



Advanced Microscopies of Next-Generation Lithium-Ion Battery Cathode Materials

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Overview

Timeline

- Start date: October 2018
- End date: September 2021
- Percent complete: 86%

Budget

- Total project funding
 - FY19 \$3,125 M (LBNL, ORNL, PNNL, UCSB)
 - FY20 \$2.375 M (LBNL, ORNL, PNNL, UCSB)
 - FY21 \$3.125 M (LBNL, ORNL, PNNL, UCSB)
- BAT376, BAT404, BAT405 and BAT406 (LBNL, ORNL, PNNL, UCSB)



Barriers Addressed

- Energy density
- Cycle life
- Cost

Partners

- Lawrence Berkeley National Laboratory
- Oak Ridge National laboratory
- Pacific Northwest National Laboratory
- UC Santa Barbara

Relevance

- This characterization endeavor is to probe the structural and chemical evolution of the next-generation cathode materials. It is relevant to the cathode deep-dive effort, targeting to delineate at atomic and electronic levels on factors that critically control the performance of the cathode materials.
- Electrochemical properties of cation-disordered rock cathode is closely related to the structural and chemical evolution of the cathode upon cycling. Revealing atomic-scale structural and chemical evolution will provide insight for designing better cathode materials.
- During the material optimization process, electron microscopic characterization will be fully integrated into each step of the process for understanding the effects of different process parameters on the capacity and long-term stability of modified cathode materials.
- Both *ex-situ* and *in situ* TEM will be used to directly observe the characteristics of the layer-based cathode materials and the electrolyte interface structures and chemistry with respect to surface coatings.



Milestones

- Establish the nature of the short-range order in DRX cathode; Reveal the CEI layer formation process in low-Co concentration cathode. (Q1, December 31, 2020; Completed)
- Determine the structural evolution of the DRX upon battery cycling; Determine the origin of the void formation in the low-Co cathode. (Q2, March 31, 2021; Completed)
- Determine the F evolution in DRX; Reveal the true nature and the origin of the cracks in the layer structured cathode. (Q3, June 30, 2021 on track)
- Identify the critical parameters that control the stability of DRX and low-Co cathode (Q4, September 30, 2021 on track)



Approach

- To get insights into the structural and chemical information at atomic resolution, aberration-corrected STEM-HAADF atomic-level imaging combined with atomic level EDS chemical analysis and EELS on atomic-level electronic structure will be used to probe the microstructural, chemical and electronic evolution of the cathode before and after the electrochemical cycling.
- EELS and EDS mapping will be used to explore the elemental distribution both within the bulk lattice and at the particle surface to gain information of local structures and the interaction of electrolyte and cathode in the structure and chemistry of solid electrolyte interphase layer.
- Direct correlation of the structural and chemical information with battery properties will provide insight on the capacity degradation mechanism of both cation-disordered rock-salt structured materials and Co-free cathode with different compositions, substitution, and surface modification.
- This characterization task will be closely integrated with the materials development and modeling tasks for guiding the designing of next-generation cathode materials toward high-performance cathode.

