Microscopy Investigation on the Fading Mechanism of Electrode Materials

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Pacific Northwest National Laboratory

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Project ID#: ES226

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Overview

Timeline

- Start date: Oct. 1, 2013
- End date: Sept. 30, 2016
- Percent complete:20%

Budget

Project funding (DOE):

- FY14: $200k

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
- Hummingbird Scientific Inc.

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Relevance/Objectives

- Develop *ex-situ*, *in situ* and *operando* high-resolution transmission electron microscopy (HRTEM) and spectroscopy to probe the fading and failure mechanism of electrode materials

- Probe the structural and chemical evolution of interfaces between the electrode and electrolyte

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

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Milestones

- Develop closed liquid-cell that enable operando TEM study of electrode materials using real battery relevant liquid electrolyte – *a prototype operando liquid-cell has been demonstrated*

- Study the interface between solid and electrolyte interface, especially Si. – *on going*

- Probe the structural stability of Li rich cathode and their correlation with capacity and voltage fading – *on going*

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Approach

- Using the state-of-the-art aberration corrected scanning/ transmission electron microscopy (S/TEM), electron energy loss spectroscopy (EELS), and energy dispersive x-ray spectroscopy (EDS) to probe chemistry and structure of electrode before and after cycling

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

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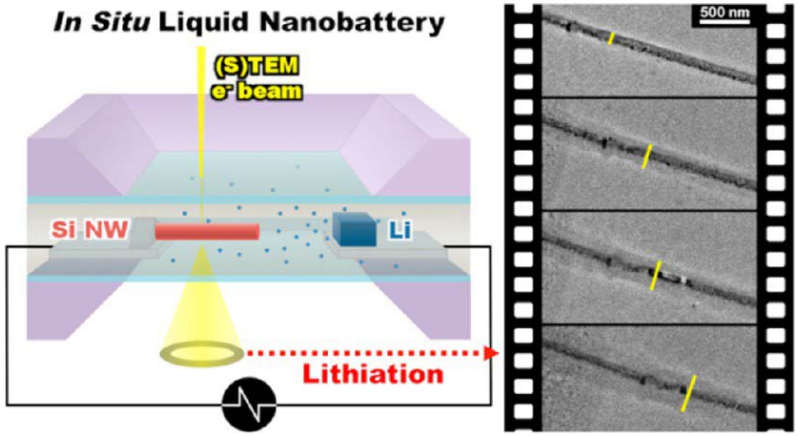
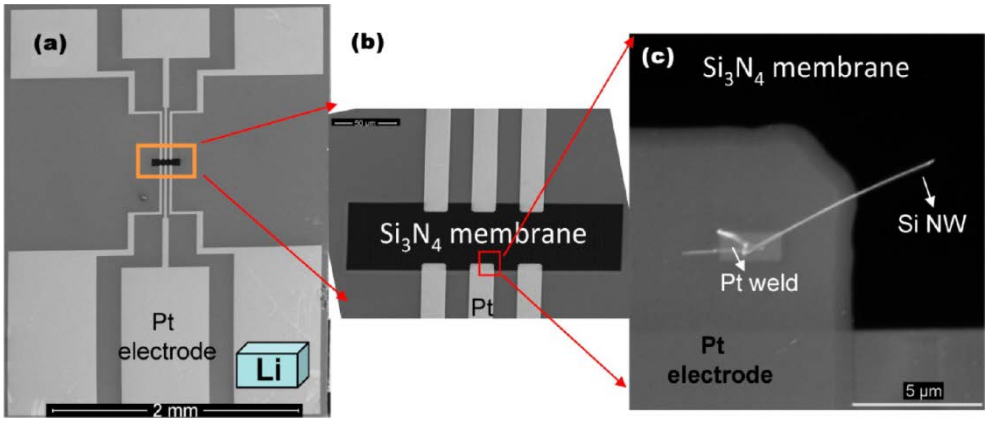
Technical Accomplishments: Development of The Operando TEM Liquid Cell





- **Prototyped the first operando liquid cell that can be operated using real battery liquid electrolyte**
- **Enabling the study of electrode materials under real battery operating condition**

