Model System Diagnostics for High-Energy Cathode Development

Guoying Chen

Lawrence Berkeley National Laboratory

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Project ID: bat225

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Overview

Timeline

- Start date: October 2016
- End date: September 2019
- Percent complete: 60%

Barriers Addressed

- Energy density
- Cycle life
- Safety

Budget

- Total project funding
  - FY2017 $550K
  - FY2018 $500K

Partners

- Interactions/collaborations: LBNL, UCB, ANL, Cambridge, ORNL, PNNL, NCEM, ALS, SSRL
- Project lead: Vincent Battaglia

Relevance/Objectives

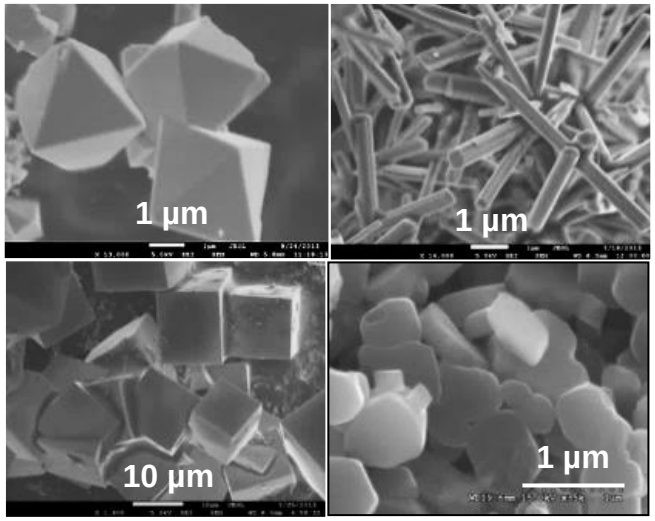
- Obtain fundamental understanding on performance-limiting properties, phase transition mechanisms, kinetic barriers, and instabilities in high-energy cathode materials
- Develop strategies to improve solid-state charge transport and optimize charge transfer at electrode-electrolyte interface
- Discover and develop next-generation electrode materials based on rational design as opposed to the conventional empirical approaches

Milestones

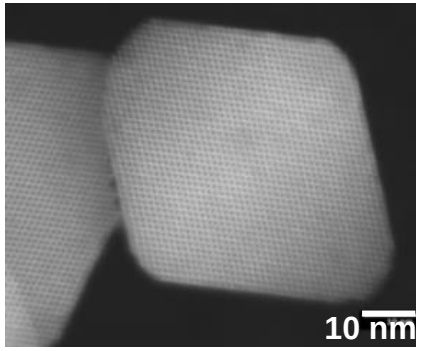
Date	Milestones and Go/No-Go Decision	Status
December 2017	Milestone Characterize O activities during charge/discharge and extended cycling of Li-TM oxides and understand their effect on cathode structural and electrochemical reversibility.	Completed
March 2018	Milestone Investigate analytical techniques to determine the kinetics of anion redox process and evaluate factors influencing rate capability of Li-TM oxide cathodes.	Completed
June 2018	Milestone Apply advanced diagnostic techniques to investigate the reactivities of model oxide surfaces and understand their impact on oxide performance and safety.	On schedule
September 2018	Go/No-Go Decision Reveal the impact of oxide chemistry and particle morphology on the extent of reversible O redox vs. lattice O loss and understand how to fine tune O activities at high voltages. No-Go if the processes of reversible O redox and lattice O loss cannot be decoupled with diagnostic studies.	On schedule

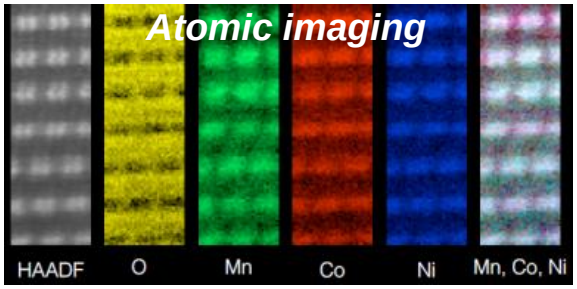
Approach/Strategy

High-quality model samples with well-controlled physical properties

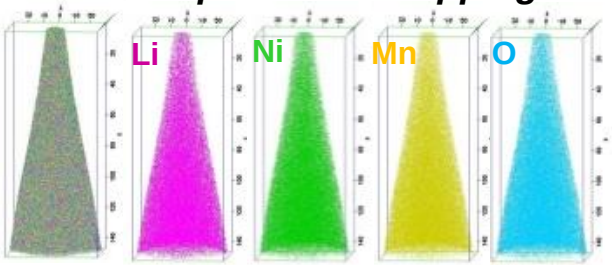


Fundamental understanding of solid-state chemistry, kinetic barriers and instabilities during battery operation





3D compositional mapping



Model-system construction

Advanced diagnostics

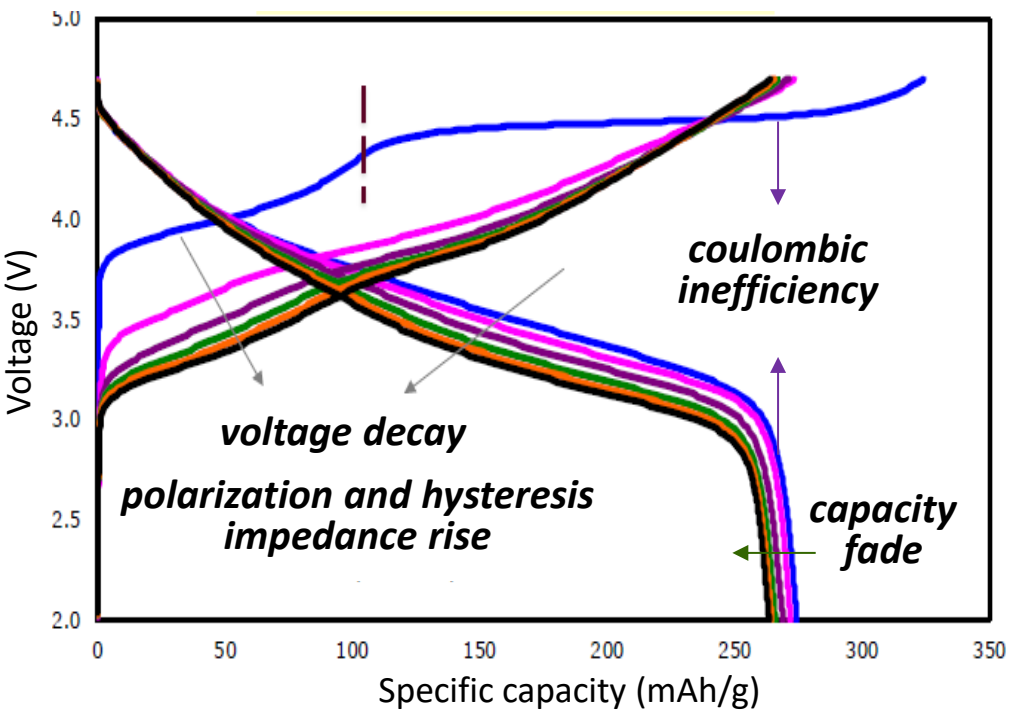
Rational design, synthesis and testing of materials

Fundamental knowledge

Layered *vs.* cation-disordered Li-rich TM oxides

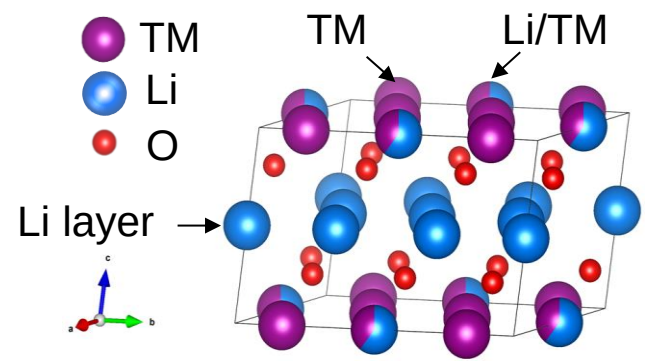
- Most studied example is layered Li- and Mn-rich NMCs (LMR-NMC) with a monoclinic structure (C2/m).
- Reversible capacity can be > 250 mAh/g but many challenging performance issues exist.

Typical cycling performance of LMR-NMC

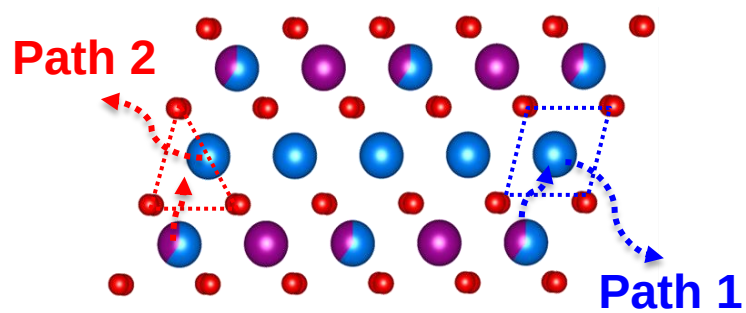


- Cation migration after Li removal main source of performance deterioration.

Layered structure



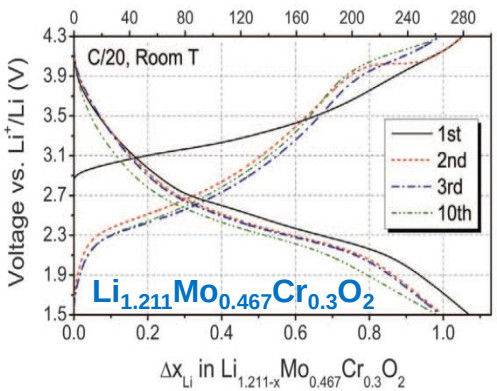
Octahedral → tetrahedral sites → **spinel**



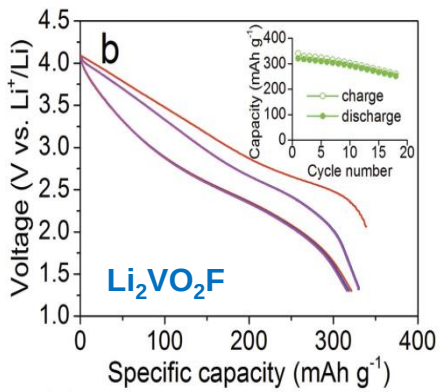
Octahedral → octahedral sites → cation disorder → **rock salt**

Layered *vs.* cation-disordered Li-rich TM oxides

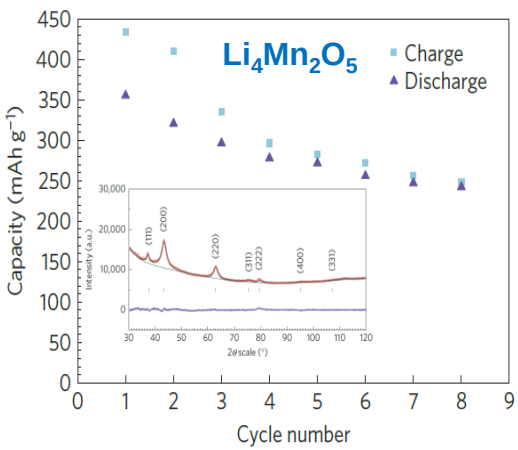
- Li-rich rock-salt oxides with cation fully randomized can also deliver high reversible capacity of ~300 mAh/g.



