CATHODE MATERIALS FOR NEXT GENERATION LITHIUM-ION BATTERIES: THEORY AND MODELING OF LOW-COBALT CATHODES

Project ID: BAT253

HAKIM IDDIR

Argonne National Laboratory

June 1-4, 2020

2020 DOE Vehicle Technologies Office Annual Merit Review

Overview

Timeline

- Start: October 1, 2018
- End: Sept. 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:

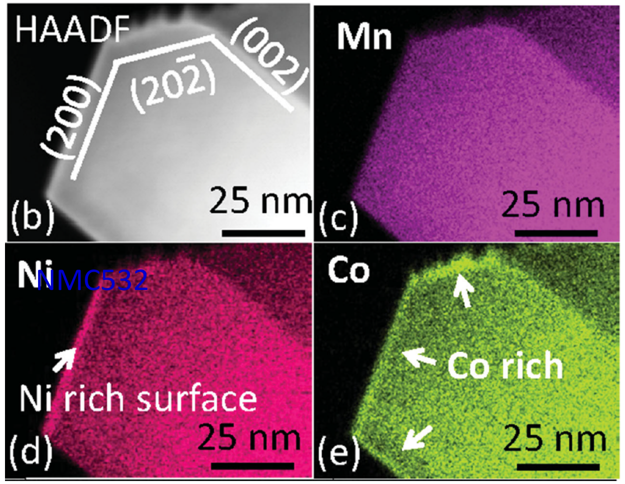
- University of Illinois at Chicago
- University of Rochester
- Oregon State University

Relevance

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



Yan, P.; et. Al. *Adv. Energy Mater.* **2016**, *6* (9), 1502455.

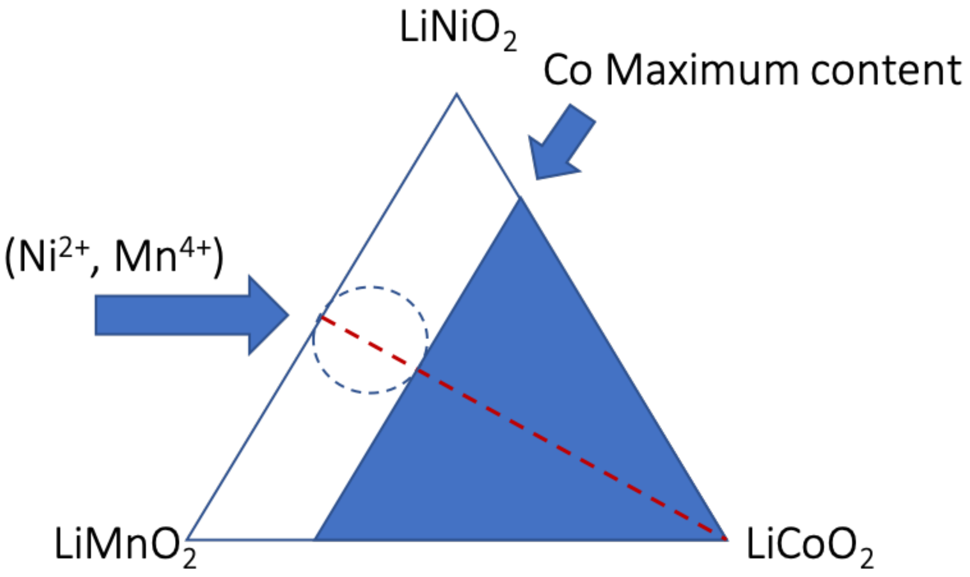
Observation of facet-dependent segregation in layered oxides

Milestones/Approach

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

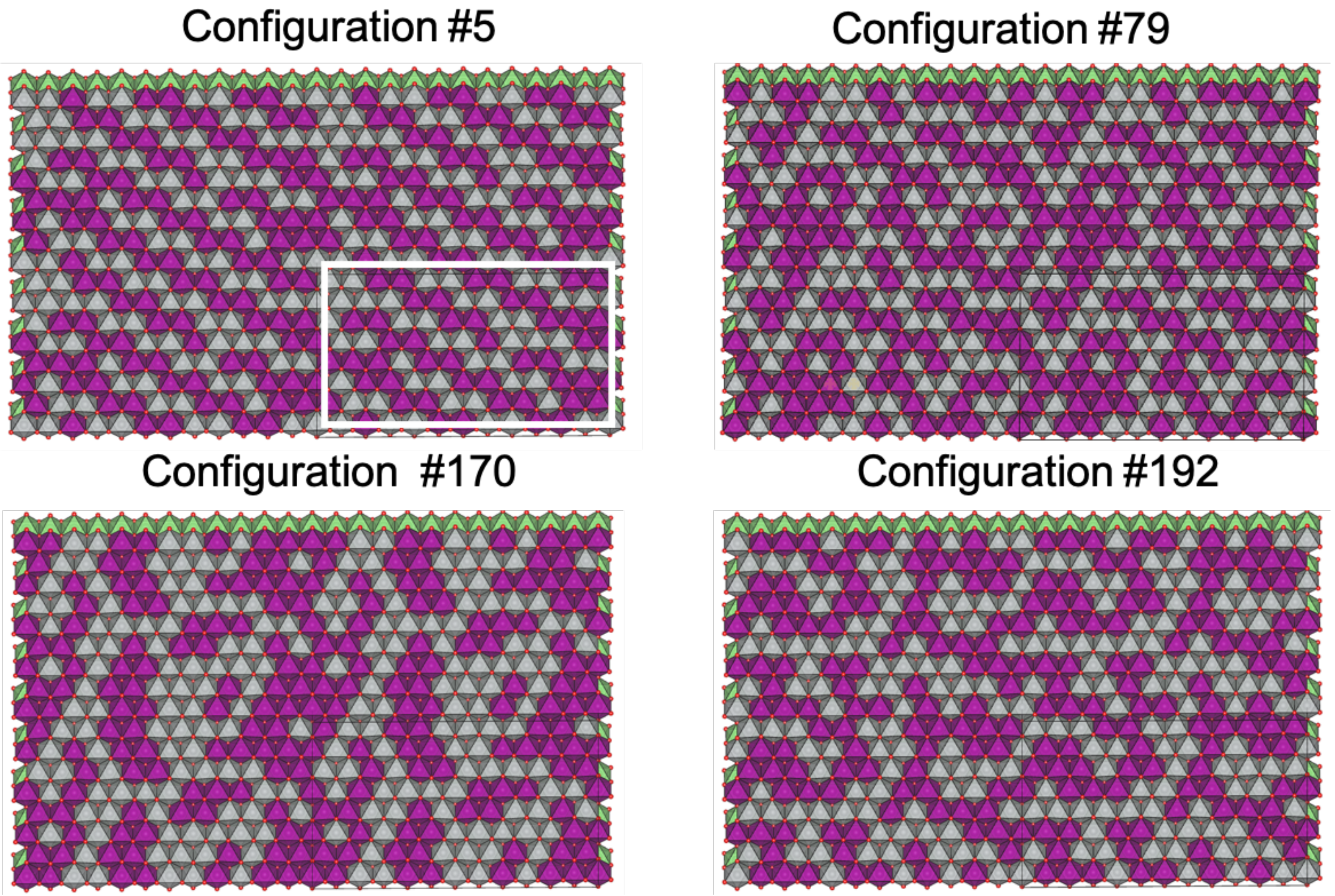
($LiMn_xNi_xCo_{1-2x}O_2$) model systems have been designed such that Ni resides in a layered structure and exists as only Ni^{2+} in order to investigate:

- The minimum amount of Co needed to maintain a layered structure against Li/Ni exchange and Ni/Mn migration – (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 – (in progress)
- Surface composition & stability of (104) & (012) facets and facet reconstruction – (in progress)
- Bulk stability (phase transitions) – (in progress)
- Surface/electrolyte interaction – (in progress)
- Identify dopants (co-dopants) that can mimic the effects of Co – (in progress)



$LiMn_{0.5}Ni_{0.5}O_2$ (MN5050) random configuration structures

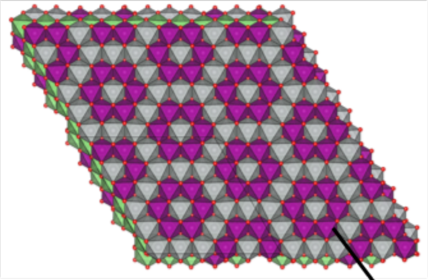
- Starting from the zigzag structure several random configurations are generated by randomly selecting a pair of Ni-Mn and swapping Ni with Mn.
- Energy is calculated using DFT (DFT+U, HSE).
- The process is repeated for hundreds of structures.
- The final goal is to understand the effect of M-M interactions on the overall energies.
- A surrogate model has been fitted to compute thermodynamic properties.



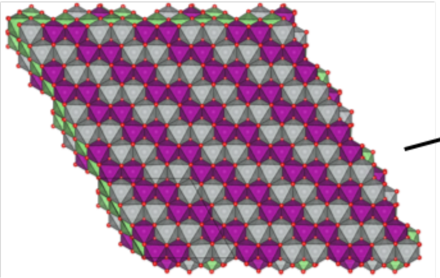
Transition metal layer (top view). Purple represents Mn sites and grey represents Ni sites.

