Microscopy Investigation on the Fading Mechanism of Electrode Materials

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Pacific Northwest National Laboratory

2015 DOE Vehicle Technologies Program Review
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Project ID#: ES226

Overview

Timeline

- Start date: Oct. 1, 2013
- End date: Sept. 30, 2015
- Percent complete:80%

Budget

Project funding (DOE):

- FY14: $200k
- FY15: $300k

Barriers addressed

- Fading and failure mechanism of electrode
- High theoretical capacity of electrode materials cannot be fully utilized

Partners

- Material synthesis group in PNNL
- Lawrence Berkeley National Lab
- Argonne National Lab
- Stanford University
- National Renewable Energy Lab
- GM Research Center
- Sandia National Laboratory
- Hydro Quebec
- EnerG2 company
- FEI Company
- Hummingbird Scientific Inc.

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Relevance/Objectives

- Develop *ex-situ*, *in situ* and *operando* HRTEM techniques for rechargeable battery research

- Use *ex-situ*, *in situ* and *operando* HRTEM to probe the fading mechanism of electrode materials

- Correlation of structural and chemical evolution with battery performance for guiding the designing of new materials

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Milestones

- Establish the methodology that enables reliably positioning of a nanowire on the chip to assembly the closed liquid cell,   December 2014, complete

- Complete quantitative measurement of coating layer and SEI layer thickness as a function of cycle number on a Si anode in a liquid cell with a practical electrolyte, March 2015 complete/on track

- Complete the operando TEM study of cathode materials with/without coating layer and the SEI layer formation, September 2015 – complete/on track

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Approach/Strategy

- Using the state-of-the-art aberration corrected S/TEM, EELS, and EDS to probe chemistry and structure of electrode

- Extend and enhance the unique ex-situ and in situ S/TEM methods for probing the fading mechanism of Li-ion battery under dynamic operating condition

- Close collaboration/integration with battery research and development groups/establishments to capture the cutting edge questions that facing the battery research/development

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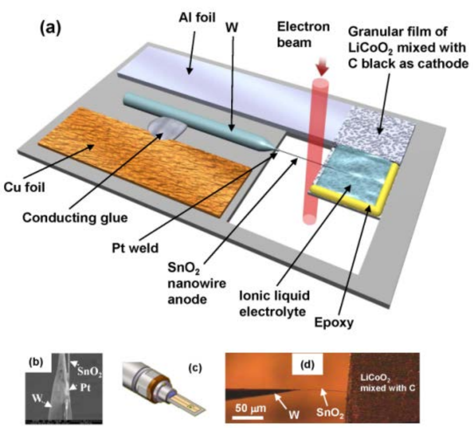
Technical Accomplishments: Developed Three Generation of In-situ and Operando TEM for Battery Research

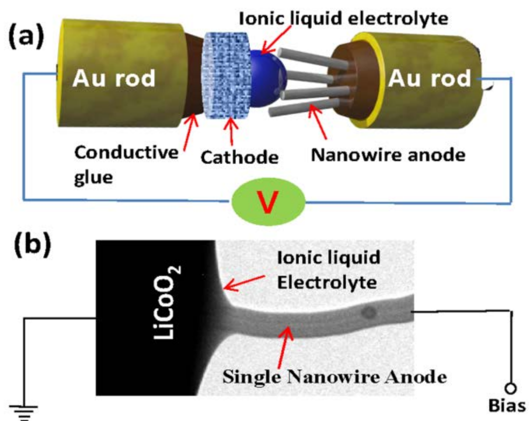
G 1: Initial concept

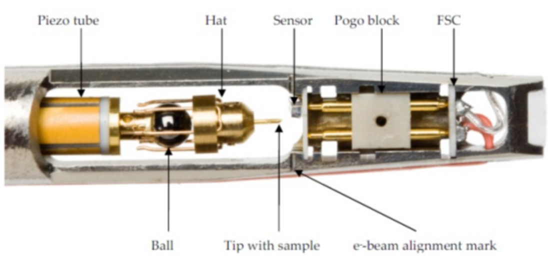


Ionic liquid based electrolyte
(10% LiTFSI in P14TFSI)

C. M. Wang, et al, J. Mater. Res., 25(2010)1541

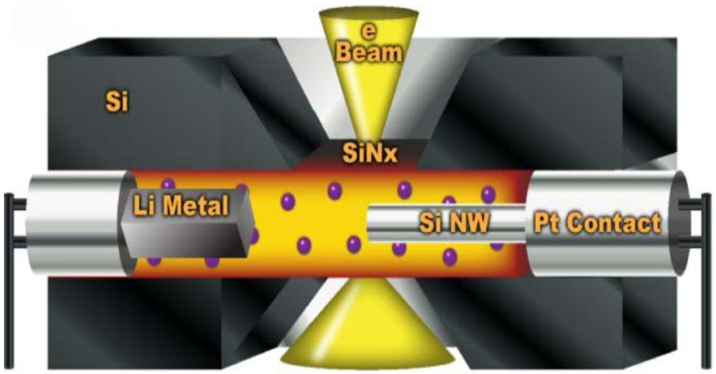
G 2: Open cell





J. Y. Huang and C. M,. Wang et al, Science, 330(2010)1515

G 3: Closed cell



M. Gu and C. M. Wang et al, Nano Letter, 13 (2013)6106

Towards real battery operating condition

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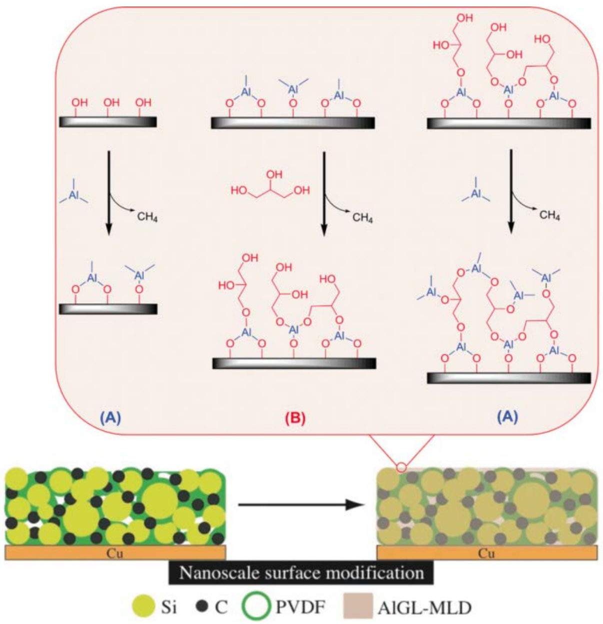
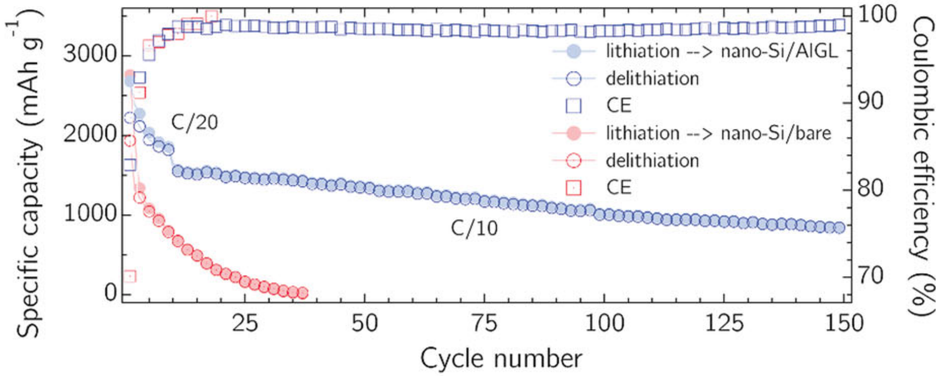
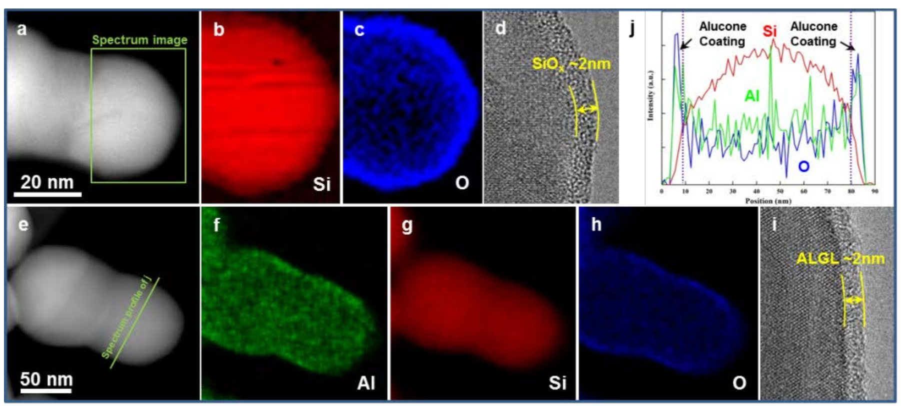
Technical Accomplishments:

Surface Coating Layer Effect on Si Cycling Properties





- Sequential, selflimiting reactions of trimethylaluminum ($Al(CH_3)_3$) and glycerol ($C_3H_5(OH)_3$)(ALGL) (Alucone) to coat nanocomposite Si electrodes



- The native silicon oxide layer of ~ 2 nm on silicon nanoparticle, the coating layer is ~ 2 nm
- Needs understanding of the fundamental mechanisms of coating layer function
- Using in-situ TEM to probe how does this coating layer function

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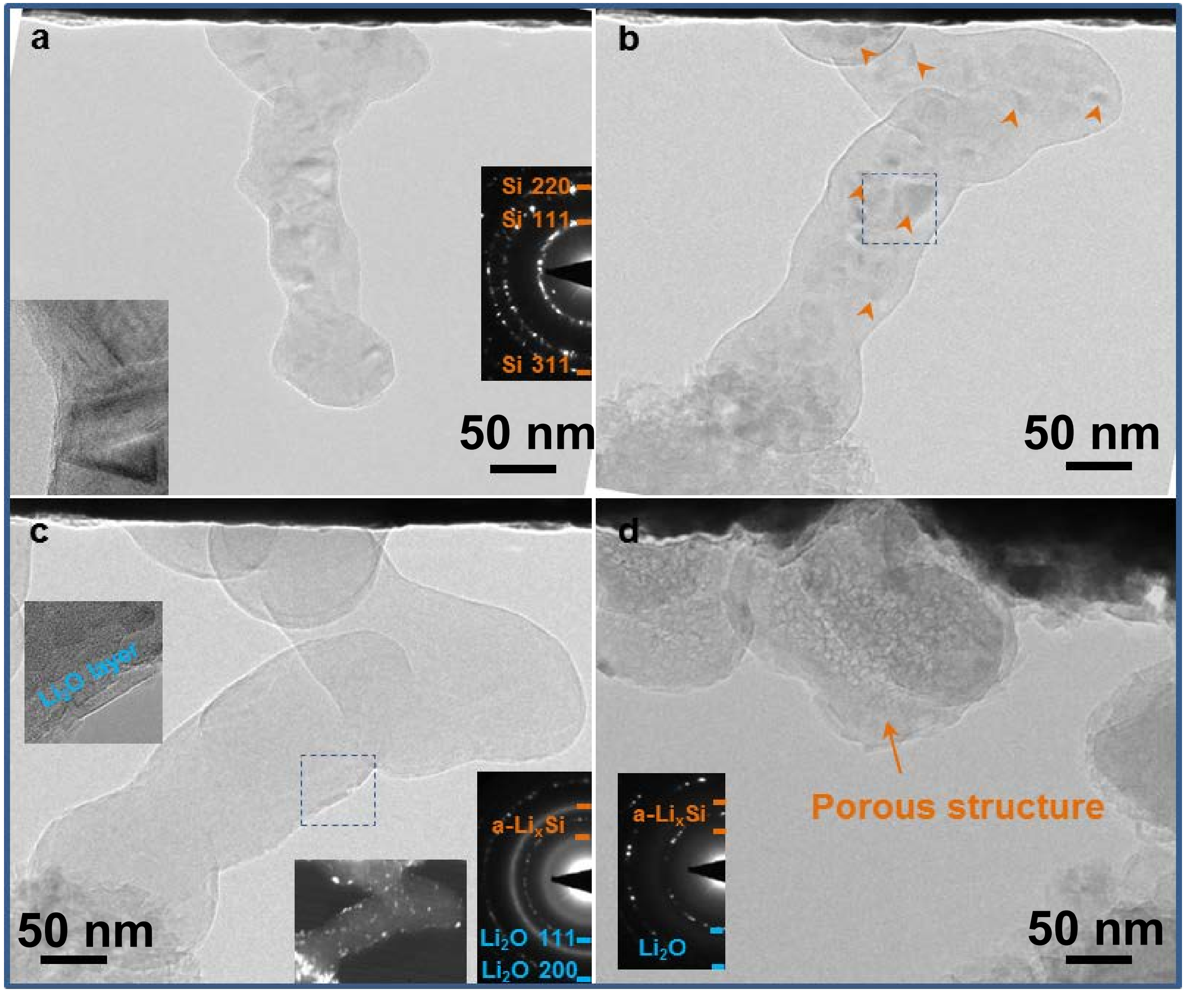
Chunmei Ban et al, Adv. Mater. 2013

Technical Accomplishments:
In-Situ TEM Observation of Lithiation and Delithiation of Uncoated Si Nanoparticle



- In-situ TEM unveils that the native oxide layer on Si anodes will create Li_2O upon lithiation
- Li_2O is a poor conductor and rather stiff

Yang He et al. 2014, ACS Nano, 8, 11816 (2014)

