Microscopy Investigation on the Fading Mechanism of Electrode Materials

Chongmin Wang

2018 DOE Vehicle Technologies Program Review

June 18-21, 2018

Project ID#: BAT226

Pacific Northwest
NATIONAL LABORATORY

Overview

Timeline

- Start date: Oct. 1, 2015
- End date: Sept. 30, 2018
- Percent complete:83%

Budget

- Total project funding: $900k
  - DOE share: 100%
- Funding received in FY 2017: $300k
- Funding for FY18: $300k

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
- UC San Diego
- 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

Relevance/Objectives

- Develop *ex-situ*, *in situ* and *operando* 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

Milestones

- Resolve the vacancy injection mechanism into the LM-NMC during the battery cycling and its correlation with battery fading mechanism (03/31/2018). **(Complete and a manuscript is submitted)**

- The functioning mechanism of electrolyte additive on the solid-liquid interphase in NMC cathode (06/31/2018). (**In progress**)

- Atomic-level understanding of the mechanism of intergranular and intragranular cracking in NMC and grain boundary structure in cathode secondary particles (9/30/2018).

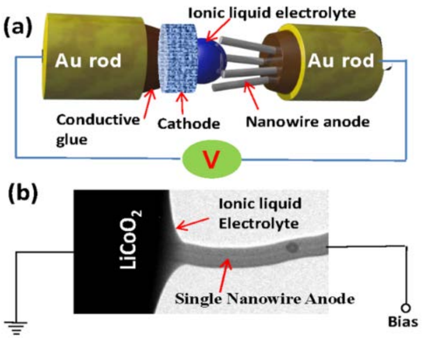
Approach

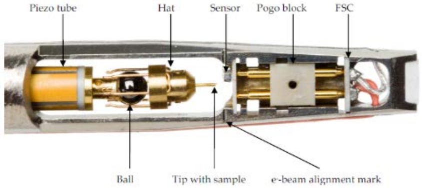
- Using the state-of-the-art aberration corrected S/TEM, EELS, and EDS and *in-situ* liquid SIMS to probe chemistry and structure of electrode
- Extend and enhance the unique *ex-situ* and *in-situ* S/TEM methods and associated spectroscopic technique for probing the fading mechanism of Li-ion battery under dynamic operating condition
- Establish close collaboration/integration with battery research and development groups to capture the cutting-edge questions facing the battery research/development

Technical Accomplishments

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

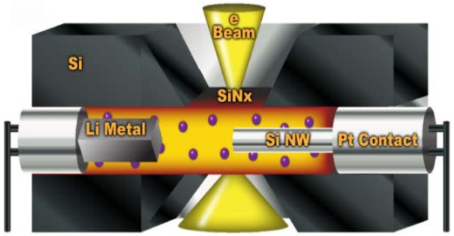
Open cell *in-situ* TEM

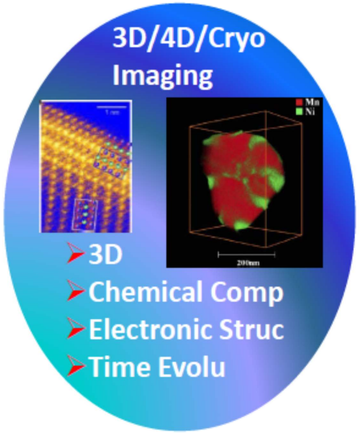




J. Y. Huang and C. M,. Wang et al, Science, 330(2010)1515

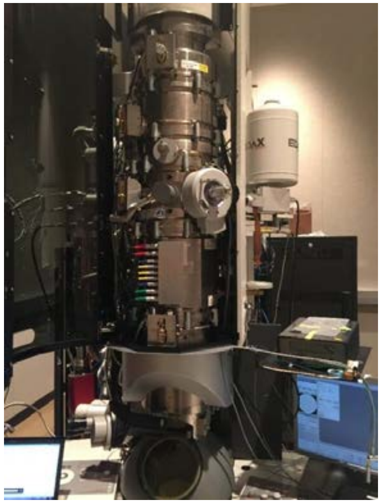
Closed cell *in-situ* TEM





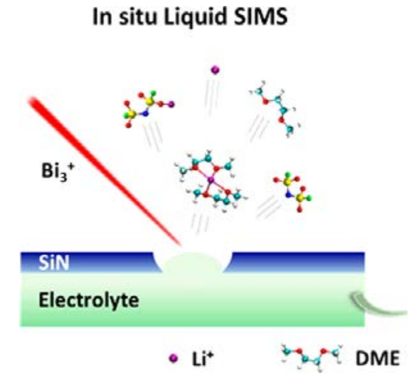
M. Gu and C. M. Wang et al, Nano Letter, 13 (2013)6106