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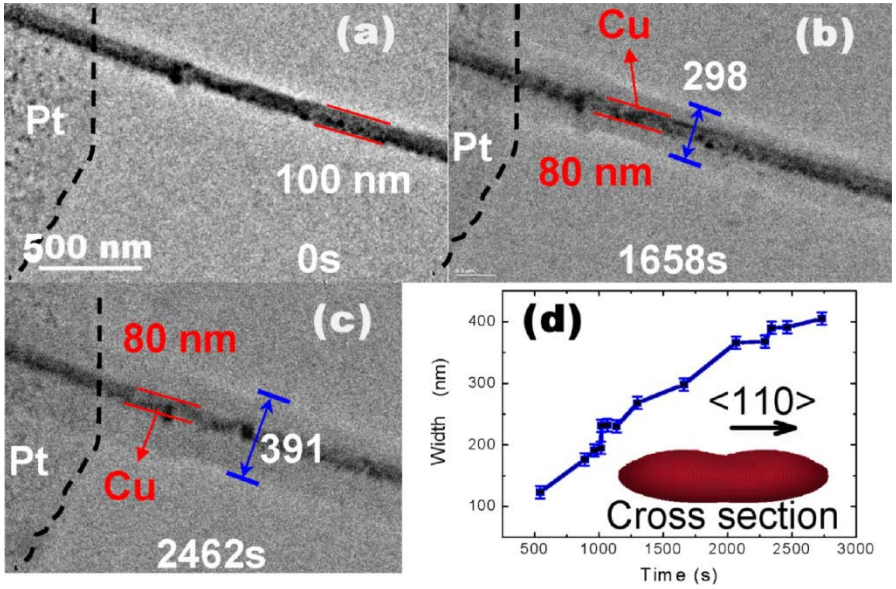
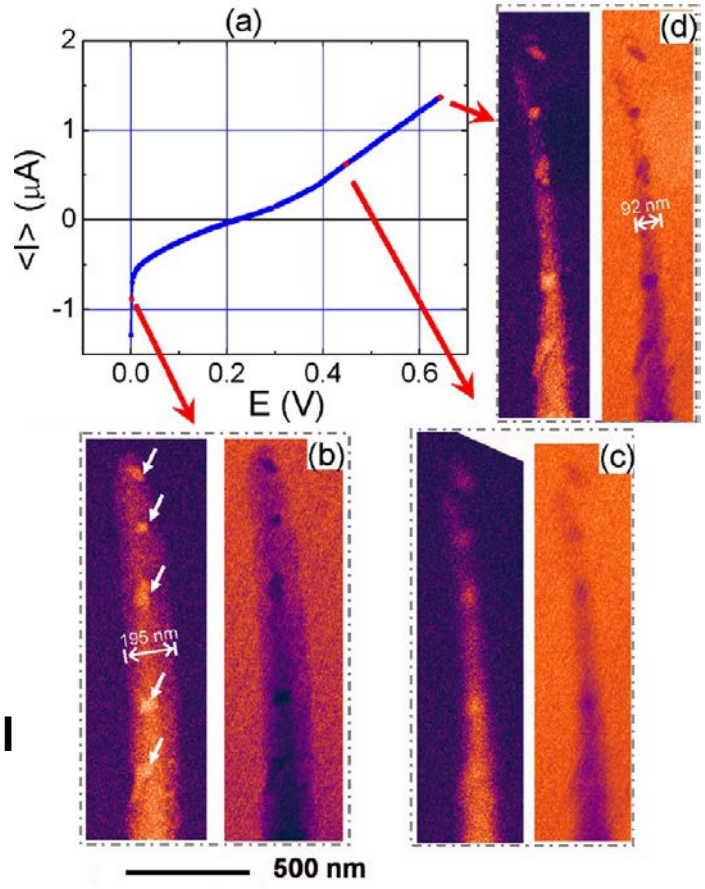
Technical Accomplishments: Operando TEM Study of Si under Real Battery Operating Condition





- The structural evolution obtained by open cell represents the intrinsic behavior of the Si
- Operando TEM allow direct correlation of structural evolution with electrochemical properties