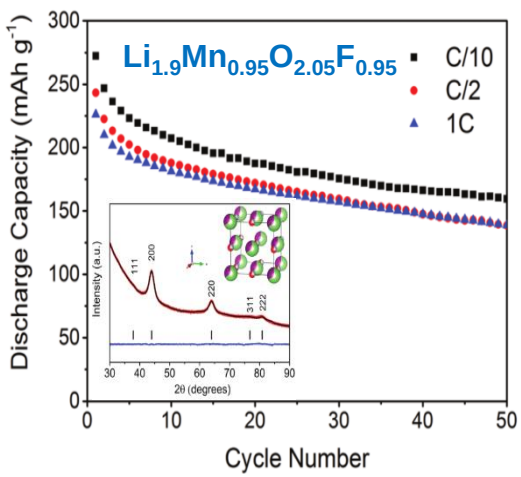
Science *343*, 519 (2014)



Adv. Energy Mater *5*, 1401814 (2014)



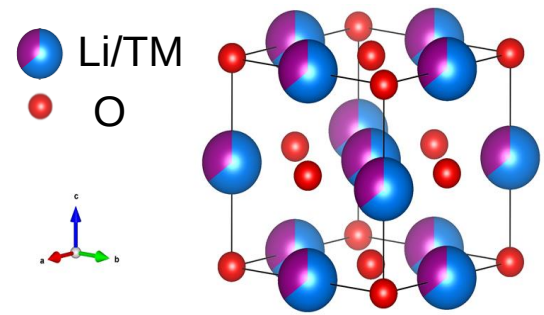
Nat. Mater *15*, 173 (2016)



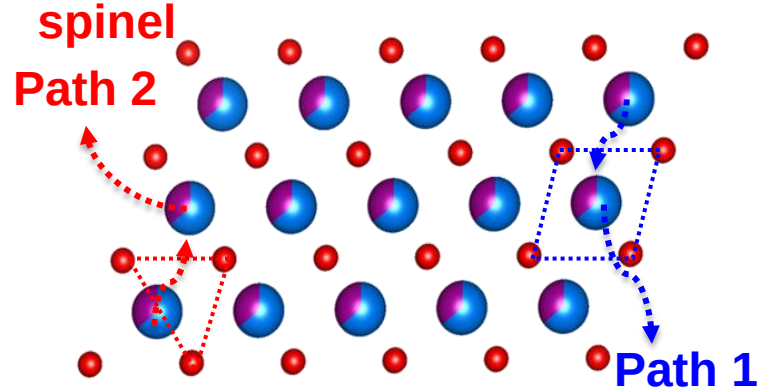
Energy Environ. Sci. (2018)

- Some may have better structural stability since cations already disordered.

Rock-salt structure

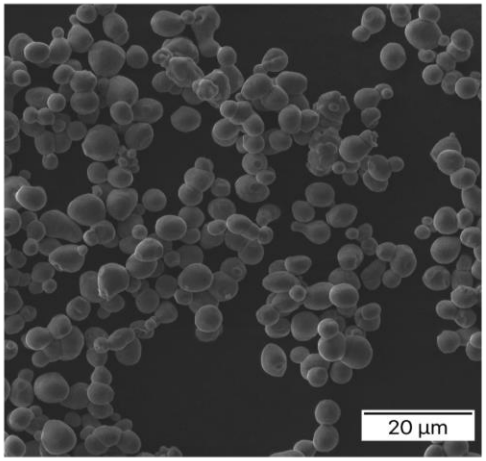


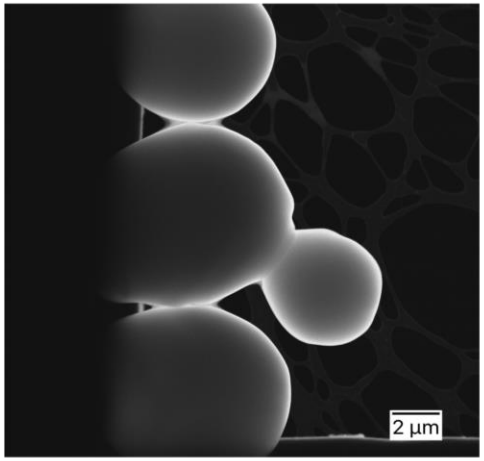
Octahedral → tetrahedral sites → **spinel**

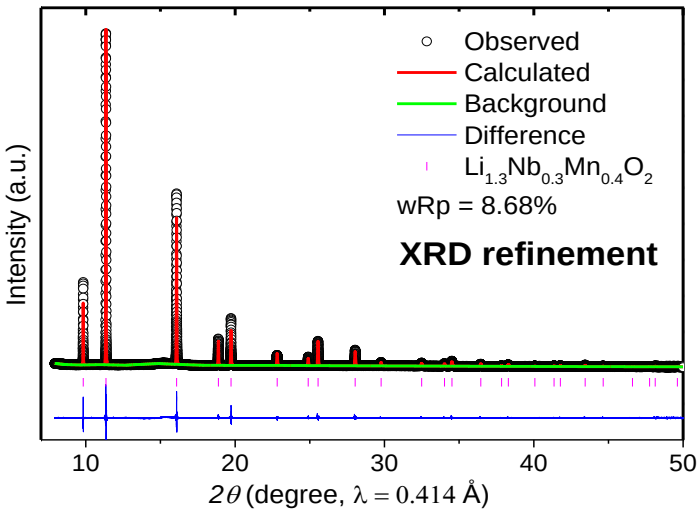


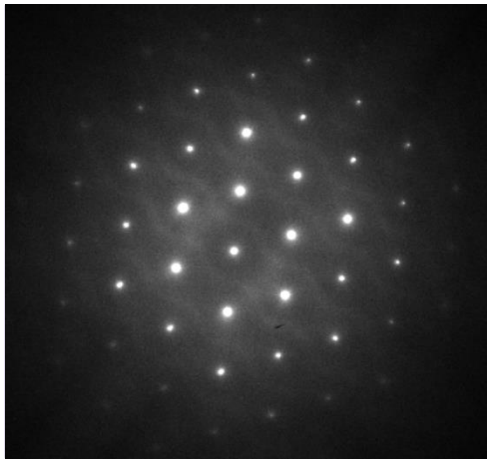
Octahedral → octahedral sites → cation disorder → ***no change***

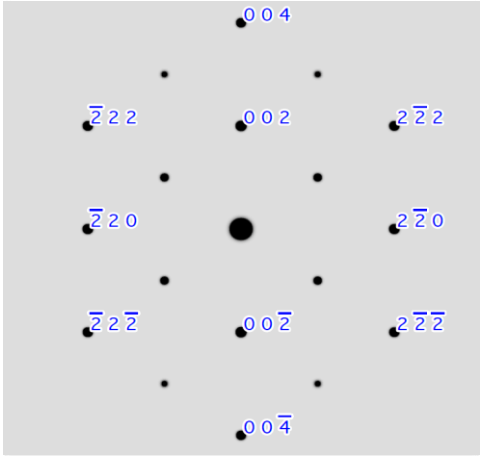
Technical Accomplishments: model Li-rich rock-salt oxide synthesized

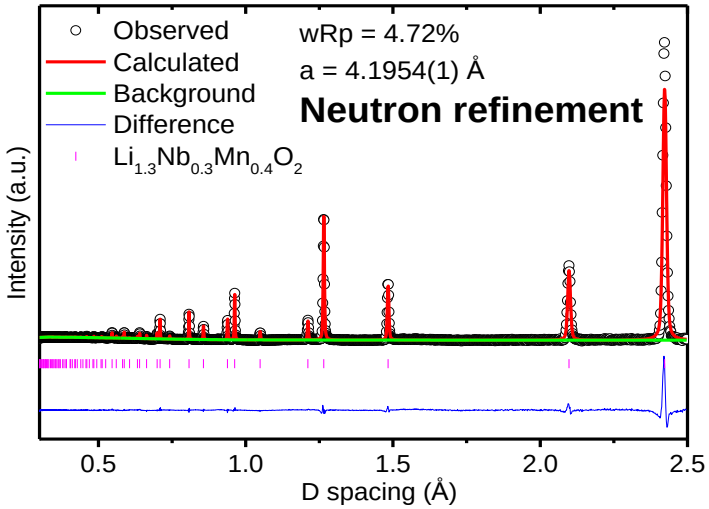






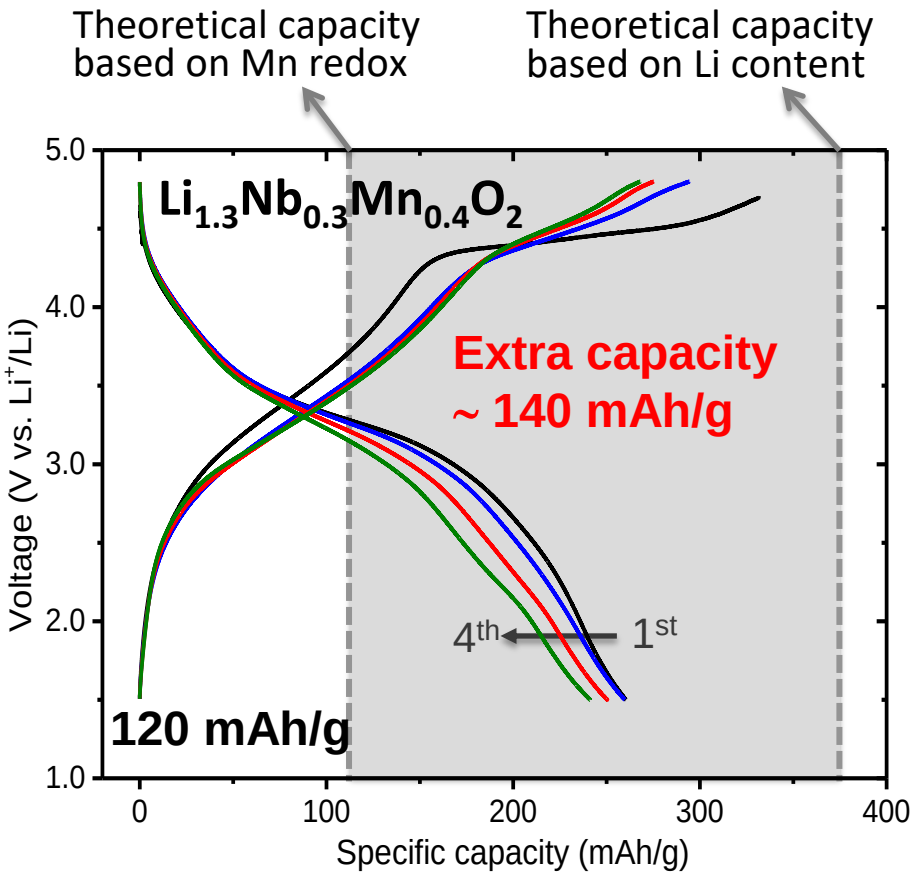






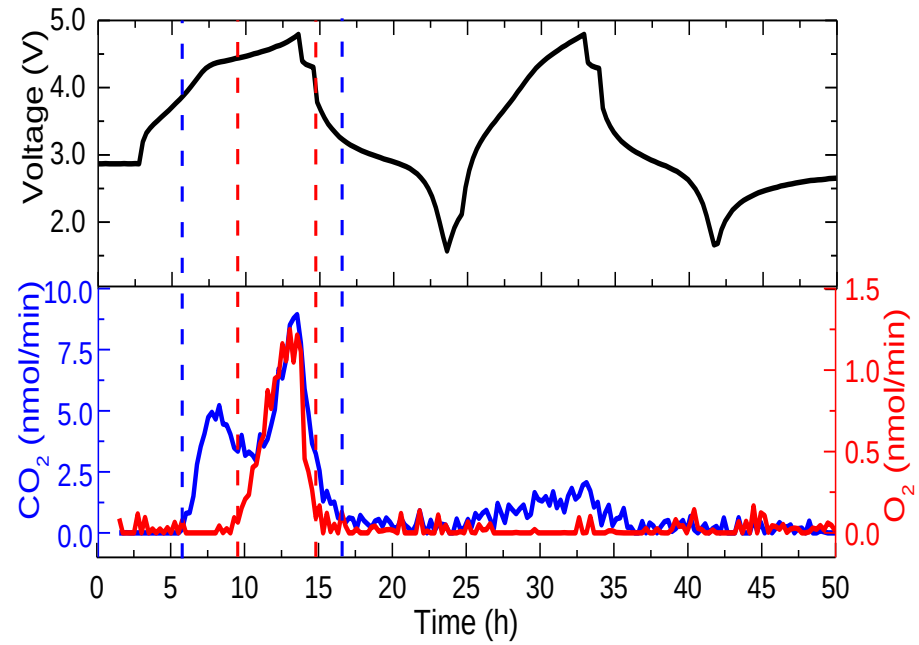
- Well-formed $Li_{1.3}Nb_{0.3}Mn_{0.4}O_2$ crystals with only one redox active TM (i.e. Mn, Nb inactive) were synthesized for study.