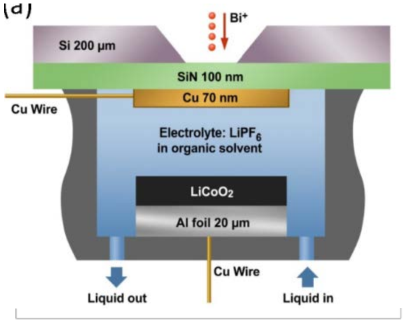
In-Situ Environmental TEM

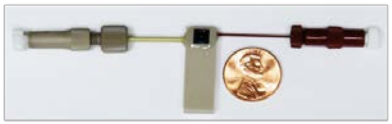


L. L. Luo and C. M. Wang et al, Nature Nanotechnology, 12(2017)535.

In-Situ Liquid SIMS







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

Towards real battery operating condition

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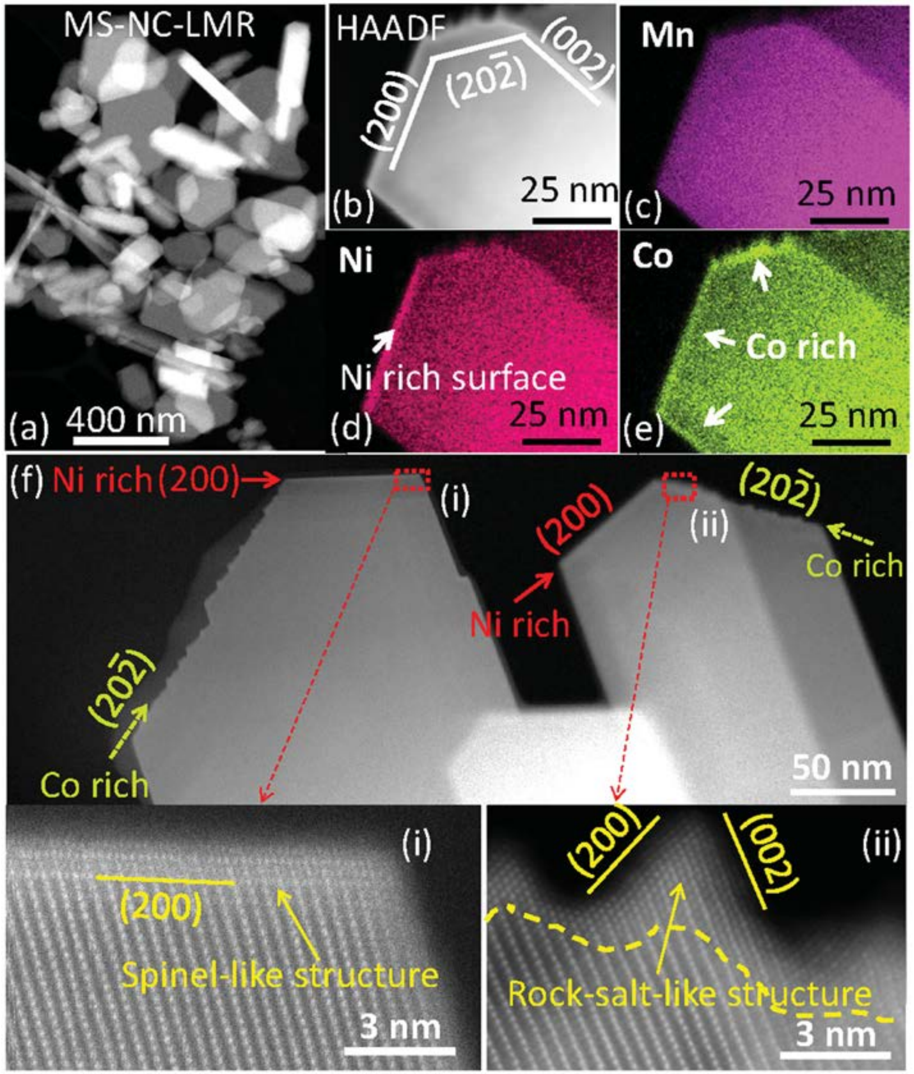
Technical Accomplishments

