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

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Vehicle Technologies Annual Merit Review

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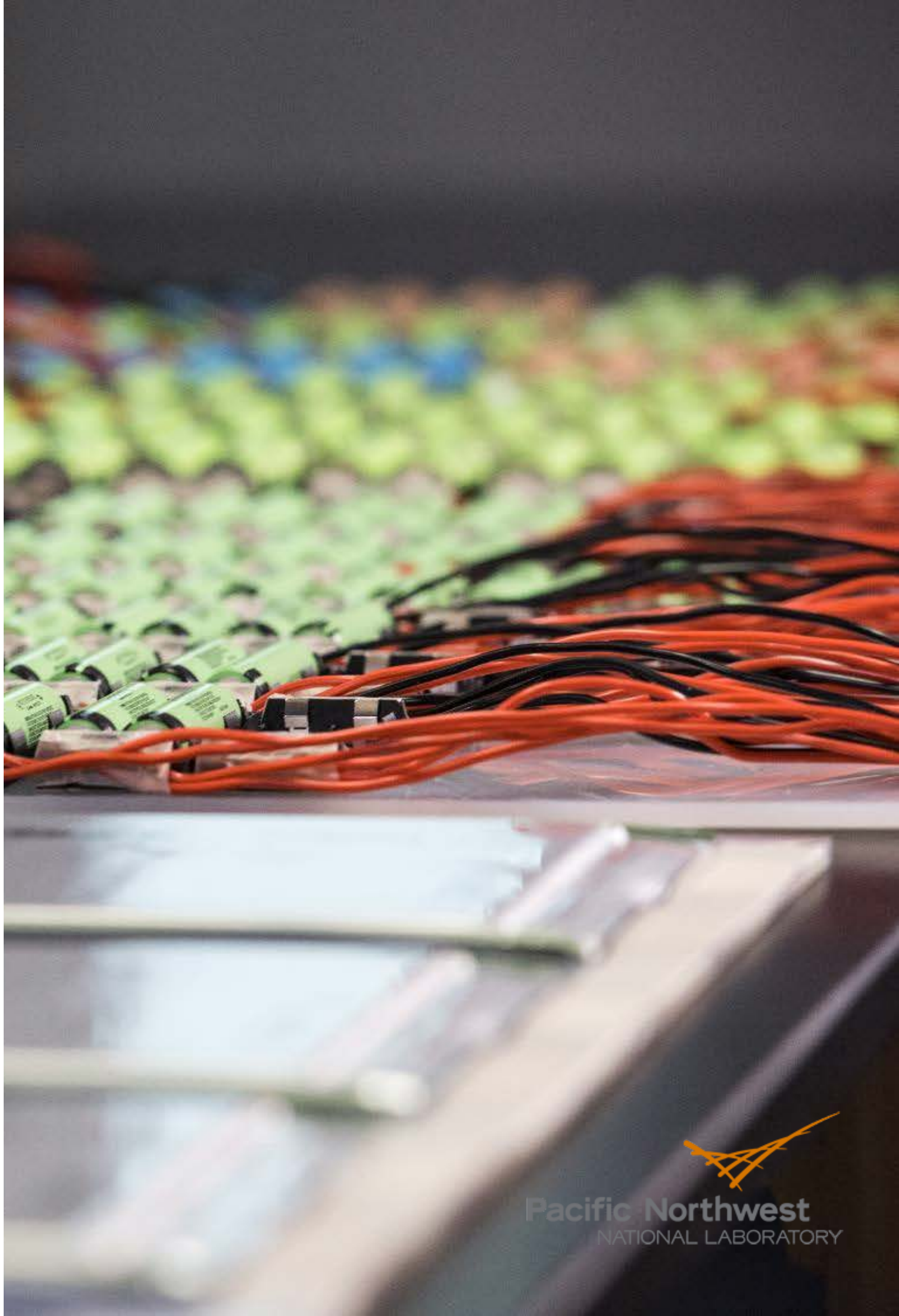
Project ID #bat405



Overview

Timeline

- Start date: Oct. 1, 2018
- End date: Sept. 30, 2021
- Percent complete:22%

Budget

- Total project funding
- DOE share: $450 (2019)
- Funding received in FY 2019: $450k

Barriers addressed

- Fading and failure mechanism of next generation cathode
- Identify critical factors that control the properties of next generation cathode

Partners

- Lawrence Berkeley National Lab
- Argonne National Lab
- Oak Ridge National Laboratory
- National Renewable Energy Lab
- Battery group in PNNL

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Relevance

- To use the state of the art microscopy and spectroscopy to probe into the structural and chemical evolution of next generation cathode materials for lithium ion batteries, typically including low-Co to Co-free metal oxide and cation disordered rocksalt structure. The work will reveal key factors that critically control the degradation mechanism of these two types of cathodes.

- Reveal the behavior and role of Co in the lithium metal oxide cathode and its correlation with the behavior of other cations (Li, Ni, Mn, and other dopant) and anions (O and relevant substitution) and consequently on the electrochemical properties of the cathode materials.

- Delineate the role of cation and anion dopants in the layer structured cathode on their electrochemical properties.

- Characterize the interaction of modified cathode surface with electrolyte and their correlation with electrochemical properties

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Milestones

- Establish correlation of short range order in the cation-disordered rocksalts cathode and their correlation with electrochemical properties; Establish the correlation of Co with other elements on the properties of the cathode materials

- Establish the lattice structural stability of the low-Co cathode with respect to the spatial distribution of the cations and anions

- Discover the correlation between surface and interface structural and chemical evolution with bulk lattice stability and their evolution on the electrochemical properties

- Reveal the mechanism on the interaction of cathode with liquid electrolyte and such interaction on cathode degradation

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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 term 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 rocksalt 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.