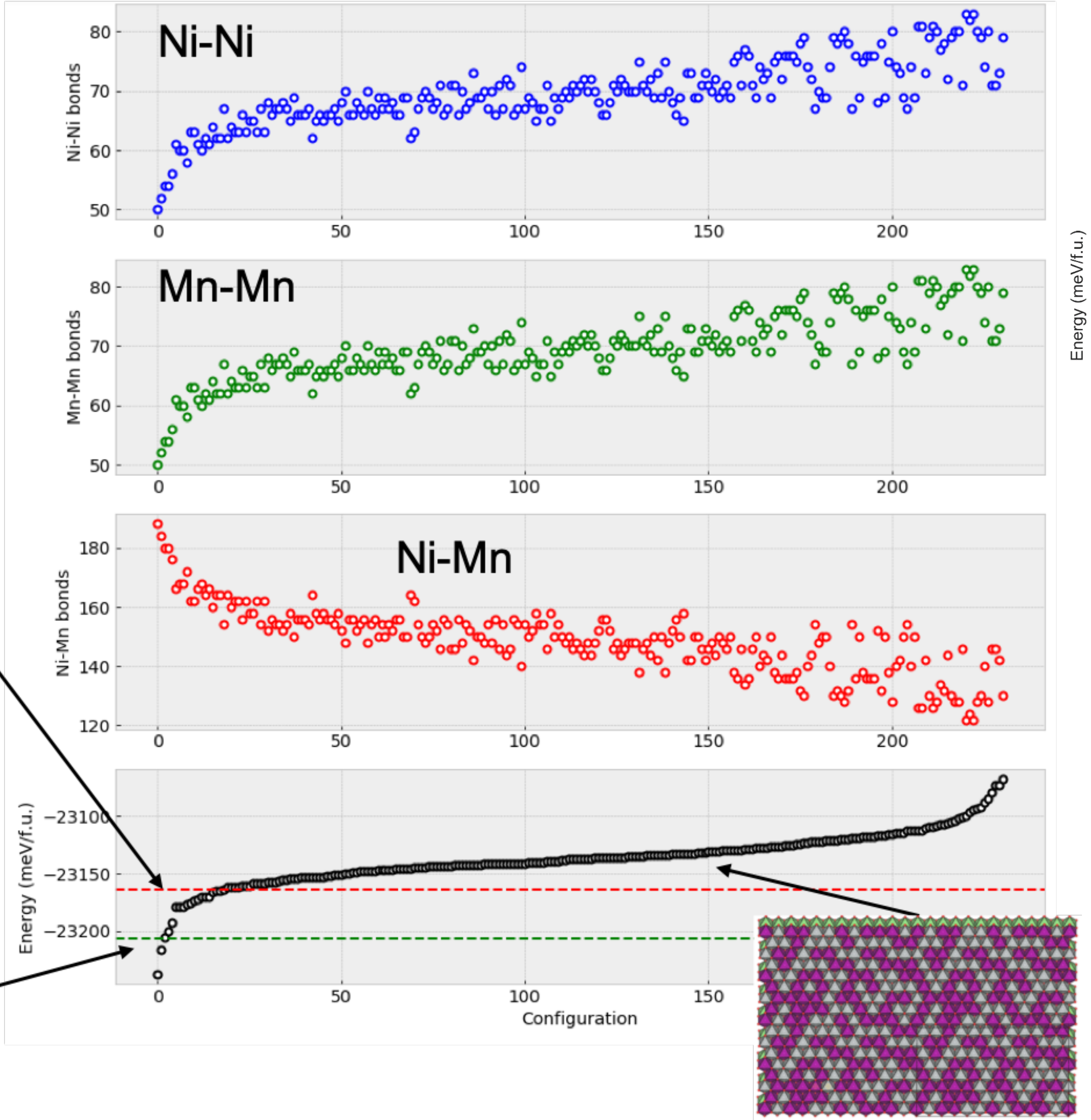
Effect of M-M interaction on the total energy of MN5050 configurations

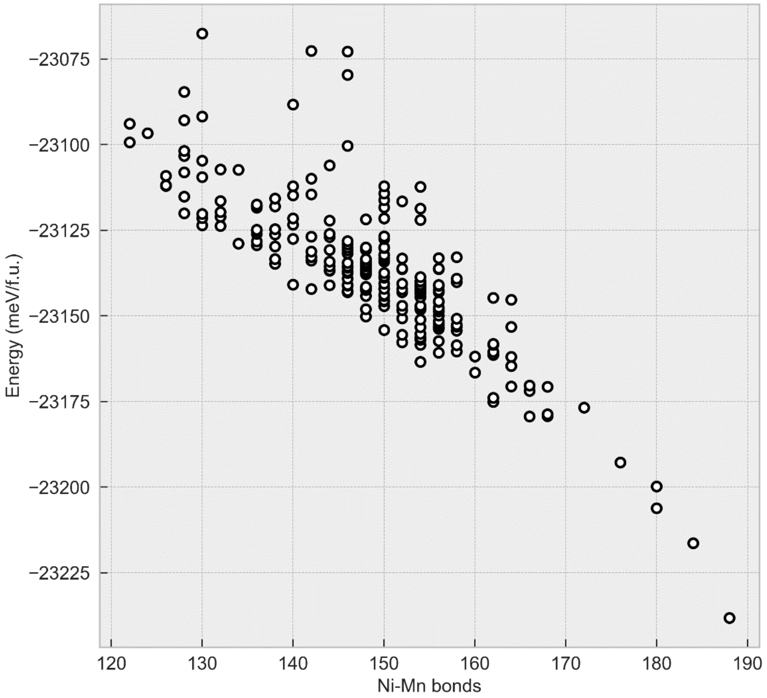
"Flower" configuration energy is indicated by the red dashed line.



" Zigzag" configuration is indicated by the green dashed line.







- There is a strong correlation between the energy and the number of Ni-Mn bonds in the configuration.
- There are less possible configurations when the number of Ni-Mn bonds is high. Hence, there is less spread in the data.

Surrogate model for MN5050

- Given the complexity of a cluster expansion model for the system under study, a simplified model is used.

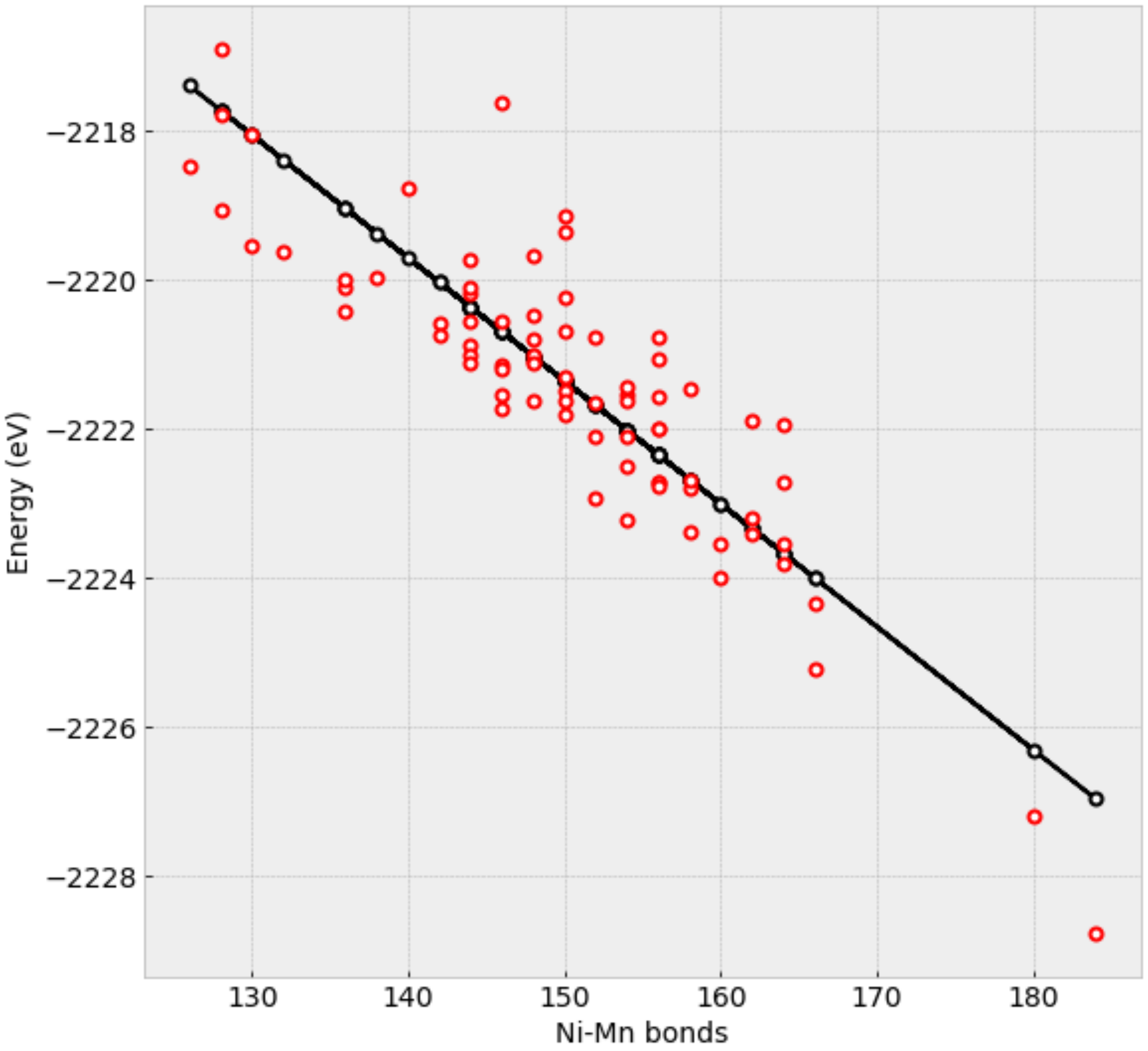
- The model is based on the two body interactions between transition metals.

$$^{*}E_{\text{fit}} = \sum_{i}^{\Omega_{\text{TM}-\text{TM}}} N_i \times E_i^{\text{TM}-\text{TM}}$$

- 20% of the data was excluded from the original pool and it was used for cross validation.

- Root Mean Square Deviation (RMSD) = 8 meV.

- The surrogate model will allow us to predict thermodynamic properties and more realistic structures.