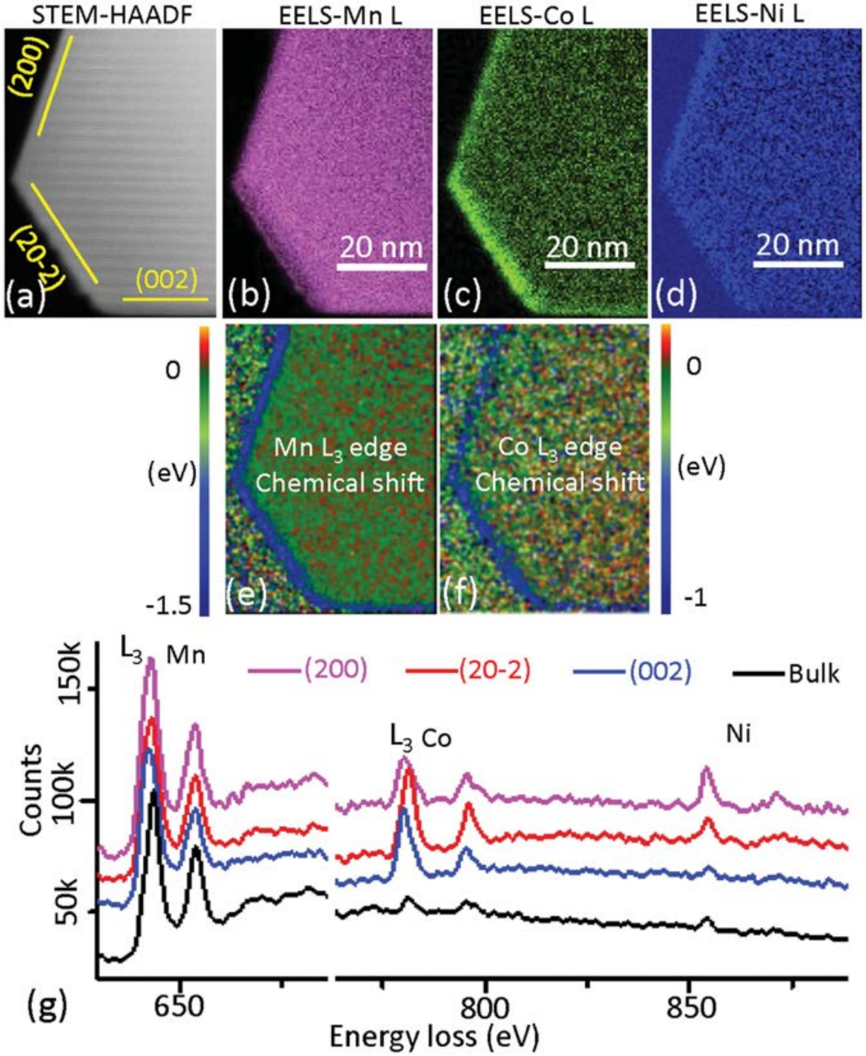
Revealed the segregation of Ni, Co, Mn in Pristine $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ and $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$



- Distinctive Surface Segregation of Ni and Co in Monoclinic LMR Cathodes
- For $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ and $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$, both Ni and Co are prone to segregation to the particle surfaces
- However, Ni and Co segregate at distinctively different surface planes:
  - Ni is exclusively segregated at the (200) m surface (the subscript m indicate monoclinic lattice)
  - Co predominately enriched on the (20−2)m surface and slight enrichment on (200)m and (002)m facets was also observed.