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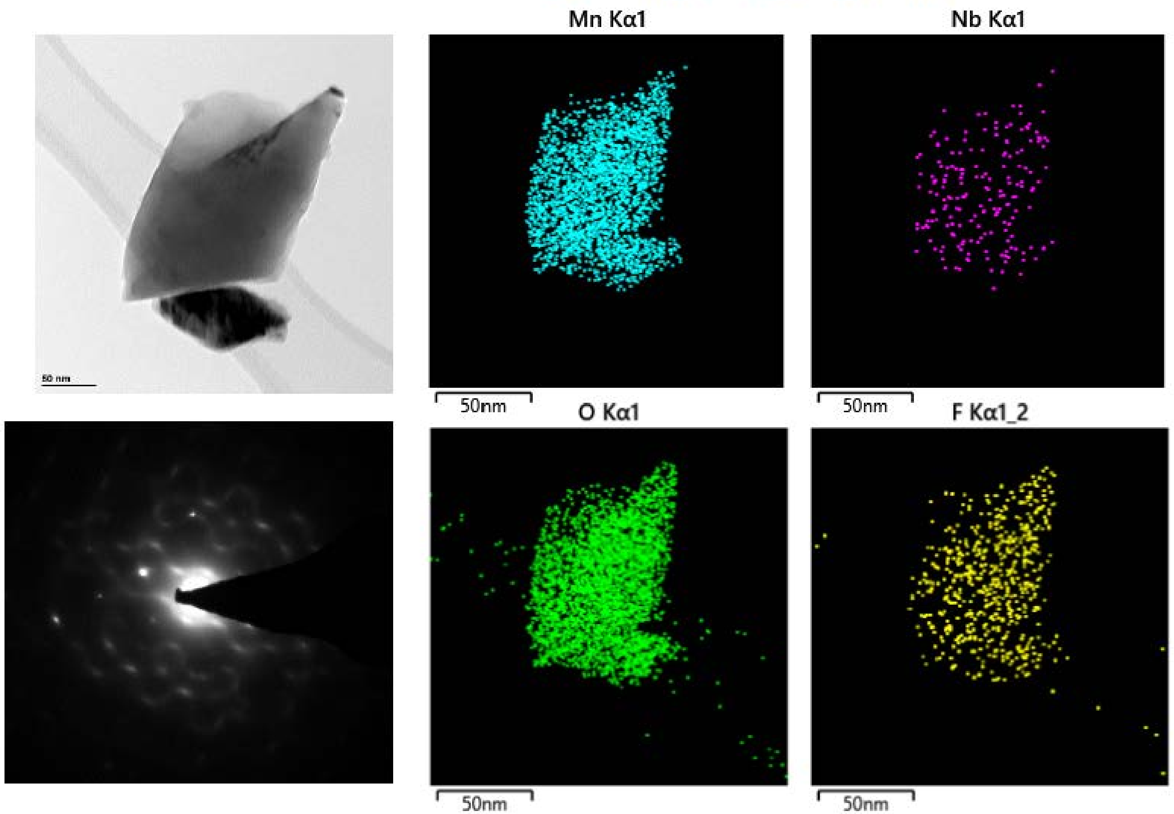
Technical Accomplishments

Revealed the elemental distribution of fluorine doped rock salt structured

$Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$



- Using STEM imaging, electron diffraction analysis, and EDS mapping to probe the structural features of pristine $Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$
- The EDS mapping indicates the F is uniformly distributed at particle level, showing no surface segregation.

