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Microscopy Investigation on the Fading Mechanism of Electrode Materials

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Vehicle Technologies Annual Merit Review

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Project ID #bat226

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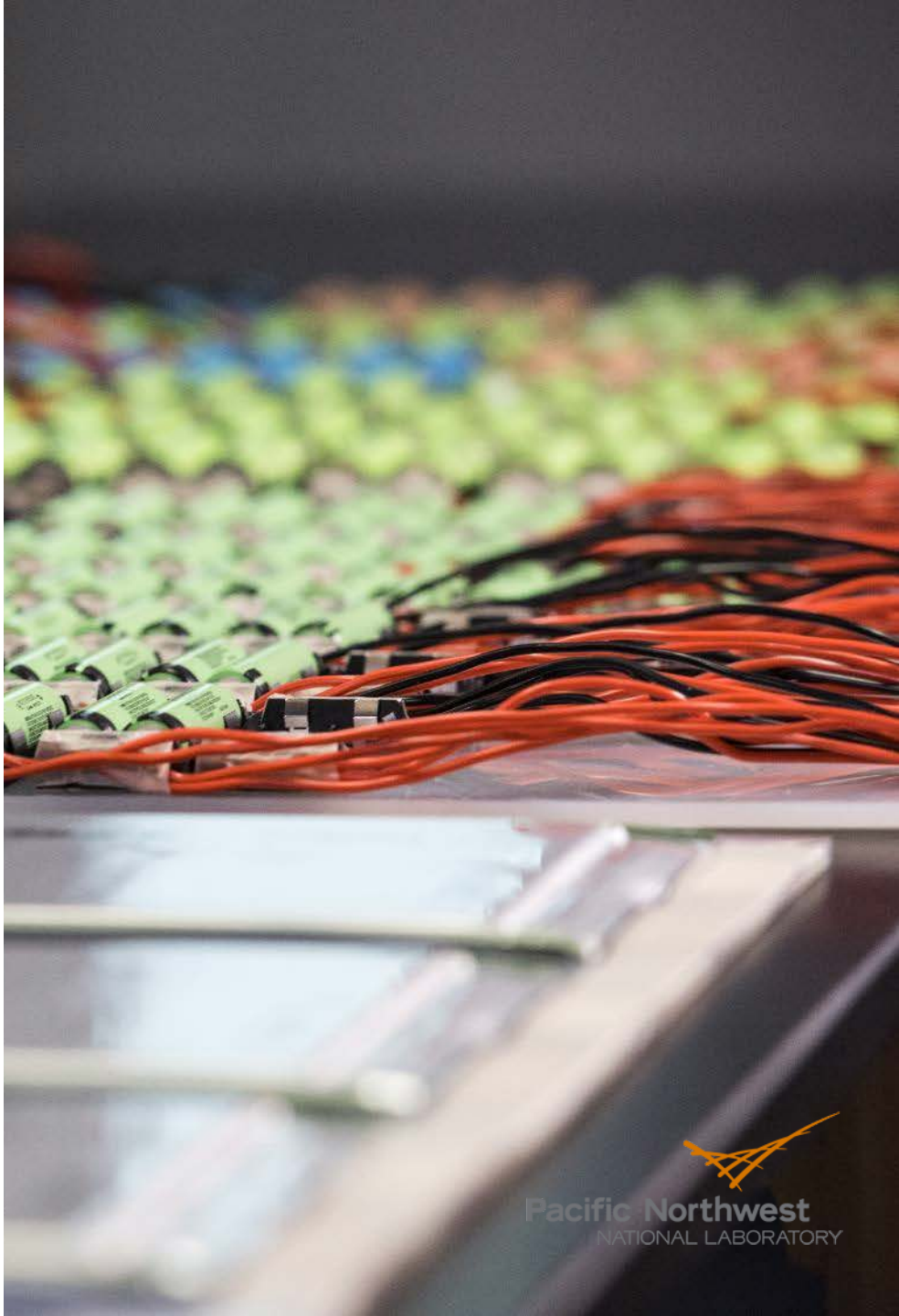

Overview

Timeline

- Start date: Oct. 1, 2016
- End date: Sept. 30, 2019
- Percent complete:83%

Budget

- Total project funding: $1000k
  - DOE share: 100%
- Funding received in FY 2018: $300k
- Funding for FY19: $400k

Barriers addressed

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

Partners

- Lawrence Berkeley National Lab
- Argonne National Lab
- Stanford University
- National Renewable Energy Lab
- GM Research Center
- University of Texas at Austin
- Hydro Quebec
- EnerG2 company
- SP-14
- FEI Company
- Hummingbird Scientific Inc.
- Material synthesis group in PNNL

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Relevance/Objectives

- Develop *ex-situ*, *in situ*, *operando and cryo* HRTEM, *in-situ* liquid SIMS and associated spectroscopic techniques for rechargeable battery research

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

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

- Obtain fundamental understanding that enables high-energy density materials required by VTO mission of long-range electrical vehicles

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Milestones and Approach

- Demonstrating how does the oxygen release happen and its correlation with anionic redox process in lithium rich layer structured cathode
- Revealing the solid-liquid interfacial reaction controls the layer to spinel phase transition
- In-situ environmental TEM revealing the coupling between electrochemically triggered thermal and mechanical effects, which can aggravate failure of layered cathode.
- Extend and enhance the unique *ex-situ* and *in-situ environmental and cryo* S/TEM methods and associated spectroscopic technique for probing the fading mechanism of Li-ion battery under dynamic operating condition

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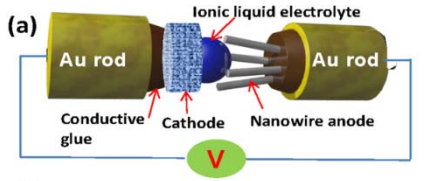
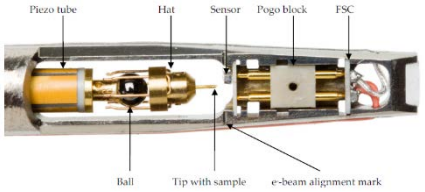
Technical Accomplishments

Enhanced *In-Situ* Environmental TEM, cryo TEM and *In-Situ* Liquid SIMS to Capture Structure, Atomic and Molecular Signature of Energy Materials