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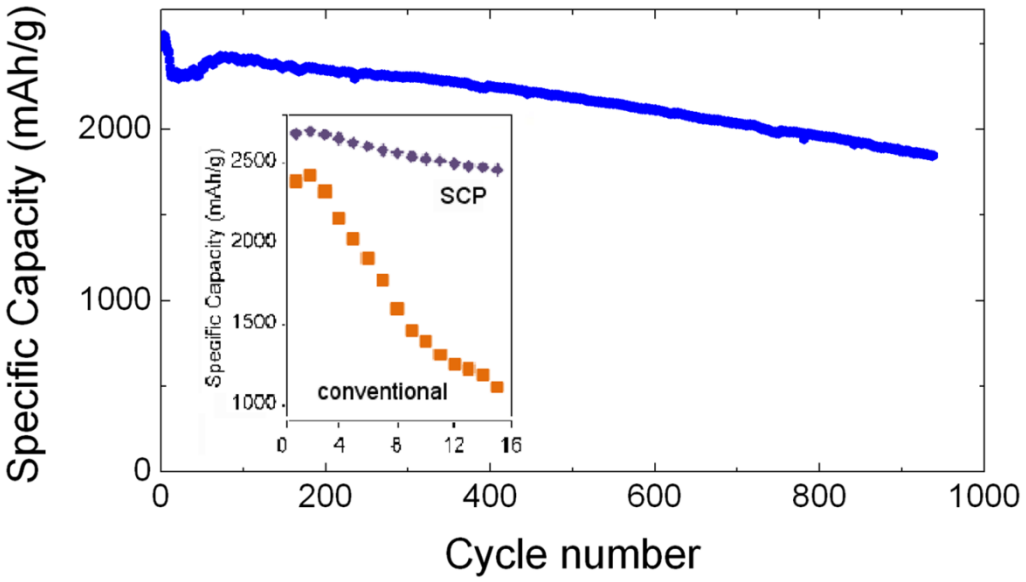
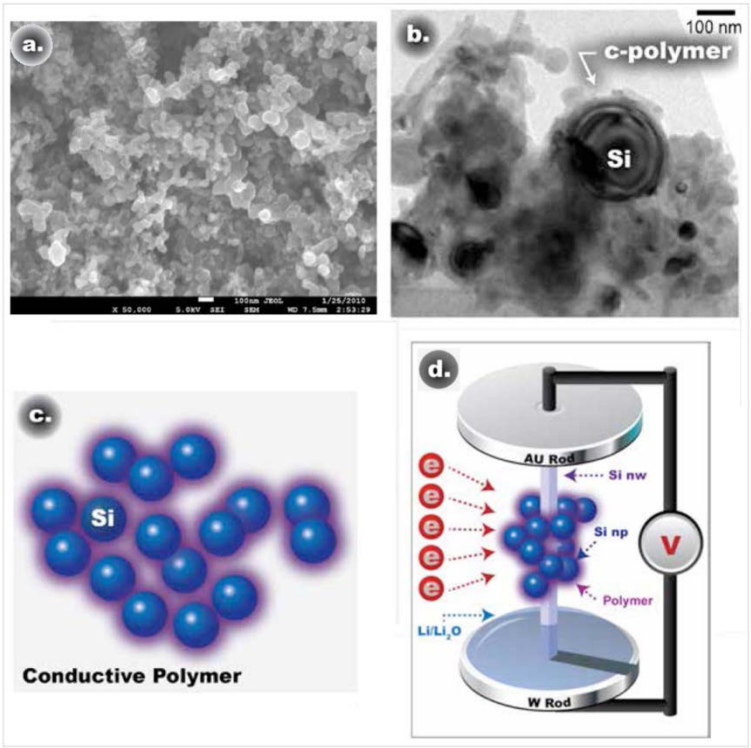
Technical Accomplishments:
Microstructure and Chemistry of Conductive Polymer Wrapped Silicon Nanoparticle





- **Conductive polymer wrapped Si nanoparticle shows great cycle stability**
- **The particle is dispersed in the polymer**