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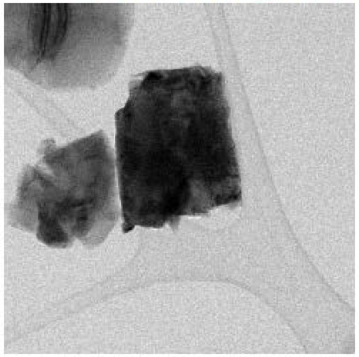
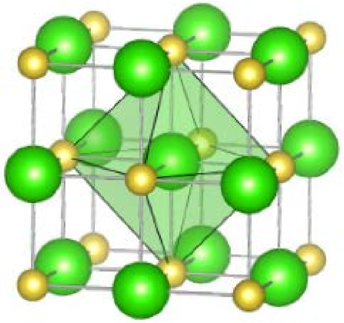
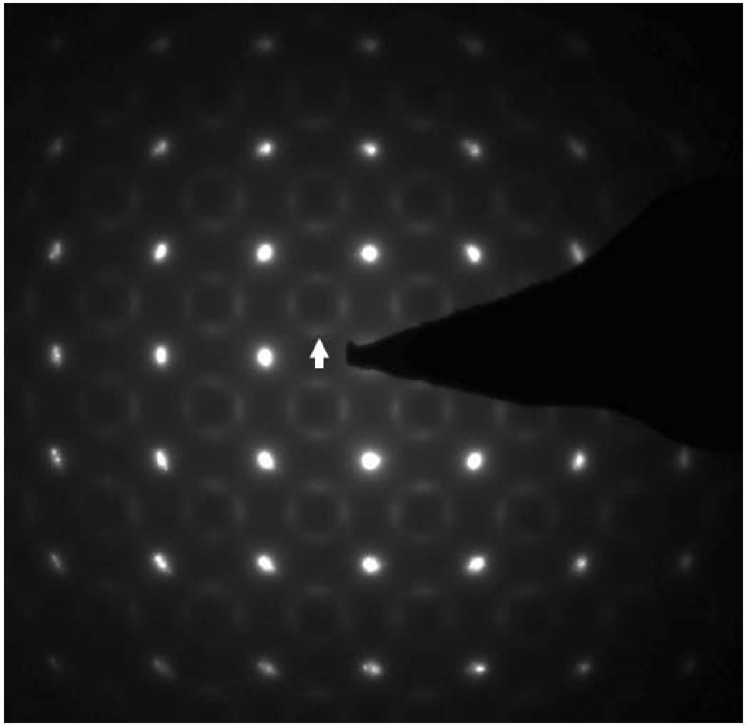
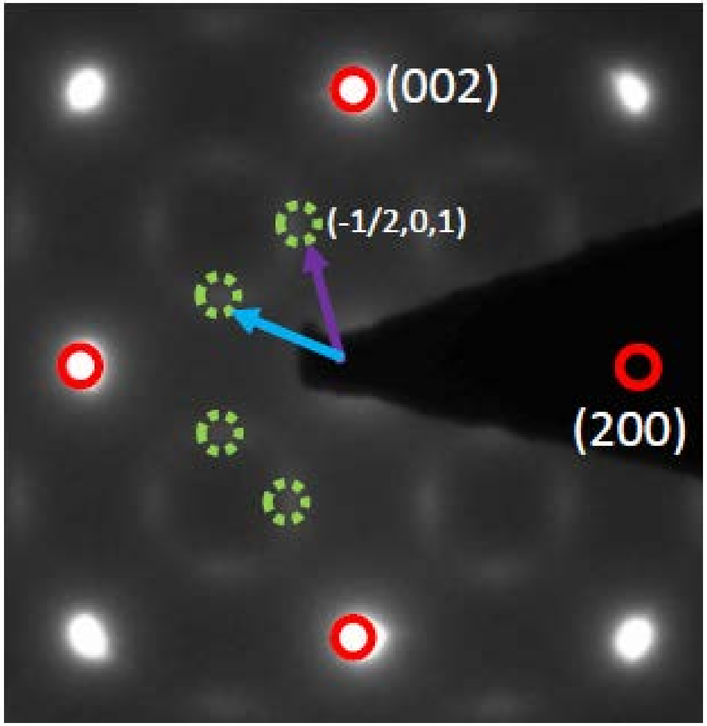
Technical Accomplishments

Electron diffraction revealed short range order in fluorine doped rock salt structured $Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$