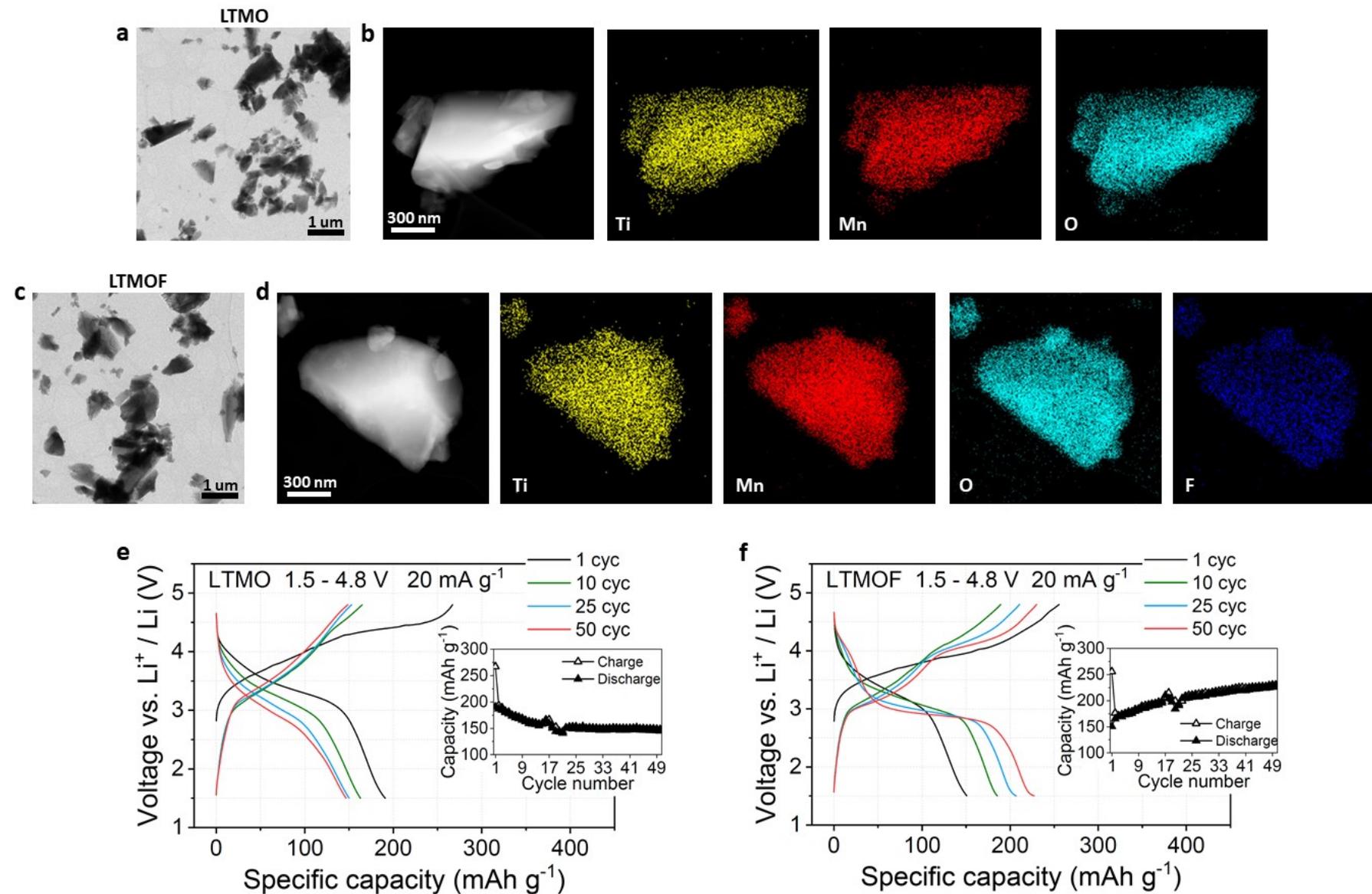


Technical Accomplishments and Progress

- Combining electrochemical measurements and scanning transmission electron microscopy, we examine the correlation between the electrochemical properties and structural evolution in cation-disordered rocksalt cathodes
- Revealed the surface structural evolution of DRX and its correlation with F dopant
- Discovered that fluorination strongly suppresses surface structural degradation, therefore greatly enhancing the cyclability of the cathode
- Discovered a novel rocksalt-to-spinel-like structural transformation, which surprisingly contributes to a gradual capacity increase during cycling
- Revealed the nature, origin, and behavior of voids that commonly seen in NMC cathode
- Using scanning transmission electron microscopy, revealed a cycling-induced vacancies aggregation behavior in a layer structured cathode
- Discovered that during the initial charging, vacancies aggregate to form nanoclusters at the outer layer of the secondary particle, which subsequently extend to the inner part of particle upon fully charged. With extended cycling, these nanoscale vacancy clusters become immobilized
- Solved a long-standing puzzle on the origin, nature, and behavior of the commonly visible vacancy clusters in the layered cathode



Morphology, composition, and electrochemical properties of LTMO and LTMOF particles



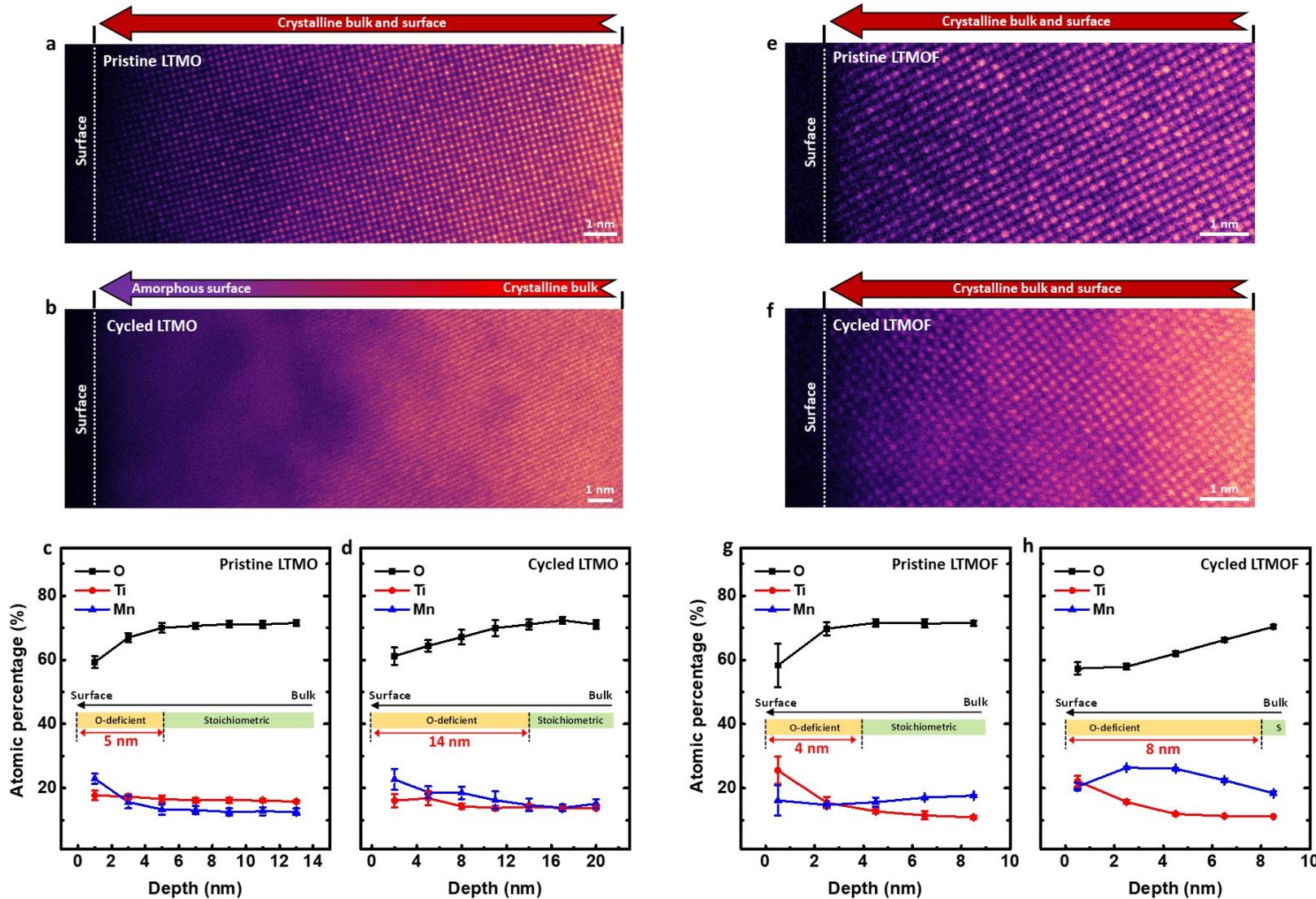
Recent studies have shown that fluorination of DRX cathodes can effectively reduce the oxygen loss and improve the cycling stability; however, the underlying atomic-scale mechanisms remain elusive