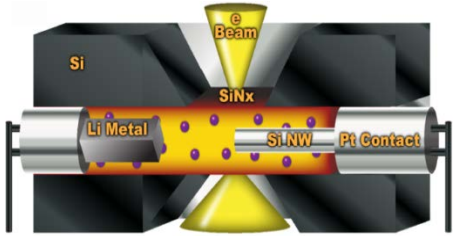
Open cell *in-situ* TEM

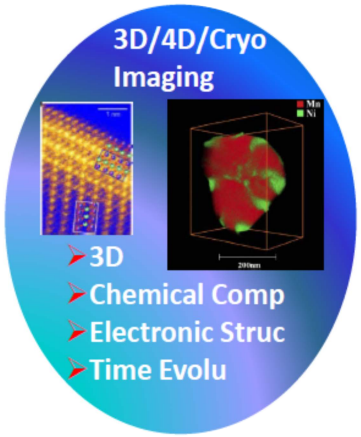




J. Y. Huang and C. M,. Wang et al, Science, 330(2010)1515

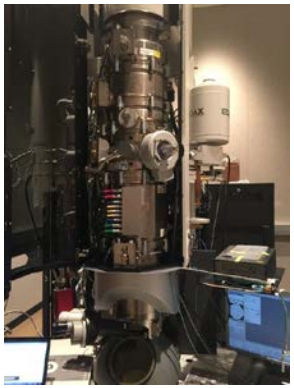
Closed cell *in-situ* TEM





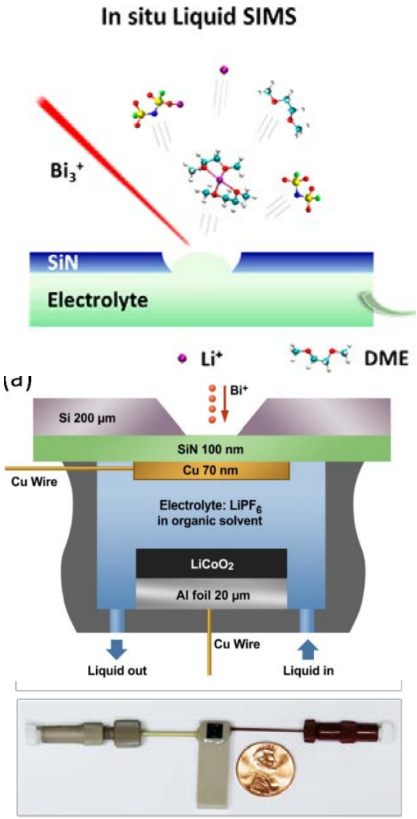
M. Gu and C. M. Wang et al, Nano Letter, 13 (2013)6106

In-Situ Environmental, cryo TEM



L. L. Luo and C. M. Wang et al, Nature Nanotechnology, 12(2017)535.

In-Situ Liquid SIMS



Zhang et al, Anal. Chem., 90 (2018), 3341−3348

Towards real battery operating condition

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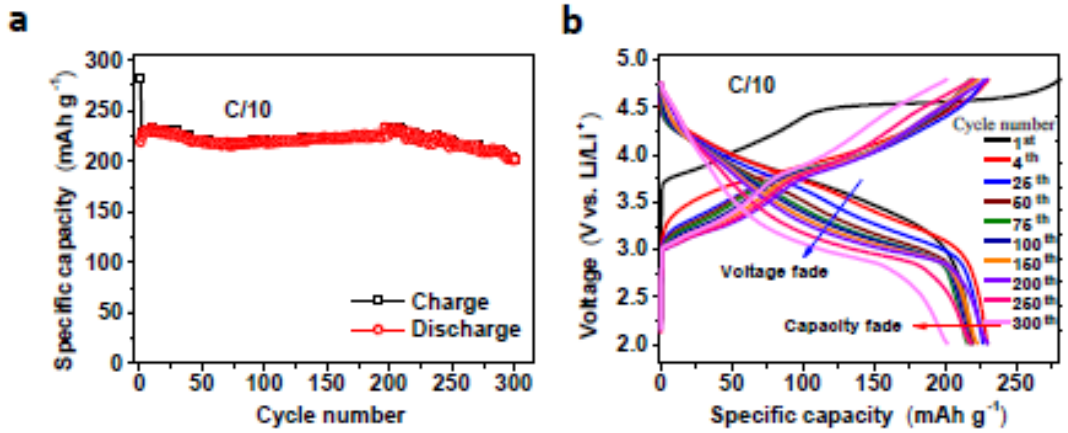
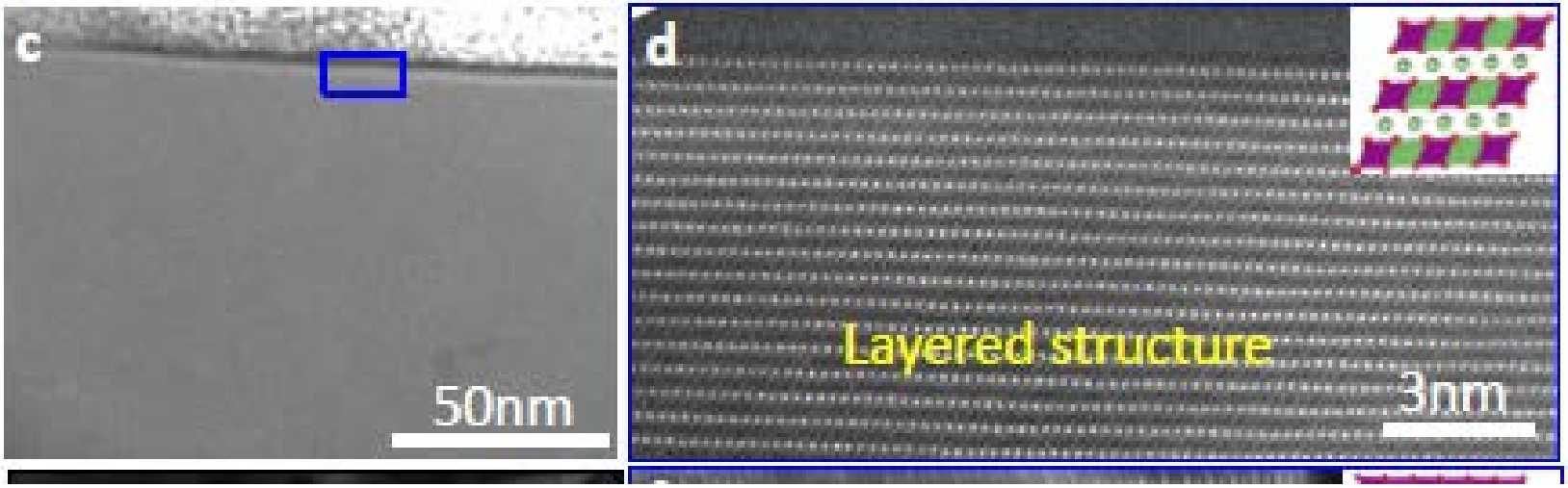
Technical Accomplishment