I. Understand the source of extra capacity



Operando DEMS

(with Bryan McCloskey, UC Berkeley)

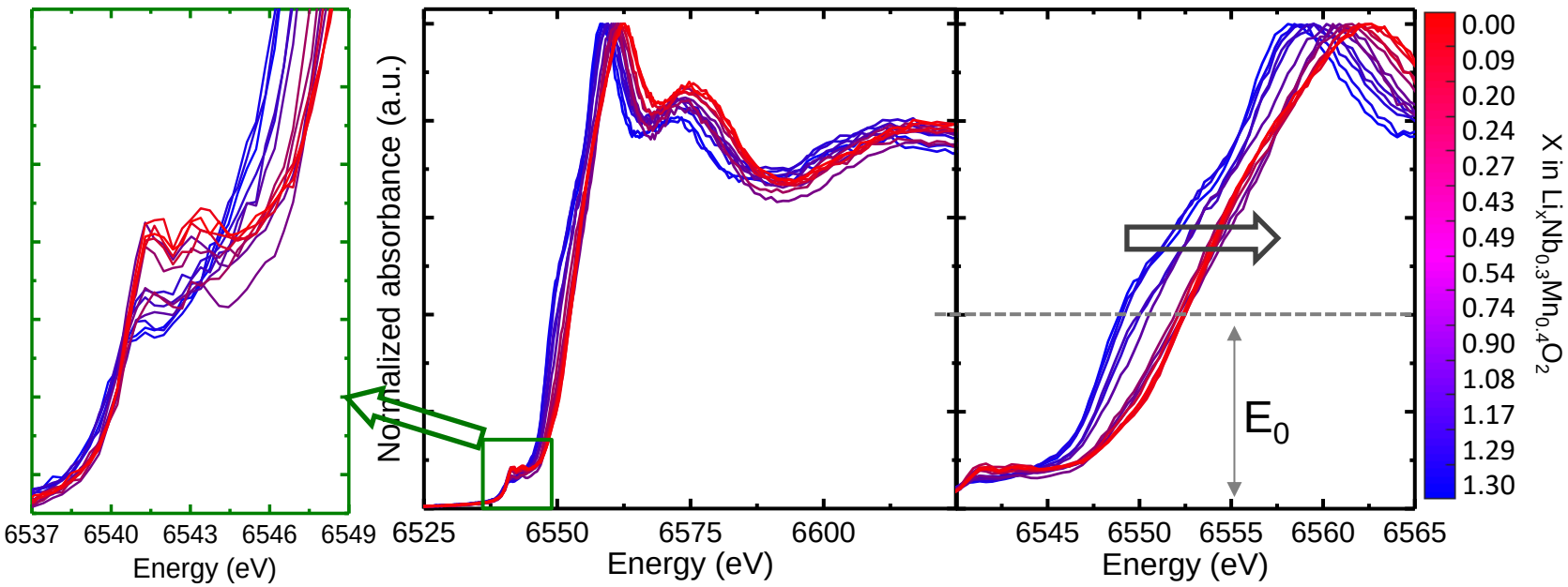


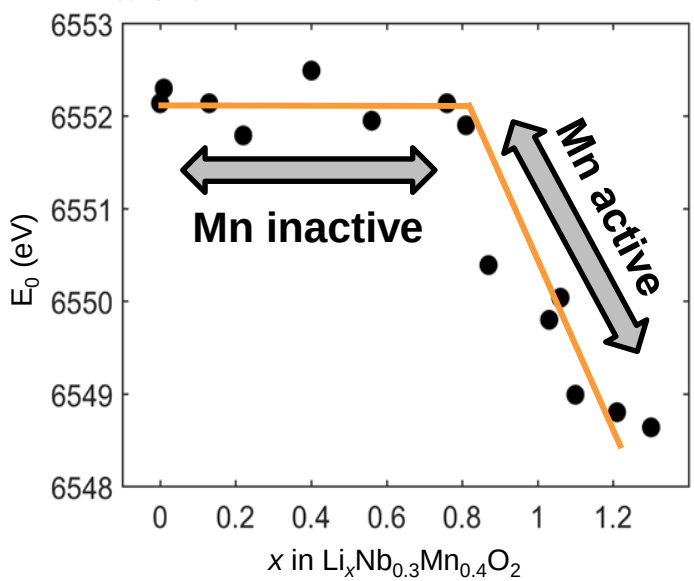
- ~ 120 mAh/g at lower voltage comes from Mn redox with 0.4 Li^+ extraction. Additional 140 mAh/g at higher voltage comes from anionic redox activities.
- O_2 evolution only detected during the 1st charge. Additional oxygen redox process must contribute to the capacity.

G. Chen et. al, *Chemistry of Materials*, **30**, 1655 (2018)

I. Understand the source of extra capacity

Mn K-edge hard XAS *(SSRL beamline 2-2)*

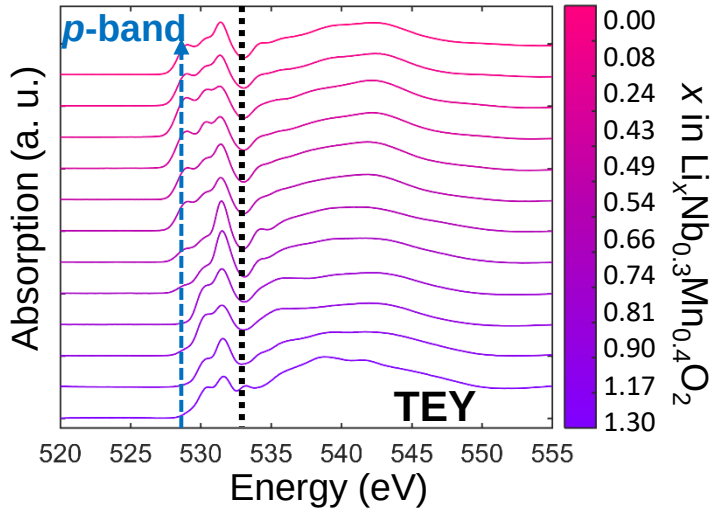


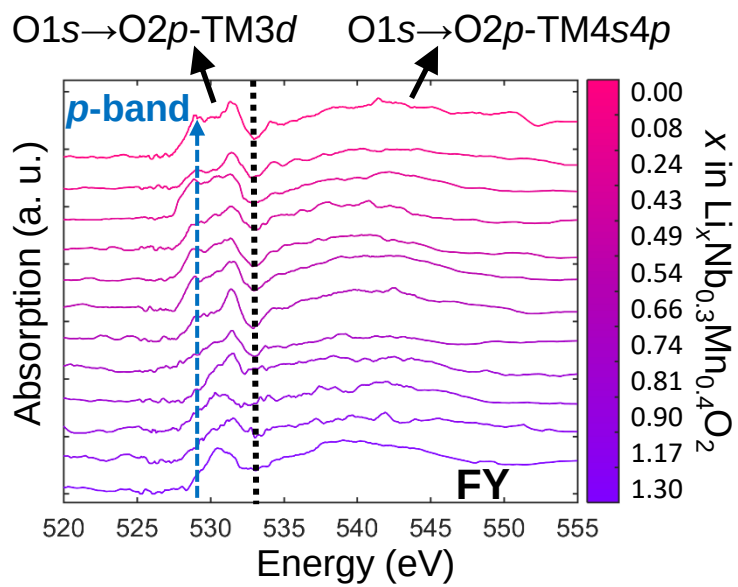


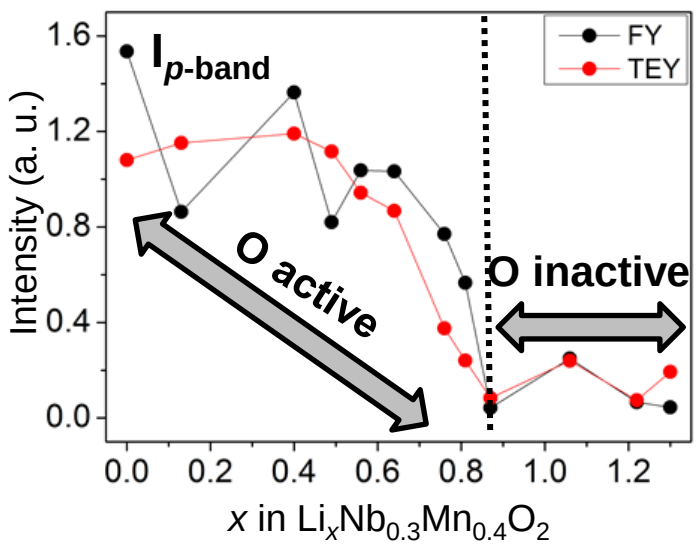
- Two distinctive regions in Mn chemical changes, divided at Li0.9 (after 0.4 Li^+ removal).
- Mn redox only occurs above Li0.9 in $Li_{1.3}Nb_{0.3}Mn_{0.4}O_2$, confirming 120 mAh/g (0.4 Li^+) from TM redox.

I. Understand the source of extra capacity

O K-edge soft XAS *(SSRL beamline 8-2)*







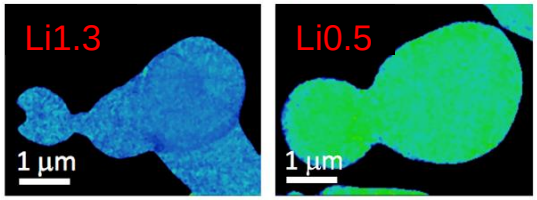
- Two distinctive regions in oxygen activities, also divided at Li0.9.
- Oxygen only active below Li0.9 – source of the additional 140 mAh/g capacity.
- Oxygen activity changes slightly from surface (TEY profiles) to bulk (FY profiles).

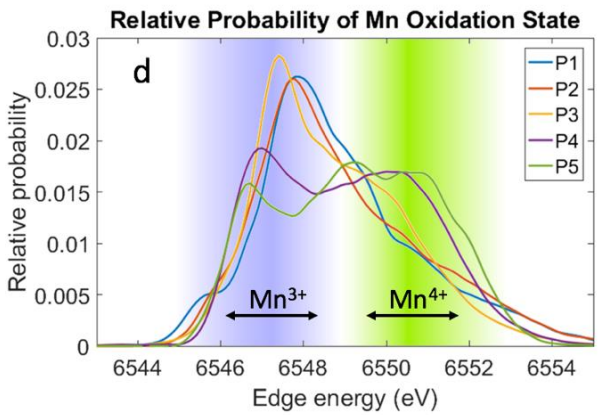
II. Kinetics: Li diffusion affected by short-range ordering

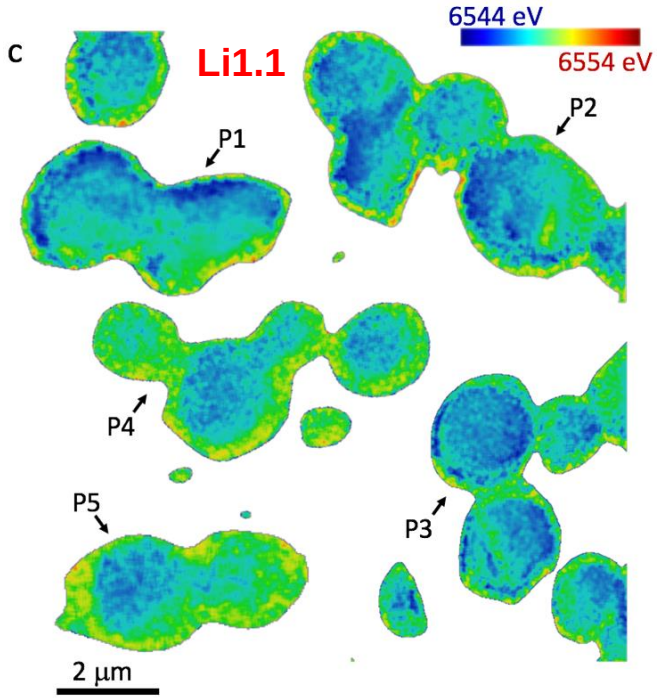
Full-field transmission X-ray microscopy combined with X-ray absorption near-edge structure (FF-TXM-XANES, *with Yijin Liu, SSRL BL 6-2c*)

Selected area electron diffraction (SAED)

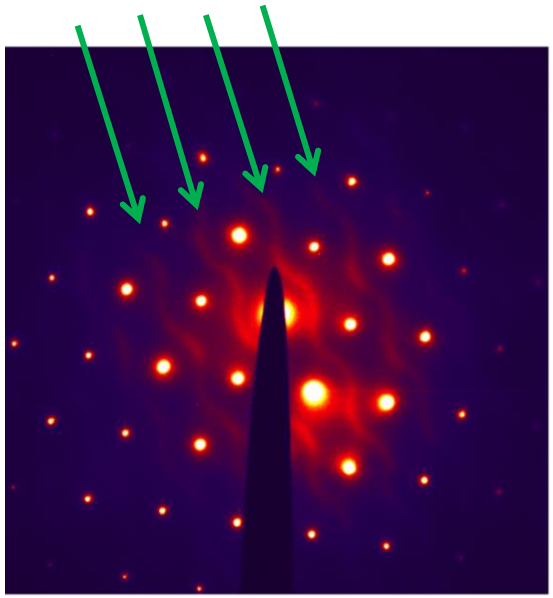
$Li_xNb_{0.3}Mn_{0.4}O_2$ (denoted as Lix)