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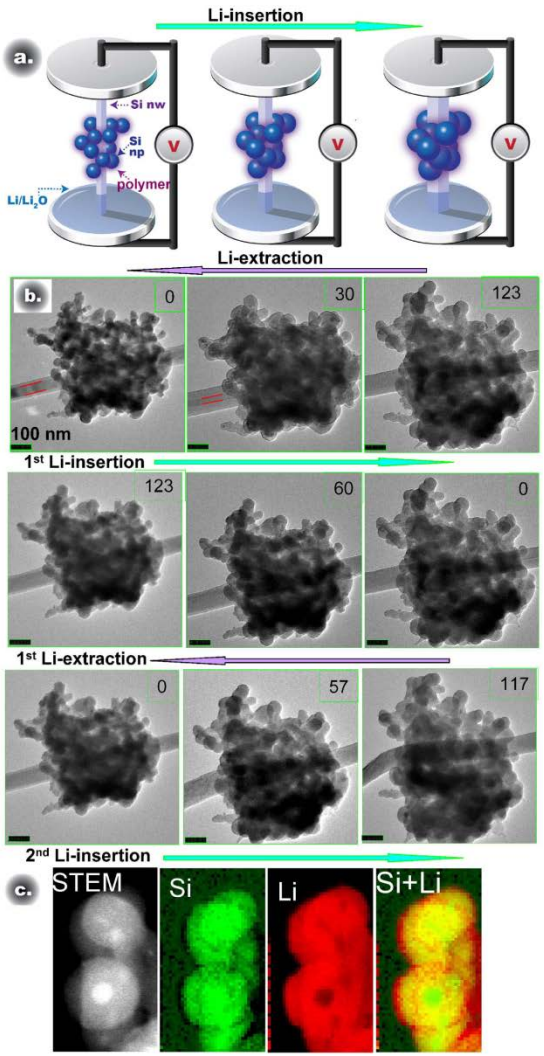
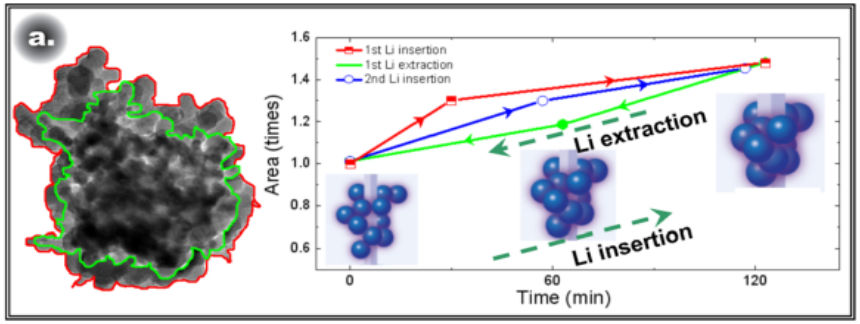
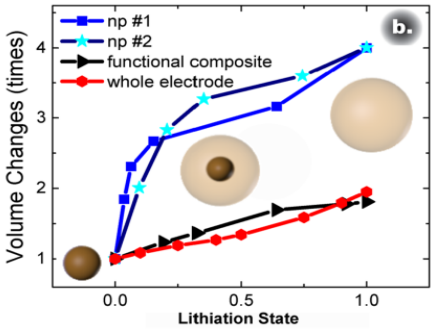
Technical Accomplishments:
Mesoscale in-situ TEM Study of Silicon Nanoparticles Wrapped by Conductive Polymer







- **In-situ TEM unveils that the enhanced cycling stability of the conductive polymer-Si composite is associated with mesoscale concordant function of Si nanoparticles and the conductive polymer**
- **The composite shows less apparent volume change upon charge-discharge**

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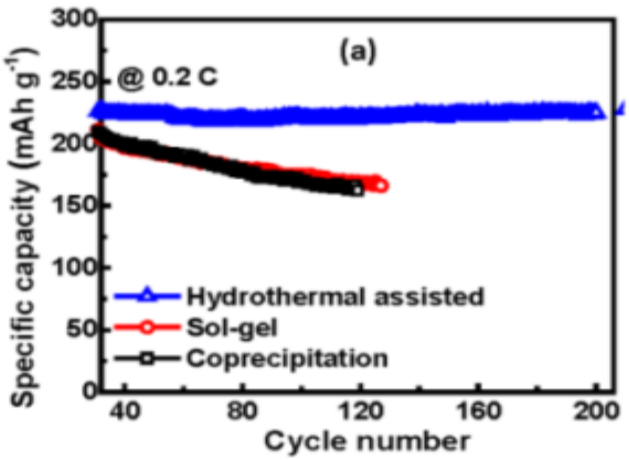
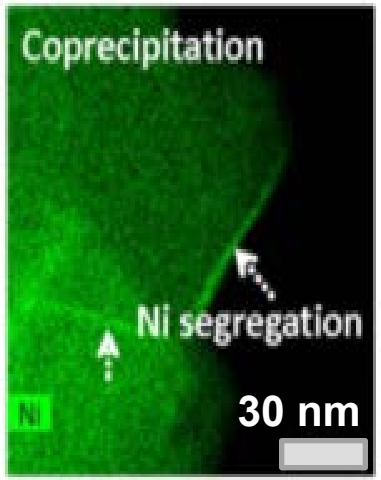
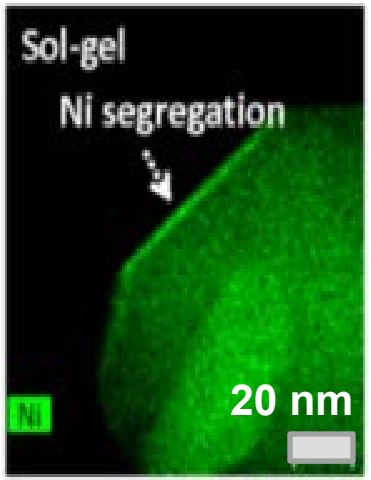
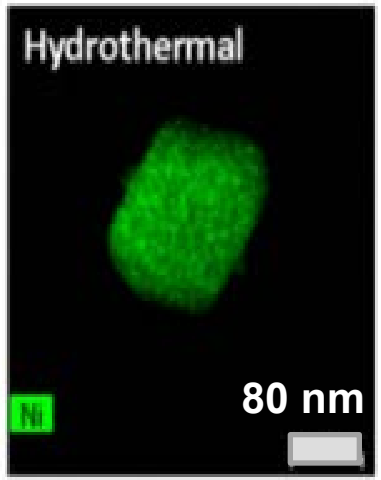
Technical Accomplishments: Correlation of Capacity Fading with Spatial Distribution of Chemicals in $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$