TEM, STEM-HAADF and STEM-EDS of the $\text{Li}_{1.2}\text{Ti}_{0.4}\text{Mn}_{0.4}\text{O}_{2.0}$ (LTMO), and its fluorinated variant, $\text{Li}_{1.2}\text{Ti}_{0.2}\text{Mn}_{0.6}\text{O}_{1.8}\text{F}_{0.2}$ (LTMOF) at pristine state

Showing a uniform elemental distribution

The LTMOF shows capacity increase upon long term cycling

Structural and chemical evolution in LTMO and LTMOF cathodes induced by cycling



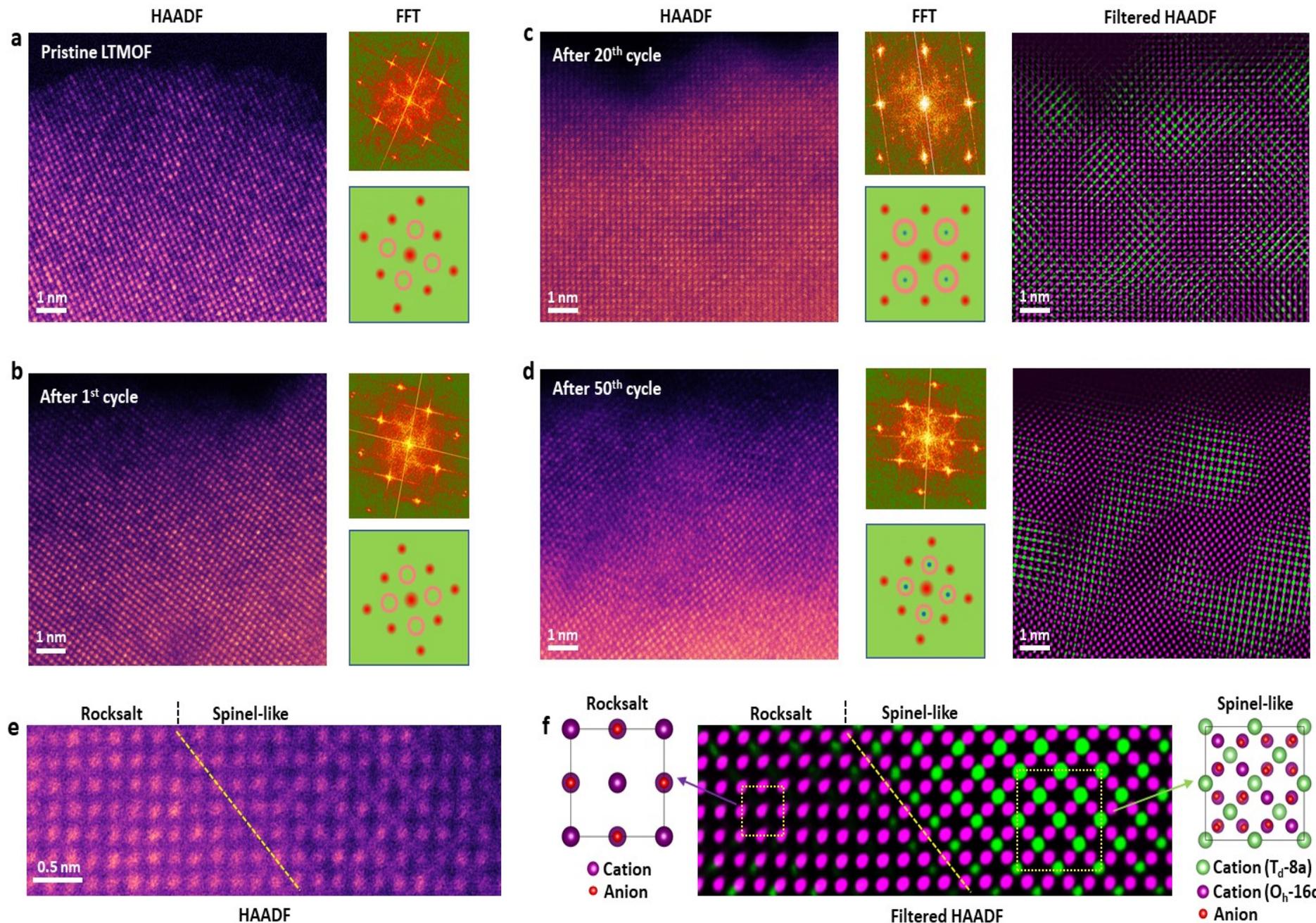
➤ Atomic-resolution STEM HAADF images of nanoscale surface regions in LTMO and LTMOF at the pristine state and at the discharged state after 50 cycles

➤ Revealing the surface amorphization and formation of vacancy clusters in the LTMO at the surface region due to oxygen loss

➤ For the case of LTMOF, upon cycling, the lattice is rather stable, indicating the addition of F stabilizes the crystalline lattice