Revealed the oxygen vacancy injection from particle surface into the bulk lattice in lithium rich cathode, such as $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ and $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$



- Electrochemical properties shows voltage fading, but not significant in capacity fading



- The pristine material shows layered lattice structure

Yan et al, Nature Nanotechnology, 2019 online

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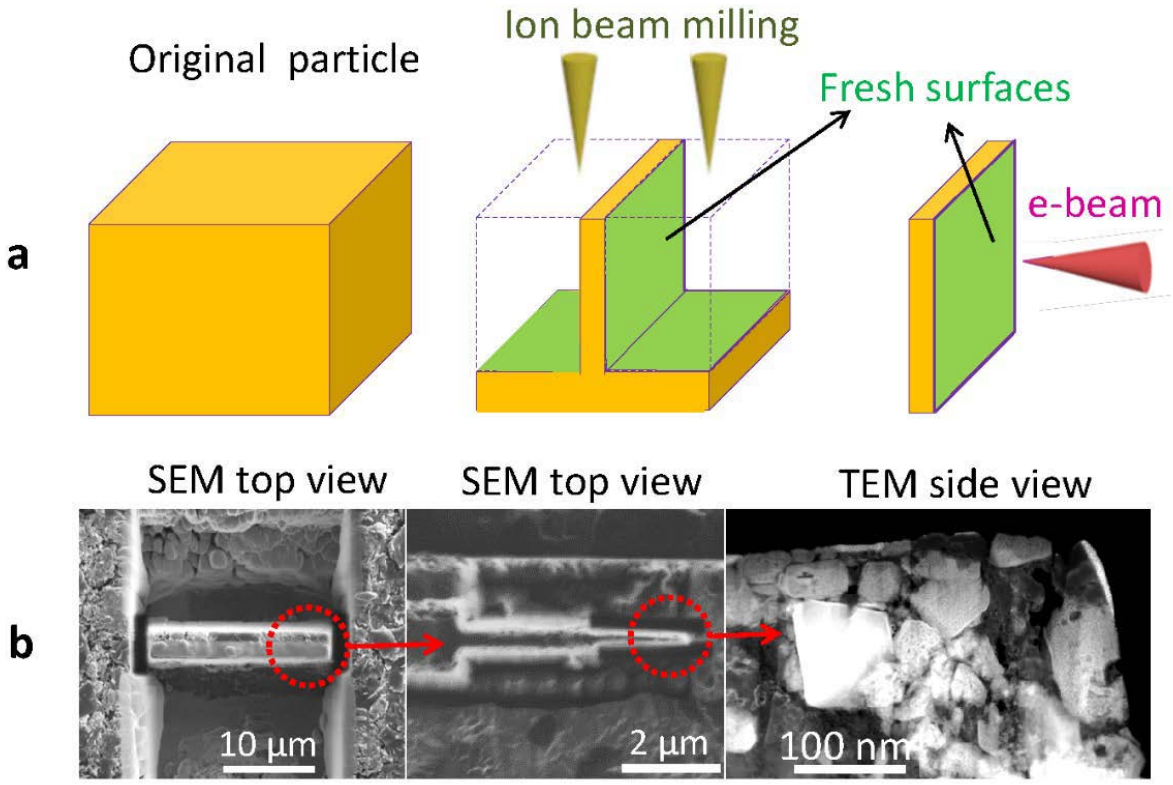

- Using focused ion beam to slice through a single particle cathode to reveal internal structure

Yan et al, Nature Nanotechnology, 2019 online

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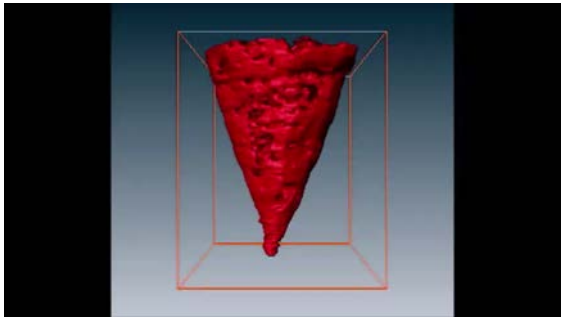