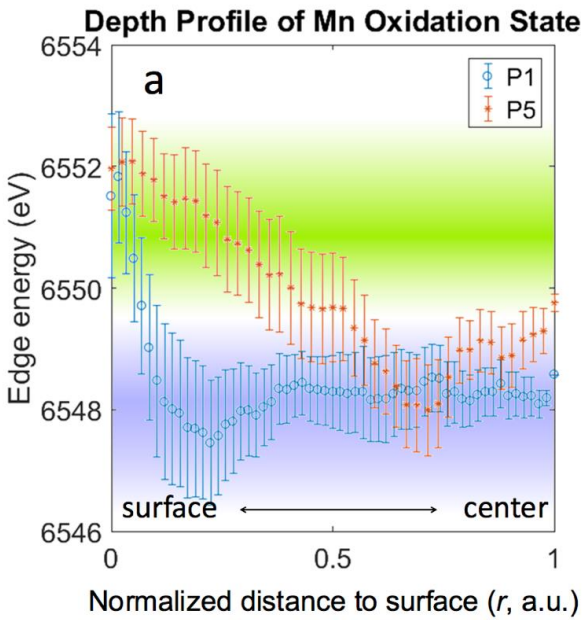


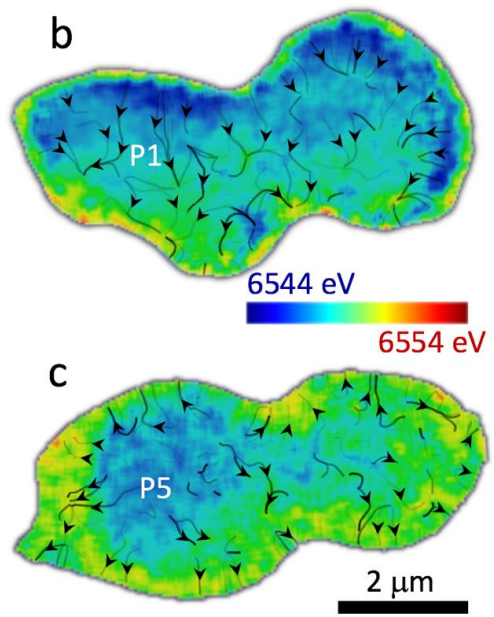
Evidence of local short-range ordering at particle-level

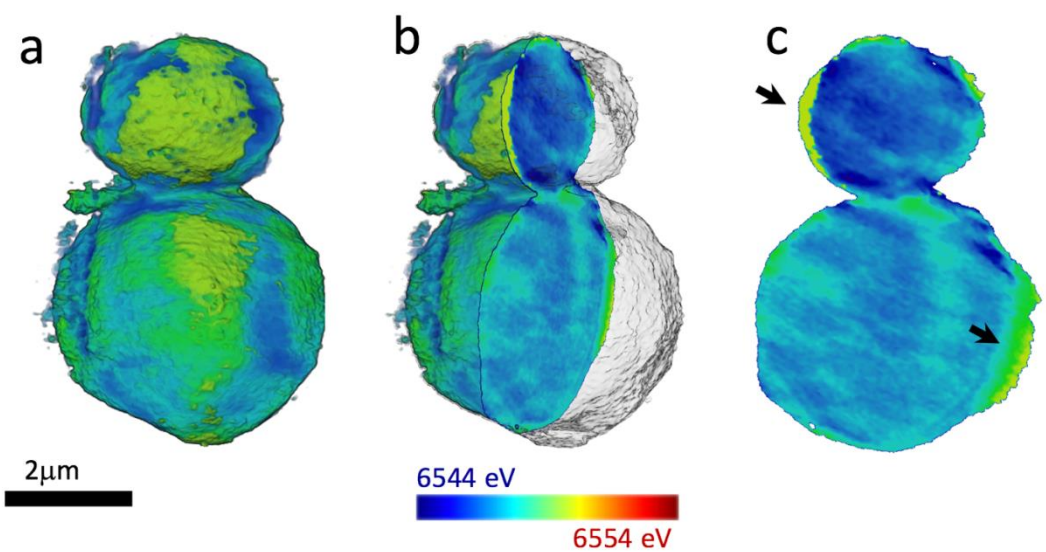


- Mesoscale chemical distribution (Mn oxidation state) as a function of state of charge visualized at sub-particle level.
- Chemical heterogeneity observed on partially delithiated particles suggests non-equilibrium diffusion pathways and impact of local short-range ordering.

II. Kinetics: Li diffusion affected by short-range ordering





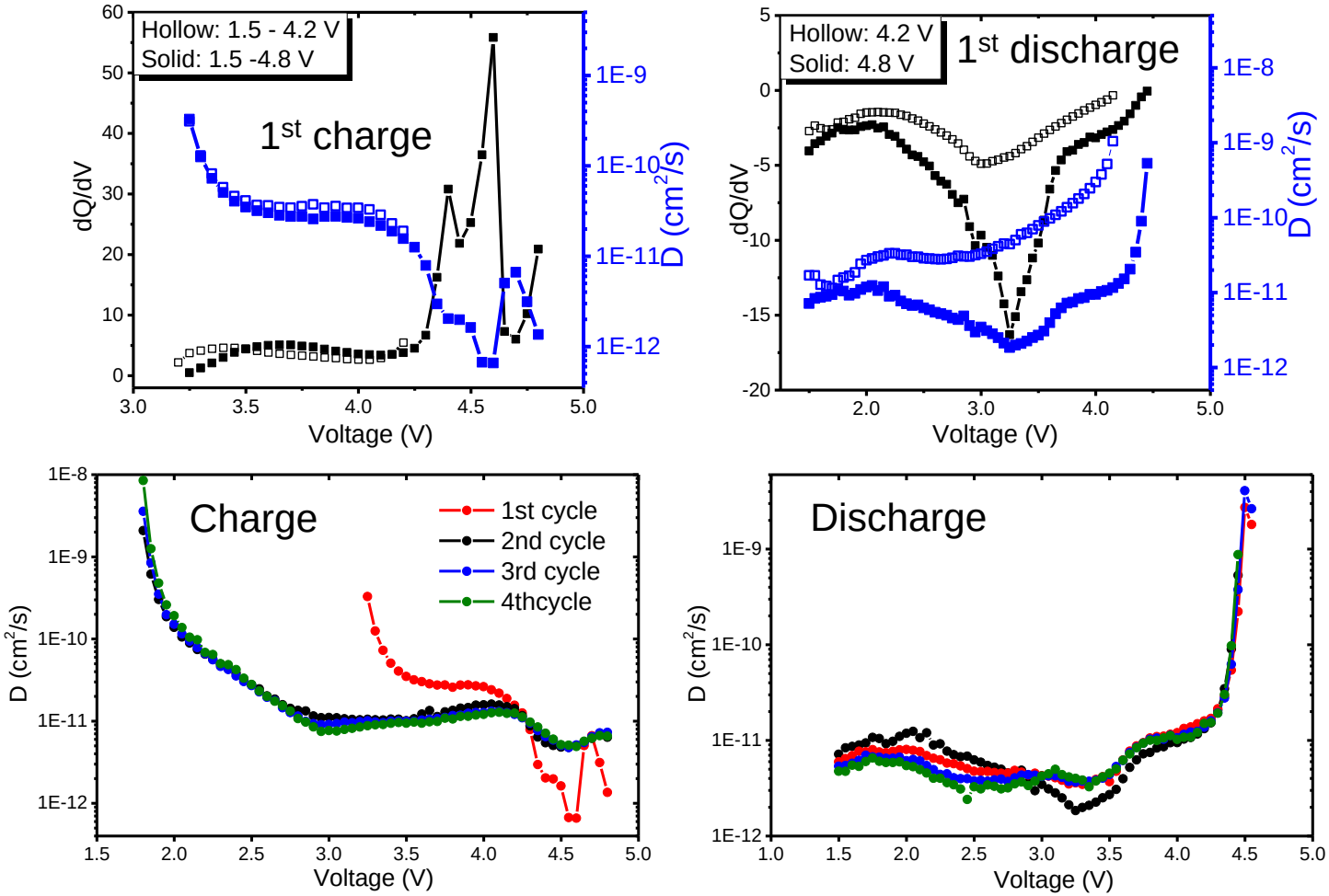


2D and 3D FF-TXM-XANES
(*with Yijin Liu, SSRL BL 6-2c*)

- The direction of lithium-ion movement (black arrows) in individual particles can be traced by following the changes in Mn cation concentration gradient.
- 3D FF-TXM-XANES reveals the presence of non-equilibrium diffusion pathways and chemical heterogeneity throughout individual particles. Drastic difference observed between the surface and the bulk.

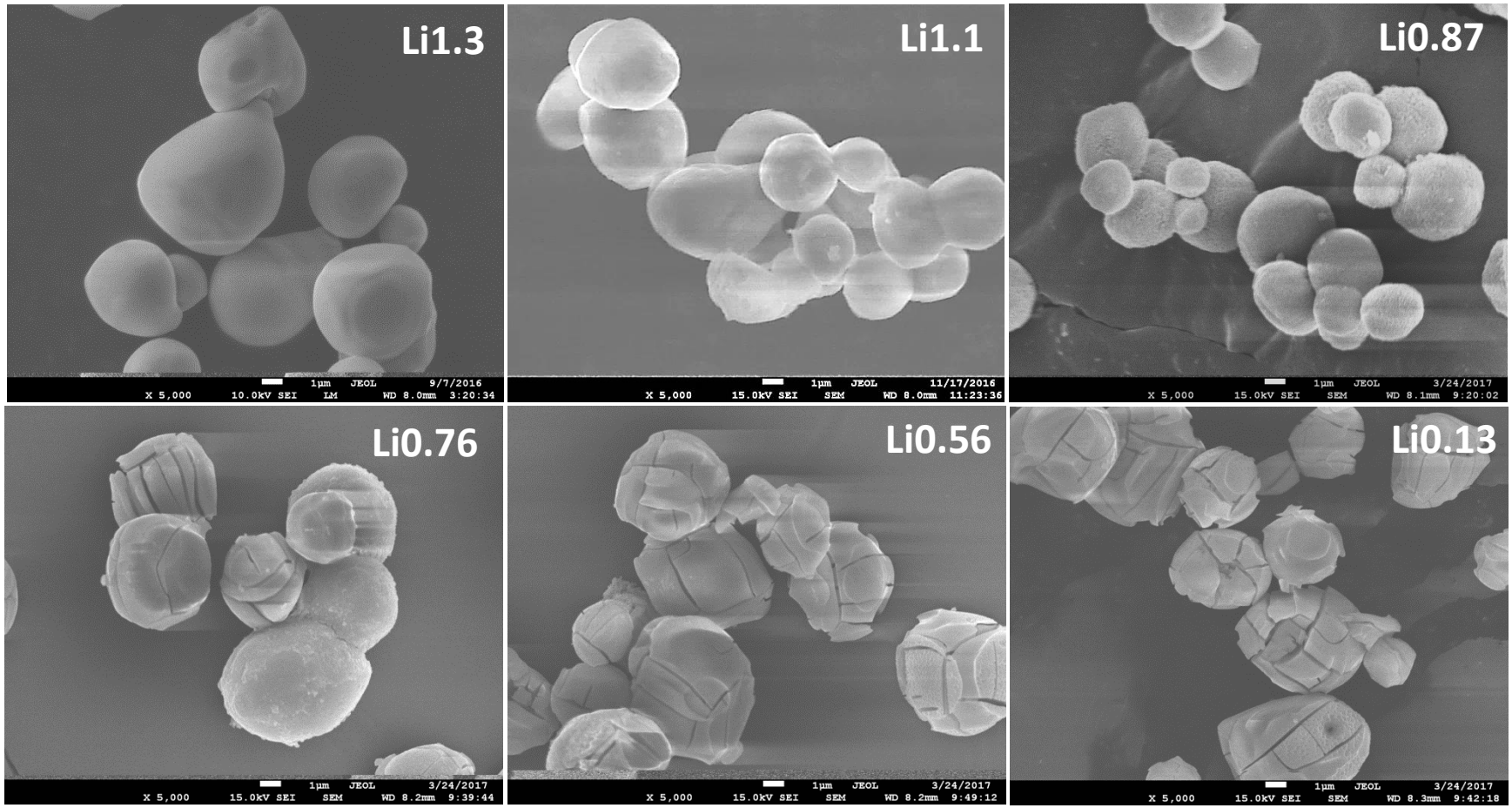
G. Chen et. al, *Chem*, under review (2018)

II. Kinetics: oxygen redox reduces kinetics



- Li diffusion during oxygen redox nearly two orders of magnitude slower than that during TM redox.
- Repeated cycling involving oxygen redox leads to kinetic deterioration in the entire voltage window.