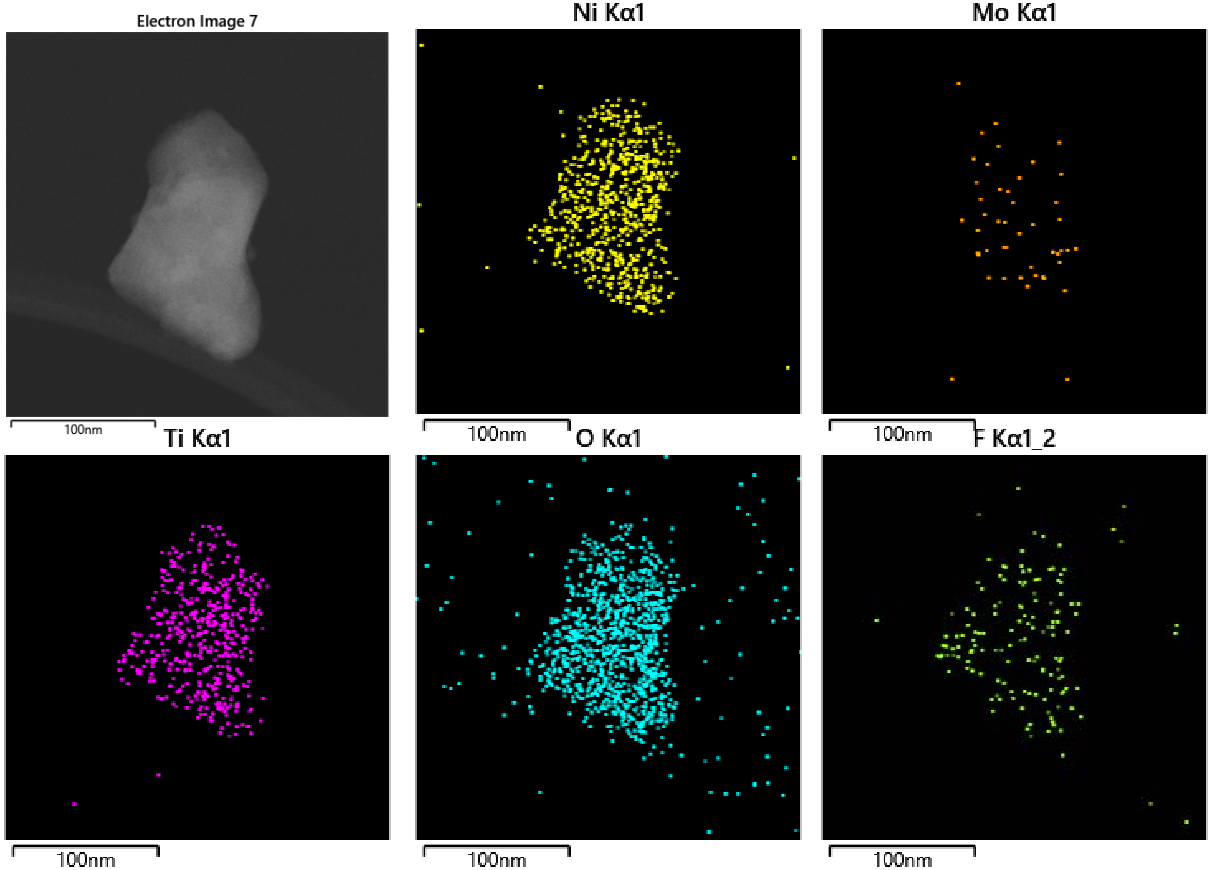




- Electron diffraction analysis shows diffuse scattering intensity, indicating the short rnage order in the pristine $Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$

Technical Accomplishments

STEM image and EDS maps revealed elemental distribution in fluorine doped rock salt structured $Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$ (NTMOF)



- Using STEM imaging, electron diffraction analysis, and EDS mapping to probe the structural features of pristine $Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$ (NTMOF).
- The EDS mapping indicates the F is uniformly distributed at particle level, showing no surface segregation.

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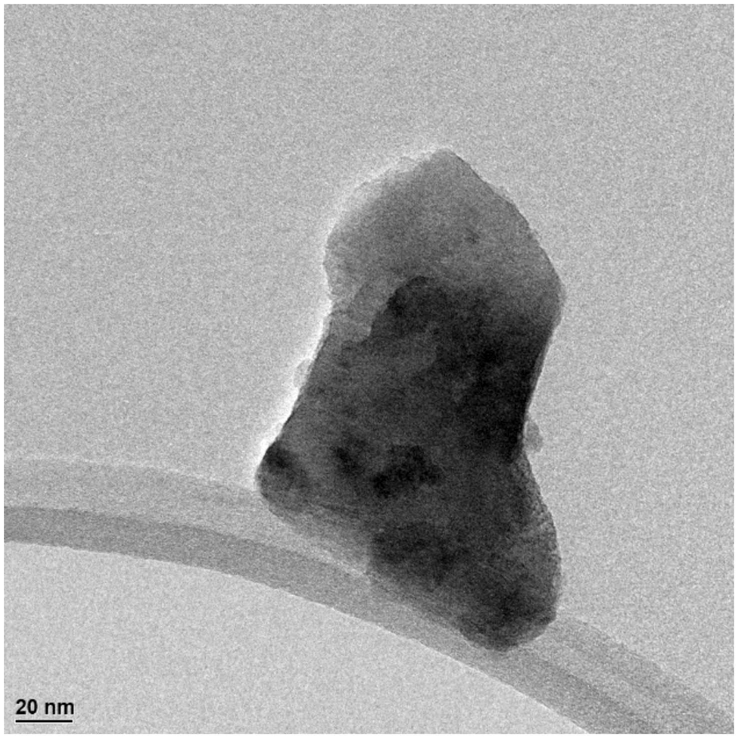
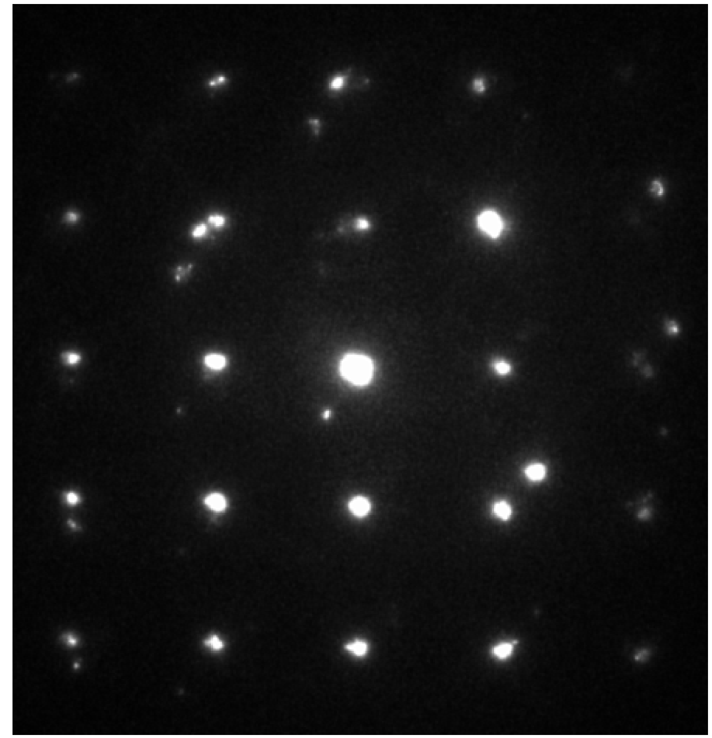
Technical Accomplishments

TEM image and electron diffraction revealed no short range order in fluorine doped rock salt structured $Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$ (NTMOF)





- Using TEM imaging and electron diffraction analysis reveal no short range order in of pristine $Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$ (NTMOF).

