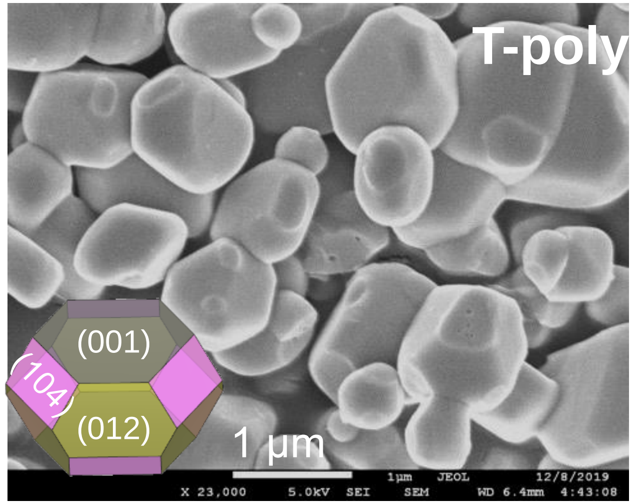
Croy, J. R.; Garcia, J. C.; Iddir, H.; Trask, S. E.; Balasubramanian, M. Harbinger of Hysteresis in Lithium-Rich Oxides: Anionic Activity or Defect Chemistry of Cation Migration. *Journal of Power Sources* **2020**, 228335.

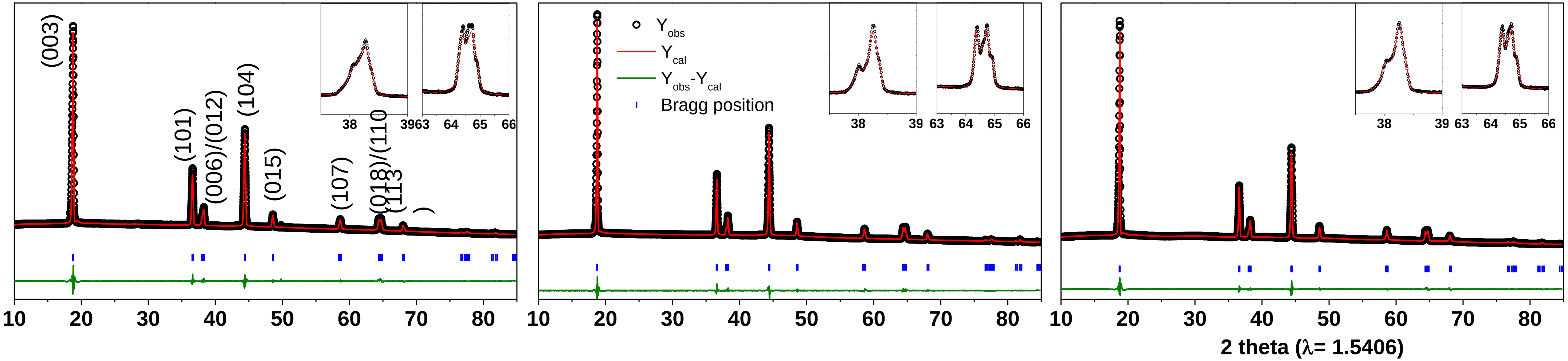
SC-LNO with different morphologies synthesized