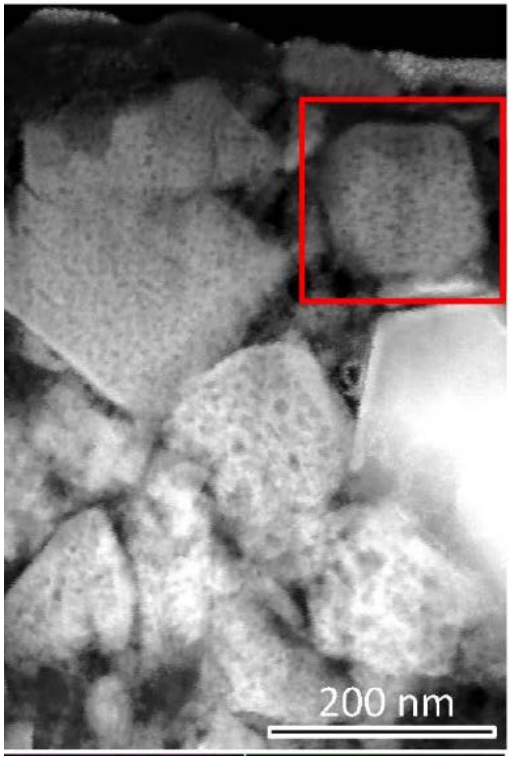

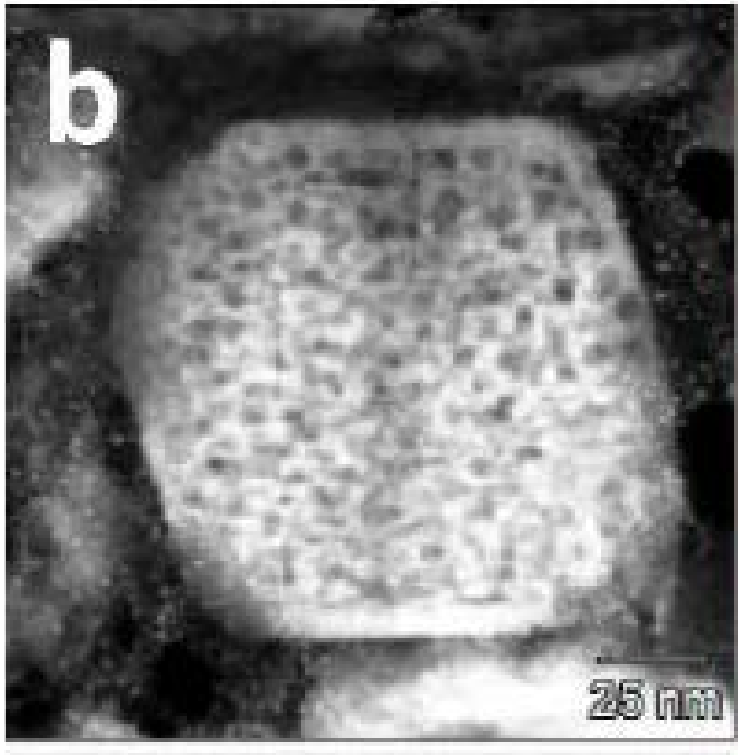

- After 300 cycles, the particle is populated with nanovoids
- 3D tomographic view of the nanovoid distribution in the bulk lattice

Yan et al, Nature Nanotechnology, 2019 online

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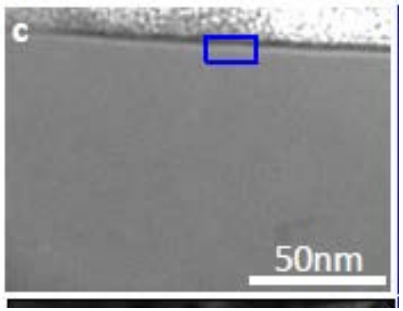
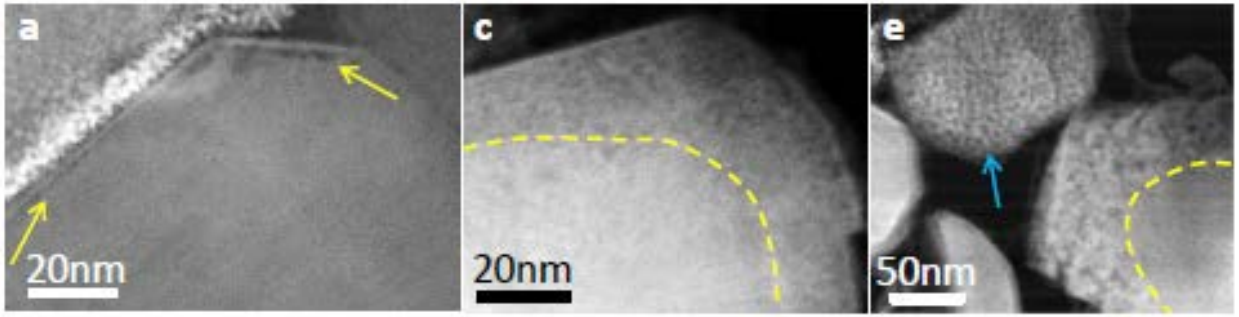
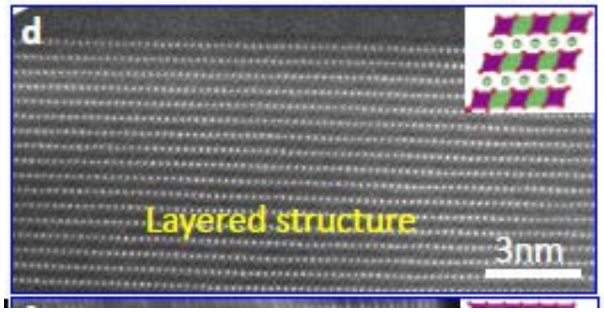
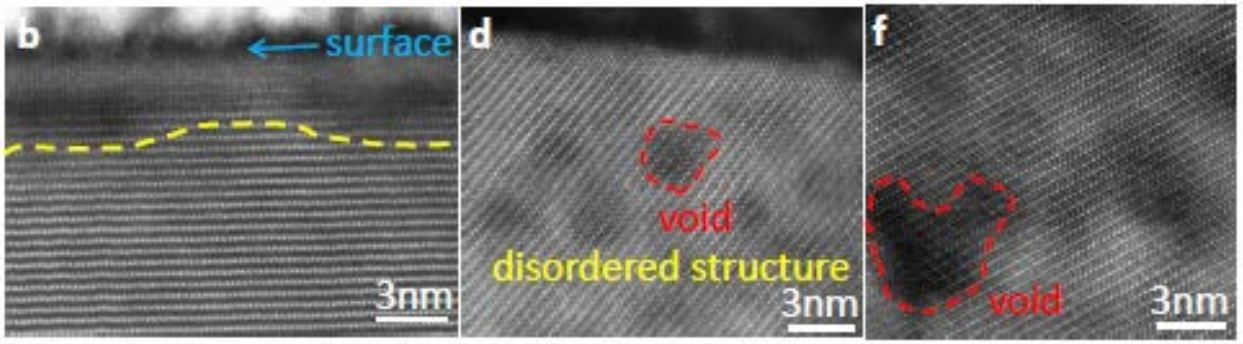


Pristine



5 cycles 45cycles 200 cycles





- Gradual propagation of nanovoids populated zone from particle surface into the bulk
- Vacancy injection indicates the oxygens are gradually diffusing out through surface vacancy mechanism