Structural transformation in LTMOF cathode induced by cycling

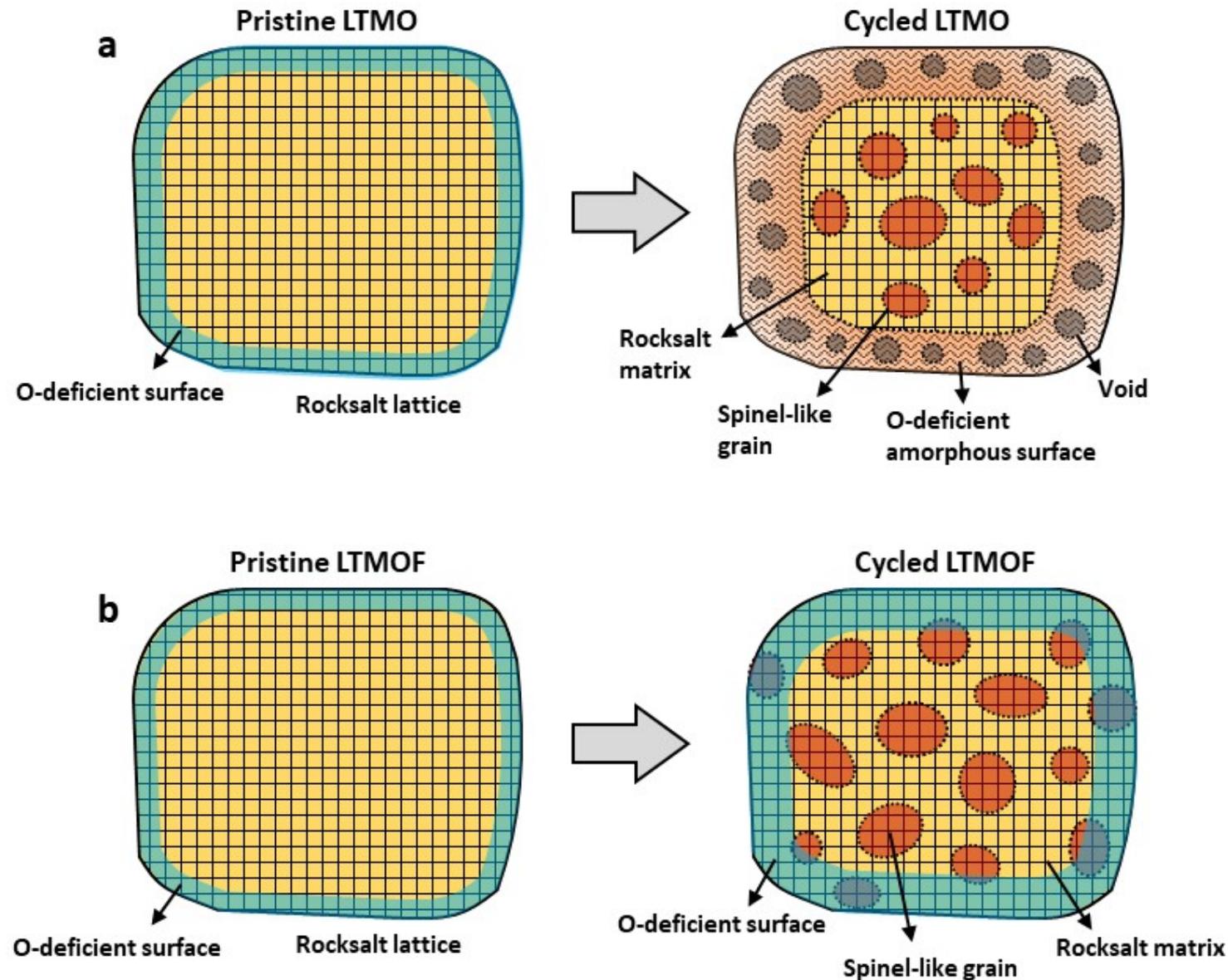


➤ Atomic STEM-HAADF image of LTMOF before and after 50 cycles reveal additional diffraction spots

➤ Indicating that upon cycling a transformation from the rocksalt to a δ -phase with spinel-like features in the LTMOF particles



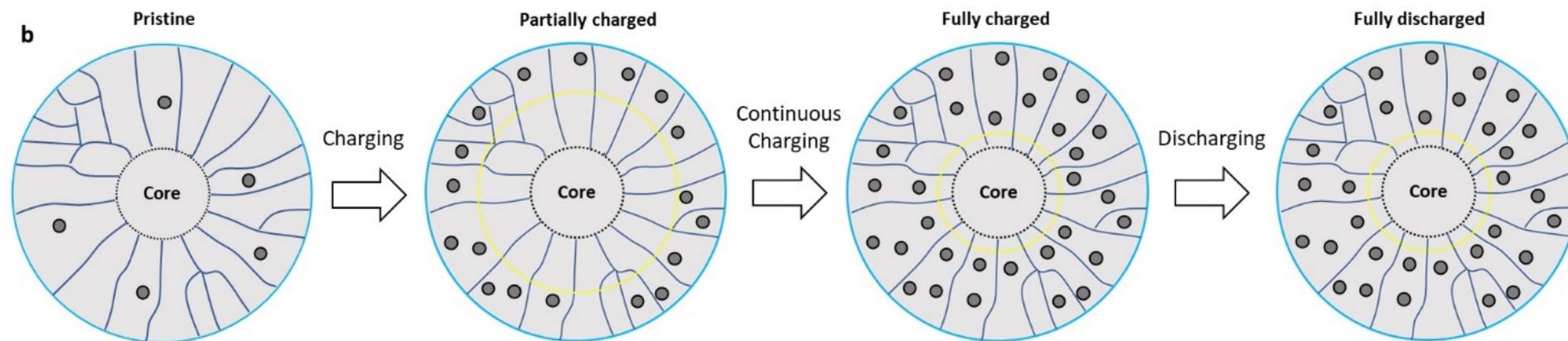
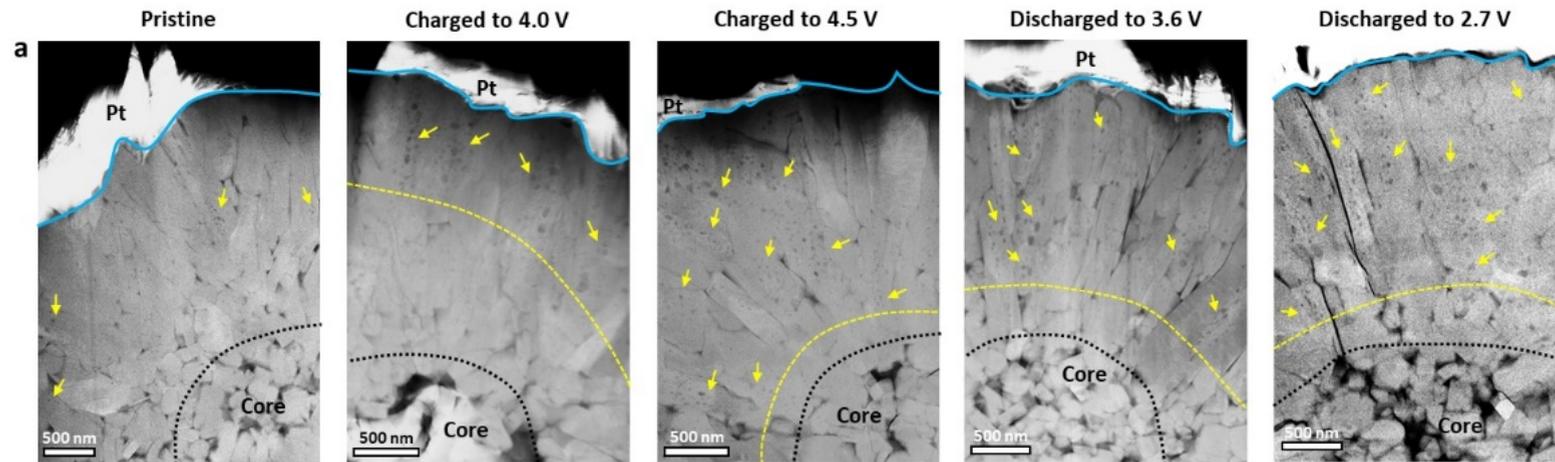
Schematic illustration of structural and chemical evolution in LTMO and LTMOF induced by cycling