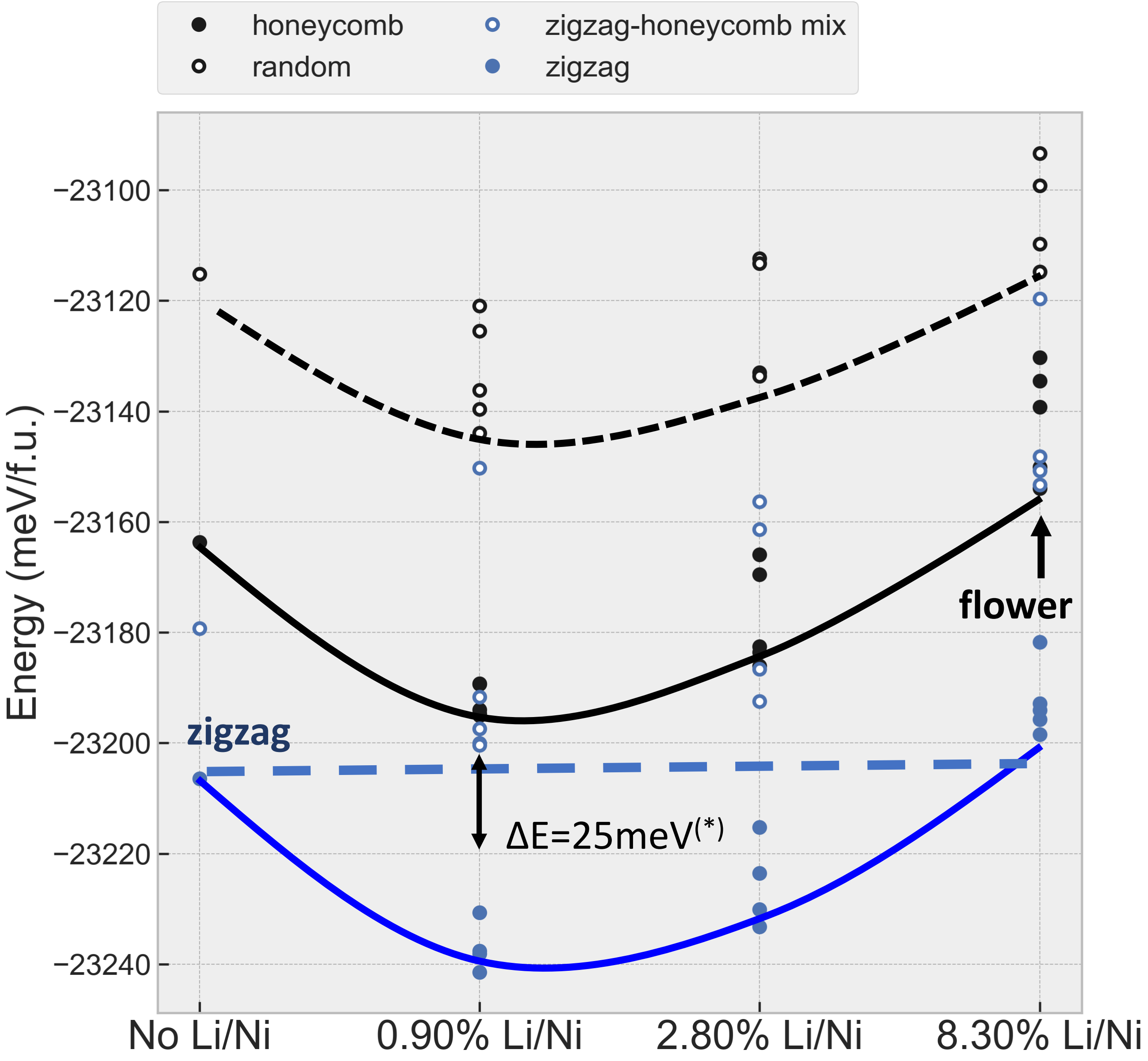
* Chaoping Liang, Fantai Kong, Roberto C. Longo, Santosh KC, Jeom-Soo Kim, SangHoon Jeon, SuAn Choi, and Kyeongjae Cho. J. Phys. Chem. C 2016, 120, 6383–6393

Effect of Li-Ni exchange on MN5050 configuration energies

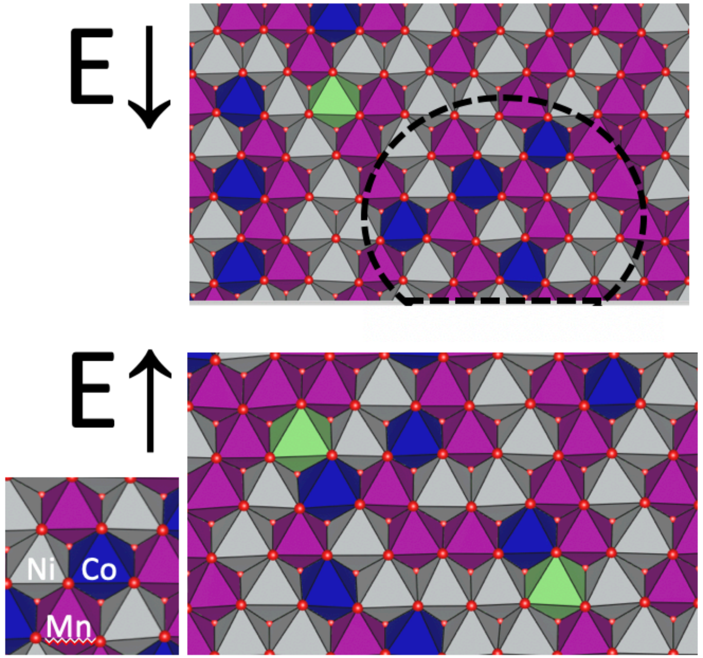
- A "perfect" flower pattern would produce 8.3% Li/Ni exchange.
- Lower energies were found for both "flower" and "zigzag" configurations with 0.9 and 2.8% Li/Ni exchange.
- 8.3% Li/Ni exchange was not found to be favorable for the flower or zigzag configurations.
- Careful annealing should lead to the predicted minimum 1-3 % Li-Ni exchange (from zigzag configuration).

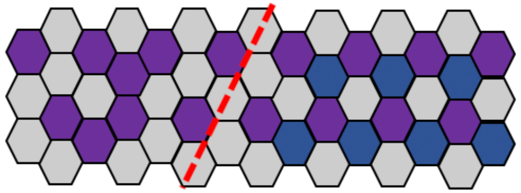
(*) 25 meV equivalent to room temperature

See also project ID: BAT251



Li/Ni antisite defect formation in MN5050 + Co

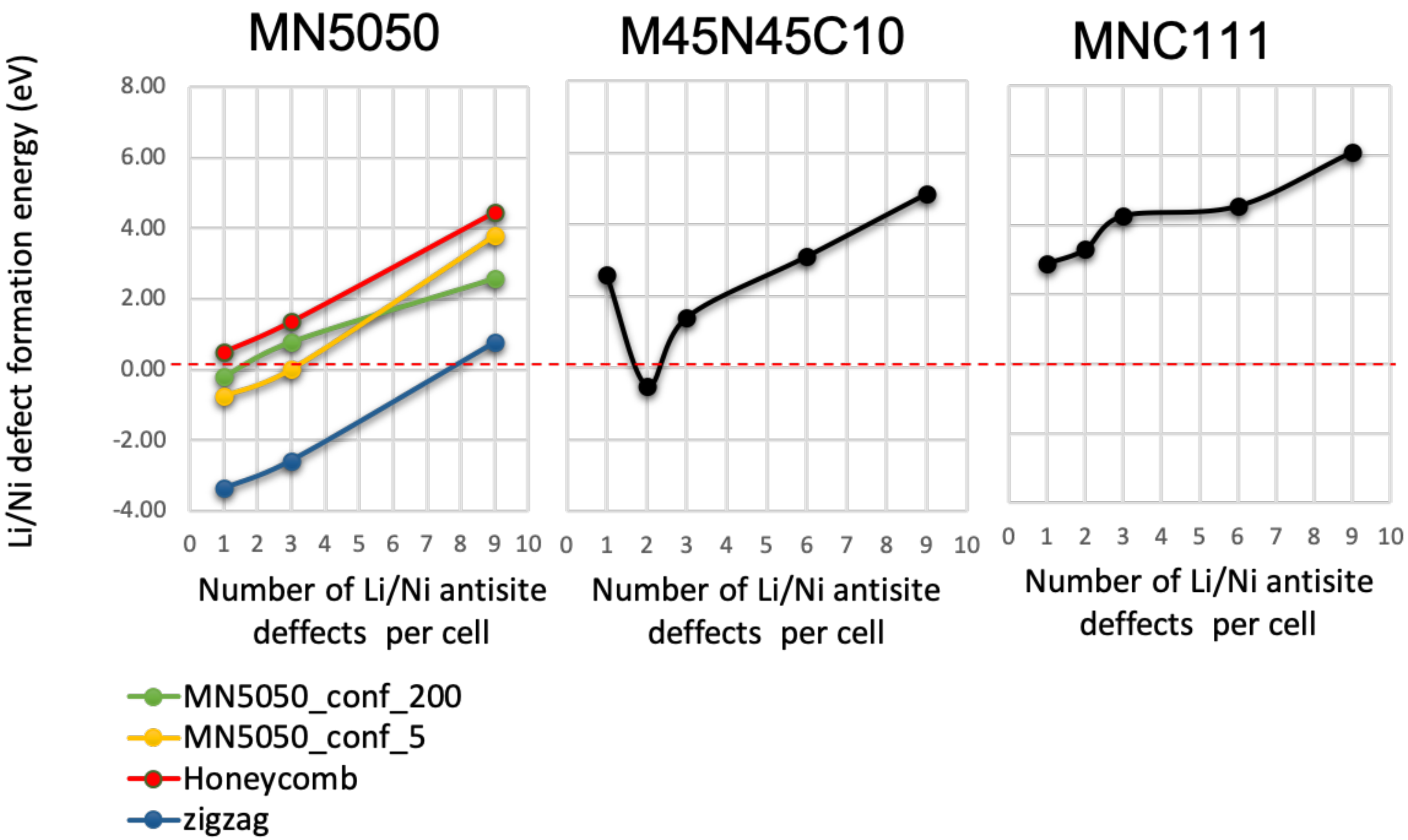




NiMn5050 region/ NMC-111 region

12 % Co → more than half of the material is ordered as NMC-111

See also project ID: BAT251

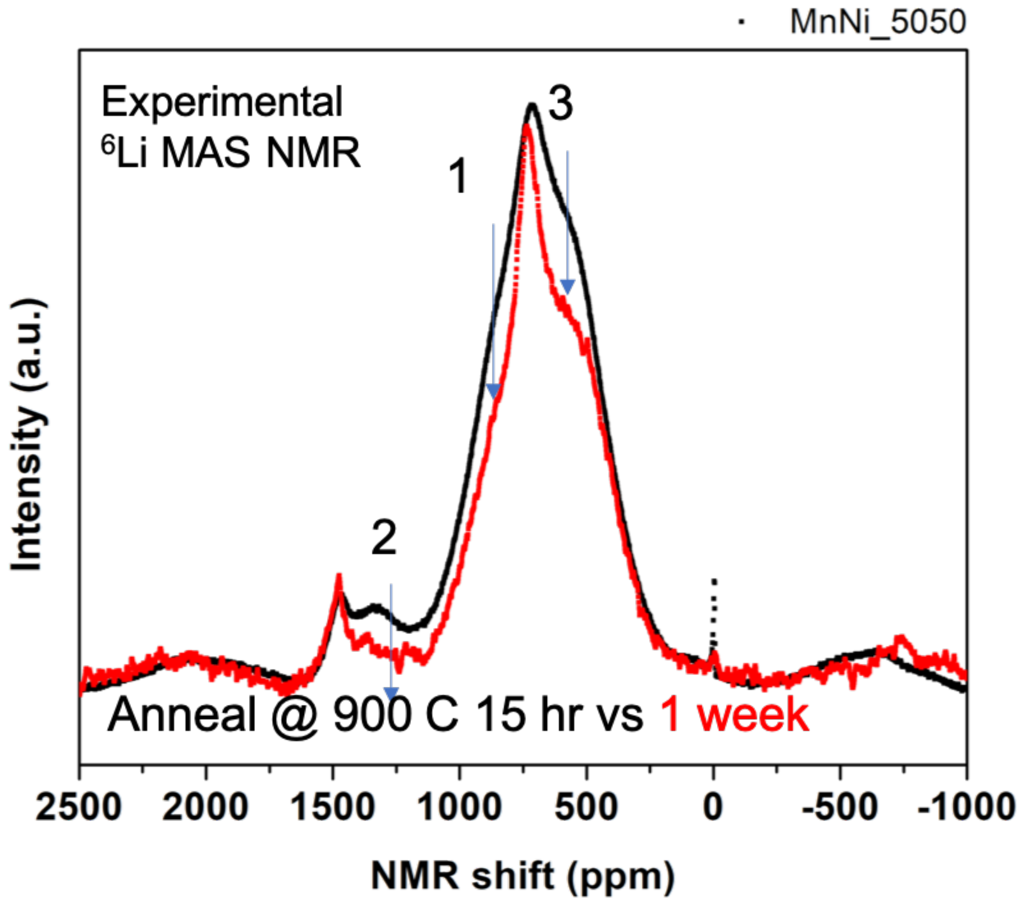


- The presence of Co increases the Li/Ni anti-site formation energy.
- Co favors the formation of ordered NMC-111 regions.
- Li/Ni anti-site defects prefer to be outside the NMC-111 regions.