- Different approaches were used to produce $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$
- Each process yield material with different degree of capacity fading
- Capacity fading of cathode is related to the atomic level distribution of Ni on single particles

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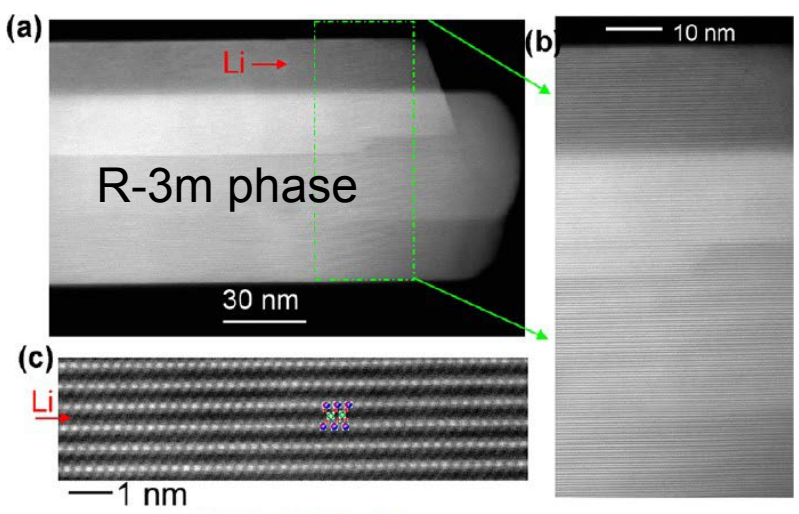
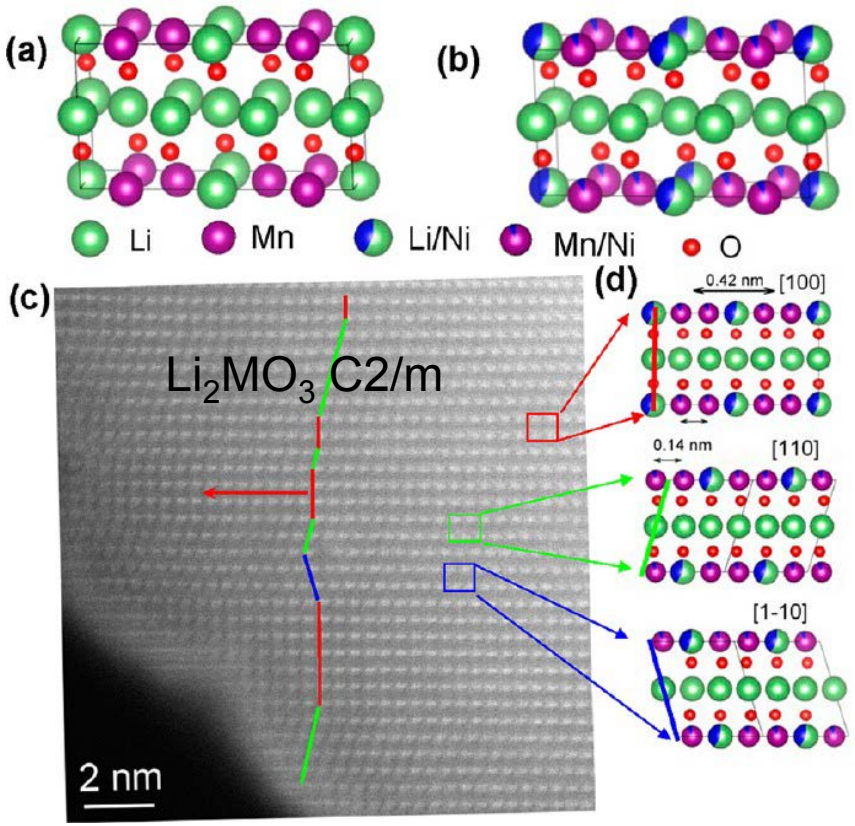
Technical Accomplishments:
Identification of The Phase Structure of Pristine $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$