Yan et al, Nature Nanotechnology, 2019 online

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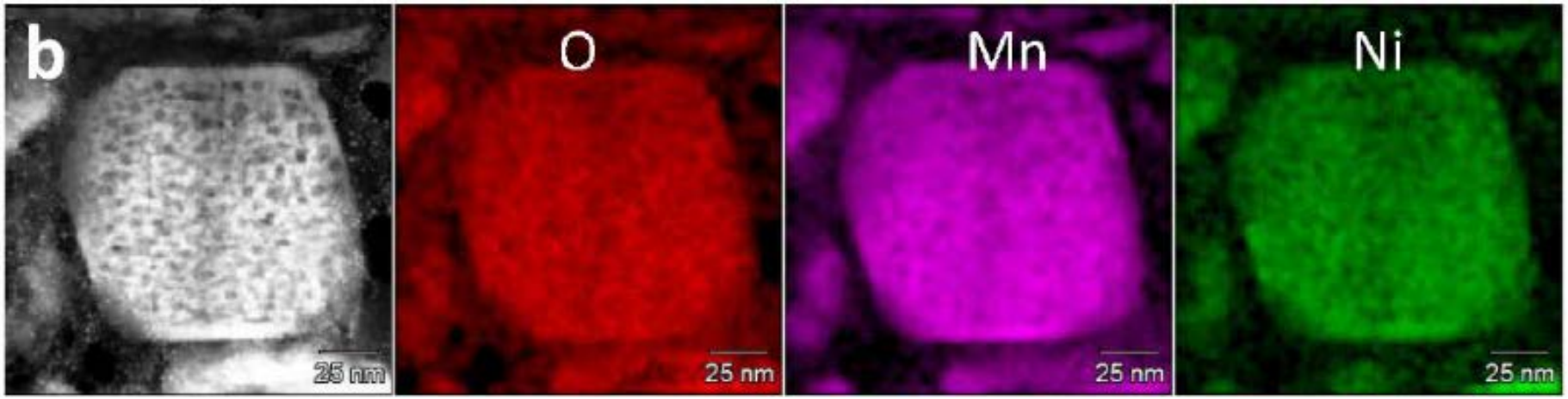

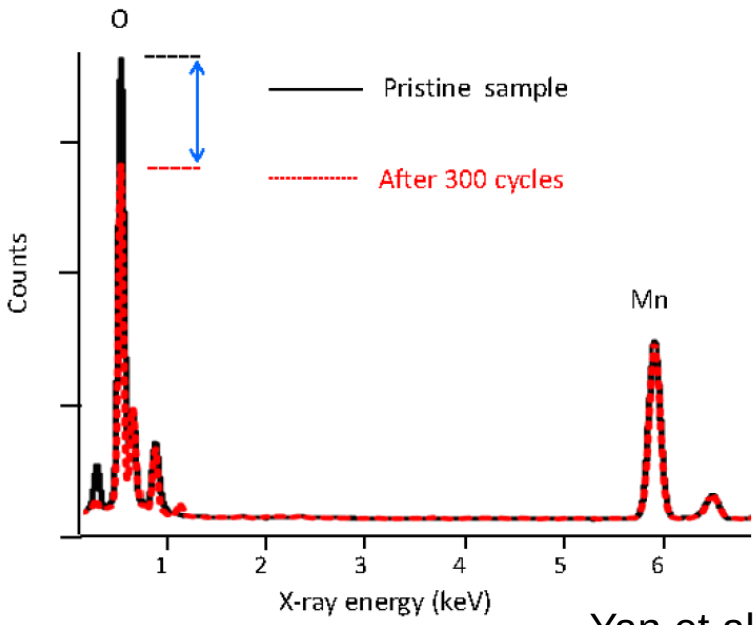

- EDS chemical mapping shows no cation segregation
- EDS reveals the loss of oxygen is ~ 20% as compared with the pristine sample

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Yan et al, Nature Nanotechnology, 2019 online

Technical Accomplishment

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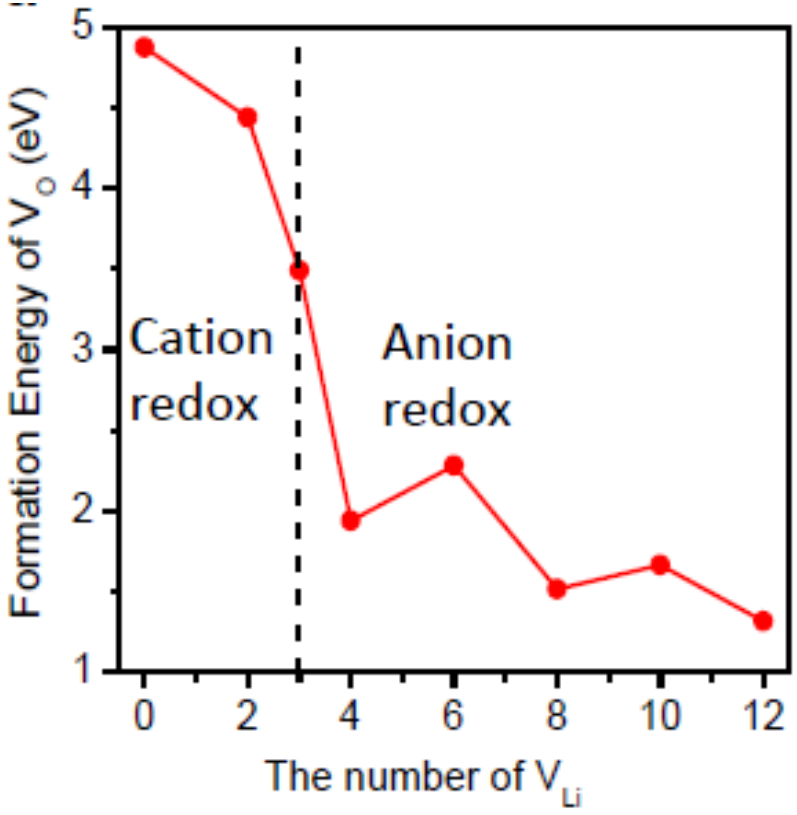

- Formation energy of oxygen vacancy in case of cation and anion redox regime

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Yan et al, Nature Nanotechnology, 2019 online

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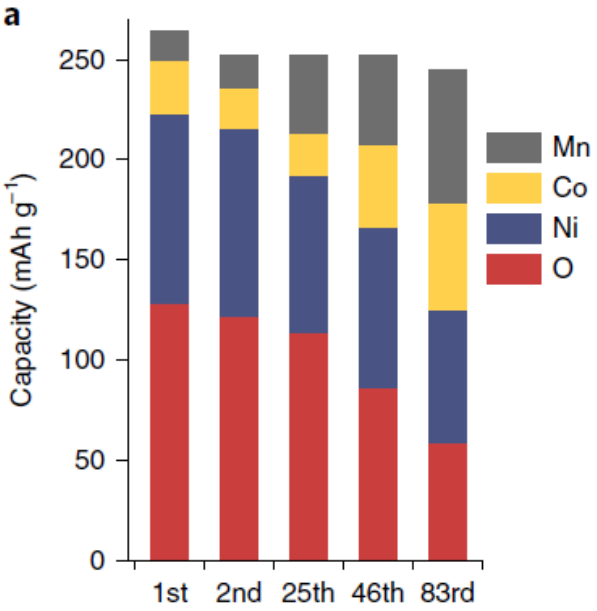