Collaboration with Guoying Chen BNL







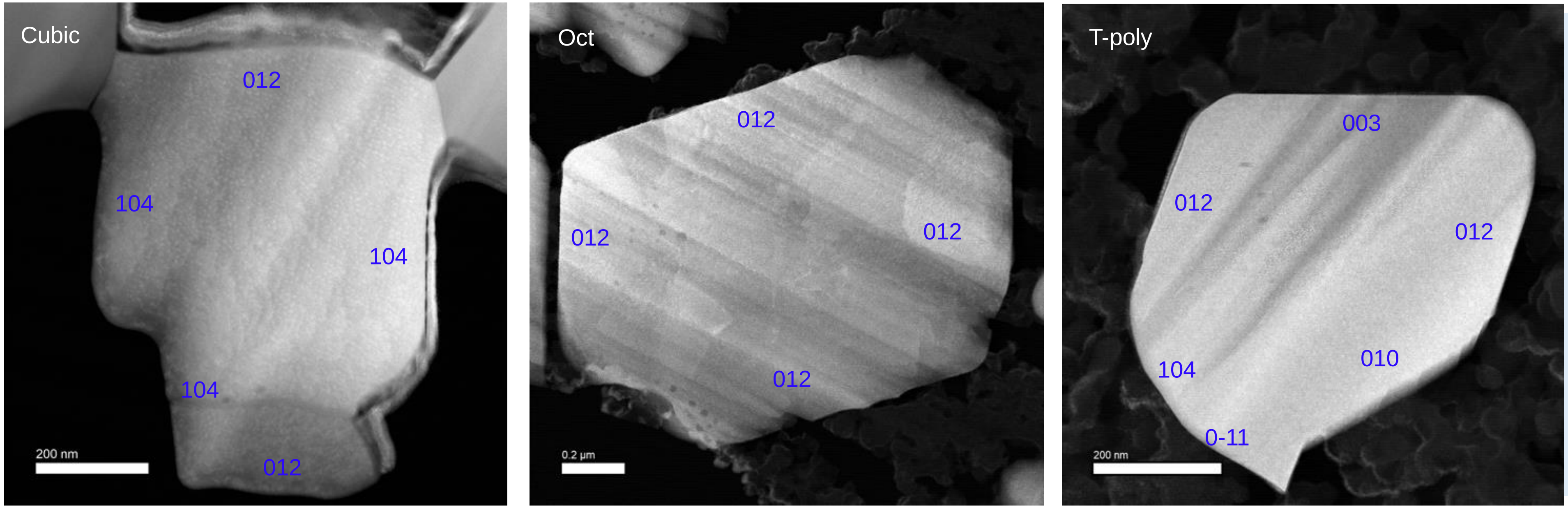


- All $LiNiO_2$ (LNO) samples made in the same size (~ 1 μm), with the same layered crystal structure and similar level of cation mixing.
- Dominating surfaces on SC-LNO – Cubic (**104** family), Oct (**012** family) and T-Poly (**mixed** 001, 104 and 012 families).

STEM-HAADF images show the surface facets of $LiNiO_2$ with different morphology

Electron Microscopy in collaboration with
Chongmin Wang
EMSOL PNNL

Focused ion beam cross section of the single crystal $LiNiO_2$ with different morphology



- FIB sectioning of the single crystal $LiNiO_2$ to determine the surface facets.
- The table list the comparison of the expected surface termination plane with that determined based on FIB sectioning of the single crystal

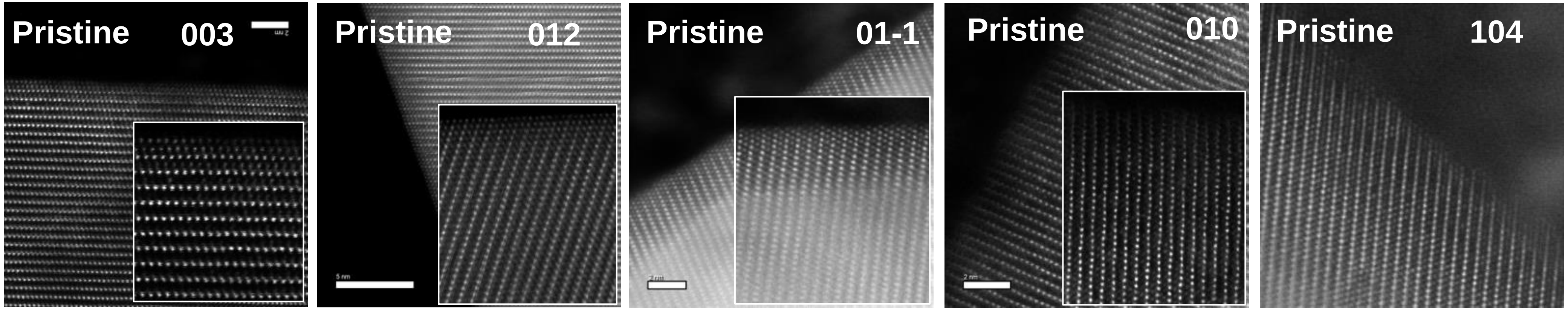
A comparison of the expected surface termination with experimentally determined surface termination for the single crystal $LiNiO_2$

	cubic	oct	T-poly
Expected surface termination	104	012	Mixing with 001
Experimentally observed surface termination	104+012	012 dominant+ a few 003	003+012+104+011+010

Dependence of the surface reconstruction layer thickness on the surface facet in $LiNiO_2$ single crystal at pristine and after battery cycling