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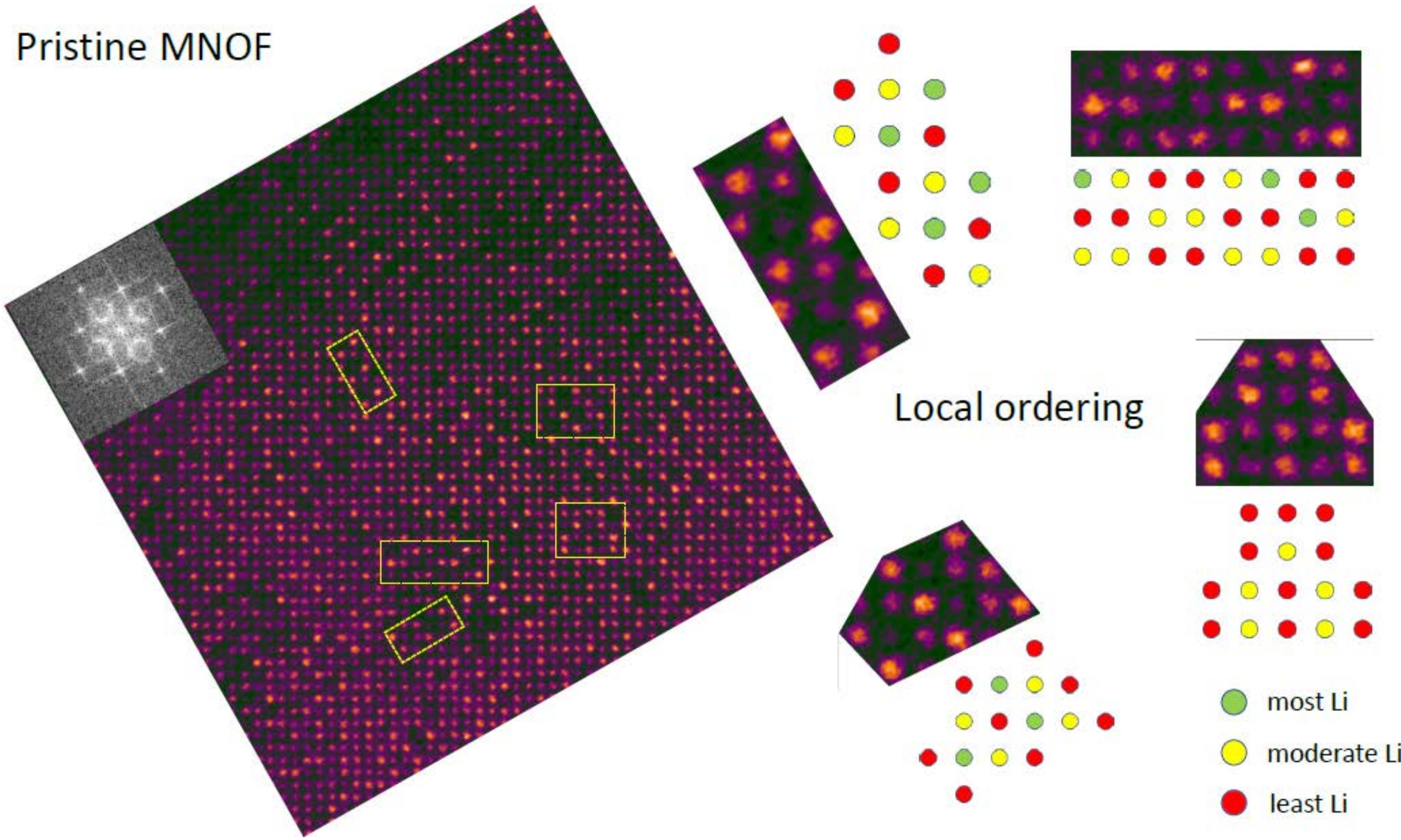
Technical Accomplishments

STEM-HAADF image to reveal short range order in fluorine doped rock salt structured $Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$



- STEM-HAADF image to directly visualize the short range order in the pristine $Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$

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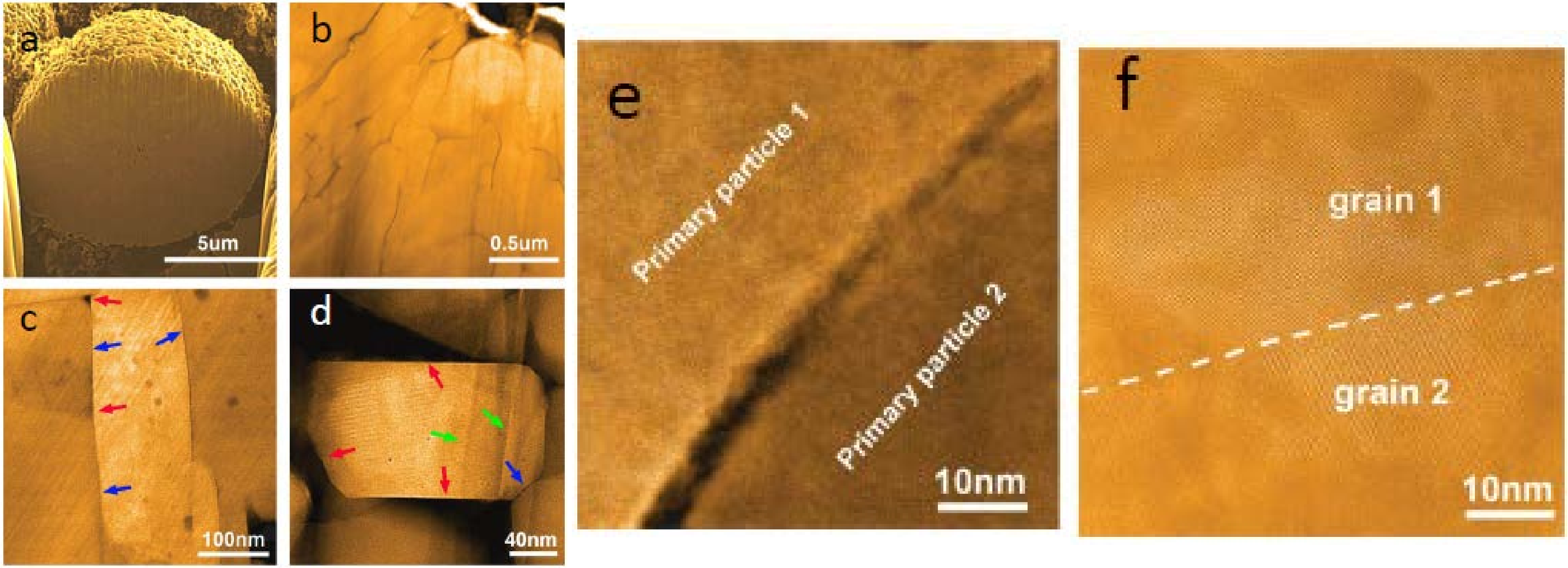
Technical Accomplishments