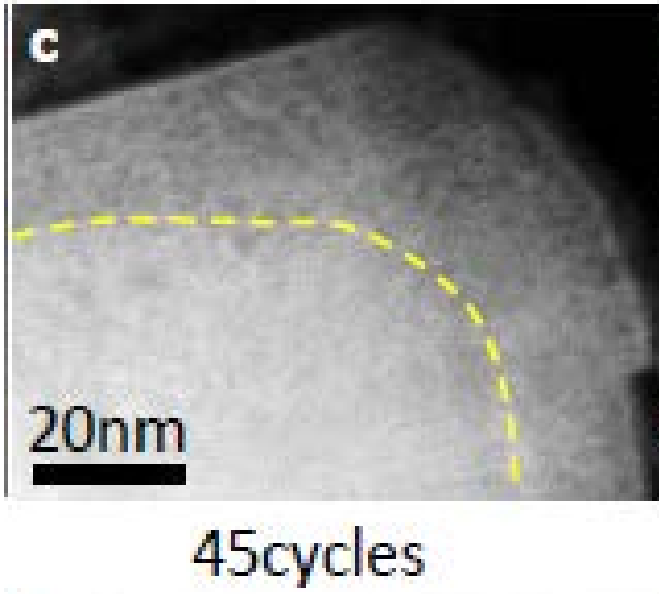

Hu et al, Nature Energy, 3, 690-698(2018)

- Excitation of anionic redox leads to vacancy injection
- Anionic redox plays contradicting role, enhance capacity, while injecting defects from surface into bulk
- Dynamic coupling of anionic redox with bulk lattice through surface oxygen loss
- To mitigate vacancy injection, preventing surface oxygen loss is a critical step

Yan et al, Nature Nanotechnology, 2019 online

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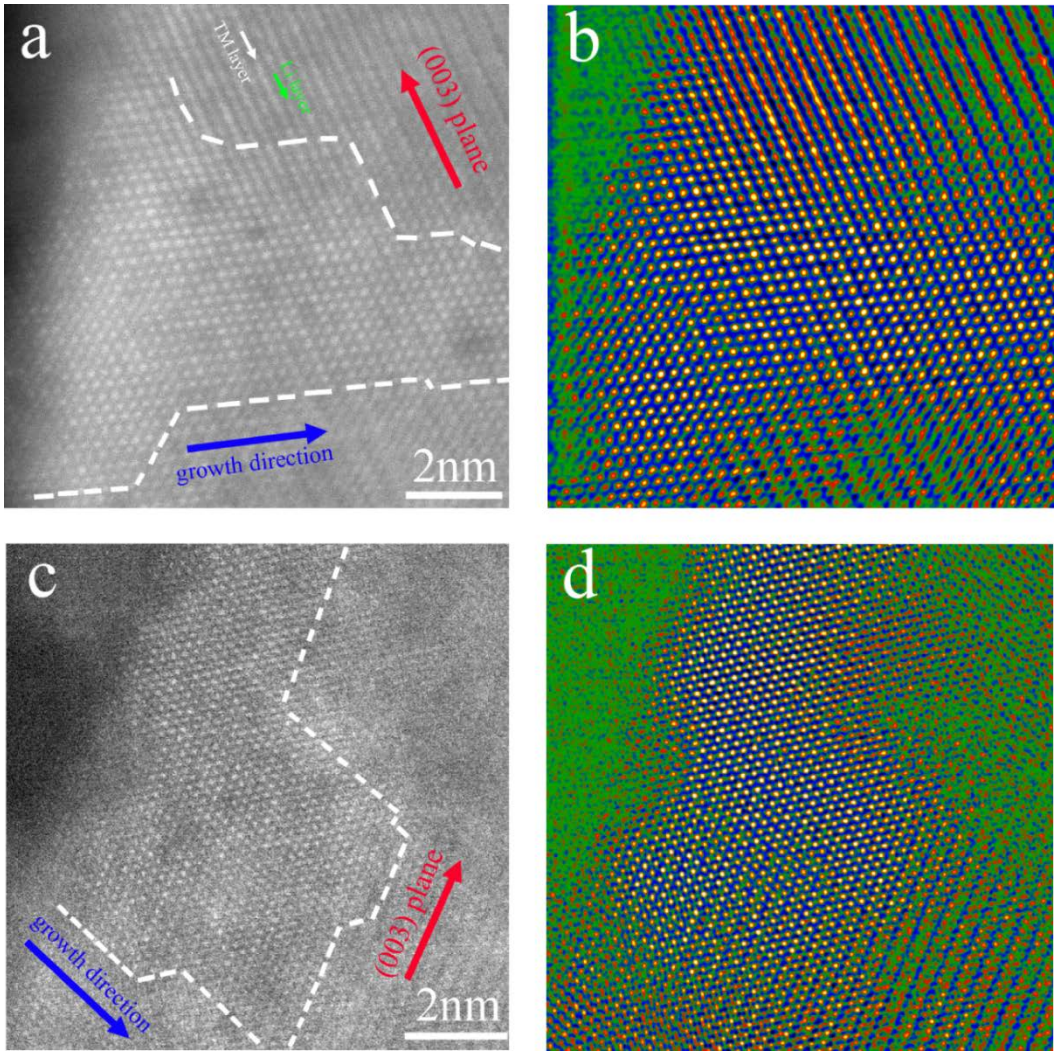
Technical Accomplishment

Revealed Interfacial reaction transverses beyond SEI layer and triggers bulk lattice phase transition ($LiNi_{0.76}Co_{0.10}Mn_{0.14}O_2$, 200 cycles)



- Anisotropic propagation of layer to rock salt transition into the bulk lattice in the baseline electrolyte: 1 M $LiPF_6$ in EC:EMC=4:6 by weight
- Coupling of interfacial process with bulk lattice