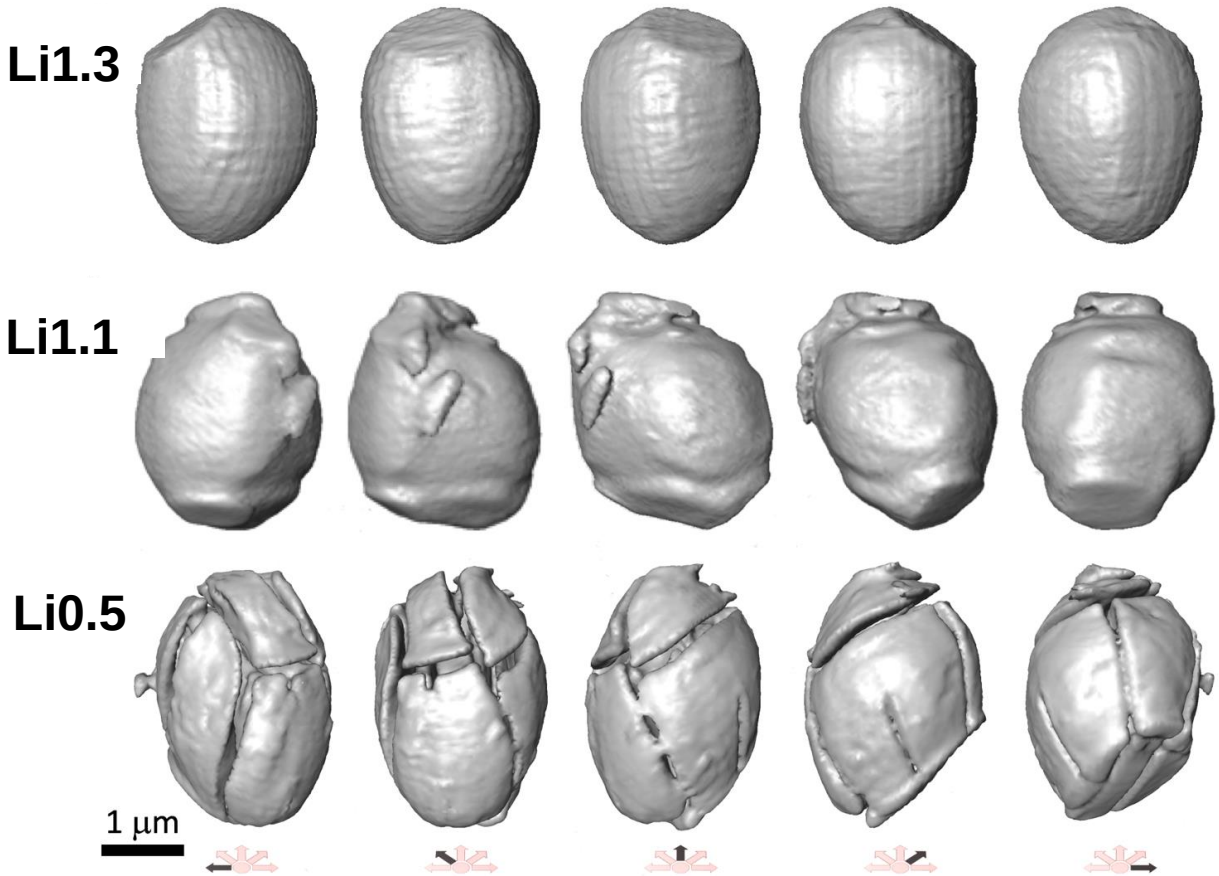
III. Understand effect of oxygen redox – morphology damage associated with oxygen redox



- No morphology changes during Mn redox ($x > \sim 0.9$).
- Cracking and fracturing broadly observed during O redox ($x < \sim 0.9$).

III. Understand effect of oxygen redox – morphology damage exposes new surface

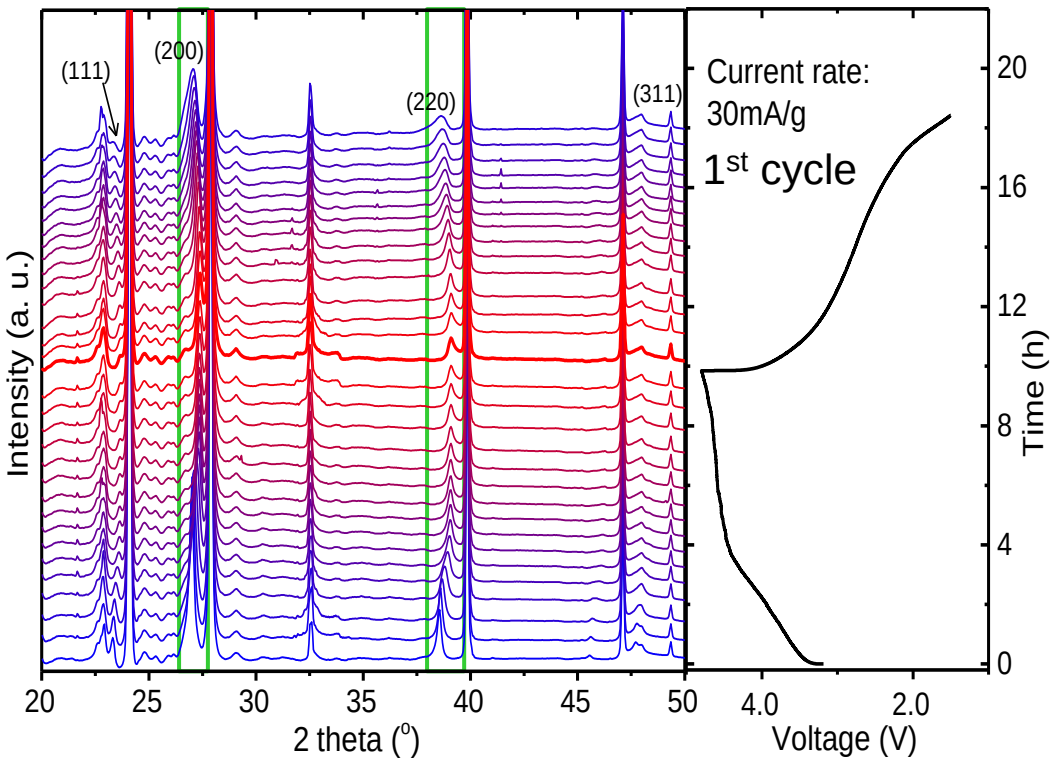
3D Transmission X-ray Microscopy (*with Yijin Liu, SSRL BL 6-2c)*

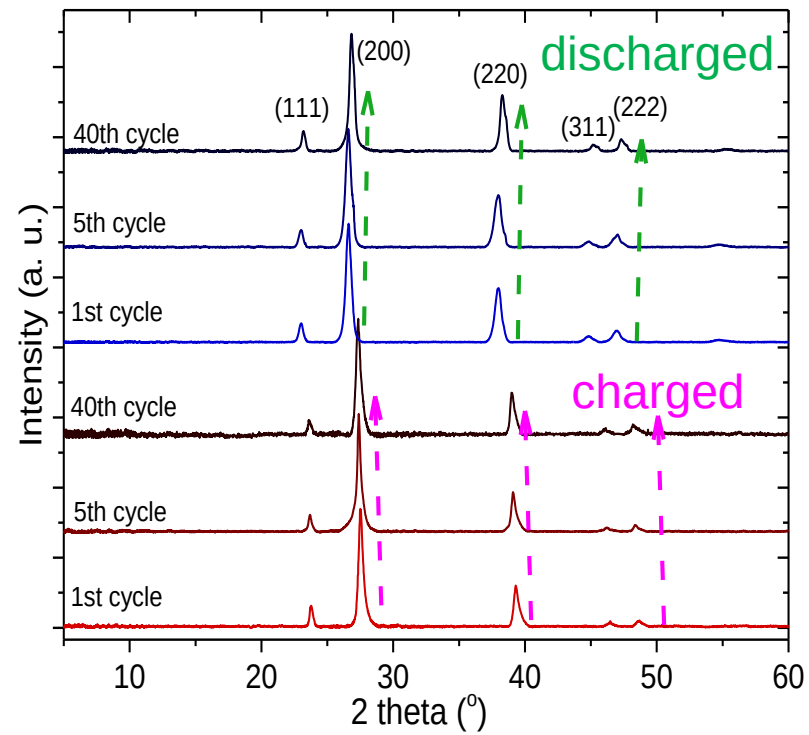


- Particle cracking creates new surface which may increase O_2 evolution.
- Surface oxygen stabilization strategies need to take consideration of morphology evolution during cycling.

III. Understand effect of oxygen redox – structural

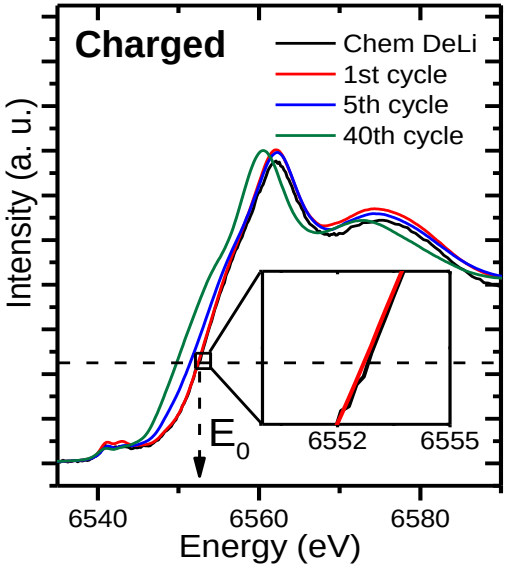
In situ and ex situ synchrotron XRD *(SSRL beamline 11-3)*



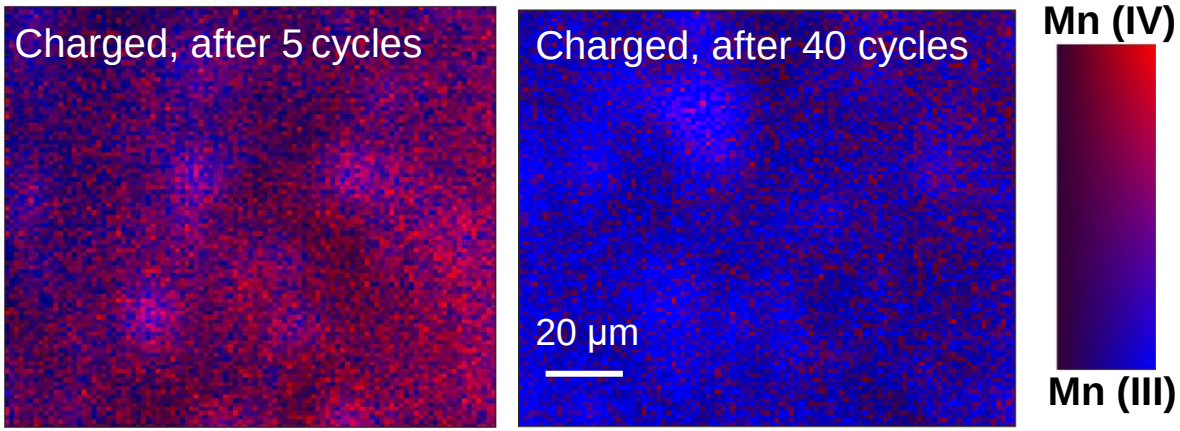


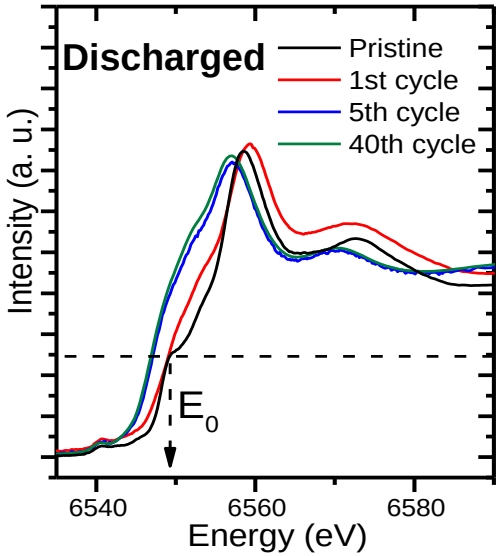
- Only rock-salt phase present during 1st cycle as well as after 40 cycles.
- No phase change detected – spinel phase not observed after cycling cation-disordered oxide cathode.