Technical Accomplishments

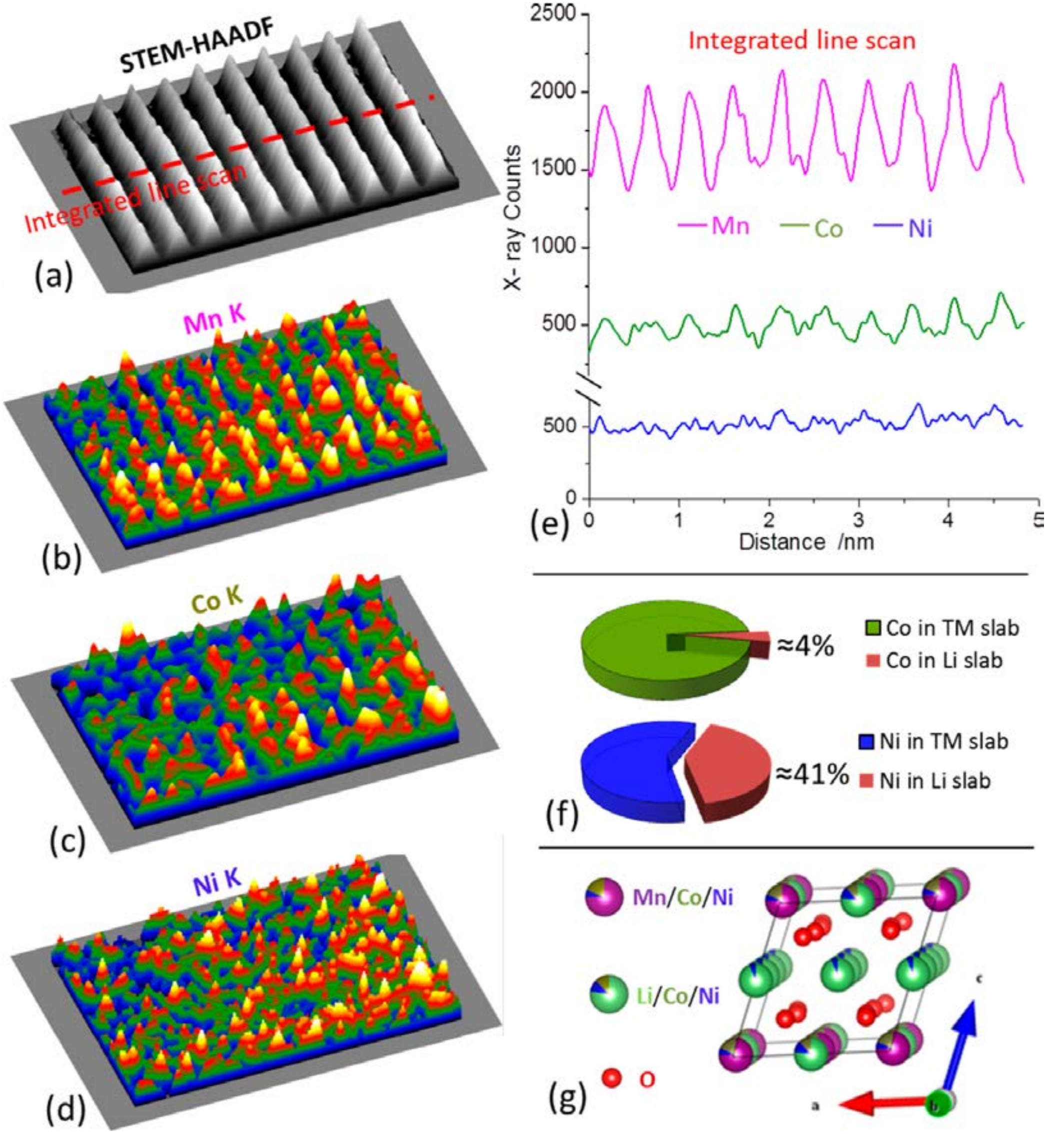
Revealed the valence state of surface segregated Ni, Co, Mn in pristine $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ and $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$



- The STEM-EELS elemental maps show Ni/Co surface segregation consistent with the results from EDS mapping
- EELS mapping allows us to extract TM valence state information based on either L-edge energy shift (so-called chemical shift) or L_3/L_2 white-line intensity ratios However, Ni and Co segregate at distinctively different surface planes.
- As shown in the Figure (e,f,) a clear chemical shift was observed on the surface for both Mn L_3 edge and Co L_3 edge as compared to that of the bulk, indicating reduced valence state of Mn and Co in the surface layer.