- ▶ In LTMO, electrochemical cycling results in surface degradation, such as amorphization and void formation, and rocksalt-to-spinel-like structural transformation within nanosized grains dispersed in the DRX matrix
- ▶ In LTMOF, electrochemical cycling results in rocksalt-to-spinel-like structural transformation within nanosized grains dispersed in the DRX matrix, whereas the crystalline surface remains well preserved



Structural evolution during the first cycle in the $\text{LiNi}_{0.76}\text{Mn}_{0.14}\text{Co}_{0.1}\text{O}_2$ cathode particles, featuring the formation of void within the primary particle



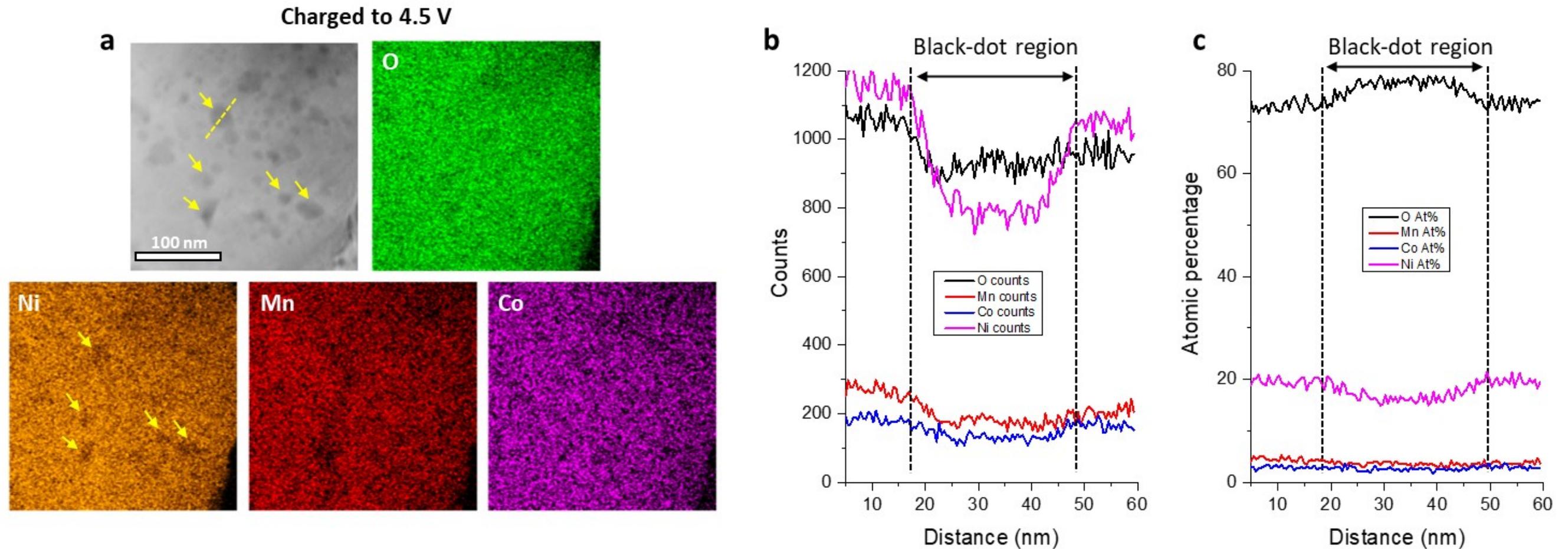
➤ STEM HAADF images and schematics to show the distribution of black-dot-like nanoregions (or “black-dots”) within the secondary particles at the pristine, partially charged (4.0 V), fully charged (4.5 V), partially discharged (3.6 V), and fully discharged (2.7 V) states in the first cycle

➤ Similar structural feature has been well recognized, while the origin, the nature and the behavior of this feature remains unclear

➤ Systematic work needs to be carried out to figure out the origin and behavior of the dark contrasted dots