Grain boundary structure in the secondary particles of NMC811



- Within NMC811 secondary particle, packing of the primary particles leads to different grain boundary structure
- Depending on the characteristics of the grain boundary structure, the liquid electrolyte may penetrate along the grain boundary

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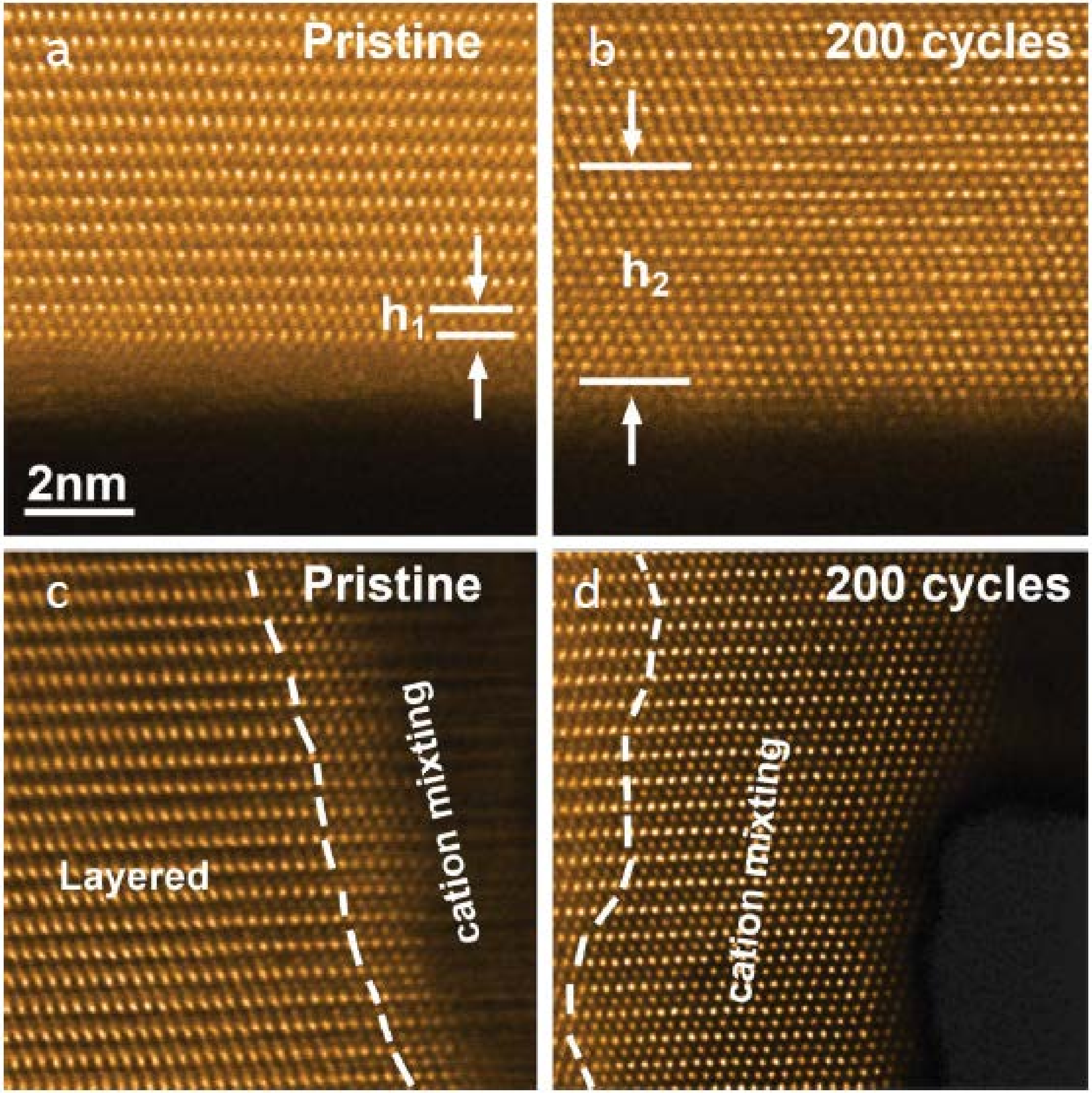
Technical Accomplishments