Technical Accomplishments

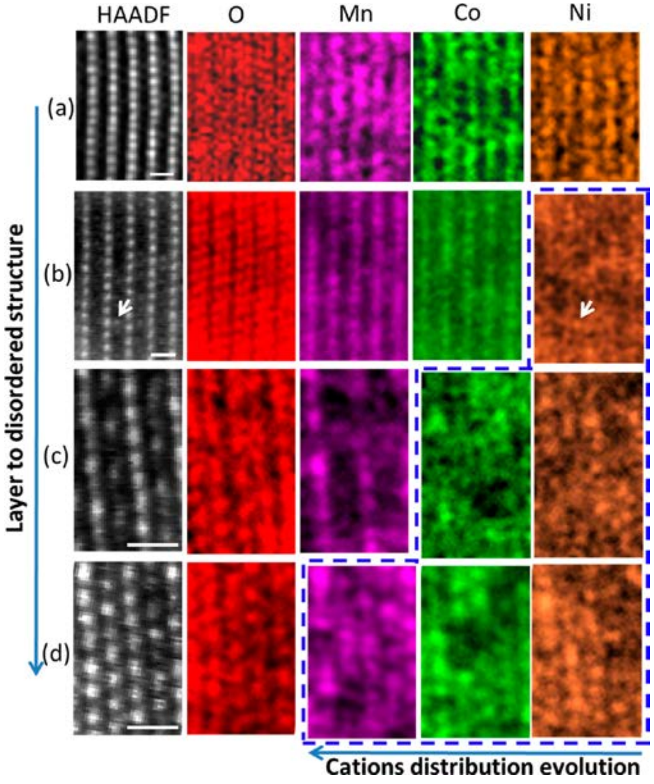
Revealed Ni, Co, Mn Mix with Li in pristine $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$



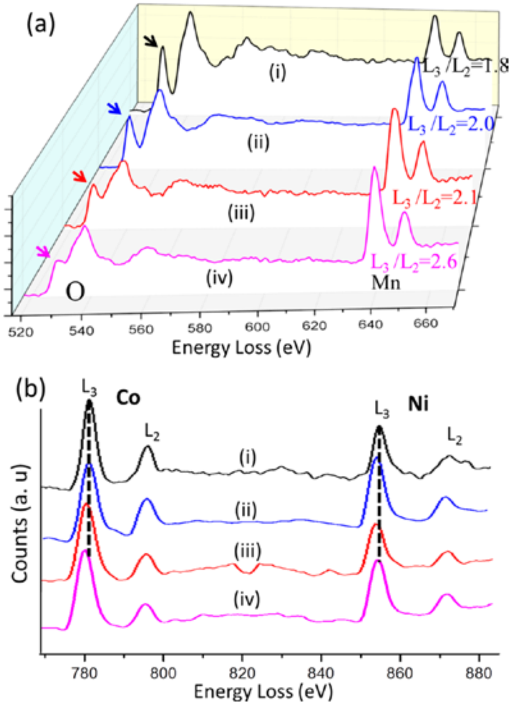
- (a) [010] zone axis STEM-HAADF image showing the EDS mapping region
- (b) Surface plot of Mn K map. (c) Surface plot of Co K map. (d) Surface plot of Ni K map. (e) Integrated line scan profile showing X-ray counts distribution across the layered structure
- (f) On the basis of counts ratio from the TM layer and Li layer, 4% Co and 41% Ni were estimated to seat in the Li layer due to interlayer mixing.
- (g) Crystal model for NC-LMR based on EDS mapping results

Technical Accomplishments

Revealed Ni, Co, Mn migration and mixing with Li layer after 100 cycles with a high cutoff voltage of 4.8 V (NMC333)



- Atomic resolution STEM-EELS mapping
- (a) From the pristine NMC333 without cycling
- (b−d) From NMC333 after 100 cycles with a high cutoff voltage of 4.8 V
- (b) From the well-preserved layered region. (c) From the disordered region
- (d) From the heavily disordered region