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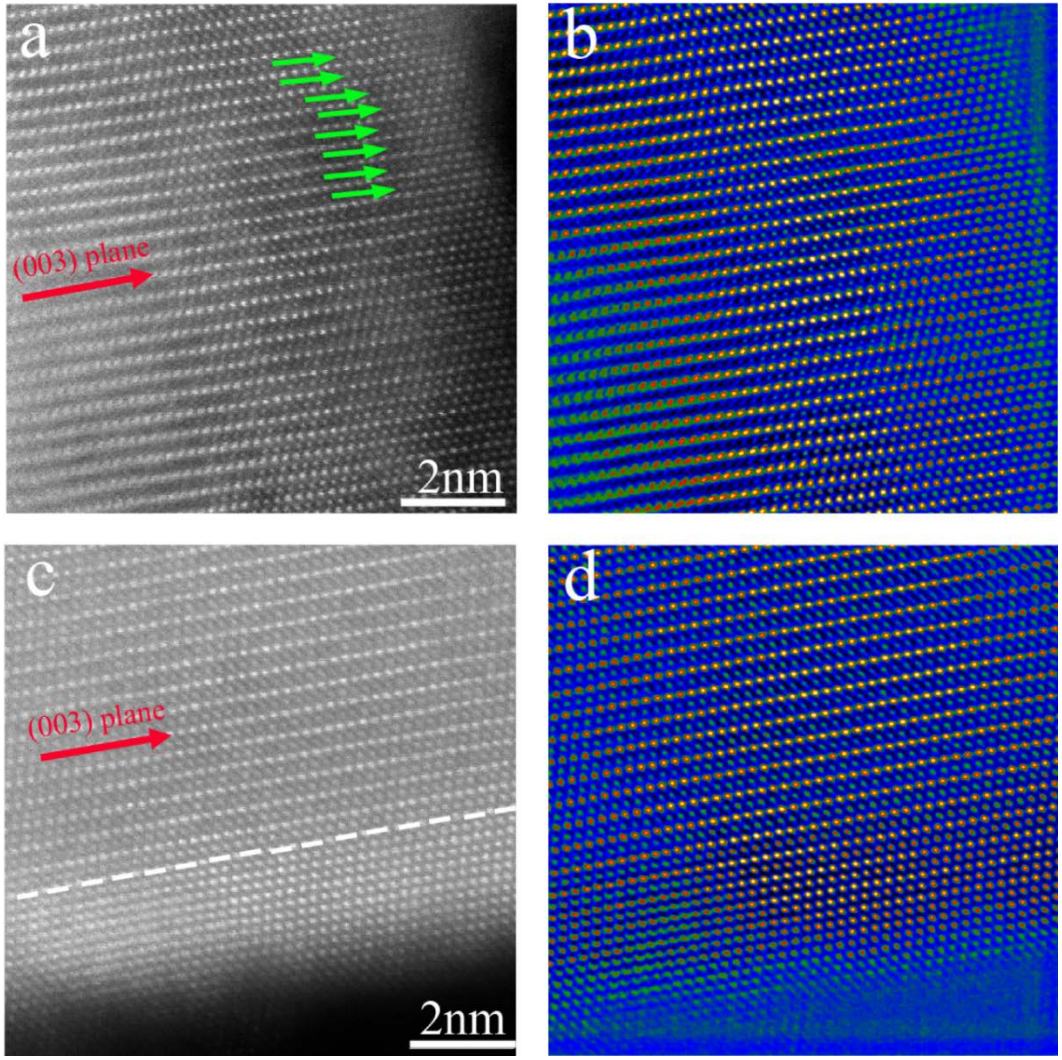
Zou et al, Chem. Mater. 30, 7016-7026(2018).

Technical Accomplishment

Change electrolyte chemistry can mitigate the interfacial reaction controlled bulk lattice phase transition ($LiNi_{0.76}Co_{0.10}Mn_{0.14}O_2$, 200 cycles)



- Mitigation of anisotropic propagation of layer to rock salt transition into the bulk lattice in the optimized electrolyte: 0.6 M LiTFSI + 0.4 M LiBOB + 0.05 M $LiPF_6$ in EC:EMC=4:6 by weight
- Control of interfacial reaction can mitigate bulk lattice degradation:
- Electrolyte chemistry; doping of bulk lattice; surface coating or modification

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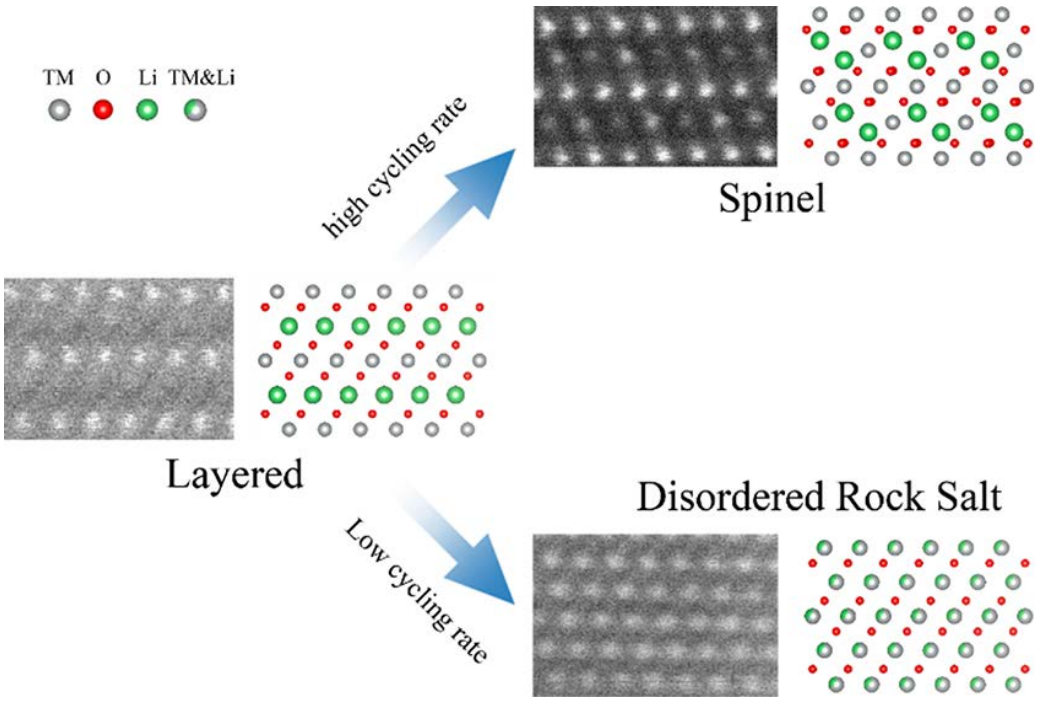
Zou et al, Chem. Mater. 30, 7016-7026(2018).

Technical Accomplishment

Revealing Cycling Rate-Dependent Structure Evolution in Ni-Rich Layered Cathode Materials ($LiNi_{0.76}Co_{0.10}Mn_{0.14}O_2$)



- High rate cycling leads to spinel phase; due to the significant kinetic barrier arising from the Li retention impedes Ni migration, leading to the growth of the spinel phase.
- Low rate cycling leads to rock salt structure; due to the sufficient Li vacancies favor the thorough mixing between transition metal and Li layers, resulting in the formation of a disordered rock salt structure

Zou et al, ACS Energy Lett. 3, 2433-2440(2018).