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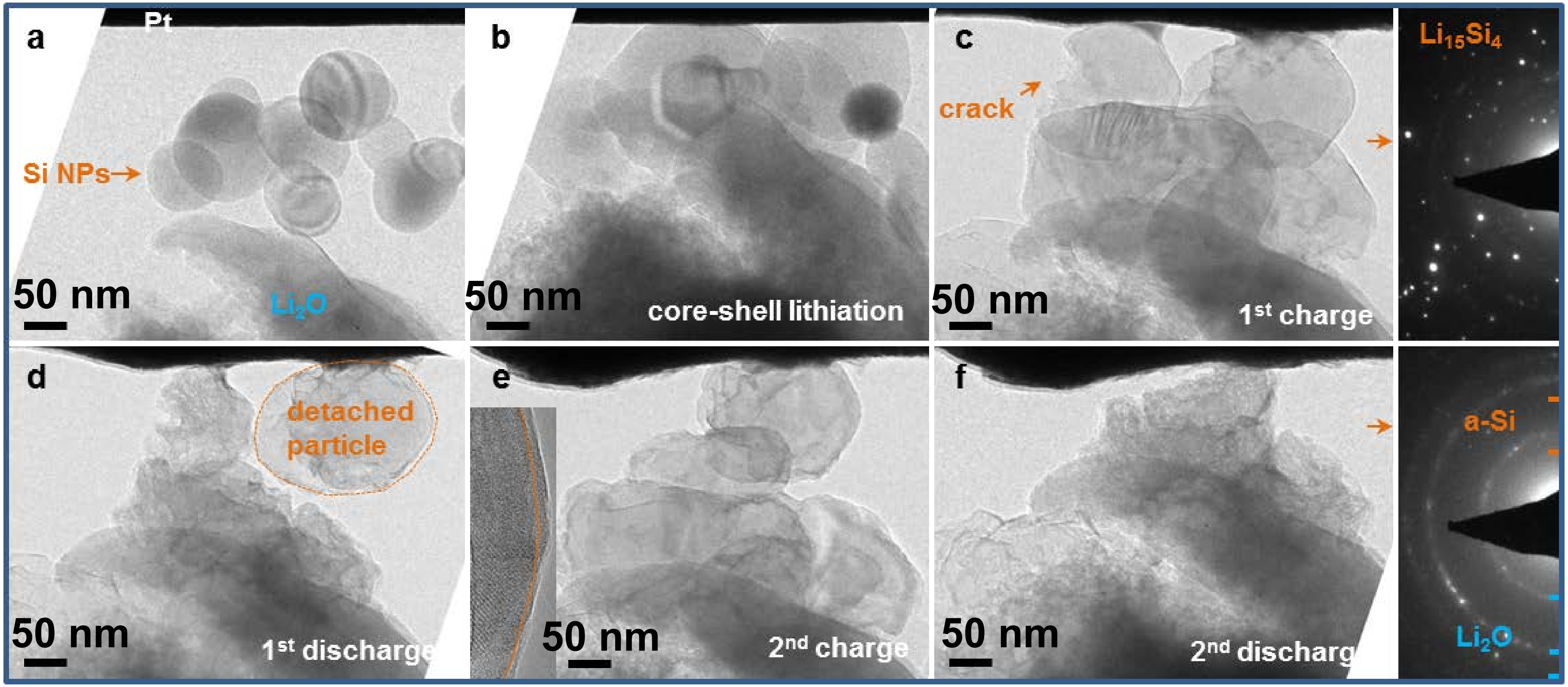
Technical Accomplishments:
In-Situ TEM Observation of Lithiation and Delithiation of Alucone Coated Si Nanoparticle



- In-situ TEM reveals that alucone MLD coating process consumes SiO_x, which subsequently passivated the particle
- Alucone behaves as plastic coating, leading to a great cyclability and high Coulombic efficiency

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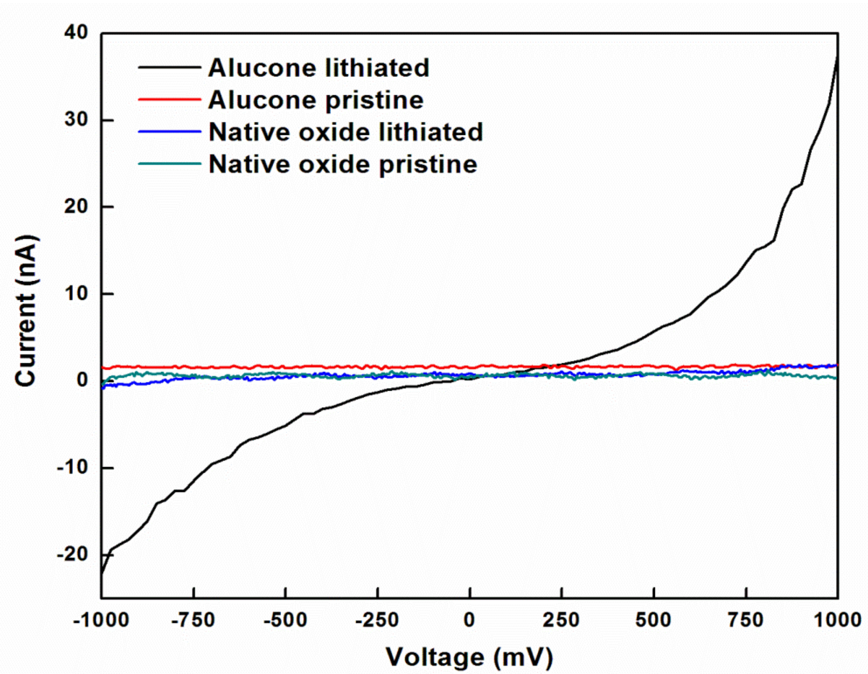
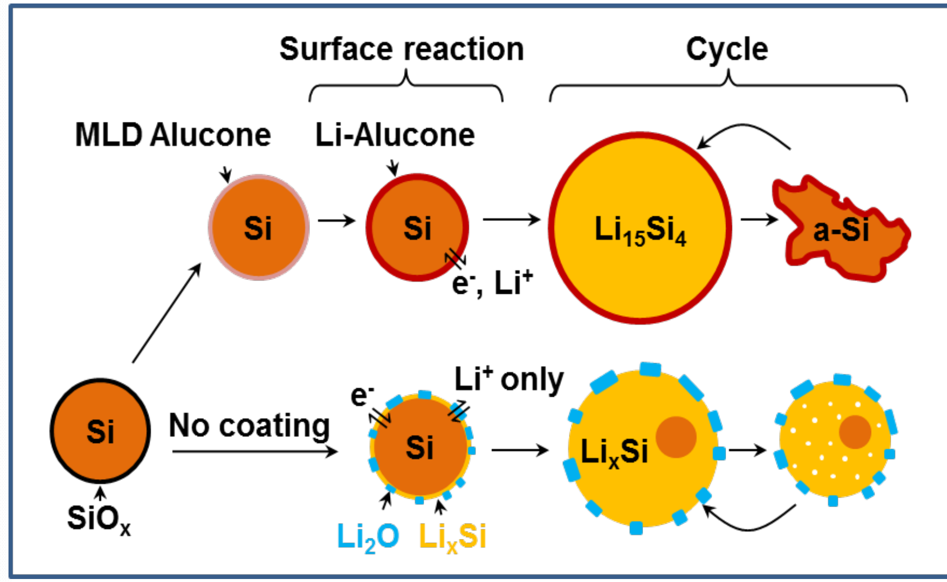
Yang He et al. 2014, ACS Nano, 8, 11816 (2014)

Technical Accomplishments:

Summary of the Behavior of the Native Oxide and Coating Layer





- Native oxide layer on Si anodes will create Li_2O upon lithiation. poor conductor
- Alucone MLD coating process consumes SiO_x, which subsequently passivated the particle!
- Alucone behaves as plastic coating, leading to a great cyclability and high Coulombic efficiency