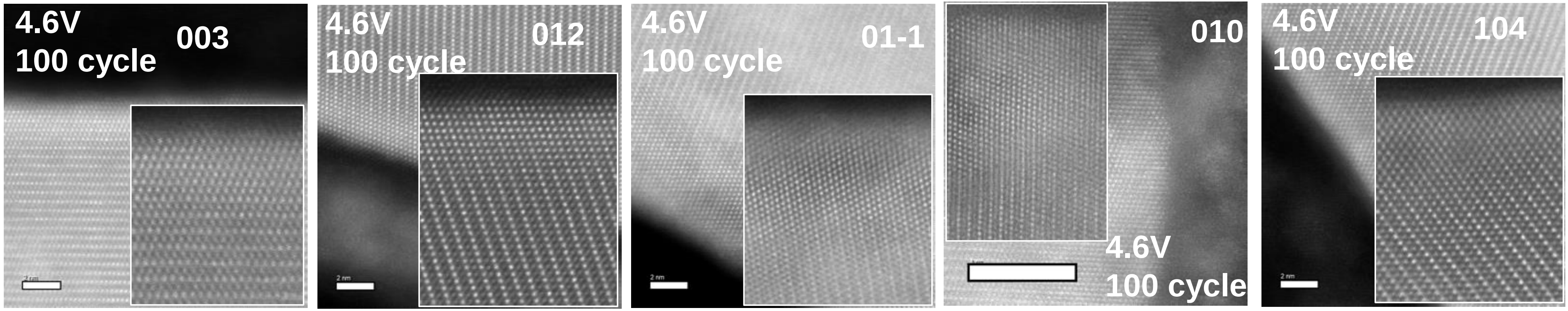
Electron Microscopy in collaboration with Chongmin Wang EMSOL PNNL

STEM-HAADF images showing the dependence of the surface reconstruction thickness on the surface facet in $LiNiO_2$ single crystal at pristine state



Surface termination	Reconstruction layer thickness
003	Serval atomic layers
104	Serval atomic layers
012	Serval atomic layers
01-1	Serval atomic layers
010	Serval atomic layers

STEM-HAADF images showing the dependence of the surface reconstruction thickness on the surface facet in $LiNiO^2$ single crystal after 100 cycles at 4.6 V