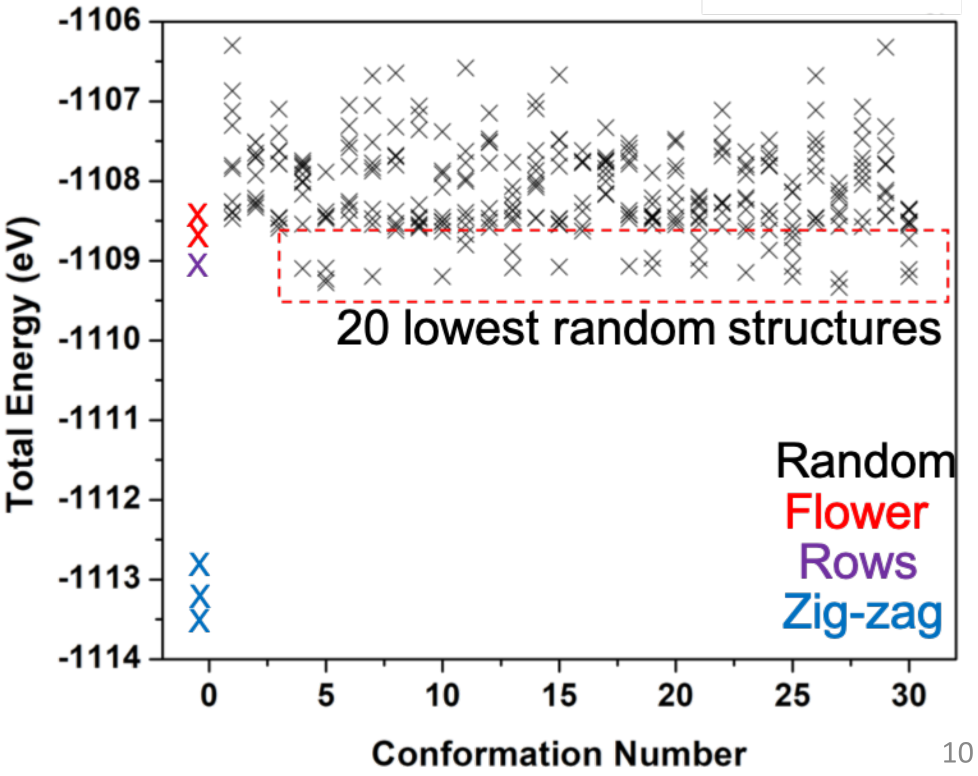
Annealing and cooling processes effects on local structure

How do syntheses conditions affect Li/Ni exchange and phase separation of $LiMn_{0.5}Ni_{0.5}O_2$ compounds?

- ^{6}Li MAS NMR is used as a fingerprint to study lithium local environments. In paramagnetic systems ^{6}Li NMR shifts are induced by Fermi contact interaction.

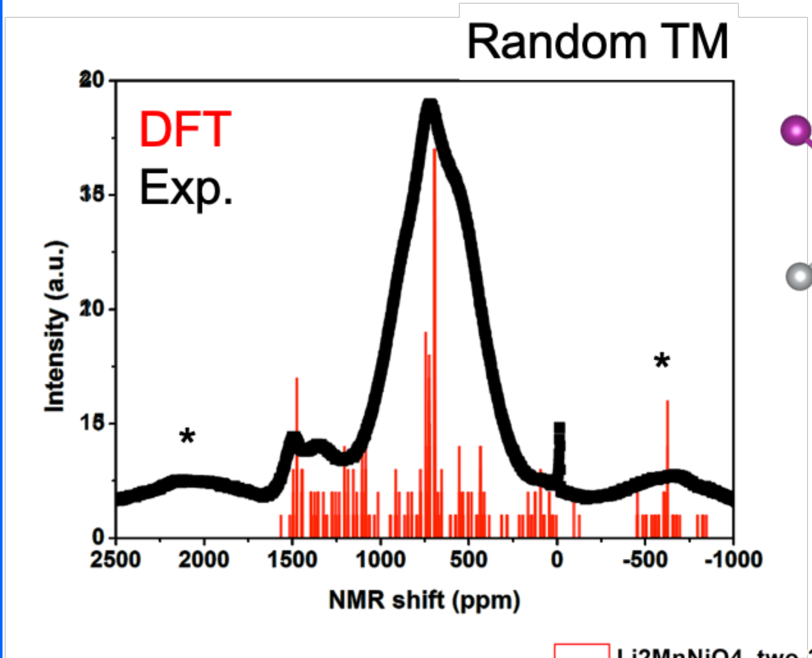


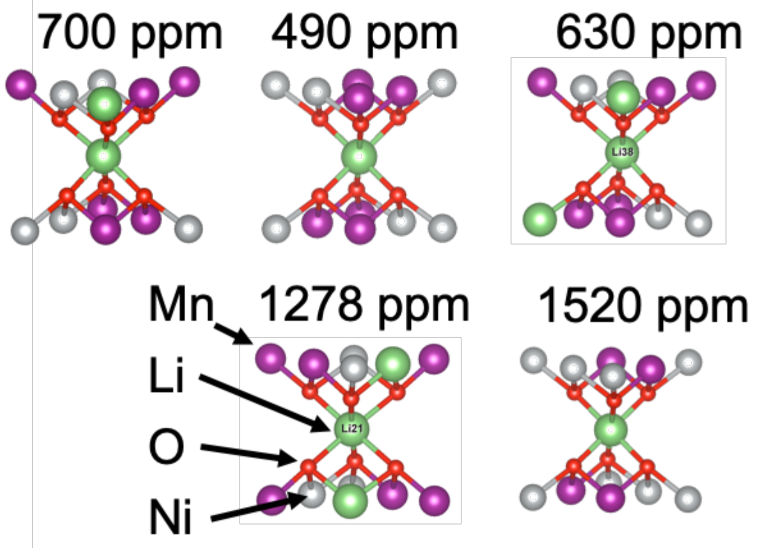
- Fermi contact term (shifts) can be computed using Density Functional Theory (DFT).
- DFT is suitable to explore a large configurational space and compute the NMR shifts of select low energy structures.

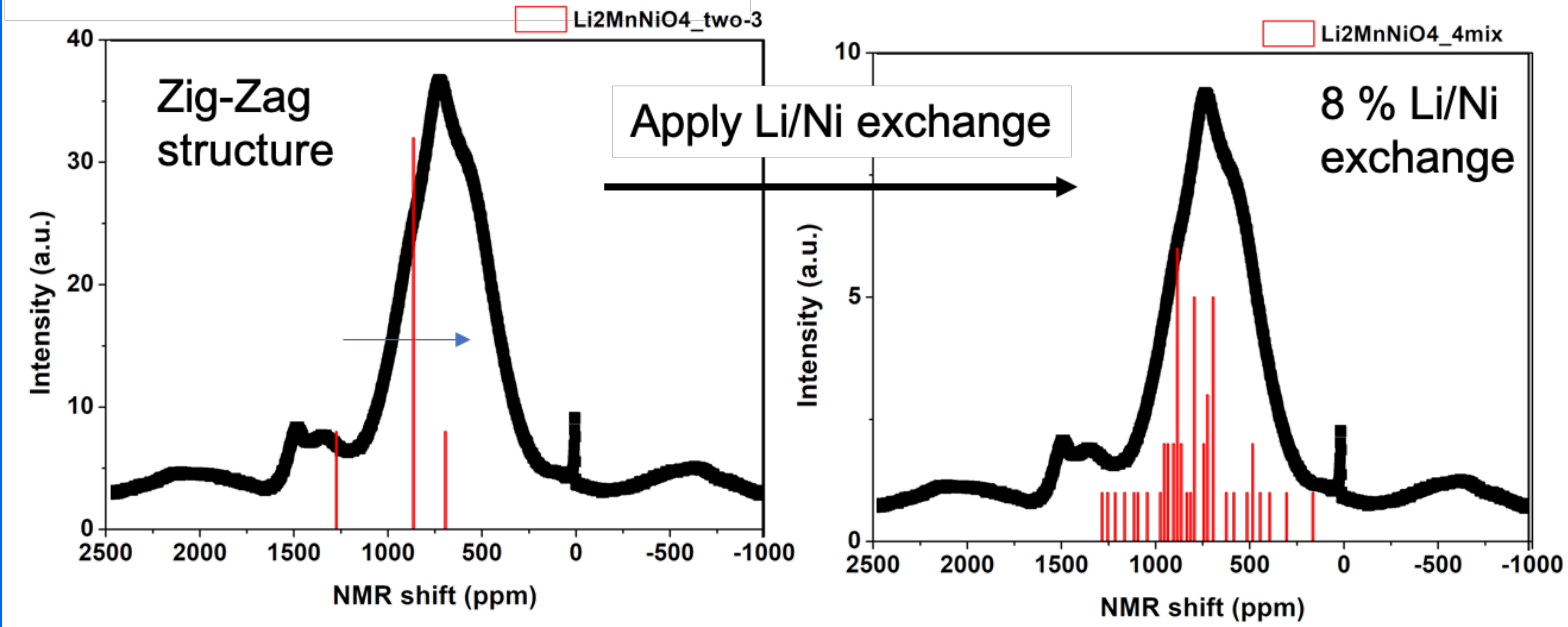


- Slow annealing produces changes in the local structures of $LiMn_{0.5}Ni_{0.5}O_2$ that reflect in the NMR spectra.