STEM-EDS mapping to reveal the black dots in the NMC are vacancy clusters



STEM HAADF image and corresponding STEM EDS elemental maps of the $\text{LiNi}_{0.76}\text{Mn}_{0.14}\text{Co}_{0.1}\text{O}_2$ particle at the fully charged state during the first cycle

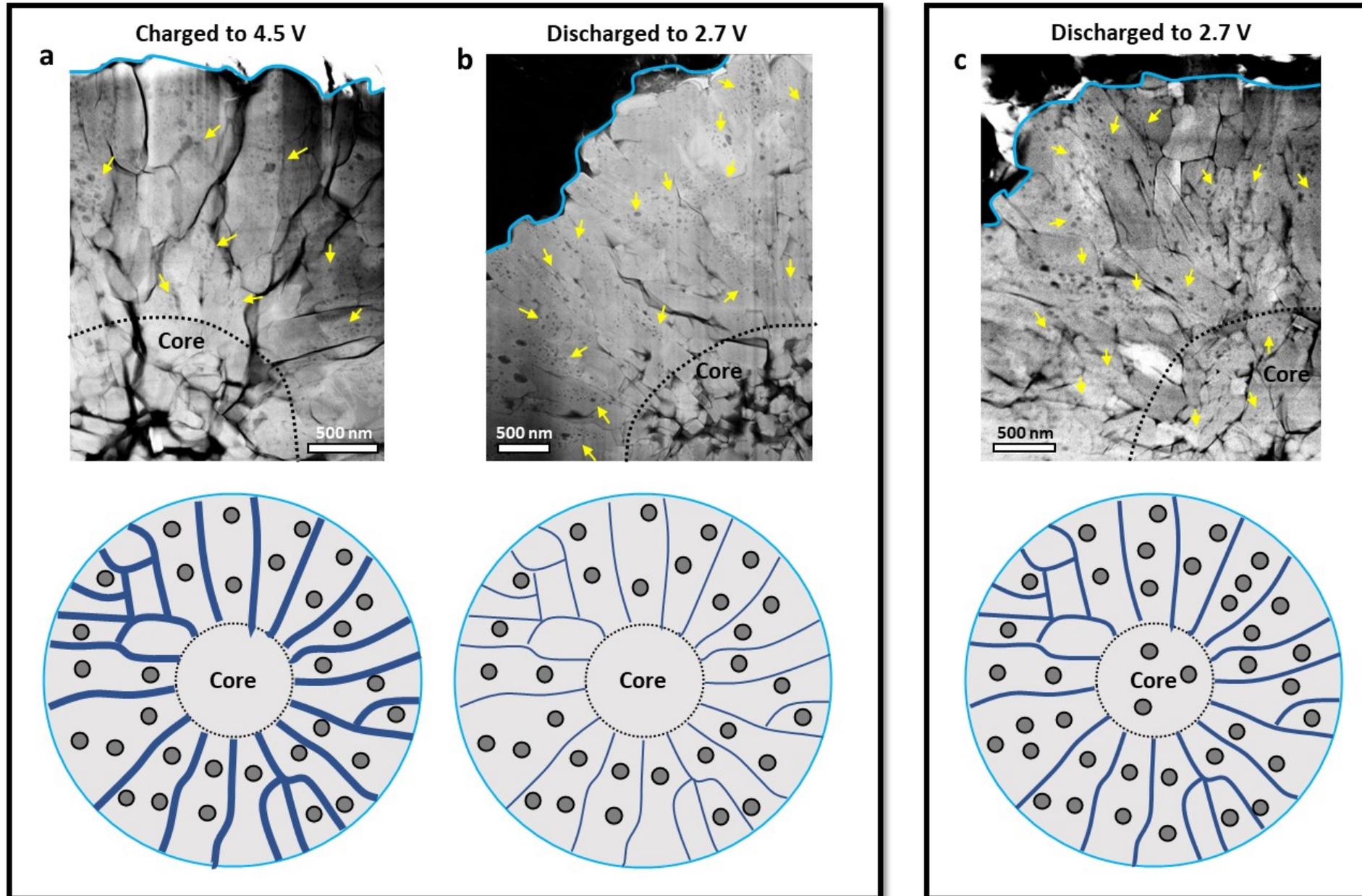
Reveal the black dots region corresponds to the materials loss in the $\text{LiNi}_{0.76}\text{Mn}_{0.14}\text{Co}_{0.1}\text{O}_2$ cathode particle



The behavior of vacancy clusters in the NMC cathode during extended cycling of the battery