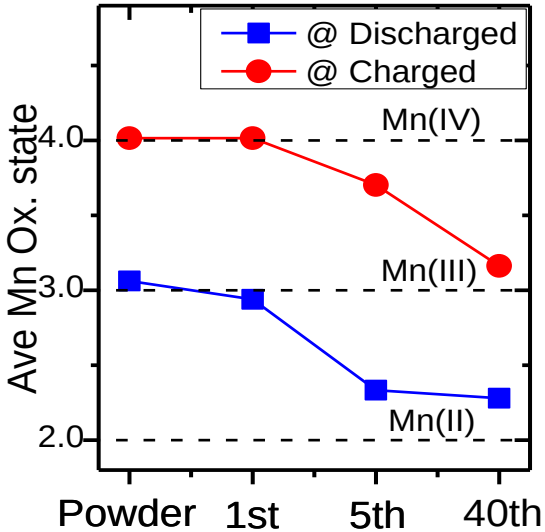
III. Understand effect of oxygen redox – chemical



Mn K-edge hard XAS spectra and mapping *(SSRL beamline 2-2)*



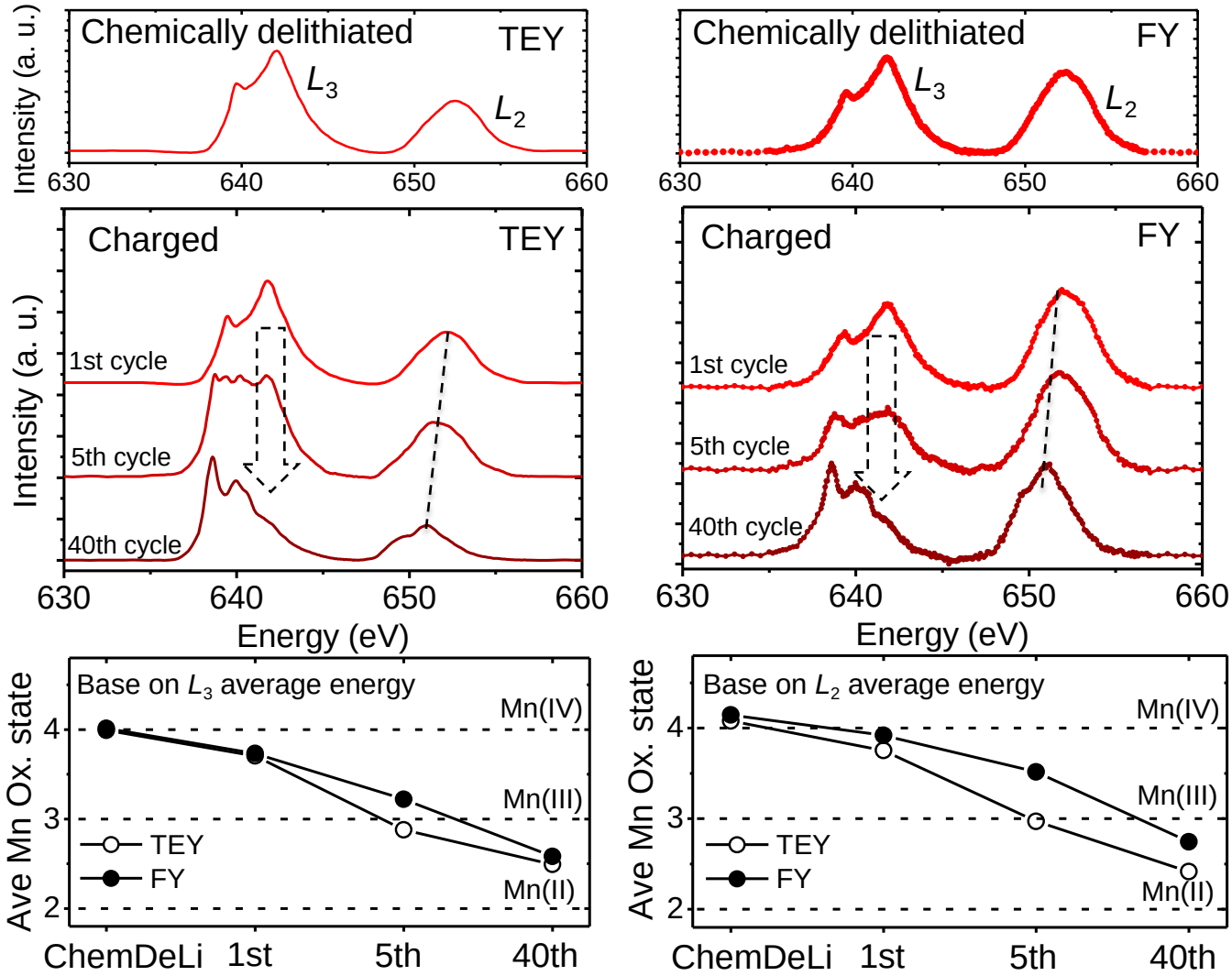




- Significant bulk Mn reduction with cycling observed in both charged and discharged states.

III. Understand effect of oxygen redox – reversibility

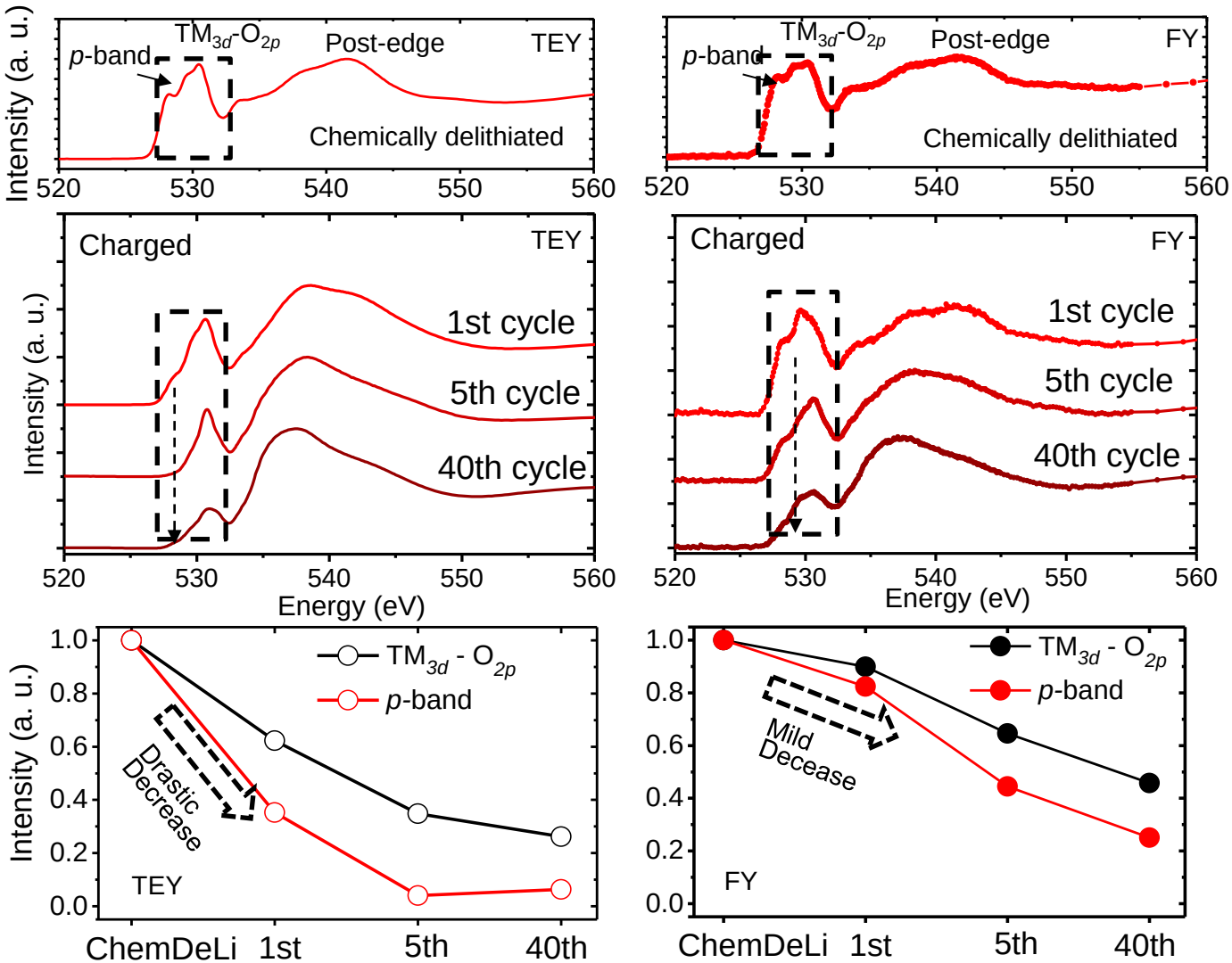
Mn L-edge soft XAS *(SSRL beamline 8-2)*



- With cycling, TM redox process becomes irreversible.
- Surface Mn reduction more severe than that in the bulk.

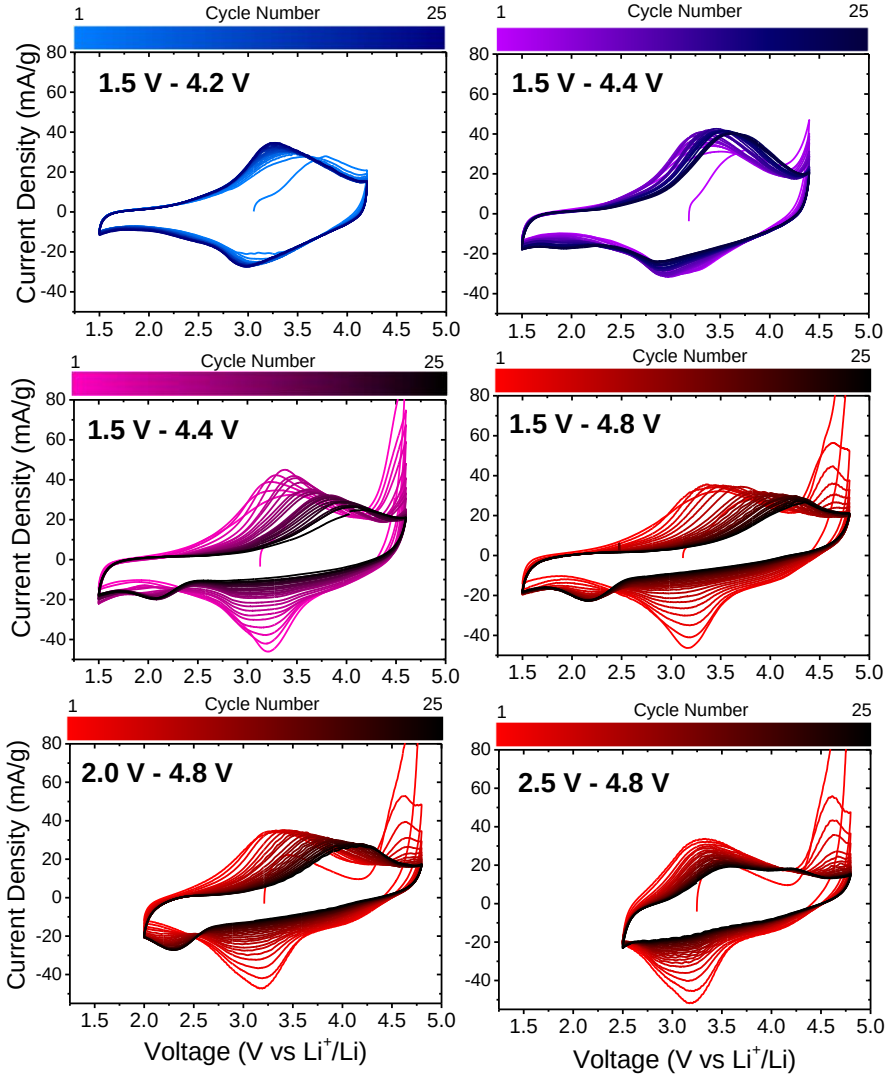
III. Understand effect of oxygen redox – reversibility