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Collaboration and Coordination with Other Institutions

Partners:

- Argonne National Lab: Preparation of cathode materials
- Lawrence Berkeley National Lab: Preparation of cathode materials
- Oak Ridge National Laboratory: Preparation of cathode materials
- Stanford University: Si nanowire based anode and surface coating
- GM Research Center: Prepared porous Si, S enclosed in carbon
- National Renewable Energy Lab: ALD coated Si samples
- University of Texas at Austin: Preparation of cathode and anode materials
- Hummingbird Scientific: Help to develop the liquid holder
- FEI Company: ETEM capability development
- Material synthesis group in PNNL: Preparation of both cathode and Si based anode materials

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Proposed Future Research

FY2019

- Revealing the role of dopant to stabilize the lattice in cathode answering why aluminum plays a critical role on cycle stability of NCA
- Resolve the true structural nature of the intragranular cracks in Ni-rich NMC and answer the questions on the origin of such a cracking behavior

FY2020

- Using in-situ TEM to probe the nucleation and growth behavior of Li dendrite, to reveal the controlling factor that induced Li dendrite
- Revealing the true structural and chemical information of Li metal anode-liquid SEI layer by cryo-TEM and EELS
- Cryo-TEM study of detailed structure of solid-liquid interphase layer Si anode and this will be combined with in-situ liquid SIMS work
- Determine the fundamental cause of the instability of Ni-rich NMC under environmental conditions

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

Summary

- For lithium rich layered cathode, oxygen vacancy is gradually injected into the bulk lattice and form nano-voids, which is a bulk degradation mechanism
- The oxygen vacancy injection in lithium rich layered cathode is associated with the excitation of anionic redox process by which the oxygen vacancy formation energy and migration energy is dramatically reduced
- For lithium rich layered cathode, the anionic redox plays a contradicting role
- For lithium rich layered cathode, the gradual releasing of oxygen through oxygen vacancy injection accounts for the gradual increasing of Mn and Co redox as well as decreasing anionic redox.
- For lithium rich layered cathode, as the releasing of oxygen is associated with surface vacancy generation, therefore mitigating surface oxygen loss is a critical step for stabilizing the structure
- Cathode-liquid interfacial reaction critically controls the bulk lattice stability through defects injection from interface into the bulk lattice
- For NMC structure, charging-discharging rate affects layer to spinel or rock salt phase transformation, high rate will lead to spinel phase, while low rate will lead to rock salt structure
- Electrochemical process will trigger thermal and mechanical effect, again in turn couples with electrochemical process to aggravate the degradation of cathode

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Technical Back-Up Slides

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Patents/Publications/Presentations

1. Pengfei Yan, Jianming Zheng, Jian Liu, Biqiong Wang, Xiaopeng Cheng, Yuefei Zhang, Xueliang Sun, Chongmin Wang, and Ji-Guang Zhang, “Tailoring Grain Boundary Structures and Chemistry of Ni-rich Layered Cathode for Enhanced Cycle Stability of Lithium-Ion Batteries”, **Nature Energy, 3, 600-605(2018).**
2. Pengfei Yan, Jianming Zheng, Tianwu Chen, Langli Luo, Yuyuan Jiang, Kuan Wang, Manling Sui, Ji-Guang Zhang, Sulin Zhang and Chongmin Wang, “Coupling of electrochemically triggered thermal and mechanical effects to aggravate failure in a layered cathode”, **Nature Communications 9, 2437(2018).**
3. Lianfeng Zou, Zhenyu Liu, Wengao Zhao, Haiping Jia, Jianming Zheng, Yong Yang, Guofeng Wang, Ji-Guang Zhang, and Chongmin Wang, “Solid−Liquid Interfacial Reaction Trigged Propagation of Phase Transition from Surface into Bulk Lattice of Ni-Rich Layered Cathode”, **Chem. Mater. 30, 7016-7026(2018).**
4. Lianfeng Zou, Wengao Zhao, Zhenyu Liu, Haiping Jia, Jianming Zheng, Guofeng Wang, Yong Yang, Ji-Guang Zhang, and Chongmin Wang, “Revealing Cycling Rate-Dependent Structure Evolution in Ni-Rich Layered Cathode Materials”, **ACS Energy Lett. 3, 2433-2440(2018)**.
5. Hanlei Zhang, Brian M. May, Jon Serrano-Sevillano, Montse Casas-Cabanas, Jordi Cabana, Chongmin Wang and Guangwen Zhou, “Facet-Dependent Rock-Salt Reconstruction on the Surface of Layered Oxide Cathodes”, **Chem. Mater. 30, 692-699(2018).**
6. Qiaobao Zhang, Huixin Chen, Langli Luo, Bote Zhao, Hao Luo, Xiang Han, Jiangwei Wang, Chongmin Wang, Yong Yang, Ting Zhu and Meilin Liu, “Harnessing the concurrent reaction dynamics in active Si and Ge to achieve high performance lithium-ion batteries”, **Energy Environ. Sci., 11, 669-681(2018).**
7. Jagjit Nanda, Chongmin Wang, and Ping Liu, “Frontiers of solid-state batteries”, **MRS Bulletin, 10 741(2018).**
8. Jaegeon Ryu, Tianwu Chen, Taesoo Bok, Gyujin Song, Jiyoung Ma, Chihyun Hwang, Langli Luo, Hyun-Kon Song, Jaephil Cho, Chongmin Wang, Sulin Zhang and Soojin Park, “Mechanical mismatch-driven rippling in carboncoated silicon sheets for stress-resilient battery anodes”, **Nature Communications, 9, 2924(2018).**
9. Yanyan Zhang, Mao Su, Xiaofei Yu, Yufan Zhou, Jungang Wang, Ruiguo Cao, Wu Xu, Chongmin Wang, Donald R. Baer, Oleg Borodin, Kang Xu, Yanting Wang, Xue-Lin Wang, Zhijie Xu, Fuyi Wang, and Zihua Zhu, “Investigation of Ion−Solvent Interactions in Nonaqueous Electrolytes Using in Situ Liquid SIMS**”, Anal. Chem. 90, 3341−3348 (2018).**

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Acknowledgements

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- ✓ Team Members:
  Lianfeng Zou, Robert Warren, Yang He, Yaobin Xu, Wu Xu, Xiaolin Li, Jie Xiao, Jun Liu, and Ji-Guang Zhang

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