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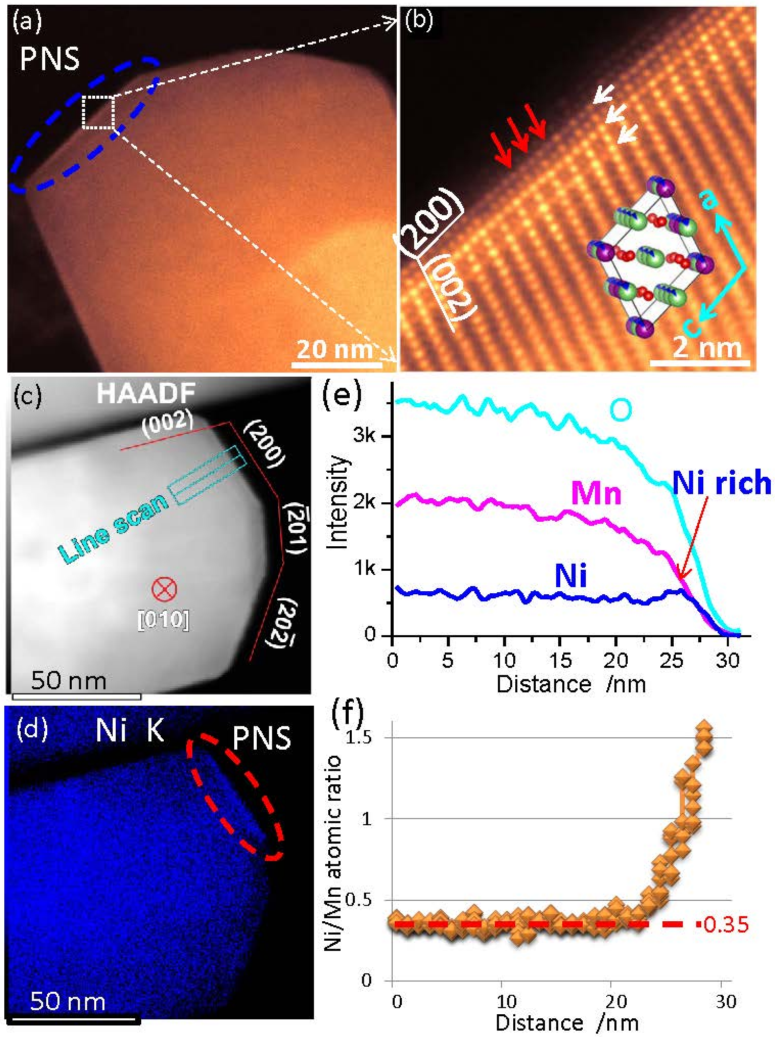
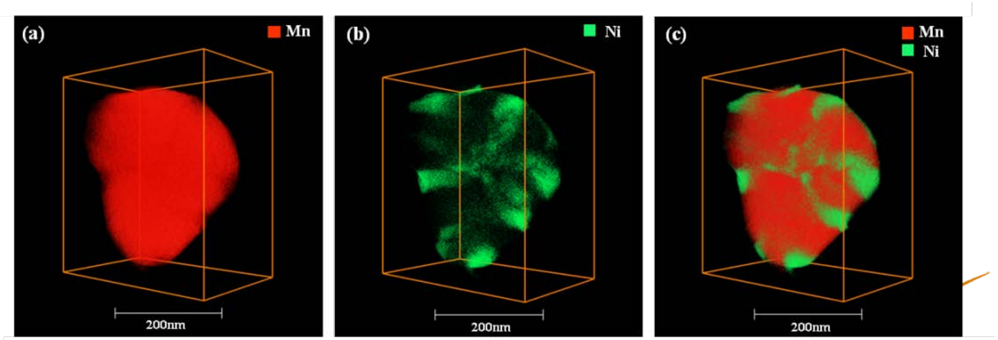
Yang He et al. 2014, ACS Nano, 8, 11816 (2014)

Technical Accomplishments:
How Does Ni Behave in LMR: Pristine $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$

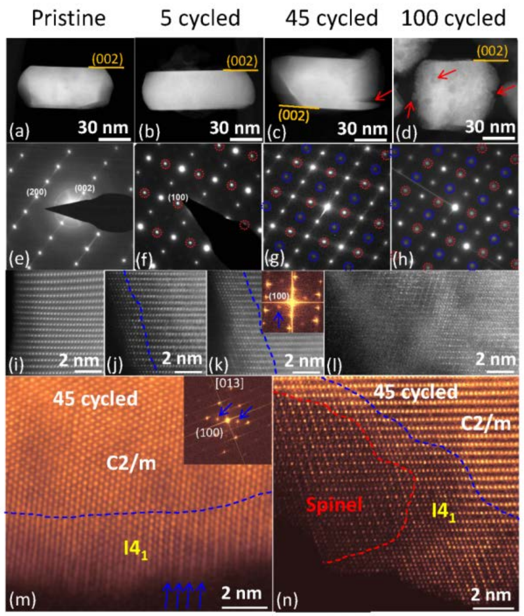


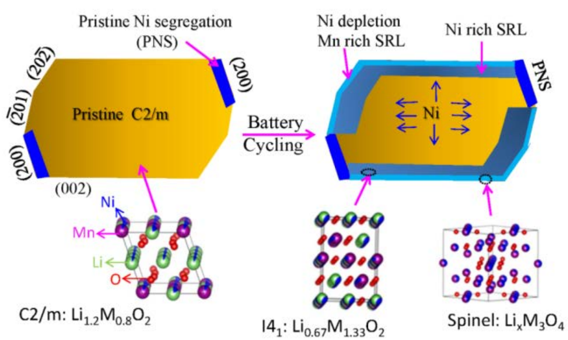
- STEM-HAADF image of A C2/m along [010] direction
- Following the fabrication, Ni shows initial segregation at (200) plane
- The Ni/Mn ratios are around 0.35 in bulk region, which is close to the designed value 0.33

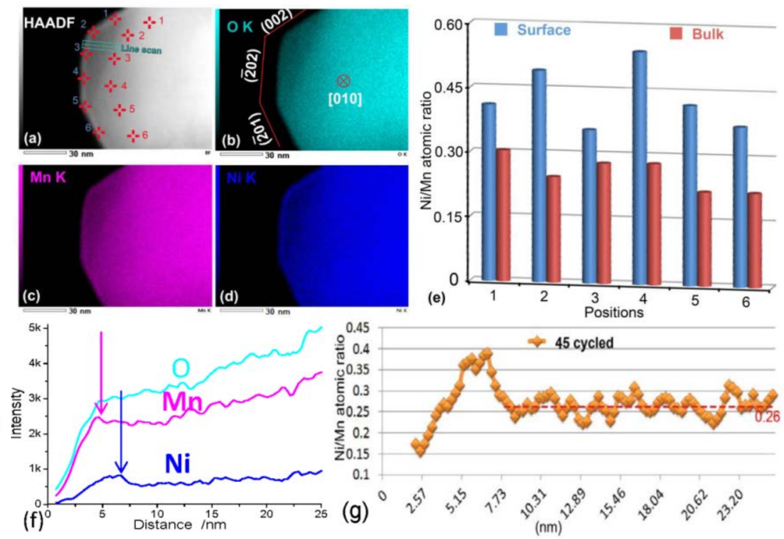


Yan et al. 2015, Nano Letters, 15, 514-522 (2015)

Technical Accomplishments:
Structure and Chemical Evolution of $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ during the Cycling of the Battery







- ➢ Cycling induced corrosion, cracks and pits formation
- ➢ (002) surface planes show strong resistance to corrosion (cation or anion only planes)
- ➢ Gradual phase transformation C2/m→I41→Spinel

- ➢ Ni concentration inside the particle decreases following cycling
- ➢ Ni and Mn at the edge showing spatial partitions, indicating dissolution of Ni into electrolyte

Yan et al. 2015, Nano Letters, 15, 514-522 (2015)