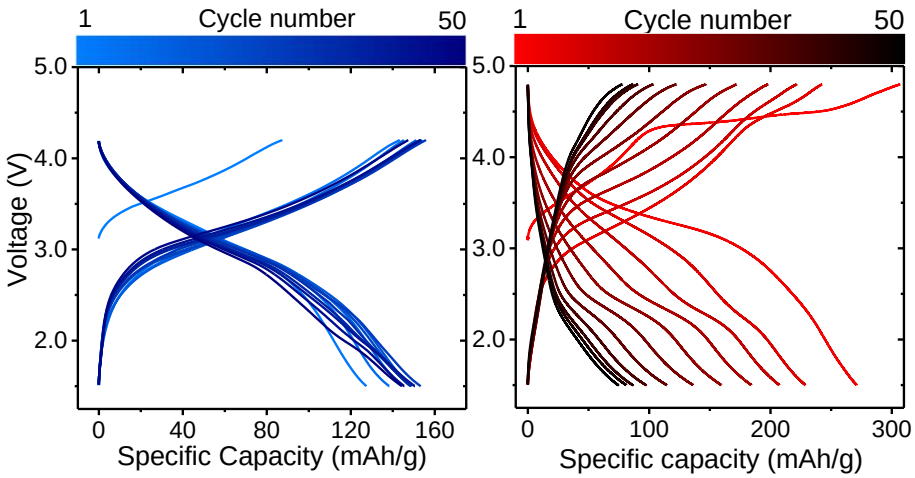
O K-edge soft XAS *(SSRL beamline 8-2)*

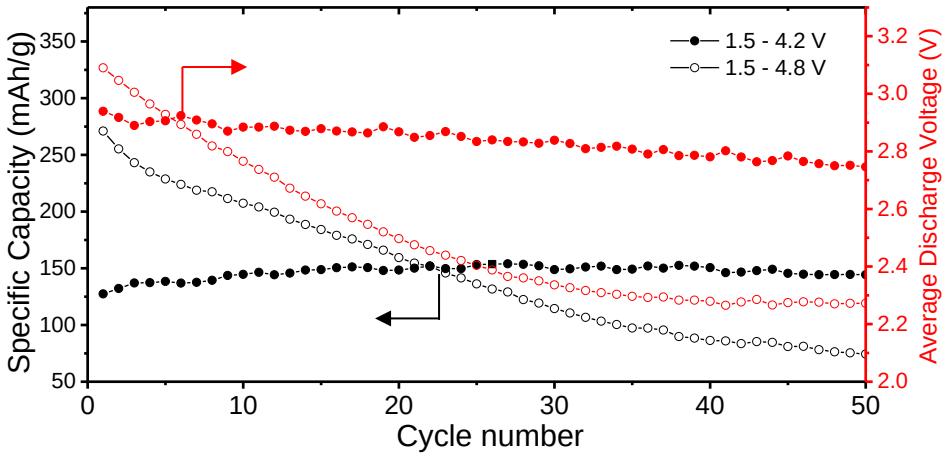


- Cycling leads to irreversible changes in oxygen redox process.
- Surface changes more severe than that in the bulk.

Controlling extent of oxygen redox key to stability

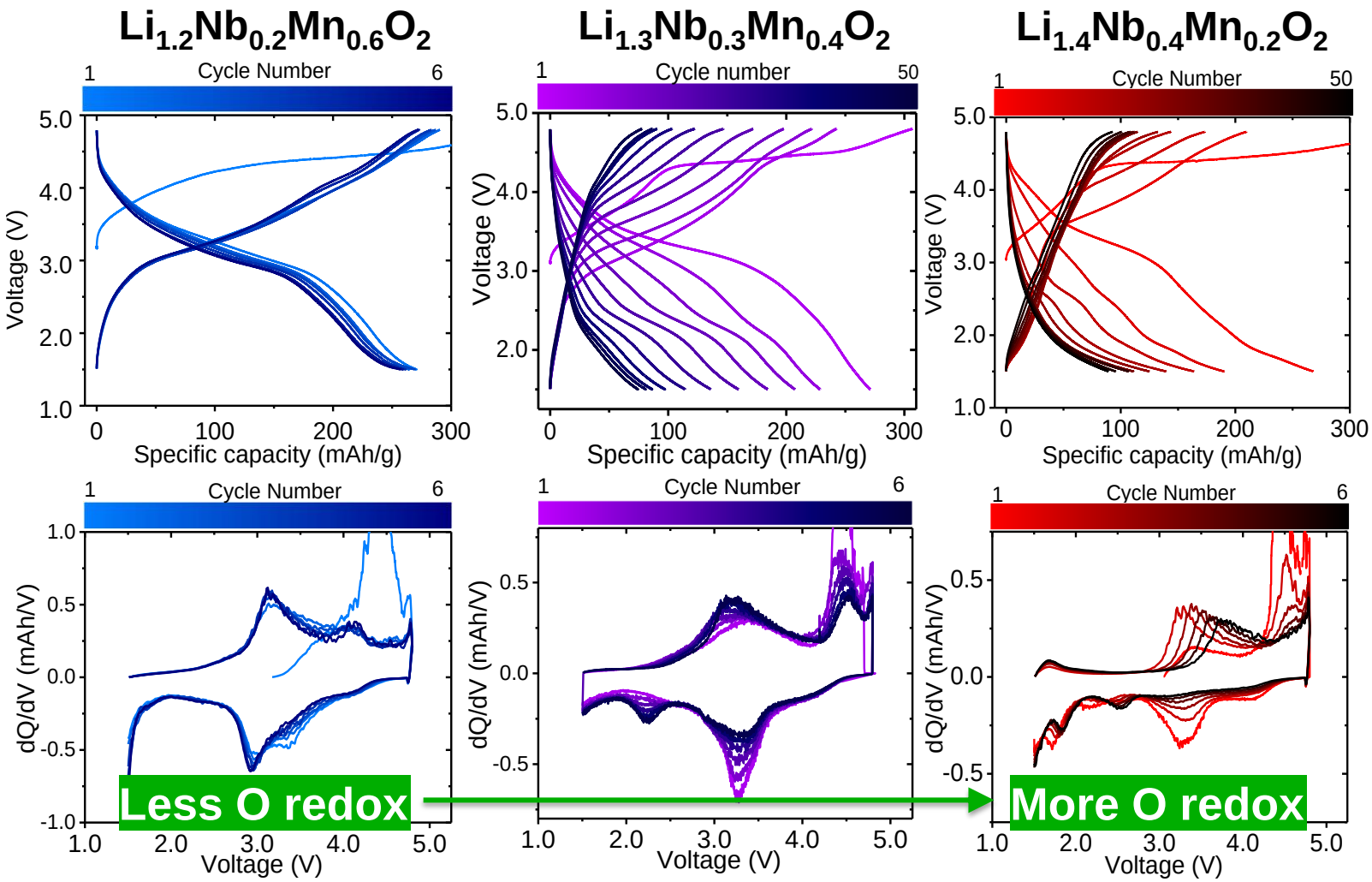






- Cycling stability (capacity and average voltage) decreases with increasing extent of O redox at high voltages.

Balancing capacity and stability



- Extent of O redox increases with Li/O ratio in the TM oxide formula.
- Material optimization critical in order to achieve stable cycling of high-capacity Li-rich oxide cathodes.

Responses to Previous Year Reviewers' Comments

DOE Merit Review, June 2017

A total of three reviewers evaluated the project. Overall, the reviewers' comments were very positive. They noted that "the PI has an excellent approach", "extensive work was performed by the research team" and "collaboration is excellent". Specific comments and suggestions are addressed below:

Recommendation/Comment: The PI please consider more direct comparison with modeling.

Response/Action: We have worked closely with modeling effort led by G. Ceder and K. Persson at UC Berkeley this year. Some of the results from the collaborative effort will be presented in the related projects.

Recommendation/Comment: The reviewer inquired if one can predict and correlate materials synthesis and processing methods with the final structures and properties.

Response/Action: This is very challenging but possible. There have been early effort in this area from some theory groups and the PI is aware of the work in progress.

Recommendation/Comment: The reviewer asked if this comprehensive study can provide some conclusive remarks on which surface, size, or shape is preferred.

Response/Action: This is one of the project goals. Extensive studies are needed in order to obtain valid conclusions but our crystal samples with carefully controlled physical properties are ideal for obtaining insights on material optimization, particularly regarding which surface, size, or shape is preferred.

Recommendation/Comment: Although the proposed future work seems logical and necessary, it did not appear to the reviewer that there was clear guidance to effectively tackle the challenges. This deficiency also was reflected in the data analysis because no clear guidance was developed to tackle the issues that caused the structure instability in the phase transformation.

Response/Action: We thank the reviewer for the comments. The cation-disordered oxide materials are relatively new to the field. In order to effectively tackle the challenges, this modeling-based project intends to first elucidate the mechanisms/processes behind the performance issues and then develop approaches to address them. We intent to shift our focus to "tackling" once we have a better grasp of the issues.

Collaborations

- Prof. Gerd Ceder and Kristin Persson (UC Berkeley) – modeling
- Dr. Venkat Srinivasan (ANL) - modeling
- Drs. Marca Doeff (LBNL), Dennis Nordlund and Yijin Liu (SSRL), and APS – synchrotron *in situ* and *ex situ* XRD, XAS and FF-TXM-XANES studies
- Drs. Ethan Crumlin and Jinghua Guo (ALS) – synchrotron XPS, XAS studies
- Prof Bryan McCloskey (UC Berkeley) – DEMS
- Dr. Ashfia Huq (ORNL) and Jack Chen (Chinese Academy of Sciences, CAS) – neutron diffraction studies
- Dr. Chongmin Wang (PNNL) – STEM/EELS

Remaining Challenges and Barriers

- Surface chemistry in Li-rich TM oxides – the formation of surface layer due to O loss and TM migration, how the layer thickness evolves and what impact it has on capacity and rate capability are not understood
- Commonly seen issues in LMR cathode materials, such as hysteresis, impedance rise, fast voltage fade and capacity fade, are they intrinsic to Li-rich oxides with oxygen redox or chemistry dependent?
- Can the trade-offs between capacity and stability in Li-rich TM oxides be addressed?
- Fundamental understanding of performance limiting mechanisms/processes in Li-rich TM oxide cathodes needed in order to verify whether O redox can be utilized to develop commercially viable high-energy cathodes

Proposed Future Work

- Further understand the interplay between cation and anion redox processes in Li-rich TM oxides and how to best utilize them both to develop high-energy cathode materials
  - Understand the redox chemistry of oxygen in Li-rich TM oxides
  - Further define the effect of oxygen redox on the performance of the cathodes
  - Determine the impact of oxide chemistry/composition, particle morphology and other modifications on O redox activities and their kinetics
- Investigate surface chemistry, particularly the formation of surface layer due to O loss and TM migration, how the layer thickness evolves and what impact it has on capacity and rate capability of the oxides
- Develop mitigating approaches to address the identified issues, particularly regarding the capacity and stability trade-offs when utilizing oxygen redox process

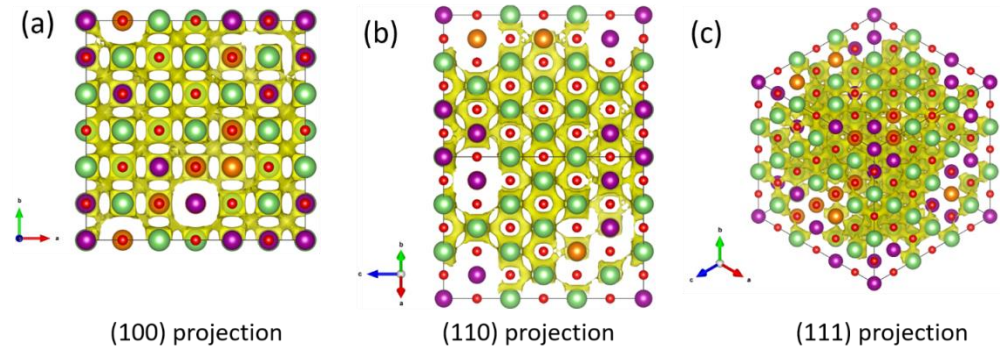
Summary

- Elucidated the charge storage mechanism in a novel high-capacity Li-rich TM oxide and experimentally validated the contribution of oxygen redox to the extra capacity.
- Evaluated kinetics of the oxide cathode. Visualized Li diffusion pathways in cation-disordered Li-rich oxides using X-ray microscopy and demonstrated how short-range ordering can be used to direct Li movement.
- Revealed the effect of involving oxygen redox on the performance of Li-rich TM oxide cathode, which includes reduced kinetics, particle morphology damage, TM reduction and chemical irreversibility.
- Provided insights on using material optimization to balance capacity and stability of cation-disordered Li-rich oxides.