Structure of free surfaces in secondary particle of NMC811



- The free surface in the secondary particle is in direct contract with the liquid electrolyte
- The free surface has a thick surface layer of phase transition at two typical crystallographic directions following the battery cycoling

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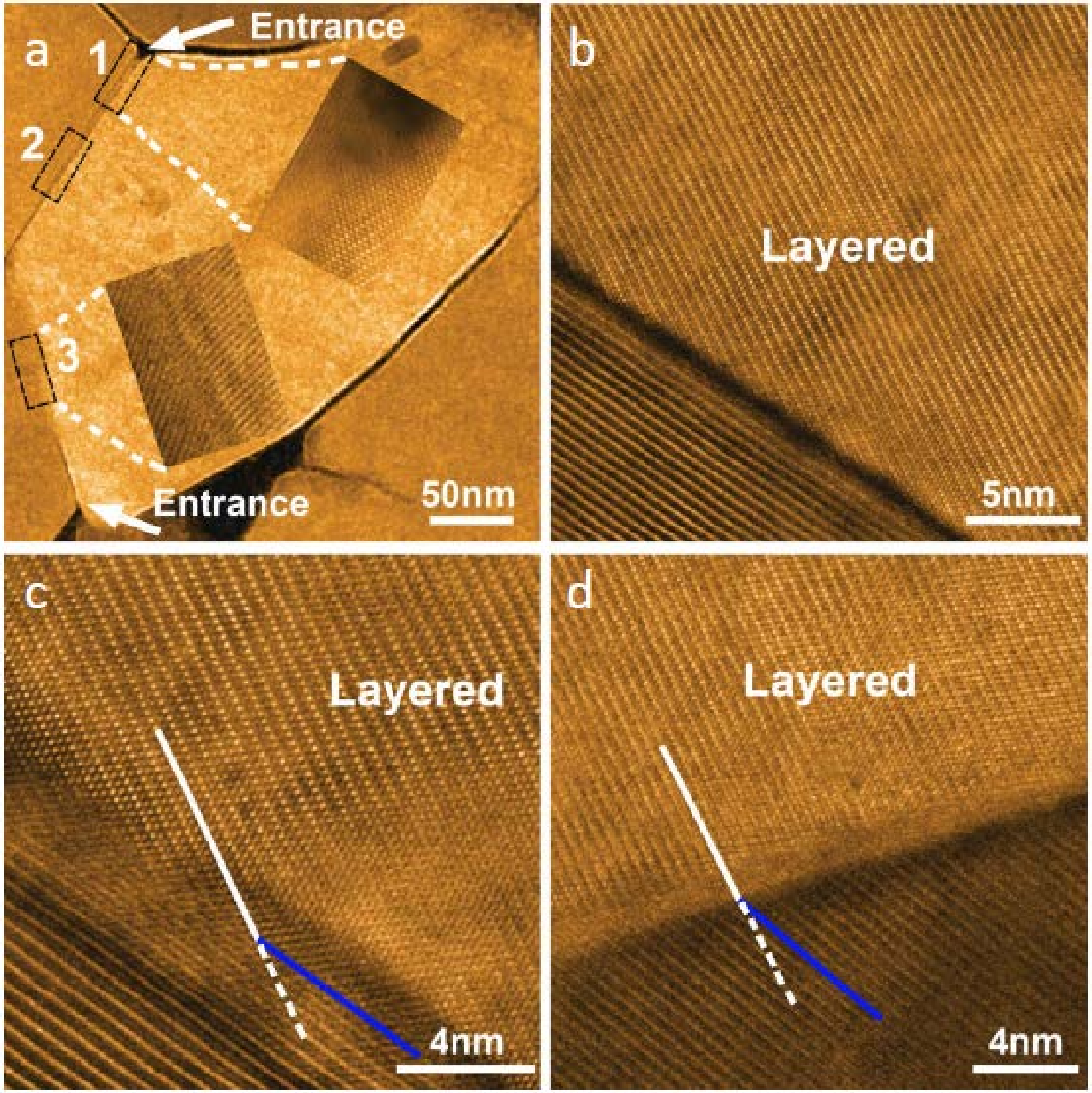
Technical Accomplishments

Dense and loose grain boundaries in the secondary particle of NMC 811



- ➢ Liquid electrolyte will penetrate the loose or wider opening grain boundaries
- ➢ Liquid electrolyte will not penetrate the densely packed grain boundaries