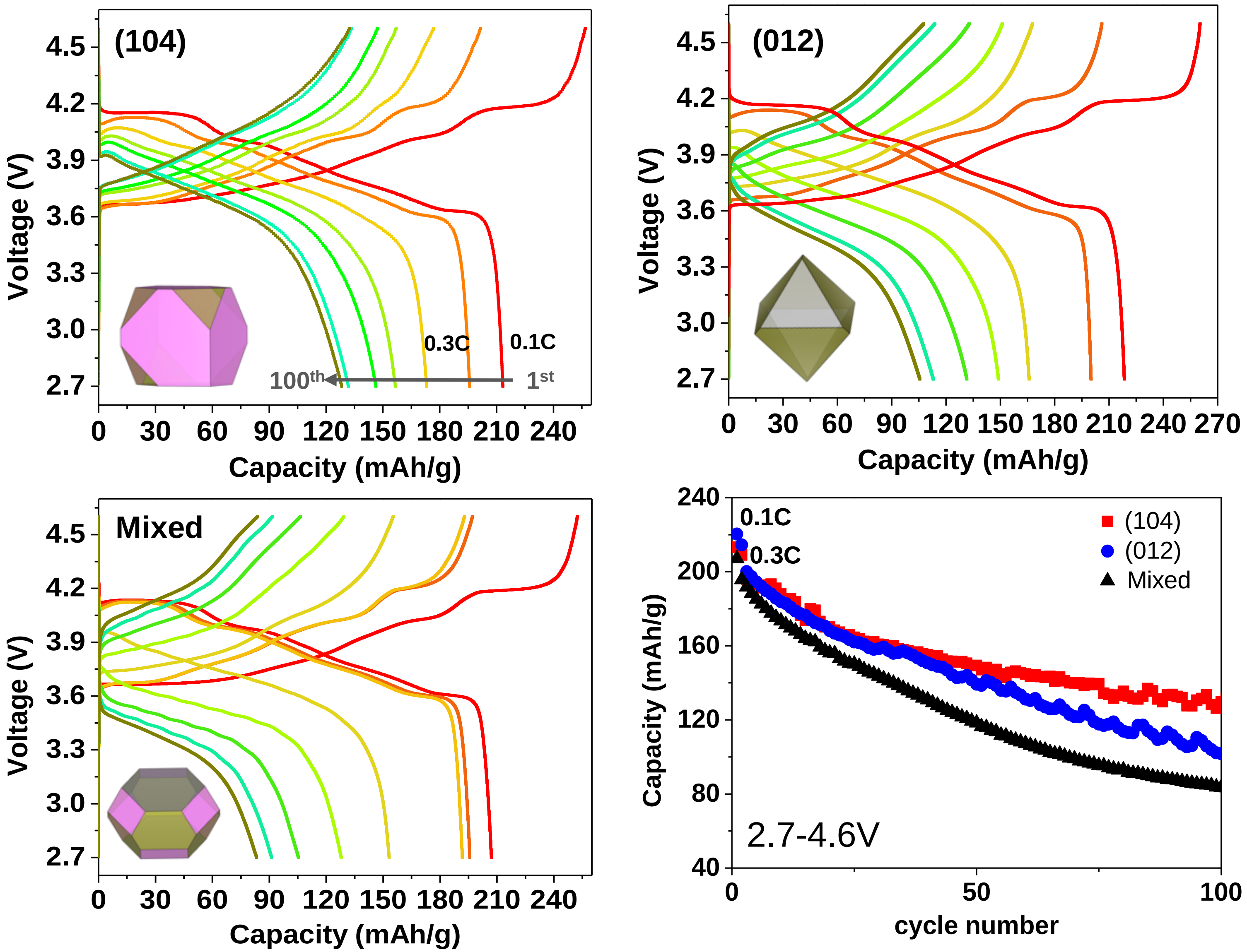


Surface termination	Reconstruction layer thickness
003	2.1nm
104	2.5nm
012	2.6nm
01-1	5.1nm
010	7.0nm

- At pristine state, all typical surface facets shows minor surface reconstruction layer.
- Following 100 cycles of the battery at 4.6 V, the thickness of the surface reconstruction layer increases, showing dependence on the surface facet.