NMR spectra of specific structures





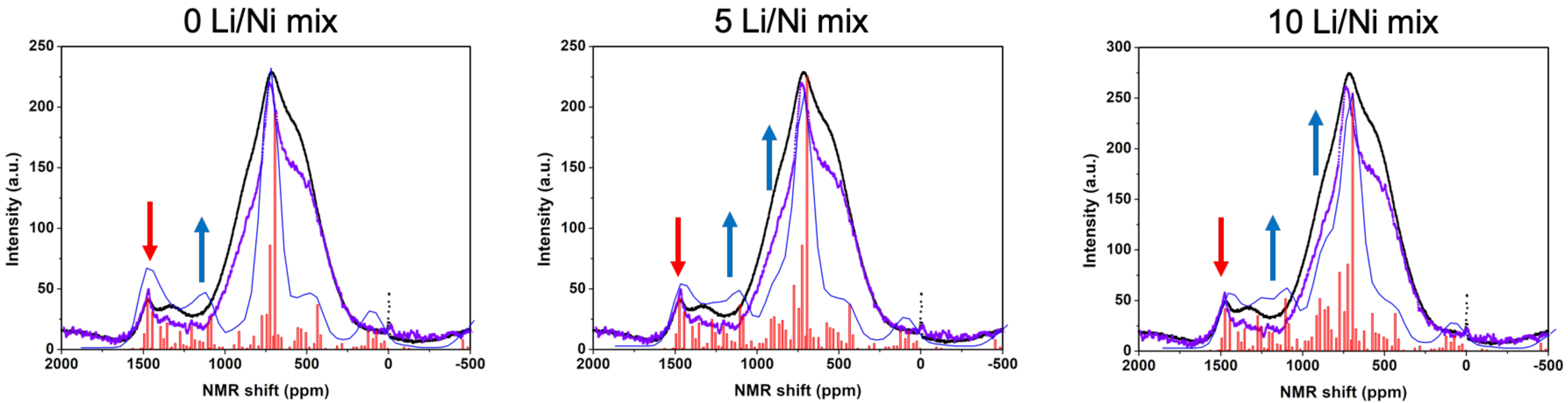


- DFT calculated ^{6}Li NMR shifts capture the main structural features reflected in the experimental NMR spectra.
- Examples of local Li environments are shown.
  - Cation mixing (Li/Ni exchange) produces new NMR shifts
  - Variations in Li-O-TM angles and distances affect the computed NMR shifts, contributing to further broadening of the overall spectra

Identification of major local Li-environments contributing the ^{6}Li NMR spectra

Black: exp (15-hrs annealing)
Purple: exp (1-week annealing)
Red: DFT-histogram
Blue: DFT-broadened

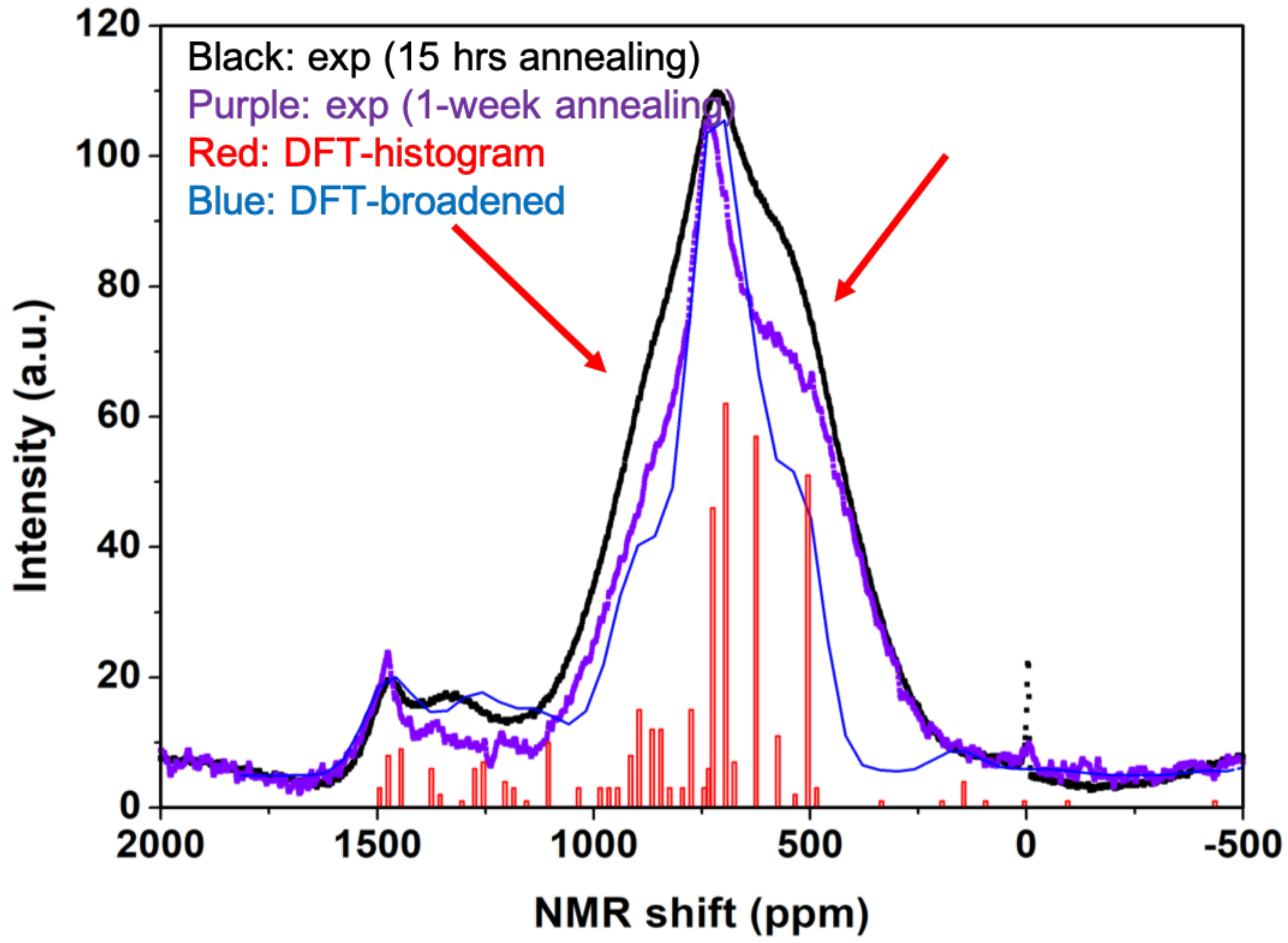
More Li/Ni exchanged configuration



Baseline: 20 random TM arrangements (excluding zigzag)

- Using energetic information and NMR shifts each of the features can be calibrated to understand the structure and its effect on the NMR spectra.

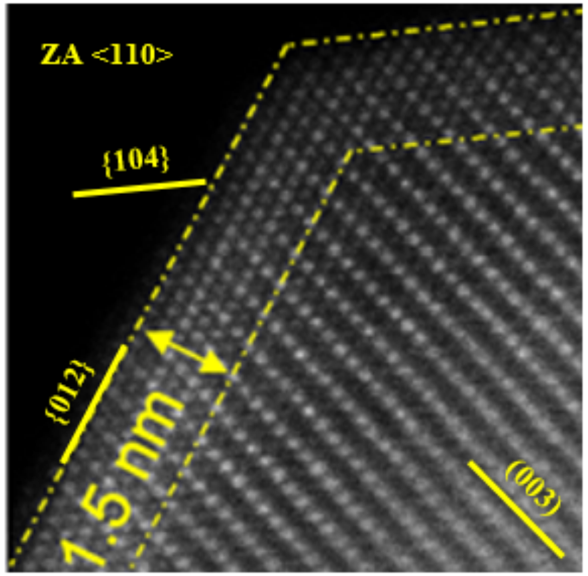
Identification of major local Li-environments contributing the ^{6}Li NMR spectra



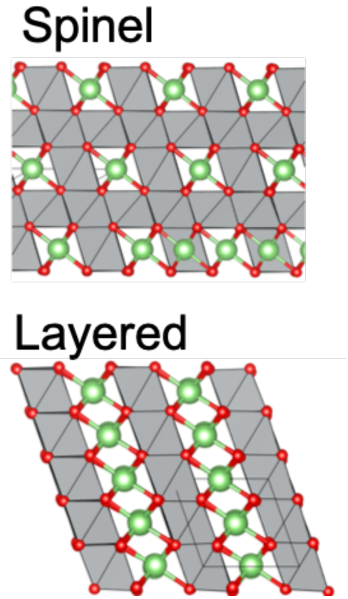
- Inclusion of zigzag configuration increases NMR shifts at ~800 ppm.
- Inclusion of more Li-Ni exchange enhances the intensity of shifts near 500 ppm as well as near 800 ppm

- $LiMn_6$ local domains seem to be present within the structure.
- Zigzag and rows configurations are the major contributors to the overall NMR spectra
- Li/Ni exchange is reduced by longer temperature annealing times.

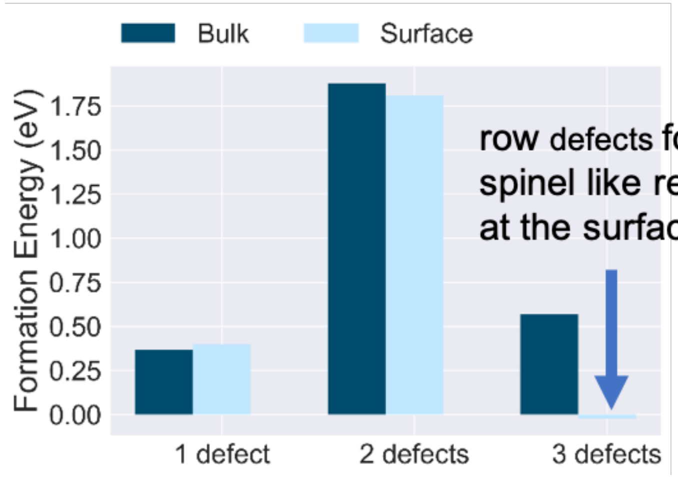
Stabilization of disordered phases pinned to layered phases