- Two phases: R-3m, and Li_2MO_3 C2/m

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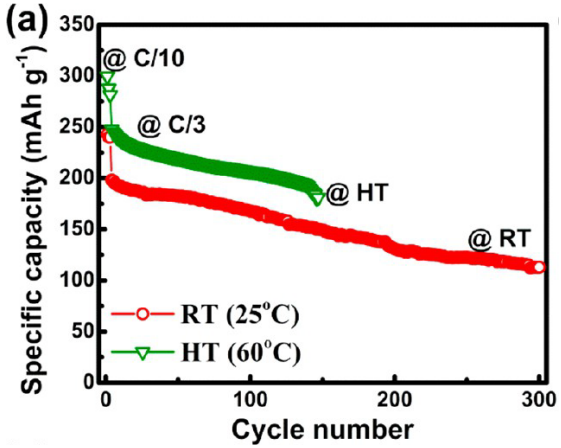
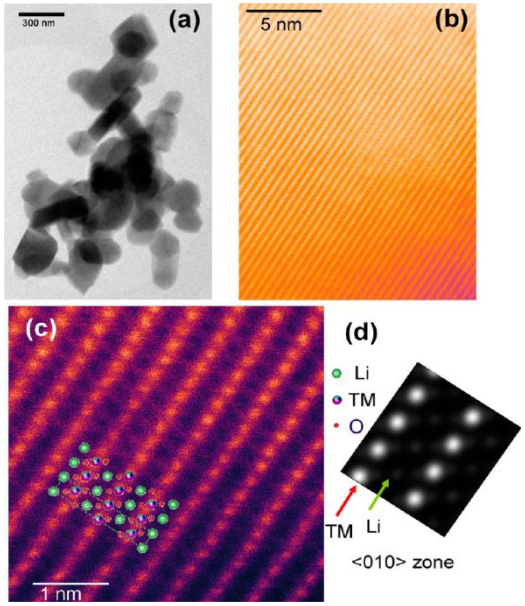
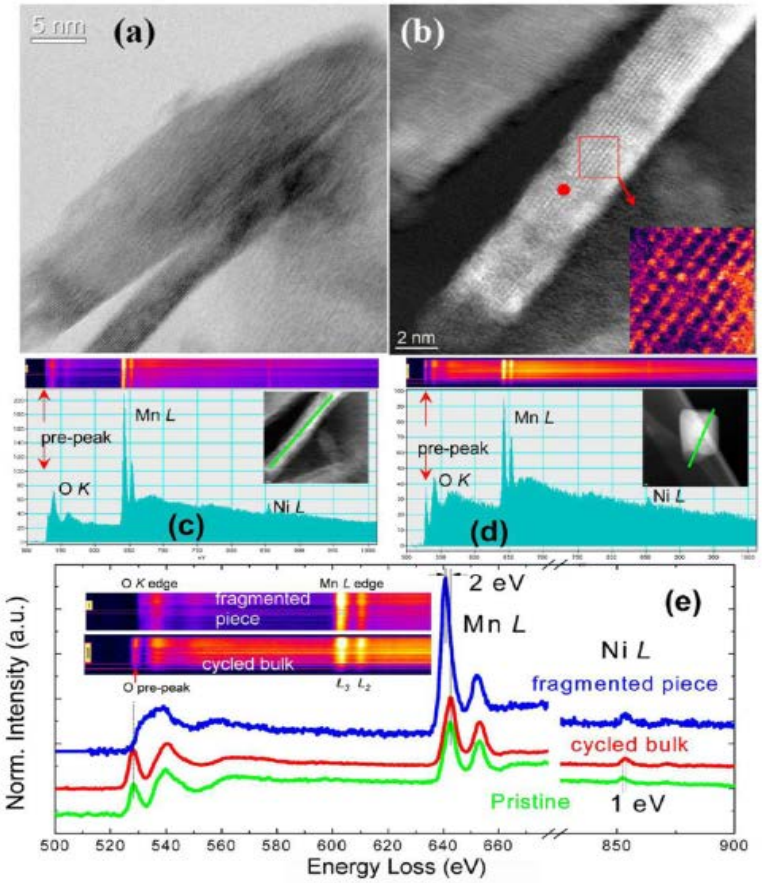
Technical Accomplishments: Failure of $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ Cathode Associated with Corrosion and Fragmentation