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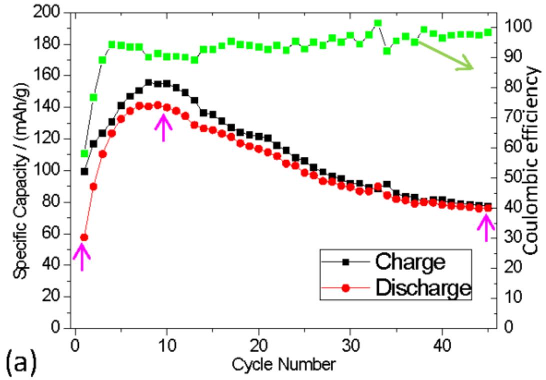
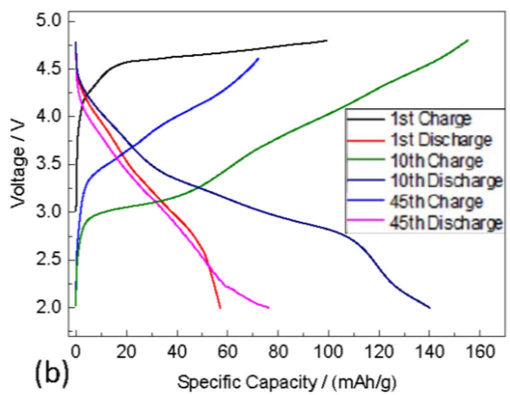
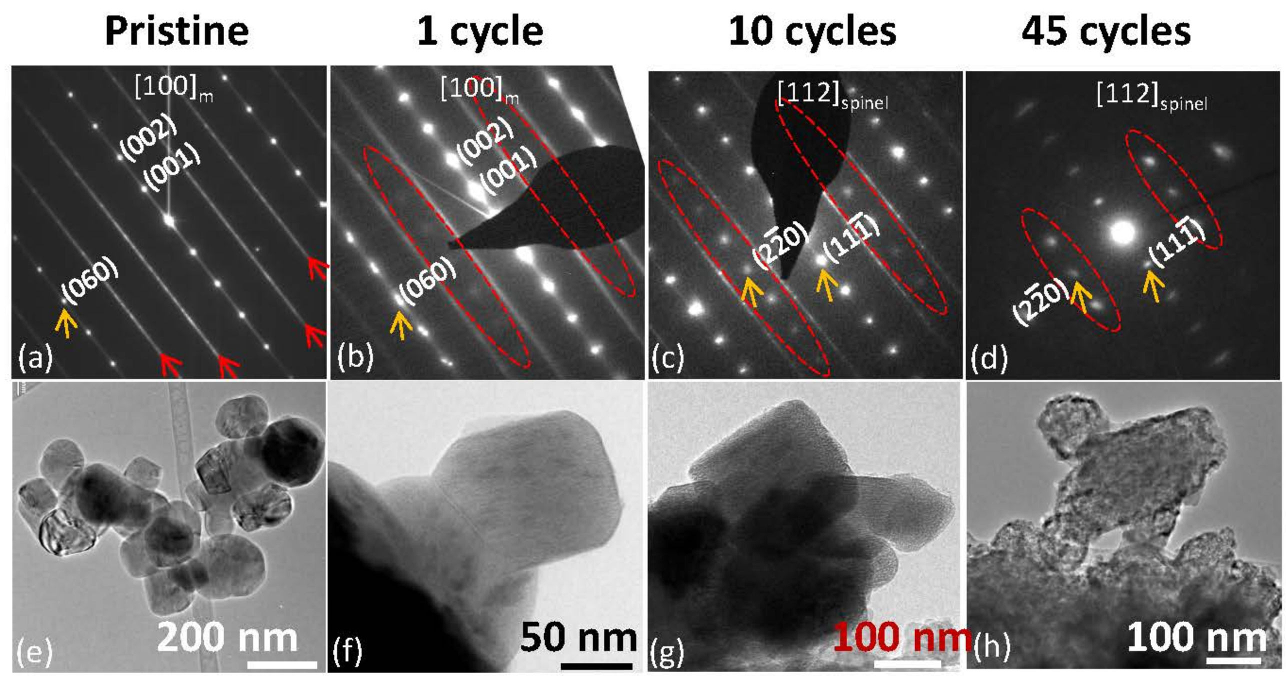
Technical Accomplishments: Correlation of Capacity Fading with Structural Evolution of Li_2MnO_3







- $[100]_m$ zone axis SAED demonstrating structural evolution of the Li_2MnO_3 as a function of cycling number
- TEM images showing particle morphology evolution from pristine to 45 cycles

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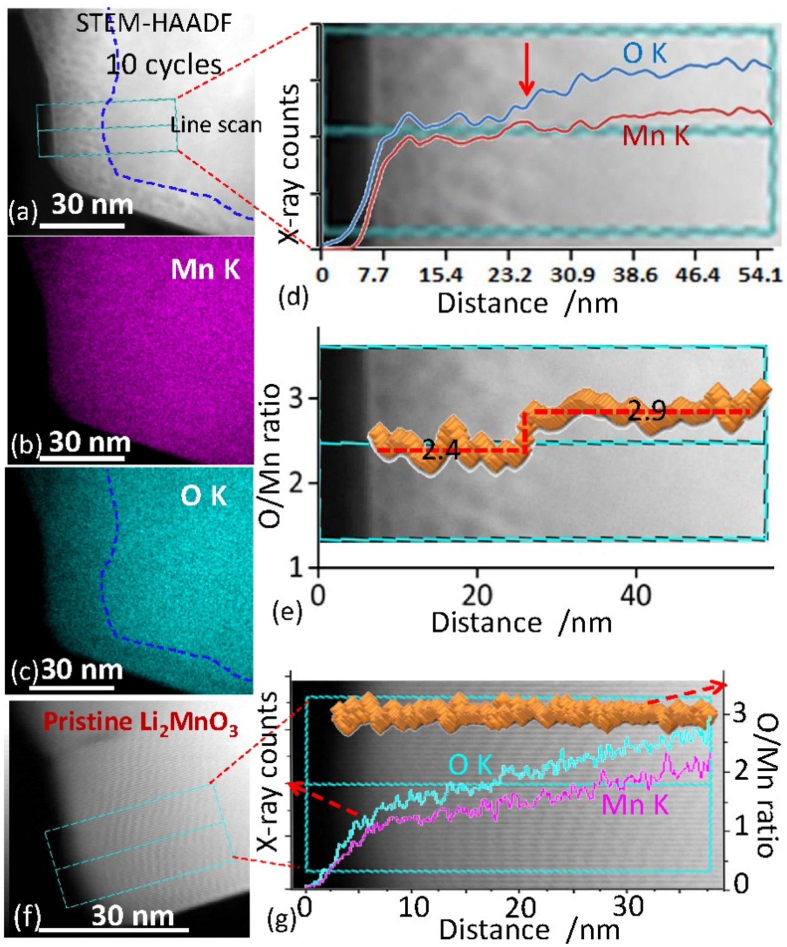
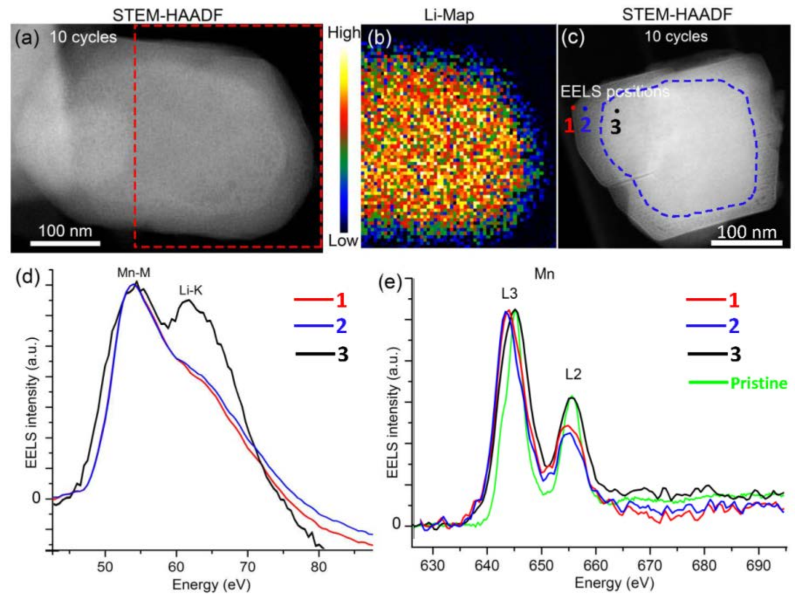
Yan et al. 2015, Chem. Mater. 27, 975-982 (2015)