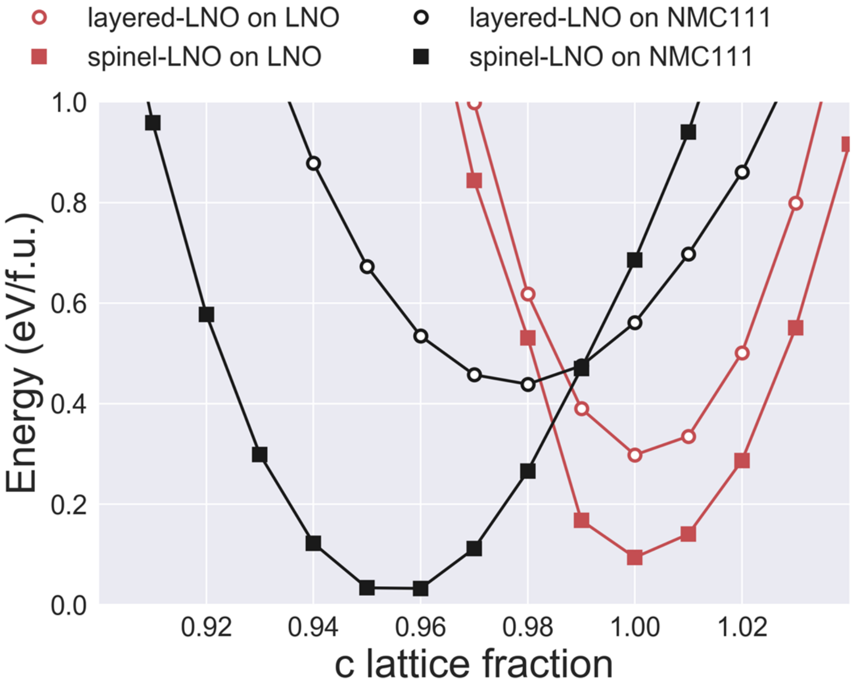


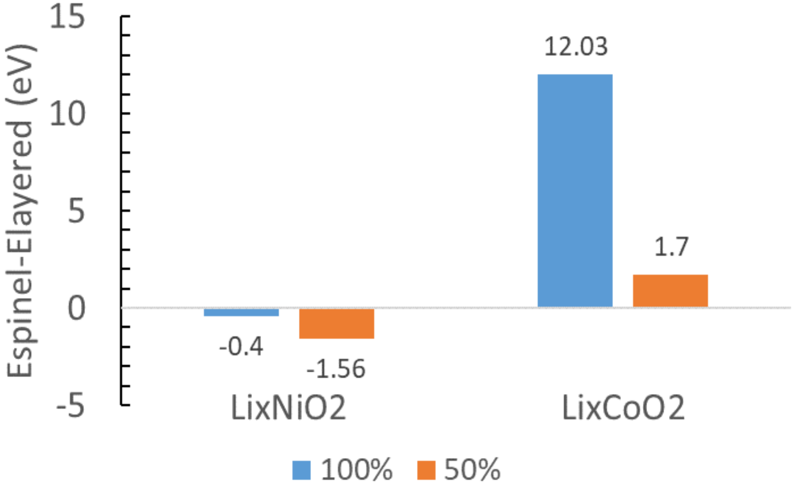
NMC532



- Ni-rich spinel-like phase unit cell is about 4% smaller than NMC-111 layered
- The reconstructed surface layer is under tensile strain.
- We have previously demonstrated that strain may favor certain phase transformations.
- On NMC-111, the strained spinel like phase shrinks and it has lower energy. It is thermodynamically favorable when it is strained.
- Delithiation increases the thermodynamic driving force for spinel formation at the surface.
- Spinel $LiNiO_2$ layers on layered $LiNiO_2$ is favorable







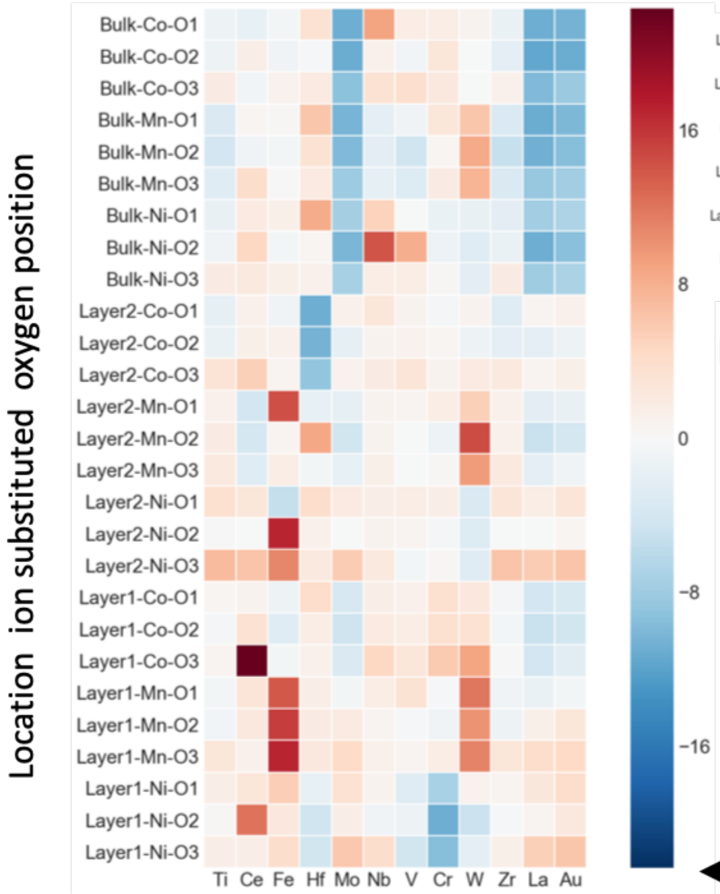
Submitted for publication

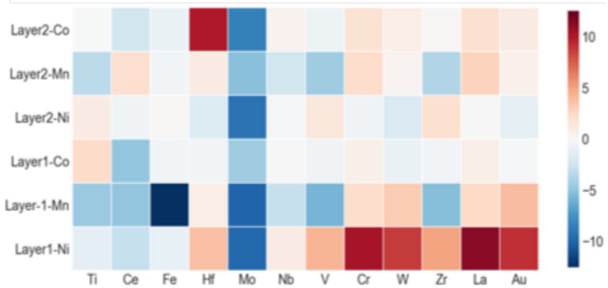
Screening for dopants in NMC and $LiNiO_2$-based oxides

$Li(Ni_{1/3}Mn_{1/3}C0_{1/3})O_2$ surface (012)

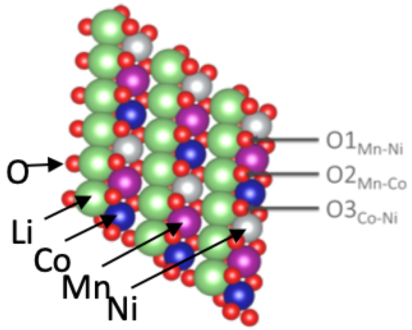
$\Delta E_{ov} = E_{ov-dopant} - E_{ov-pristine}\ (eV)$

$\Delta E = E_{surface-dopant} - E_{bulk-dopant}\ (eV)$



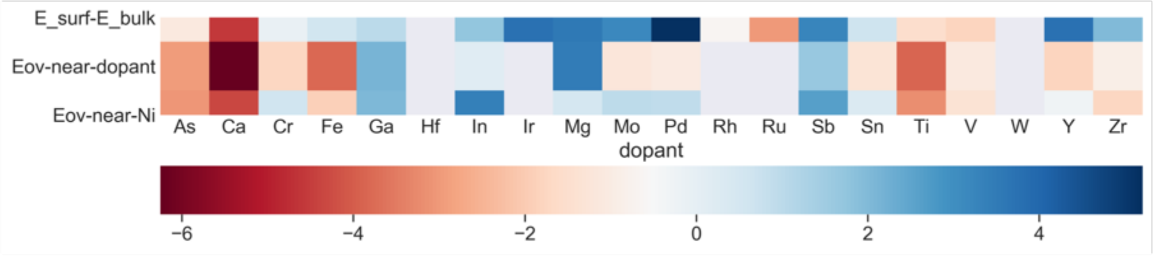


Blue → dopant prefers surface

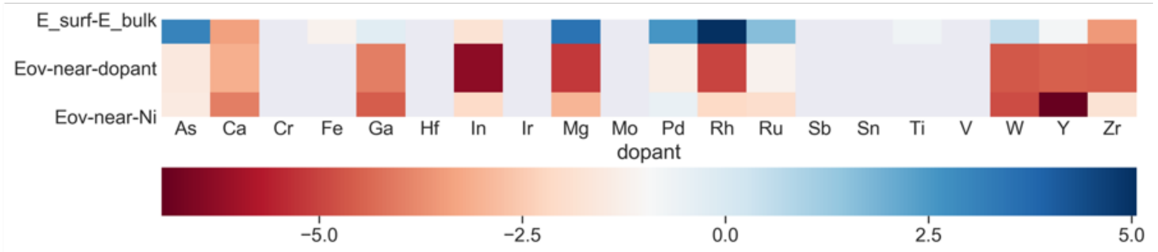


Blue → doped surface is more reactive.

$LiNiO_2$ surface (012)

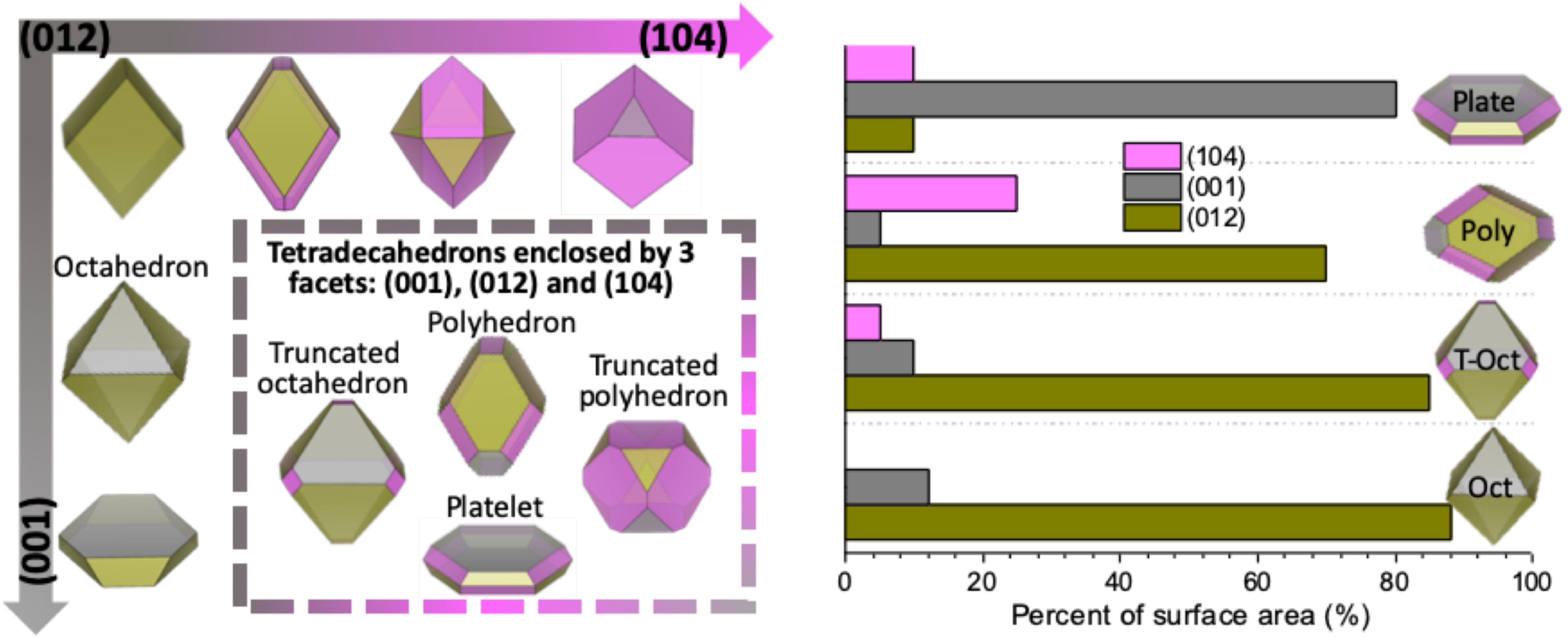


$LiNiO_2$ surface (104)



- For dopants in $LiNiO_2$, the first row of the heatmaps indicates a preference to segregate to the surface (blue).
- The second and third row of the heatmaps indicate reactivity (red means the surface is less reactive when doped, based on oxygen vacancy formation energy).
- For $LiNiO_2$ the dopant segregation is facet dependent.
- Therefore, the reactivity of doped $LiNiO_2$ can change with particle shape.