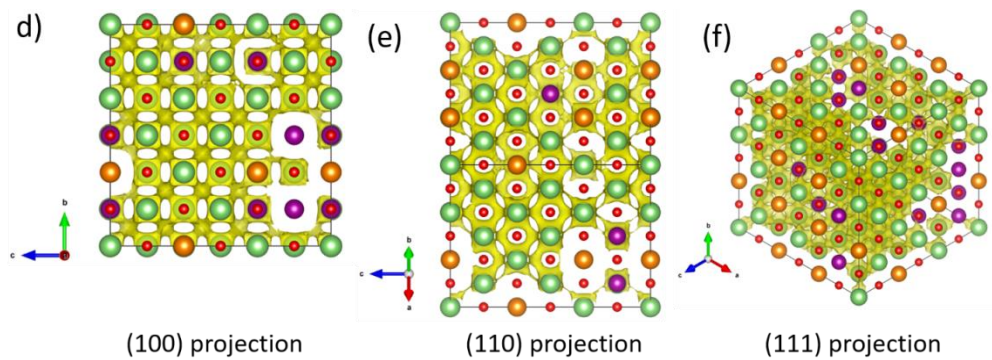
Technical Back-Up Slides

Short-range ordering disrupts Li-ion conduction network in rock-salt oxides

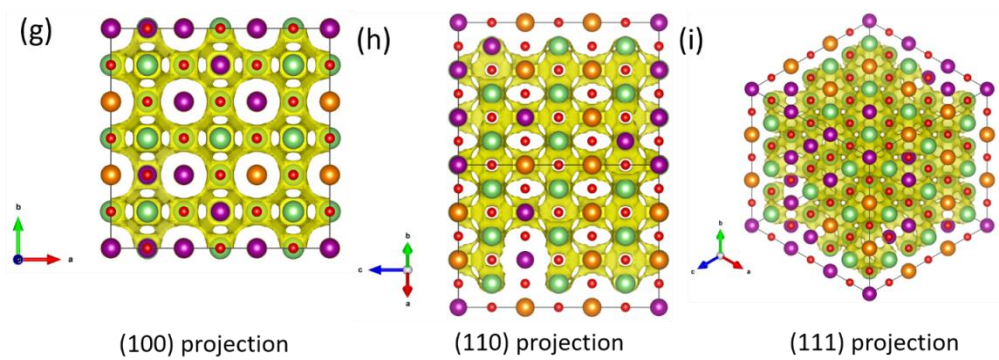
Random cation configuration



Nb cation ordering

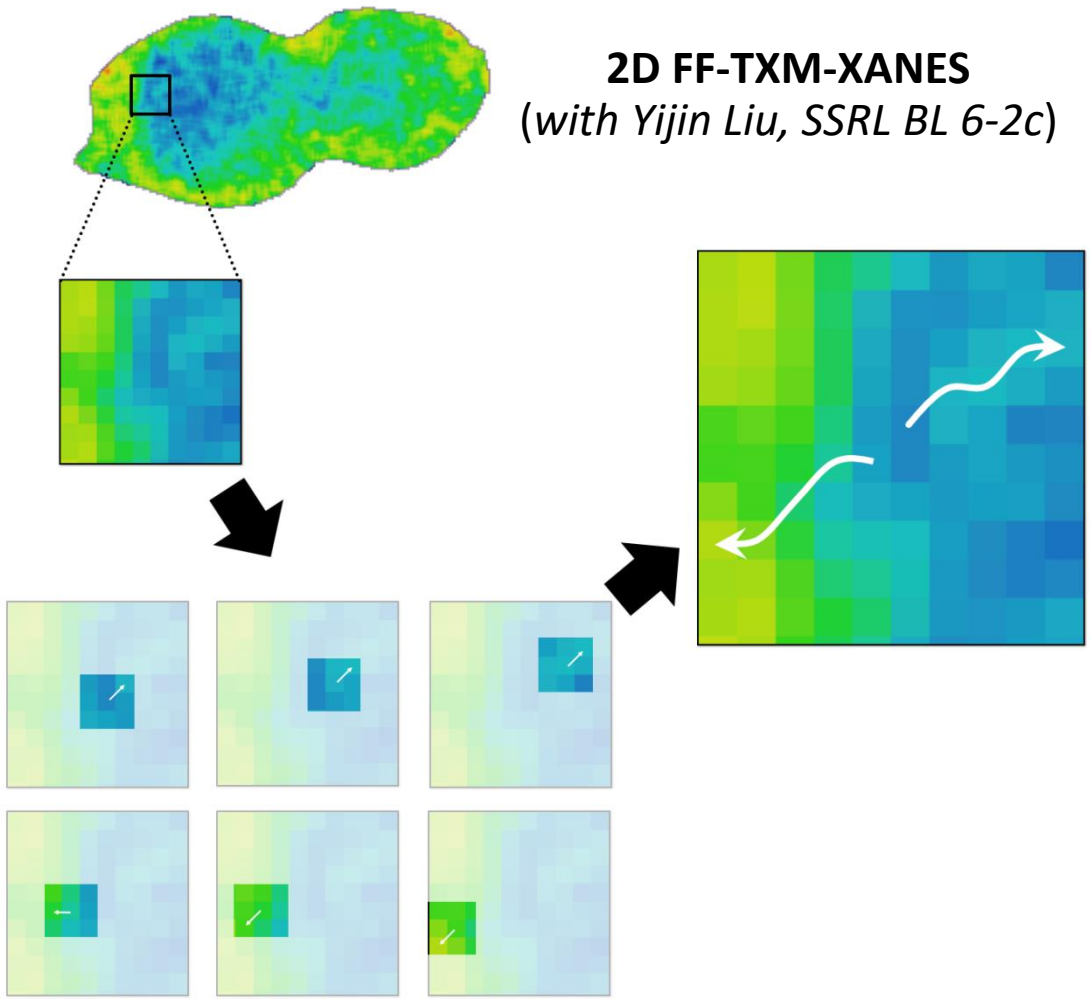


Mixed Mn-Nb cation ordering with Nb enrichment



- 3D contour surfaces for Li-ion percolation network at various projections were constructed from BVS mismatch calculation of $Li_{1.3}Nb_{0.3}Mn_{0.4}O_2$ supercells with different cation configurations.
- Structural ordering causes disruption in otherwise percolating network for Li diffusion.
- Strong impact of the local structural feature on the Li-ion diffusion pathways in cation-disordered rock-salt oxides revealed.

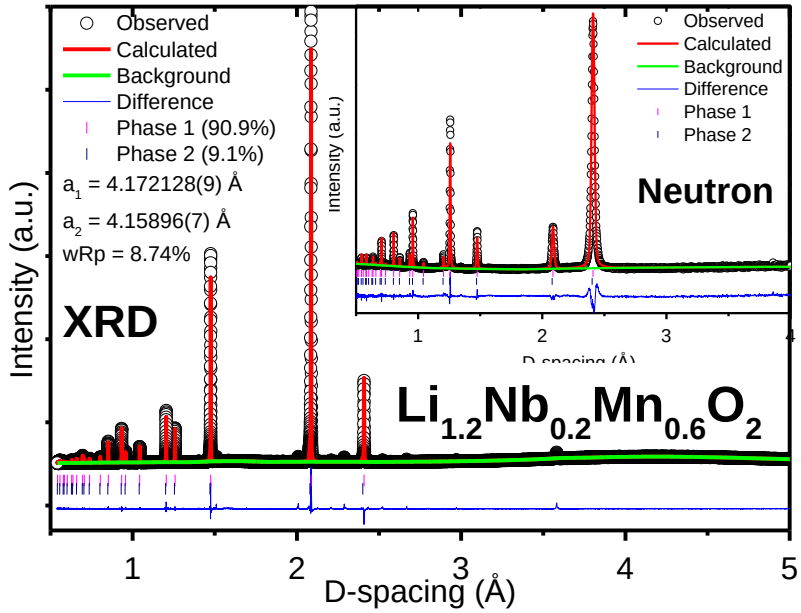
Numerical method for tracing Li diffusion pathway

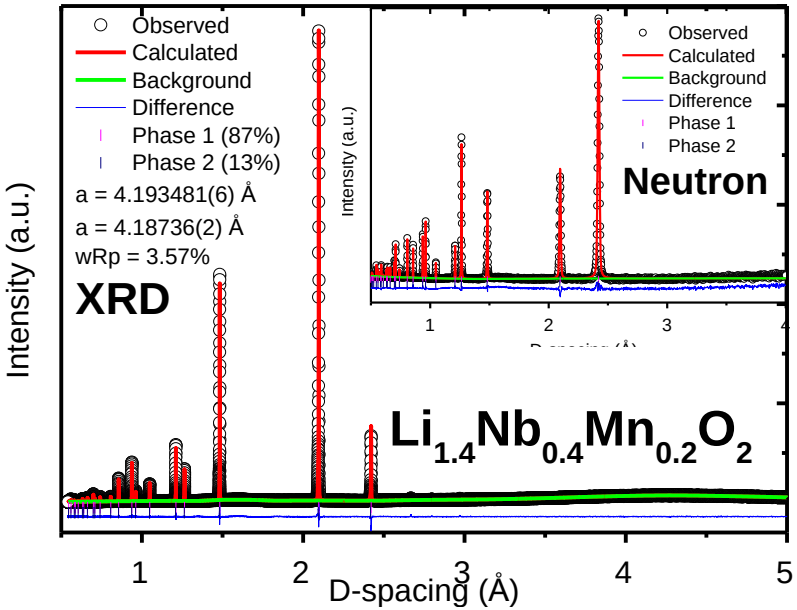


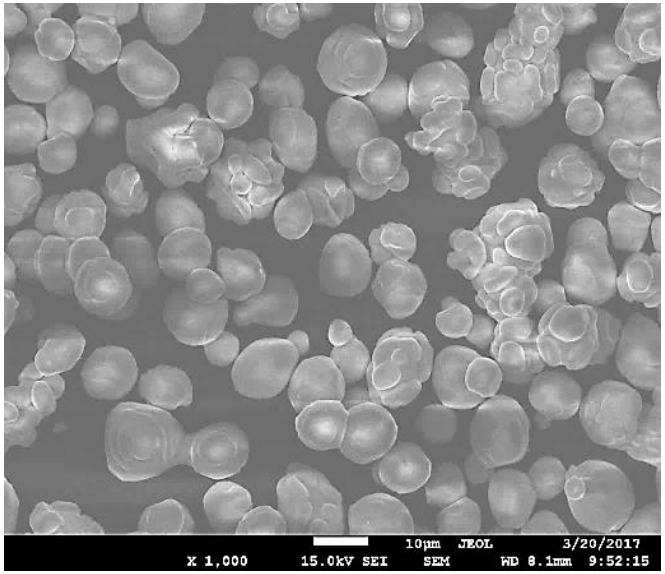
Li diffusion pathway traced by means of the largest local chemical gradient within a reasonable range

- For every single pixel, the local chemical gradient is calculated to identify the direction of the optimal local over-potential.
- The center pixel is then moved to the neighboring pixel with the optimal local over-potential.
- This process is iterated to trace the Li diffusion pathway pixel by pixel. Two of the examples are shown.

Structure and morphology of synthesized oxides







- Structural data obtained through combined refinement of synchrotron XRD and neutron patterns show pristine samples were phase pure rock-salts with no oxygen vacancies.
- Particle morphology similar to that of $Li_{1.3}Nb_{0.3}Mn_{0.4}O_2$ sample.