50th Cycle

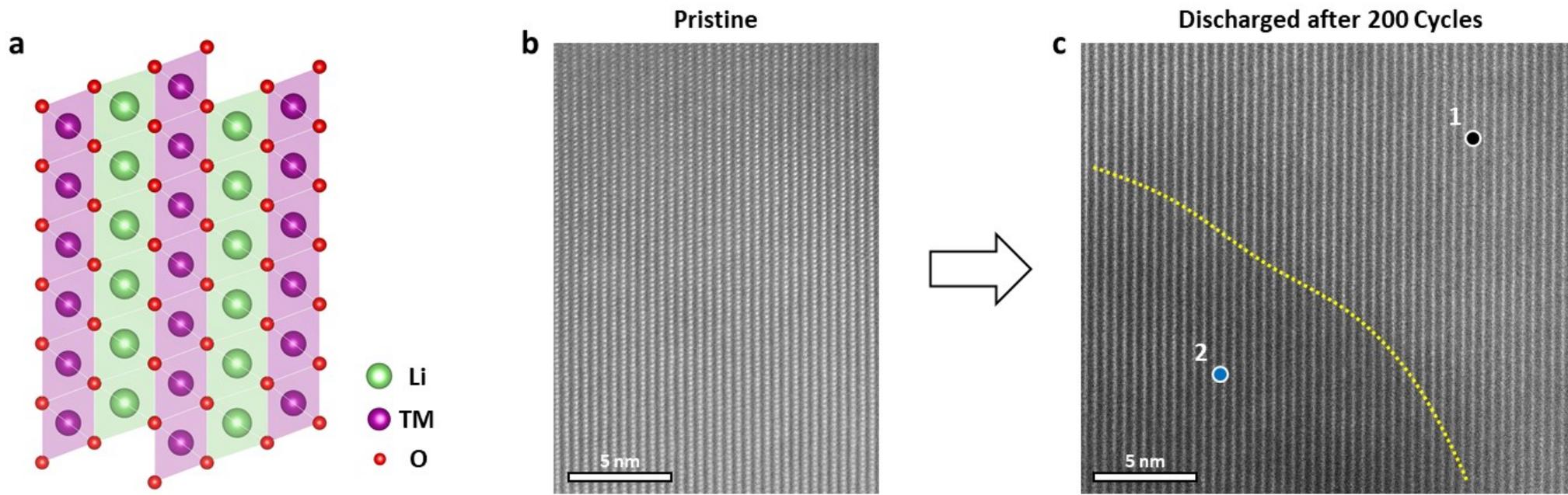
200th Cycle



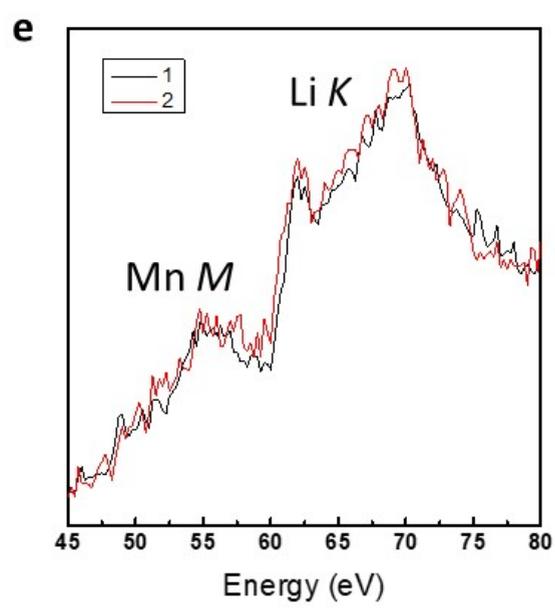
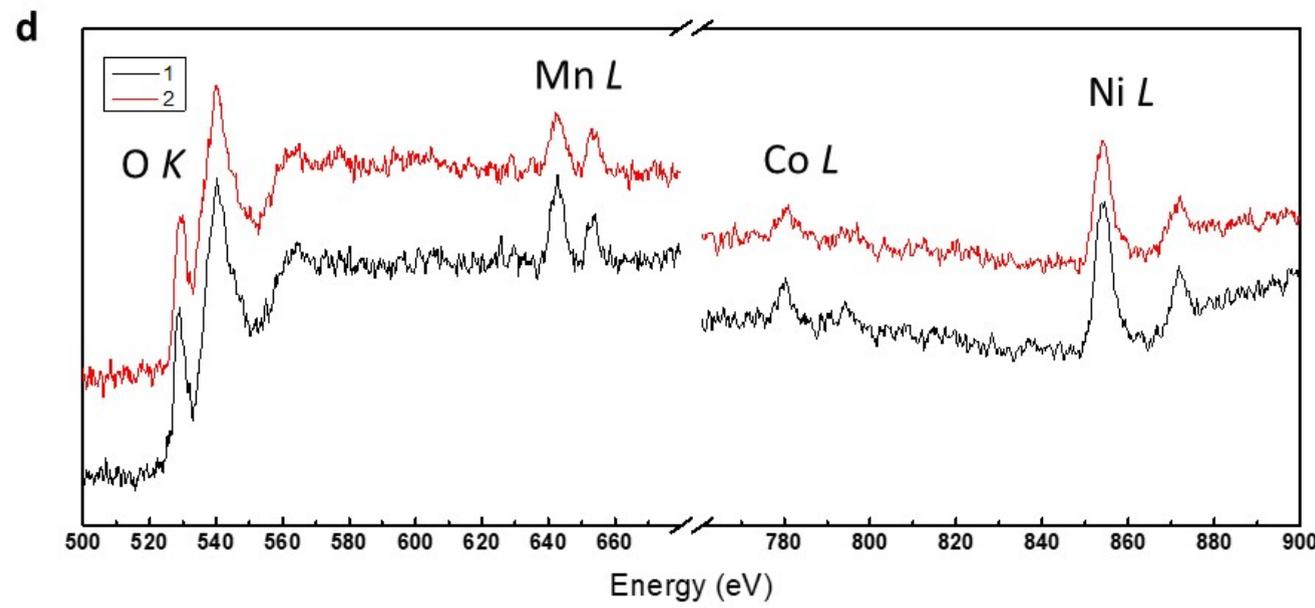
- STEM-HAADF images and schematic to show the Structures of the $\text{LiNi}_{0.76}\text{Mn}_{0.14}\text{Co}_{0.1}\text{O}_2$ cathode particles after 50 and 200 cycles
- The black-dot has been identified to be vacancy clusters
- With cycling, high density of the vacancy clusters begin to populate the primary particle
- With extended cycling, the vacancy clusters grow large and becomes immobilized