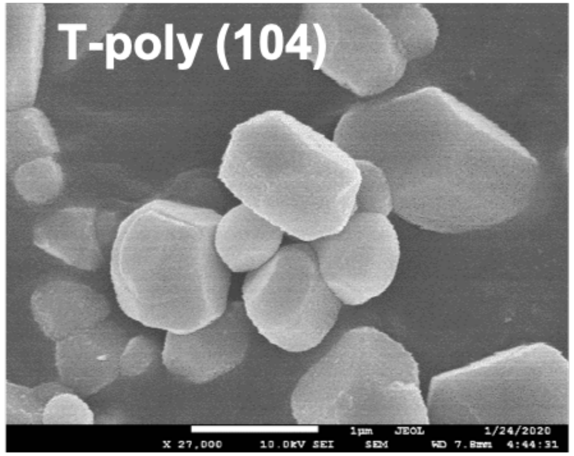
Surface-specific layered oxide crystals – typical morphology

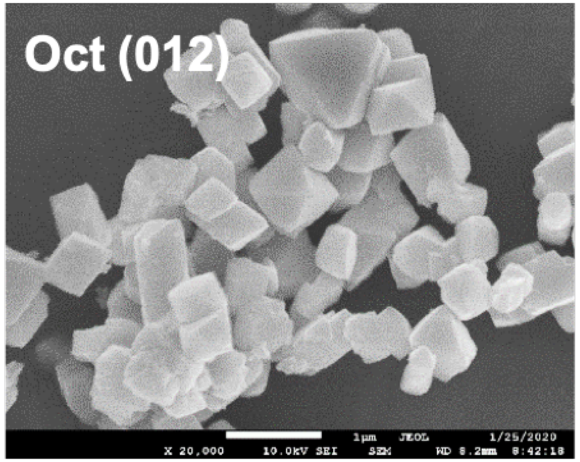


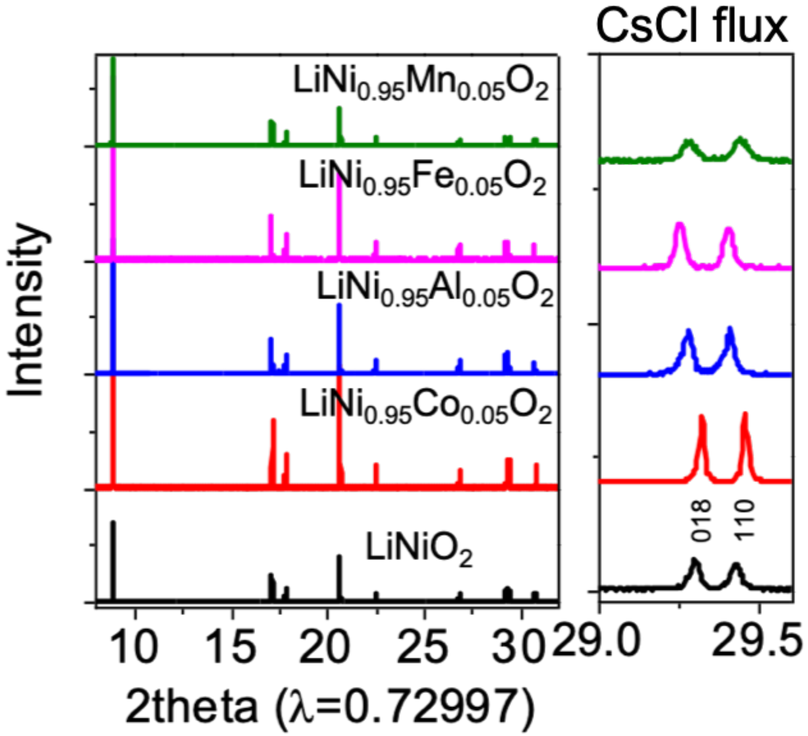
- A molten-salt based synthesis method is used to systematically tune particle morphology and surface

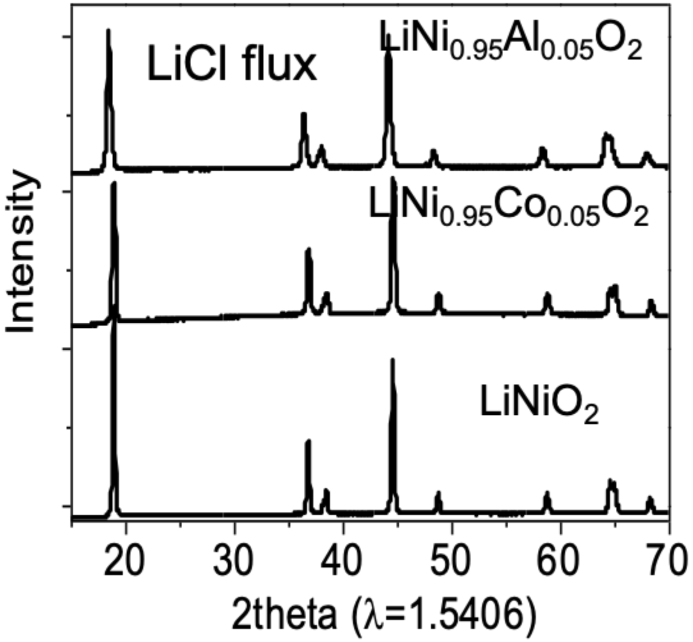
Slides from Guoying Chen (LBNL), Chongmin Wang (PNNL)

Surface-specific crystals – synthesis of $LiNiO_2$-based oxides





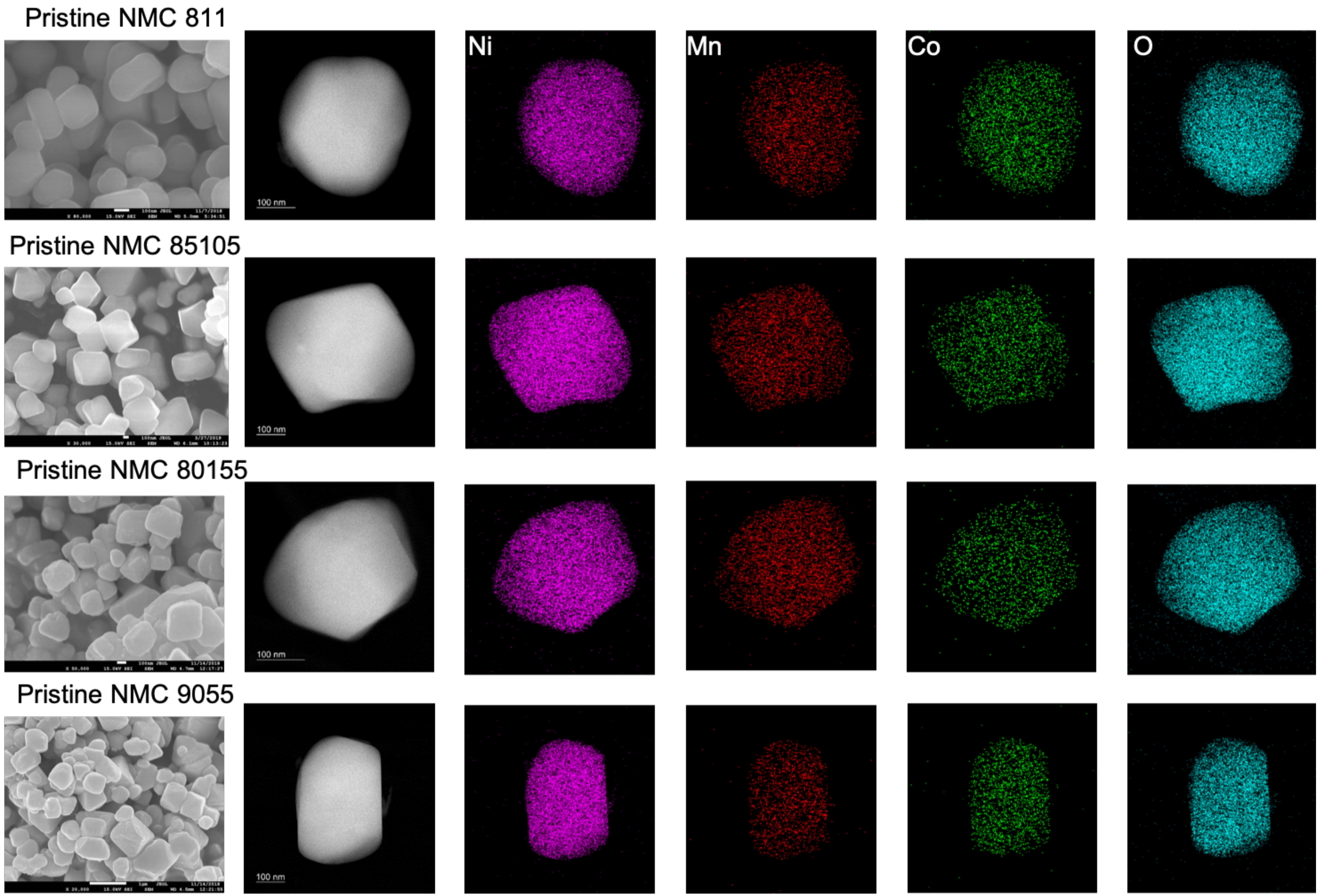




- LNO and 5% TM substituted LNO samples with truncated polyhedron (T-poly) and octahedron (Oct) morphologies have been prepared.
- Dominating surfaces are (104) for T-poly and (012) for Oct.