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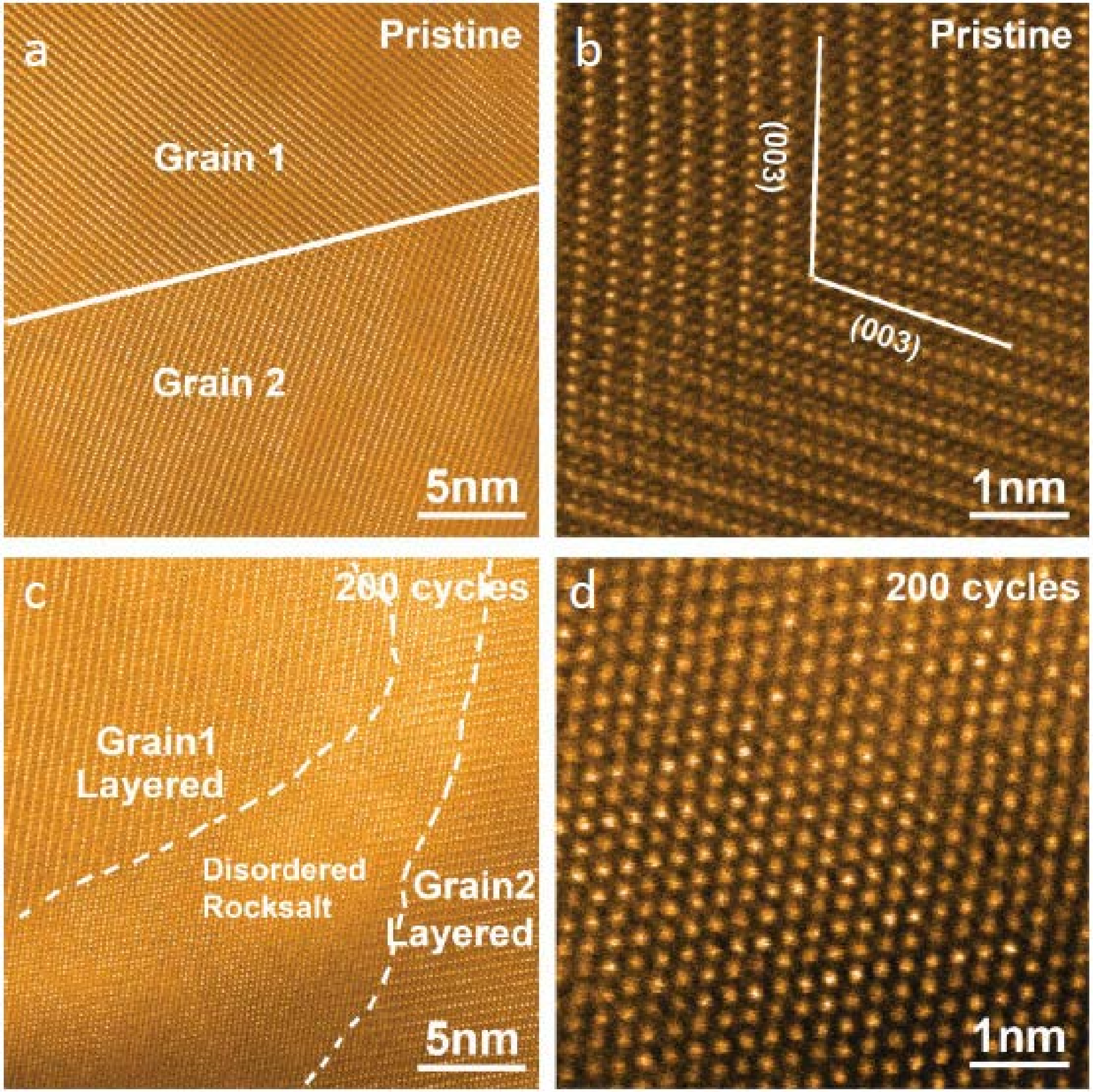
Technical Accomplishments

Special grain boundaries in secondary particle of NMC 811



- Liquid electrolyte will not penetrate along the special grain boundaries formed by the secondary particle
- Even liquid electrolyte will not penetrate along the special (dense) grain boundary, the grain boundary is still acting as a fast channel for mass transport, therefore leading to the phase transition adjacent to the grain boundary during the battery cycling

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Responses to Previous Year Reviewers' Comments

This is a new project and there is no review for previous year

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Collaboration and Coordination with Other Institutions

Partners:

- Argonne National Lab: Preparation of cathode materials, ALD coating
- Lawrence Berkeley National Lab: Preparation of cathode materials
- Oak Ridge National Laboratory
- National Renewable Energy Lab: ALD coated Si samples
- Hummingbird Scientific: Help to develop the liquid holder
- FEI Company: ETEM capability development
- Battery Research Group in PNNL: Preparation of cathode

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Remaining Challenges and Barriers

- The true structural nature of the short range order in disordered rock salt structure
- What factors control or affect the short range order in disordered rock salt structure
- How does the short range order evolve with the cycling of the battery?
- What is the correlation between short range order and electrochemical properties
- What is ideal dopant for low Co and Co-free next generation cathode?
- How does the structure evolve of the low Co and Co-free cathode?

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Proposed Future Work

FY2019

- Explore the atomic model of short range order in disordered rock salt structure
- Fading mechanism of disordered rock structure
- Explore the critical factors that control the stability of low Co and Co free cathode

FY2020

- Probe the structural and chemical evolution of the the short range order in the disordered rock salt structure
- Determine the atomic correlation between short range order and electrochemical properties
- Explore the dopant effect on the cycling stability of doped and surface coated low Co and Co-free cathode
- Determine the fading mechanism of low Co and Co free cathode

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

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Summary

- Fluorine doped disordered rock structure shows short range order as revealed by the electron diffraction and STEM-HAADF imaging
- The true structural nature of the short range order and their correlation with electrochemical properties need more detailed investigation
- Grain boundaries in secondary particle shows a range of characteristics, ranging from open, loose to dense and special grain boundaries
- The structural nature of the grain determines if the liquid will penetrate or not into the grain boundary.
- Typically, the loose or open grain boundary will be penetrated by the liquid electrolyte and cause solid-liquid reaction, while the dense or special grain boundary will not be penetrated by the liquid electrolyte
- Due to the grain boundary provide a fast mass transport channel, therefore, the phase transformation preferentially happens along the grain boundary

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Technical Back-Up Slides

Patents/Publications/Presentations

1. Manuscript under review

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Acknowledgements

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- ✓ Team Members:
  PNNL, LBNL, ANL, ORNL, NREL

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