Surface impacts cycling stability

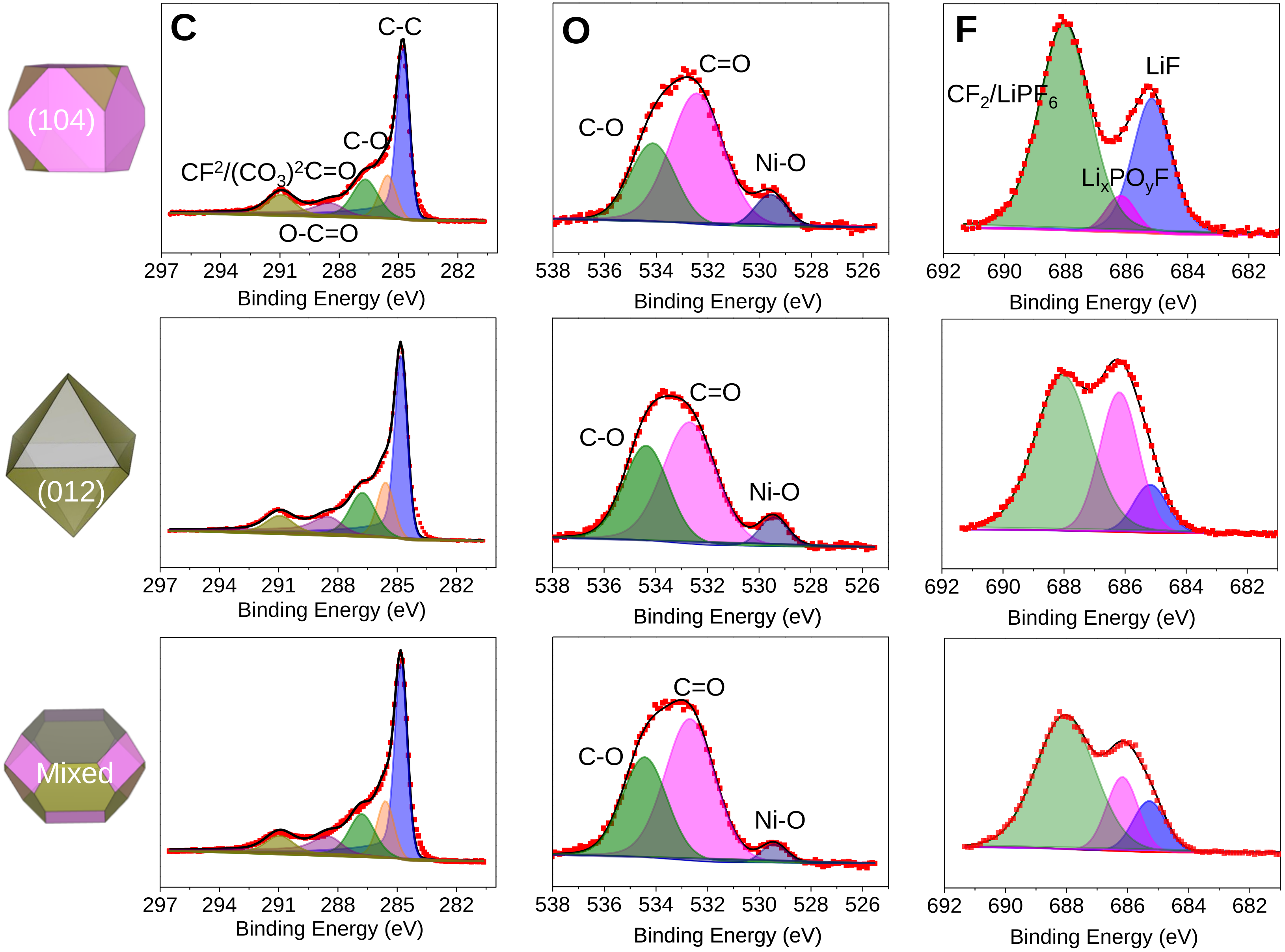
Collaboration with Guoying Chen BNL



- SC-LNO half-cells cycled between 2.7 V and various upper cutoff voltages (UCVs). Results of 4.6 V UCV cycling are shown.
- Increasing UCV reduces cycling capacity retention.
- Best cycling performance achieved on the Cubic sample with dominating (104)-family surface.
- Advantages of (104) surface are more significant in higher UCV cycling.

Surface analysis – XPS

Collaboration with Guoying Chen BNL



In collaboration with I. Bloom (ANL)

- All SC-LNO samples recovered after 100 cycles at 4.6 V UCV.
- Significant differences observed on F spectra. Much higher LiF/LixPOyF ratio detected on Cubic LNO.
- Mechanism of more LiF formation on (104) surface under investigation.

Summary

- **$LiMn_{0.5}Ni_{0.5}O_2$:**
    - Inclusion of zigzag configuration increases NMR shifts at ~800 ppm.
    - Inclusion of more Li-Ni exchange enhances the intensity of shifts near 500 ppm as well as near 800 ppm.
    - Li/Ni exchange is slightly reduced by longer temperature annealing times.
    - Spinel phase more stable than the layered phase at low temperatures.
- **Ni-Rich NMCs:**
    - Strain drives surface reconstruction and cation segregation in layered $Li(Ni_{1-x-y}Mn_xCo_y)O_2$ (NMC) cathode materials.
    - The reactivity of the (012) facet, usually the most abundant, decreases for all surface dopants with a positive oxygen vacancy formation energy, for instance: Ca, Fe, Ti, Cr, V, Sn, Ru, Rh, As.
    - The (104) facet is less reactive than the (012), and all the tested dopants decrease the reactivity even more.
    - Higher states of charge (SOC) promote Ni migration from the Li layer to the TM layer.
    - Once Ni is back in the TM layer, Li/Ni defect formation has a positive energy: irreversible process at high SOC.
- **Hysteresis in Li rich oxides:**
    - Calculations show that neither oxygen nor Ti contribute to the electrochemical capacity of this material.
    - Oxidation of Cr^{3+} to Cr^{6+} is concomitant with both Cr and Ti migration from octahedral to tetrahedral sites, enhanced by a d^0 configuration.
    - Subsequent re-lithiation of the oxide is subject to an energy penalty due to the unfavorable occupation of lithium surrounding the tetrahedral sites.
- **Model systems (single crystals):**
    - Experimental results using single crystal models showed facet-dependent reactivity behavior.
    - Surface reconstruction is present in pristine samples and its thickness increases with cycling.
    - Surface reconstruction thicker on edge facets.

Future Work

- **$LiMn_{0.5}Ni_{0.5}O_2$:**
  - Investigate the effect of dopants/substitutions on the initial Li/Ni exchange ratio.
  - Investigate the effect of dopants/substitutions on the kinetics of Ni migration during annealing and cooling.