Technical Accomplishments: Oxygen and Lithium Depletion with the Progression of Cycling of Li_2MnO_3

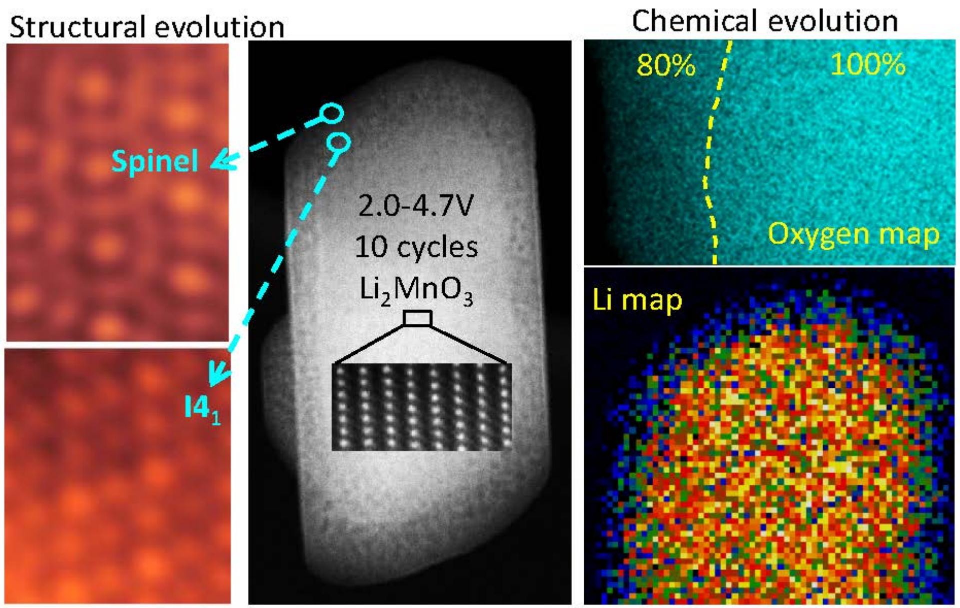


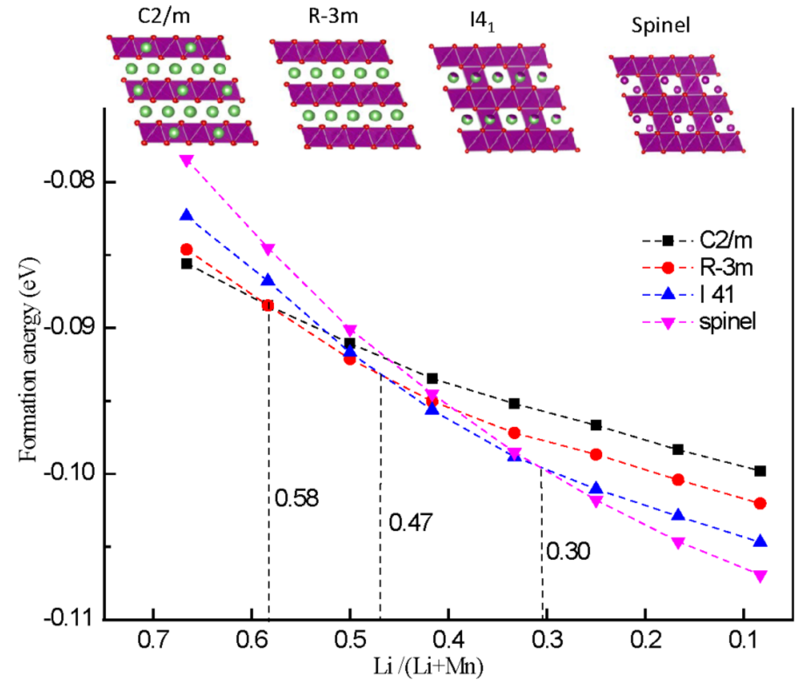


- Loss of oxygen at the surface region
- EELS map reveals the depletion of Li at the surface layer and reduction of Mn

Yan et al. 2015, Chem. Mater. 27, 975-982 (2015)

Technical Accomplishments:
Correlation of Capacity Fading with Structural and Chemical Evolution of Li_2MnO_3





- Gradual phase transformation, C2/m →I41→Spinel
- Oxygen loss and lithium depletion near the surface region
- The surface layer shows dependence on the crystallographic direction
- Tailoring of materials with minimal instable surface will lead enhanced stability

Yan et al. 2015, Chem. Mater. 27, 975-982 (2015)

Responses to Previous Year Reviewers' Comments

The reviewers comments are generally positive, especially about the development of the in-situ and operando TEM cell for battery: ...good to see the atomic level dynamics; ...interesting and innovative approach; ...nice in situ TEM work; …the development of the operando TEM liquid electrolyte cell is a real step forward

Comment: Suggested to comparison with other techniques, such as x-ray absorption
Response: Totally agree. Essentially, EELS and XANES are comparable, but with different spatial resolution

Comment: How does this study guide designing of materials for resolving the real problem, such as voltage fading of cathode, and inefficiency of cycling Si
Response: Direct correlation of structure and chemistry with properties of both cathode and anode can guide the design of better materials

Comment: Suggested considering benchmarking with other materials
Response: Agree, closely integrated with the materials system in the BMR team

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Collaboration and Coordination with Other Institutions

Partners:

- Material synthesis group in PNNL: Preparation of both cathode and Si based anode materials
- Argonne National Lab: Preparation of cathode materials
- Lawrence Berkeley National Lab: Prepare and tested the LMR materials
- Stanford University: Grown the Si nanowire
- GM Research Center: Prepared porous Si, S enclosed in carbon
- National Renewable Energy Lab: ALD coated Si samples
- Sandia National Laboratory: part of STEM observation
- Hummingbird Scientific: Help to develop the liquid holder
- FEI Company: Part of EDS mapping

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Remaining Challenges and Barriers

- A primary challenge for in-situ and operando TEM study of battery is the loading of Li metal anode into the liquid cell. Attacking this problem will rely on microfabrication technique and configuration of the in-situ cell
- TEM and STEM imaging resolution needs to be optimized by minimizing the liquid layer thickness. This can be achieved by designing of the liquid window geometry to minimize the bulging effect
- Due to the complicated steps of assembling the in-situ cell, the reliability and reproducibility of the in-situ and operando TEM cell need to be improved

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Proposed Future Work

- **FY2015**

- Complete the study of the effect of deformable coating layer on Si
- Continue the study of the SEI layer characteristics and Co, Ni, and Mn in LMR, NCM, and NCA based cathode and correlate with fading mechanism
- Study the faceting plane stability of LMR correlation with fading mechanism

- **FY2016**

- Using various microscopic and spectroscopic techniques, including open-cell and the newly developed in-situ and *operando* TEM and in-situ liquid SIMS system, HRTEM, EDS, STEM-HAADF, to diagnose the structural and chemical evolution of electrode materials upon cycling of the battery
- Anode materials fading mechanism, focusing on Si-C composite system
- Cathode voltage and capacity fading, focusing on NCM and NCA system
- Prevention of Li dendrite growth, focusing on chemistry and morphology of lithium dendrite growth and correlation with electrolyte chemistry