Slides from Guoying Chen (LBNL), Chongmin Wang (PNNL)

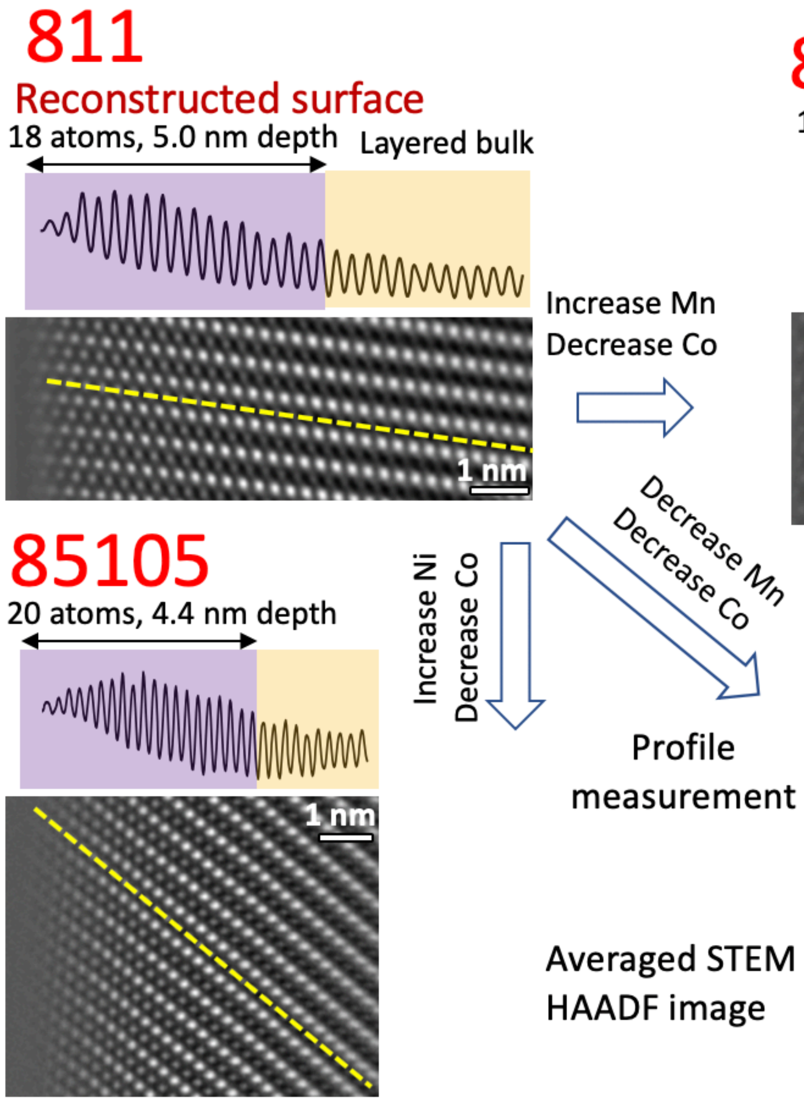
Uniform composition distribution (at particle level) in pristine cathodes

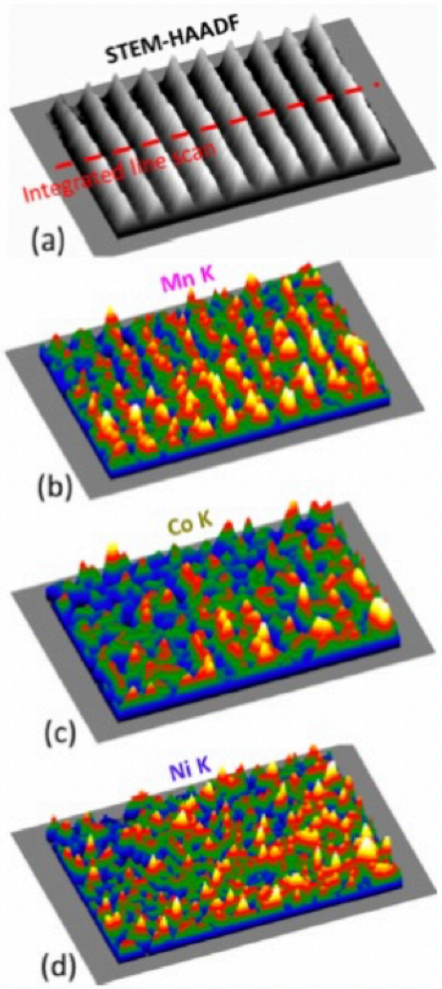


- Uniform distribution of components.
- Higher resolution studies are underway to focus on the elemental distribution near the surface layers

Slides from Guoying Chen (LBNL), Chongmin Wang (PNNL)

Surface structural feature of Pristine NMC single crystal





- At pristine state, all particle surfaces have a reconstruction layer.
- The reconstruction layer increases with increasing Ni concentration.
- This is consistent with our previous observation that Ni is the most mobile and migrates to the Li layer, followed by Co, then by Mn

Migration sequence is Ni > Co > Mn
Yan et al. Chem. Mater. 2015, 27, 5393

Slides from Guoying Chen (LBNL), Chongmin Wang (PNNL)

Response to Previous Year's Reviewer Comments

This project was not reviewed last year

BAT253

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
- Alison Dunlop
- Jessica Durham
- Jeff Elam
- Juan Garcia
- Linxiao Geng
- 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
- Chen Liao
- Qian Liu
- Wenquan Lu
- Mei Luo
- Anil Mane
- Jagjit Nanda
- Nate Phillip
- Bryant Polzin
- Krzysztof Pupek
- Yan Qin
- Yang Ren
- Marco Rodriguez
- Aryal Shankar
- Boyu Shi
- Woochul Shin
- Ilya Shcrob
- Seoung-Bum Son
- Adam Tornheim
- Stephen Trask
- Bertrand Tremolet de Villers
- John Vaughey
- Anh Vu
- 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

Support for this work from the ABR Program, Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged – Peter Faguy, David Howell

Proposed Future Research

Modeling:

- Extend the screening for elemental composition for Co substitution for $LiNiO_2$-based oxides.
- Refining NMR fitting and expansion of configuration space.
- Include screening criteria for phase stability of $LiNiO_2$-based oxides.
- Effect of elemental segregation on surface reconstructions.

Model systems:

- Characterize doped oxide crystals and determine the effect of dopant on the bulk and surface properties of the pristine samples
- Perform electrochemical and diagnostic studies to evaluate the effect of dopant on chemical and structural changes as well as cycling stabilities under battery operating conditions

Any future work is subject to change depending on funding levels

Summary

- First-principles calculations predict a minimum of 1-3% Li/Ni exchange for all $LiMn_{0.5}Ni_{0.5}O_2$ configurations. These results reveal that there is no theoretical barrier to achieving low Li/Ni exchange in LiNi0.5Mn0.5O2 and suggests that advanced design and synthesis should be pursued in this regard

- The presence of Co induces the formation of ordered domains within the transition metal layer, which decreases the driving force for cation mixing and promotes more layered structures.

- There is a strong correlation between the total energy and the number of Ni-Mn bonds in the configuration.

- Surface reconstruction layers (spinel phase) form even on pristine stoichiometric materials. The formation and stability are further enhanced by the strain developed between the two phases. The higher the Ni content the thicker the reconstruction layers.

- Surface segregation and oxygen vacancy formation energies are used to screen for new substitutes for Co. The elemental segregation and chemical reactivity are facet dependent.

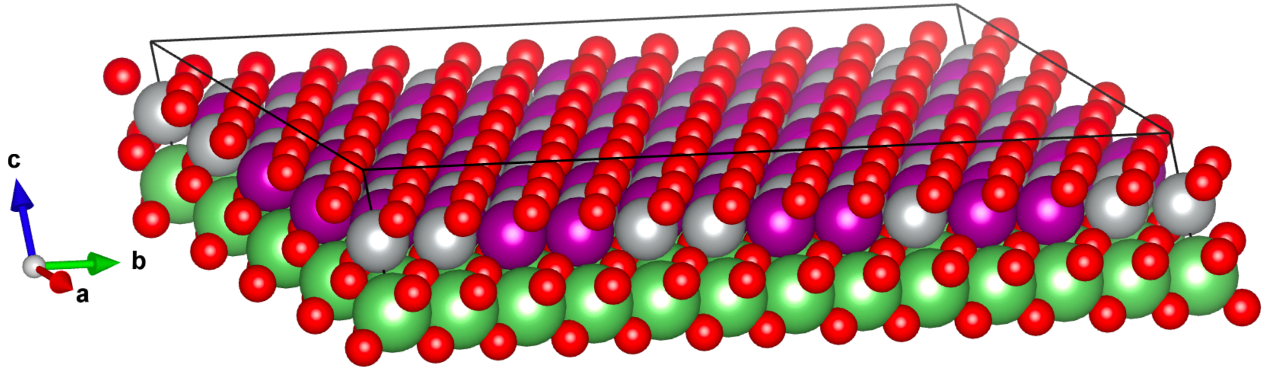
- The DFT predicted NMR spectra of $LiMn_{0.5}Ni_{0.5}O_2$, show that Li/Ni exchange induces local structural distortions that give rise to new shifts and increases signal broadening. The analysis of the experimental NMR spectra suggests a structure with a combination of low energy configurations and ~8% Li/Ni exchange.

Technical Backup Divider Slide

Density Functional Theory methodology

Periodic boundary slab models used to perform Density Functional Theory (DFT) based calculations.

- Spin-polarized density functional theory
- Generalized gradient approximation (GGA) parametrized by Perdew, Burke, and Ernzerholf (PBE).
- The GGA+U scheme is used for applying the on-site correlation effects among 3d electrons of the transition metals (TM)./
- After geometry optimizations within the DFT+U framework, electronic relaxation was performed using a single point calculation with the hybrid functional HSE06 for selected simulations.
- Bulk solvent effects are accounted for by using an implicit solvation (VASPsol) when needed.



Representative supercell for the $LiMn_{0.5}Ni_{0.5}O_2$ system. It has 384 atoms in a cell with periodic boundary conditions. Purple spheres represent Mn, silver spheres represent Ni, green spheres represent Li and the smaller red spheres represent oxygen.

- This supercell is suitable to explore transition metal configurations within the transition metal layer.
- For NMR calculation a smaller cell, with three transition metal layers was used. Such a cell is more suitable to explore the local chemical environment around Li ions in the R-3m symmetry.