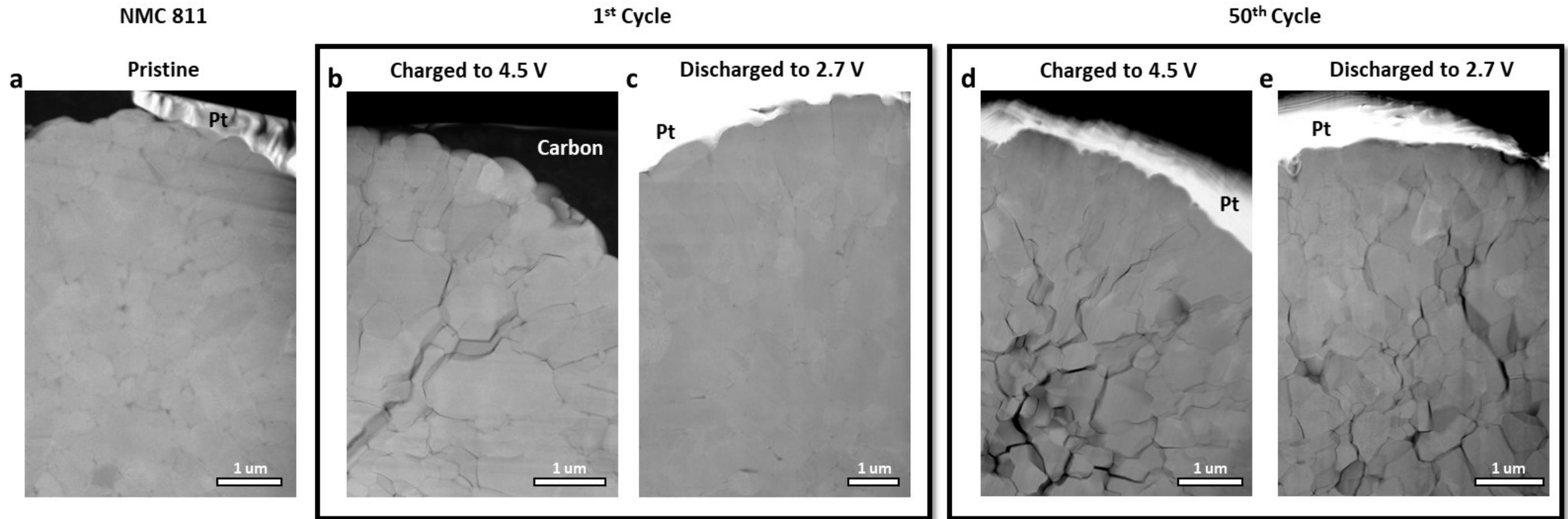
Atomic and electronic structures of the $\text{LiNi}_{0.76}\text{Mn}_{0.14}\text{Co}_{0.1}\text{O}_2$ cathode particles



➤ STEM-HAADF image and STEM-EELS reveal the electronic structure at the vacancy cluster region shows no difference as compared with that of pristine state



Using commercial NMC811 as a benchmark material to reveal the origin of the vacancy cluster as seen in some NMC



- STEM-HAADF images of the NMC811 cathode particles at pristine and following different cycles
- No vacancy cluster can be seen in the commercial NMC811
- Demonstrating that the vacancy clusters seen in some NMC are introduced during the materials fabrication, which aggregates during the battery cycling

Responses to Previous Year Reviewers' Comments

- ▶ Made a poster presentation; the project was not reviewed in 2019



Collaboration and Coordination with Other Institutions

Partners:

- Lawrence Berkeley National Laboratory: Preparation of disordered rock-salt-structured cathode materials and computational modeling
- Argonne National Laboratory: Preparation of low-Co and Co-free cathode materials
- Oak Ridge National Laboratory: Low-Co and Co-free cathode materials, disordered rock-salt-structured cathode
- Hummingbird Scientific Inc.: Help to develop the liquid holder
- Thermo Fisher Scientific Inc.: *In situ* and ETEM capability development
- Battery Research Group at PNNL: Preparation of low-Co and Co-free cathode



Remaining Challenges and Barriers

- How does the short-range order evolve upon battery cycling?
- How do F, O, and Li correlate in the DRX lattice and affect the electrochemical properties?
- What is the structure and composition of the cathode electrolyte interface in DRX?
- How does the bulk lattice evolve in LiNiO_2 ?
- How does oxygen evolve in the cathode of both layered and disordered rock salt structures?
- What is the origin of the intragranular cracking in the layered cathode?



Proposed Future Work

FY2021

- Explore Mn valence distribution in the DRX with and without F dopant upon battery cycling
- Probe into the bulk lattice phase transition of LiNiO_2 during the cycling of the battery

FY2022

- How does F behavior during the battery cycling of DRX
- What is the dynamic nature of the short-range order in DRX
- Explore the cathode electrolyte interphase in DRX
- Establish the correlation between oxygen release and intragranular cracking in the layer structured cathode
- Determine the correlation between cathode electrolyte interphase and cathode lattice stability with low Co concentration

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



Pacific Northwest
NATIONAL LABORATORY

Summary

- Fluorination of disordered rocksalt structure cathodes can effectively reduce the oxygen loss and improve the cycling stability
- Revealed the correlation between the electrochemical properties and structural evolution in Mn-redox-based DRX cathodes, $\text{Li}_{1.2}\text{Ti}_{0.4-x}\text{Mn}_{0.4+x}\text{O}_{2.0-x}\text{F}_x$ ($x = 0$ and 0.2).
- Discovered that fluorination strongly suppresses structural amorphization and void formation initiated from the particle surface, therefore greatly enhancing the cyclability of the cathode.
- Reveal a novel rocksalt to δ -phase spinel-like structural transformation in the DRX bulk, which contributes to a gradual capacity increase during cycling. Gained important insight for the design of novel DRX cathodes with high capacity and long cycle life.
- Revealed a cycling-induced vacancies aggregation behavior in a layer structured cathode.
- Discovered that during the initial charging, vacancies aggregate to form nanoclusters at the outer layer of the secondary particle, which subsequently extend to the inner part of particle upon fully charged, and with extended cycling, nanoscale vacancy clusters become immobilized.
- Reveal that the generation of these vacancy clusters is correlated to the material-synthesis conditions.
- Solved a long-standing puzzle on the origin, nature, and behavior of the commonly visible vacancy clusters in the layered cathode, providing insights on correlation between properties and dynamic behaviors of atomic-scale defects in layered oxide cathodes.