- The cathode particles subject to corrosion and fragmentation during the cycling
- The fragmentation and corrosion induced defects contribute to the capacity fading and final failure

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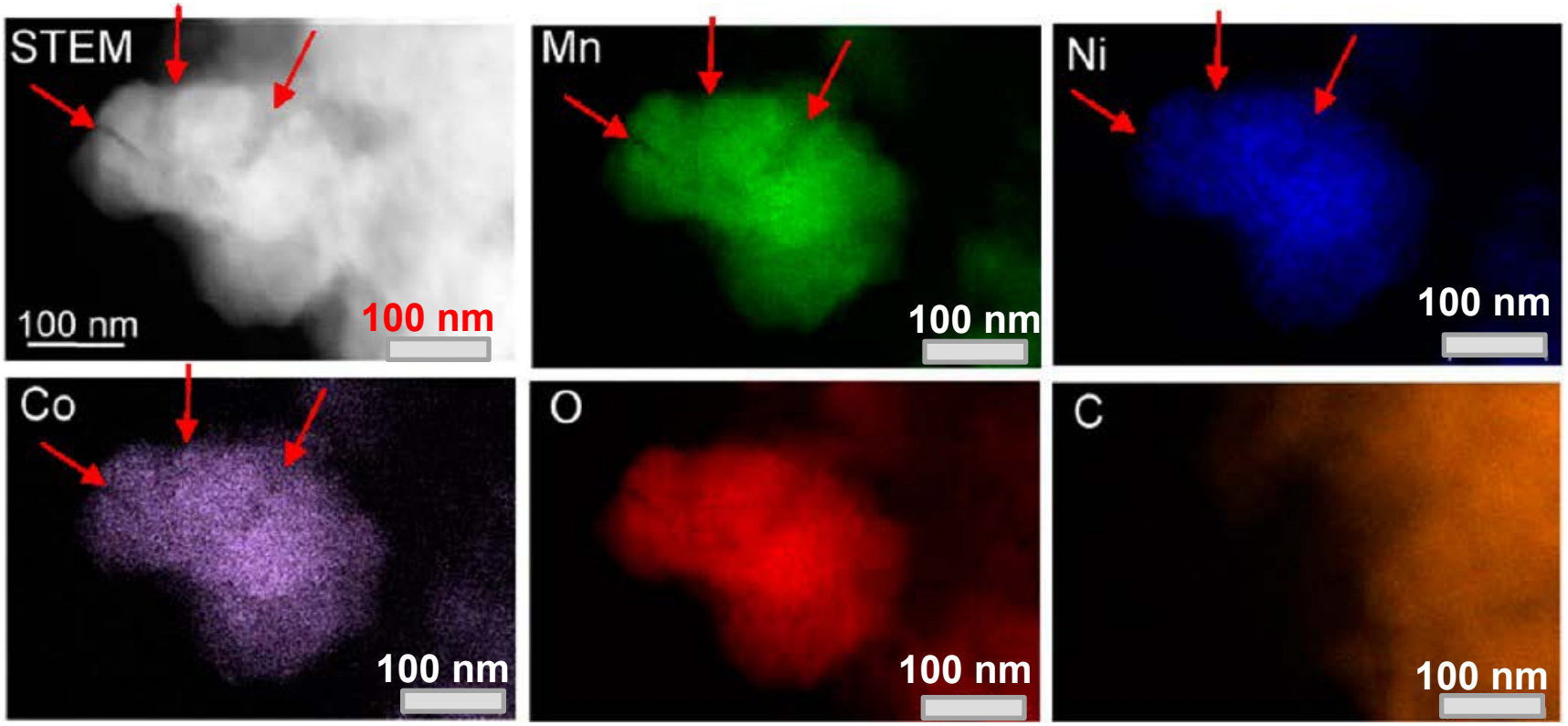
Technical Accomplishments: Cracking of the Particle upon Cycling Contributed to The Capacity Fading