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Summary

- In-situ HRTEM clarified the detrimental effect of native oxide on Si particle;
- The coating layer will change the lithium ion transport kinetics: charge/discharge rate and more work is needed.
- For LMR, voltage and capacity fading are related to phase transformation, which initiates from the particle surface and propagates towards the inside of the particle
- The phase transformation is governed by migration of transition metal to Li layer, oxygen loss makes the transition metal migration easier, mitigating oxygen loss will prevent the migration of transition metal to Li layer, therefore to prevent the capacity fading
- For the layer structured LMR, the pure cation or anion type surface facet is more stable than that with a cation and anion mixed plane: guiding to a direction of designing better materials by controlling the surface faceting

Technical Back-Up Slides

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Patents/Publications/Presentations

1. **"Evolution of Lattice Structure and Chemical Composition of the Surface Reconstruction Layer in $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ Cathode Material for Lithium Ion Batteries"** Pengfei Yan, Anmin Nie, Jianming Zheng, Yungang Zhou, Dongping Lu, Xiaofeng Zhang, Rui Xu, Ilias Belharouak, Xiaotao Zu, Jie Xiao, Khalil Amine, Jun Liu, Fei Gao, Reza Shahbazian-Yassar, Ji-Guang Zhang and Chong-Min Wang, *Nano Lett.*, 15, 514-522(2014).

2. "Probing the Degradation Mechanism of Li_2MnO_3 Cathode for Li-Ion Batteries**"**, Pengfei Yan, Liang Xiao, Jianming Zheng,‡Yungang Zhou, Yang He, Xiaotao Zu, Scott X. Mao, Jie Xiao, Fei Gao, Ji-Guang Zhang, and Chong-Min Wang, Chem. Mater., 27, 975−982 (2015)

3. "Observation of Electron-Beam-Induced Phase Evolution Mimicking the Effect of the Charge−Discharge Cycle in Li-Rich Layered Cathode Materials Used for Li Ion Batteries", Ping Lu, Pengfei Yan, Eric Romero, Erik David Spoerke, Ji-Guang Zhang, and Chong-Min Wang, Chem. Mater., 27, 1375−1380 (2015).

4. "In Situ Transmission Electron Microscopy Probing of Native Oxide and Artificial Layers on Silicon Nanoparticles for Lithium Ion Batteries." Yang He, Daniela Molina Piper, MengGu, Jonathan J. Travis, Steven M. George, Se-Hee Lee, Arda Genc, Lee Pullan, Jun Liu, Scott X. Mao, Ji-Guang Zhang, Chunmei Ban, and Chongmin Wang, ACS *Nano*, 8, 11816-11823, 2014.

5. Invited Review: "In situ transmission electron microscopy and spectroscopy studies of rechargeable batteries under dynamic operating conditions: A retrospective and perspective view", Chongmin Wang, **J. Mater. Res.** 30, 326-339 (2015)

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Acknowledgements

- ✓ Supports from the U.S. Department of Energy, Office of Vehicle Technologies Program are gratefully appreciated.

- ✓ Initial supports from Laboratory Directed Research and Development Program of PNNL, EMSL user facilities, and BES are highly appreciated.

- ✓ Team Members:
  Pengfei Yan, Jianming Zheng, Meng Gu, Wu Xu, Xiaolin Li, Jie Xiao, Jun Liu, and Jason Zhang

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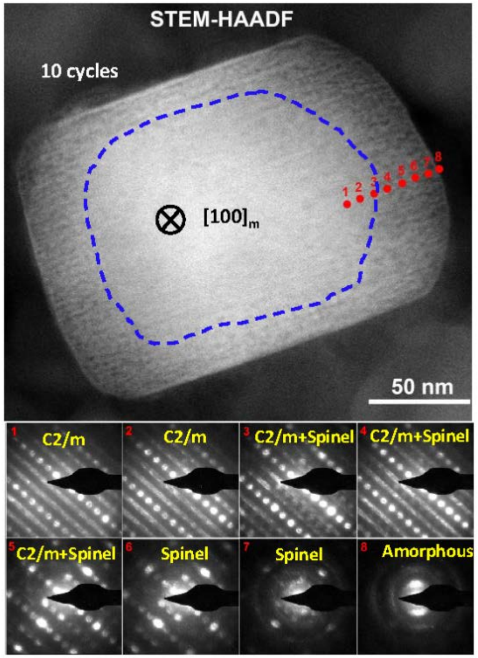
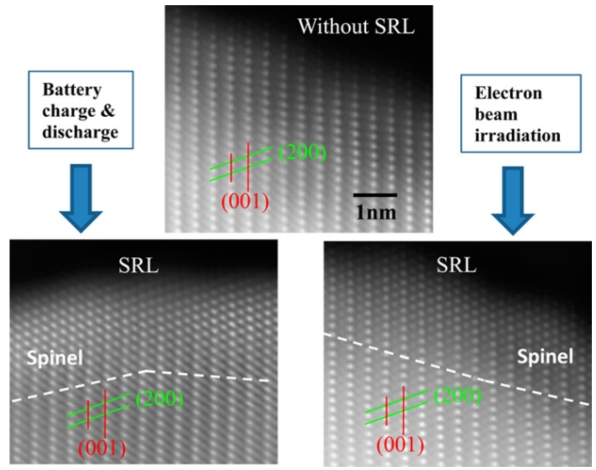
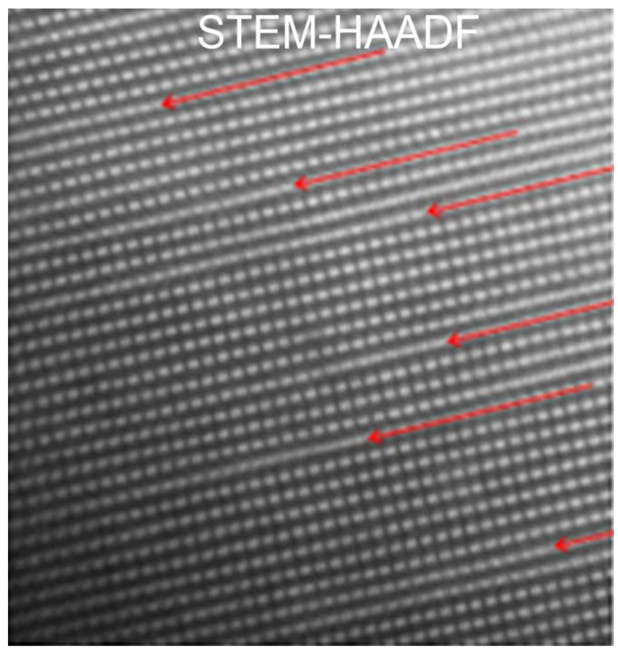
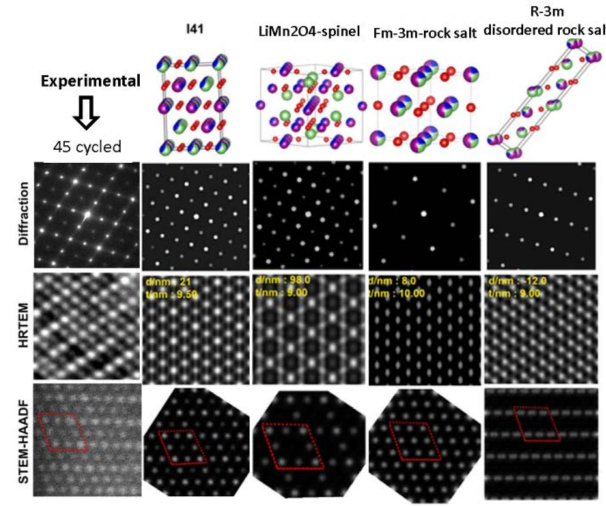
The Structure Change Route of Li_2MnO_3 Synthesized by CP Method



8-position line scan of a 10-cycles sample using nano beam electron diffraction. The crystal orientation can be assigned to [100] for C2/m structure and [112] for spinel structure.