- **Ni-Rich NMCs:**
  - Extend the configuration and concentration space for the screening of dopants/substitutions.
  - Effect of dopants/substitutions on the initial surface reconstruction and evolution during cycling.
  - Effect of the surface reconstruction layers on the surface reactivity with the electrolyte and additives.

- **Model systems (single crystals):**
  - Atomic scale probing of spatial distribution of dopants/substituents on various surfaces of SC-LNO.
  - The nature of the stacking fault in the $LiNiO_2$ and formation process.

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

Collaboration and Coordination

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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

Comments:	Responses:
This modeling work is appropriate to link very many experimental projects that are ongoing on low-Co cathode material design. The project could help link various studies together in providing a unified understanding that will help move the field forward.	We thank the reviewer for the comments and questions. We have tried to present modeling work that supports our experimental efforts from the group as well as exploratory work for screening purposes, i.e. predictions for future experiments. However, we always strive to strengthen our connection to most team members.
The production of facet-dependent segregation in layered oxides was very interesting to the reviewer. It could be of great interest to really understand why the calculations predict a minimum of 1-3% Li-Ni exchange for all $LiNi_{0.5}Mn_{0.5}O_2$ configurations. Another interesting result is about the “zigzag” configuration on the Mn5050 oxide. **Is it more stable because there is additional Mn-Ni atomic overlap in that geometry?**	We thank the reviewer for the comments and questions. The new low energy configurations with 1-3% Li-Ni exchange result from special extended defects states, that have not been considered before and obtained here because of the periodic boundary conditions and specific cell sizes used in the modeling (optimized for large a-b planes to investigate Ni-Mn ordering). New results with larger cells in the c-direction are included in this year’s presentation.

Response to Previous Year’s Reviewer Comments

Comments:	Responses:
Various insights are interesting, including energy correlation with Ni-Mn bonds, the difference between structures containing flower and zigzag patterns for Li-Ni exchange, dopant effect, and the dependence on the crystal facets. The principal investigator (PI) should show the comparison with the experimental electrochemical data to develop a confidence in the modeling results even though the NMR and lattice data are presented and compared.	We thank the reviewer for the comments and questions. We appreciate the suggestion from the reviewer. Indeed, we have worked towards this goal, and new experimental results using single crystals with controlled morphology have been included in this year’s presentation. The results, are consistent with our modeling predictions, with respect to reactivity-facet dependency. The results coming from the LiMn0.5Ni0.5O2 composition show a finite Li-Ni exchange that was not possible to reduce with temperature control (synthesis and post-annealing). The combination of XRD , NMR and modeling show that the amount of Li-Ni exchange and Mn, Ni ordering with the transition metal layers are mostly determined during the synthesis process and mostly remain during annealing and further cooling of the samples. The electrochemistry results show that the amount of this disorder (Mn-Ni, Li-Ni) negatively impacts the performance. Dopants results are still in progress.
The team has generated useful insights into role of Mn-Ni interaction and effect of Li-Ni exchange. The impact of calcination and cooling conditions is also elucidated. Screening of dopants was comprehensive, but the reviewer struggled to understand the conclusions.	We thank the reviewer for the comments and questions. We have tried to better present the results on dopants in this year’s update, as we have added more dopants and more descriptors to screen for possible good candidates. In short, the best candidates responding to our screening criteria, would be the ones that prefer surface/near surface sites and better resistance to oxygen vacancy formation (less reactive with the electrolyte and less oxygen loss).

Response to Previous Year’s Reviewer Comments

Comments:	Responses:
The refining NMR fitting seems very important, and it seemed to the reviewer that it gave useful hints about the local Li-environments. It could be of interest to know how truncated polyhedron and octahedron morphologies have been prepared without revealing confidential information. That could be important at some point to judge if the process is scalable.	We thank the reviewer for the comments and questions. Both samples were made by a molten-salt method. More details can be found in the published paper: J. Mater. Chem. A, 2019, 7, 5463–5474.
Effect of element segregation would be useful. The reviewer was not sure if the kinetic modeling can be done that will be of useful (long enough) time scale.	We thank the reviewer for the comments and questions. Great suggestion. We assume that the transition metals migration/diffusion is more facile during synthesis conditions. However, inclusion of migration barriers at lower temperatures into a kinetic model would certainly help as suggested. We have not continued in this direction but would like to consider it if aligned with the rest of the program.