- **STEM image and Mn, Ni, Co, O, C, EDS maps showing the crack formation in LNMCO after 60 cycles; the red arrows indicate the crack locations in the image and maps**

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Responses to Previous Year Reviewers' Comments

- New Project. It was not reviewed last year

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Collaboration and Coordination with Other Institutions

Partners:

- Material synthesis group in PNNL: Preparation of cathode and Si based anode materials
- Argonne National Lab: Preparation of cathode materials
- Lawrence Berkeley National Lab: Prepare and tested the conductive polymer wrapped silicon nanoparticle composite
- Stanford University: Grown the Si nanowire
- National Renewable Energy Lab: ALD coated Si samples
- Hummingbird Scientific: Help to develop the liquid holder

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Future Work

- Using the operando TEM technique to investigate the formation and evolution of SEI layers on Si based anode
- Further improve the operando TEM technique to increase the reliability and rate of success of the operando experiment
- Study the coating layer effect on the structural evolution of both anode and cathode
- Probe the detailed phase transformation mechanism and correlation with chemical composition for cathode materials
- Study of cathode structural evolution using operando TEM

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Summary

- ✓ Developed operando TEM cell, enabling direct observation of structural evolution of battery materials under dynamic operating condition
- ✓ Use in-situ TEM studied identified mesoscale structure change of silicon nanoparticles wrapped by conductive polymer
- ✓ Discovered that capacity/voltage fading of $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ cathode is closely related to the corrosion, cracking, fragmentation, and gradual phase transformation of material
- ✓ Revealed that Ni segregation in the $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ is directly related to the capacity and voltage fading

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Patents/Publications/Presentations

1. **"Mitigating Voltage Fade in Cathode Materials by Improving Atomic Level Uniformity of Elemental Distribution,"** Jianming Zheng, Meng Gu, Arda Genc, Jie Xiao, Pinghong Xu, Xilin Chen, Zihua Zhu, Wenbo Zhao, Lee Pullan , Chongmin Wang, and Ji-Guang Zhang, *Nano Lett.*, Article ASAP, **DOI:** 10.1021/nl500486y,April 7, 2014.

2. **"Corrosion/Fragmentation of Layered Composite Cathode and Related Capacity/Voltage Fading during Cycling Process",** Jianming Zheng, Meng Gu, Jie Xiao, Pengjian Zuo, Chong-Min Wang, and Ji-Guang Zhang,, Nano Lett. 13, 3824−3830 (2013)

3. **"Mesoscale Origin of the Enhanced Cycling-Stability of the Si-Conductive Polymer Anode for Li-ion Batteries"**, Meng Gu, Xing-Cheng Xiao, Gao Liu, Suntharampillai Thevuthasan, Donald R. Baer, Ji-Guang Zhang, Jun Liu, Nigel D. Browning, and Chong-Min Wang, Sci. Rep., 4, 3684, 2014.

4. **"Demonstration of an Electrochemical Liquid Cell for Operando Transmission Electron Microscopy observation of the Lithiation/Delithiation Behavior of Si Nanowire Battery Anodes."** Gu, M; Parent, L.R; Medhi, B.L; Unocic, R.R; McDowell, M.T; Sacci. R. T; Xu, W; Connell, J.G; Xu, P.H; Abellan, P; Che, X.L; Zhang, Y.H; Perea, D. E; Evans. J.E; Lauhon, L. J; Zhang, J.G; Liu, J; Browing, N. D; Cui, Y; Arslan, I and Wang, CM. *Nano Letters*, 13(12): 6106-6112, 2013. DOI: 10.1021/nl403402q.

5. **"In-Situ TEM study of Lithiation of Si and Phase transformation",** CM Wang, M Gu, Z Wang, F Gao, JG Zhang, DR Baer, S Thevuthasan, N Browning, J Liu, Microscopy and Microanalysis 19 (S2), 1468-1469 (2013)

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Acknowledgements

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

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