Comparison between experimental results and simulation results of different crystal models for the SRL from the [010] zone axis. I41 structure matches best in the four crystal models.

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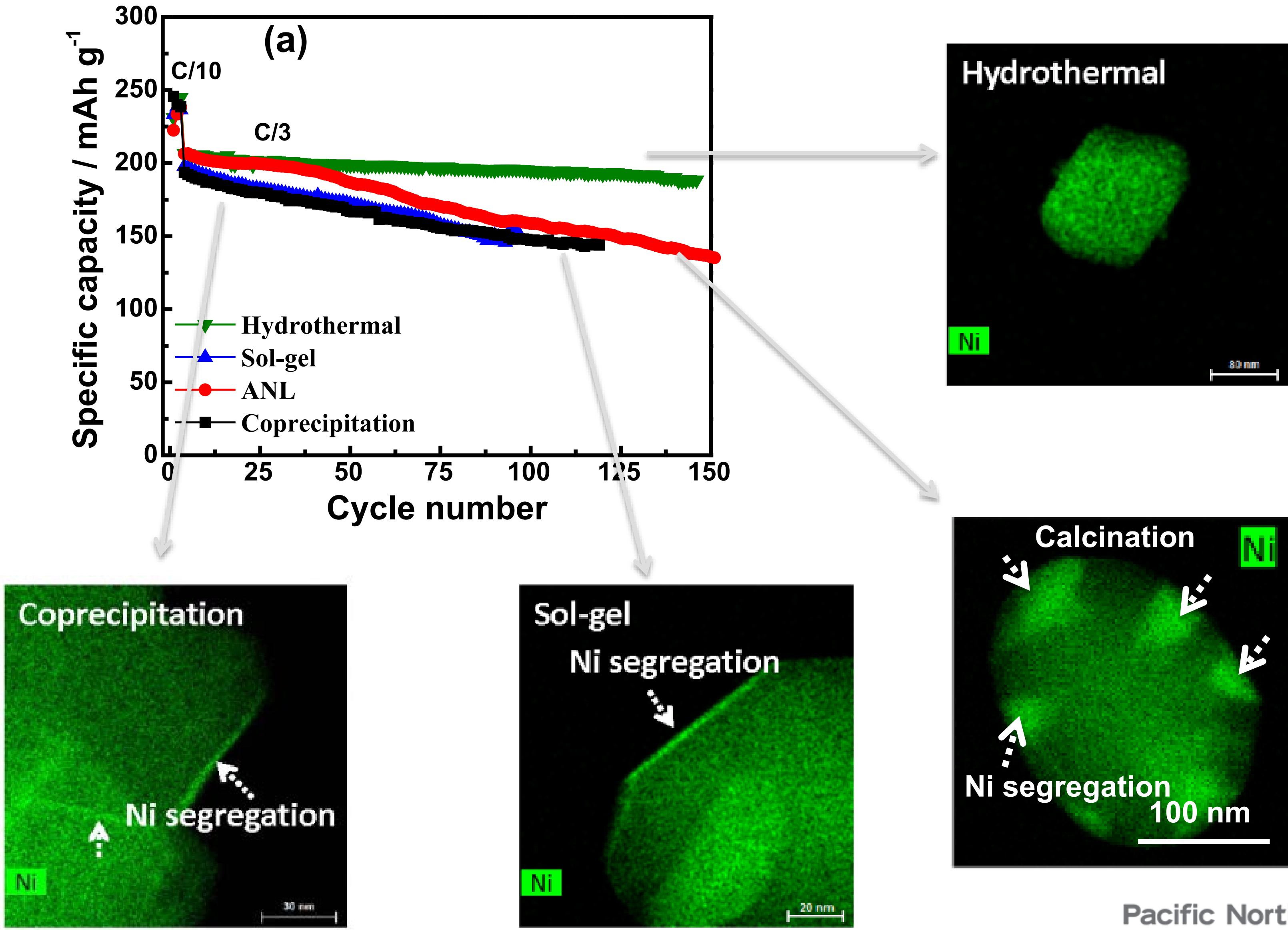
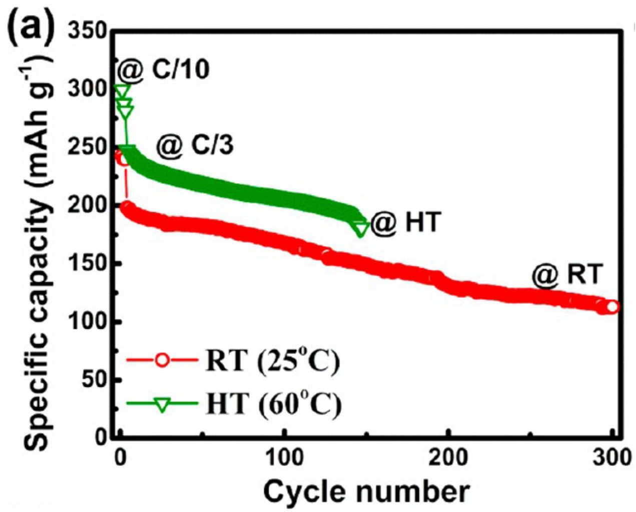
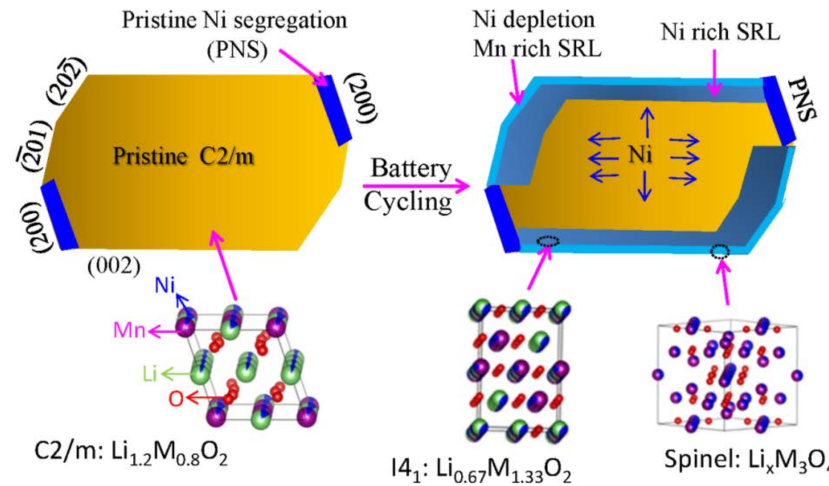
Direct correlation of the spatial distribution of chemical species with capacity fading



Technical Accomplishments: Structural and Chemical Evolution and Correlation with Capacity and Voltage Fading





- For the pristine LMR particles, Ni prone to segregate at (200) facets
- Upon cycling, LMR particle developed a surface restructured layer (SRL), SRL thickness increases with cycling numbers
- Ni ions migrate from the bulk lattice to the surface, leading to decrease of Ni in the bulk lattice and Ni enriched SRL
- The surface facet of pure cation/anion is more stable than that with a mixture of cation and anion

Yan et al. 2015, Nano Letters, 15, 514-522 (2015)

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