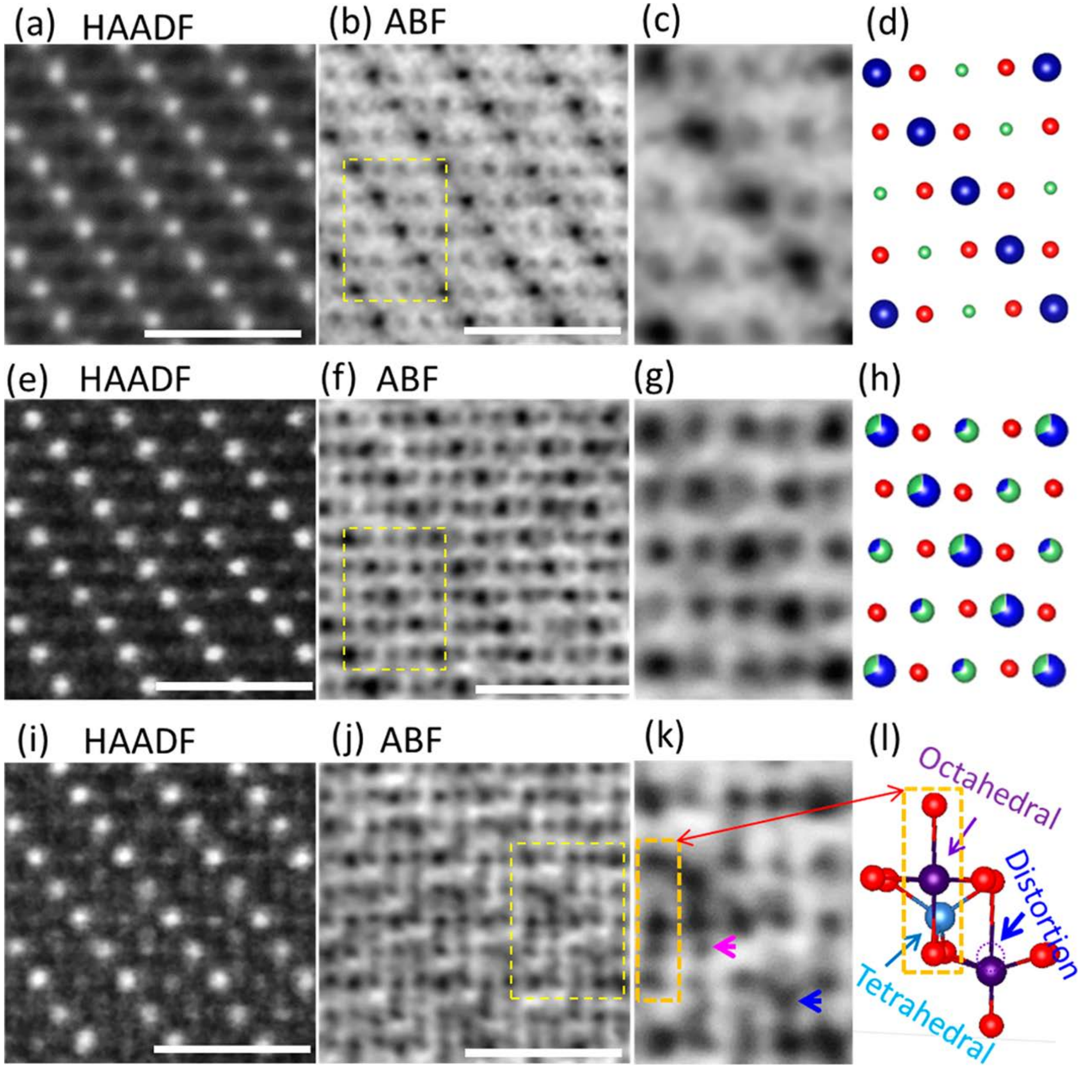


- EELS spectra (a) O K-edges and Mn L-edges; and (b) Co L-edges and Ni L-edges
- As marked in panel a, with the gradual increase of the lattice disordering, the pre-peak on the oxygen K-edge gradually decreases, indicating formation of oxygen vacancies; while s and the L3/L2 ratio on Mn-L edge gradually increases, indicating the reduction of Mn
- As indicated by the black dashed line in panel b, the chemical shift of L-edge for both Ni and Co indicates the reduction of Ni and Co

Pengfei Yan et al, Nano Lett., 17, 3946-3951(2017)

Technical Accomplishments

Revealed at atomic level the migration path of Ni in NMC333 cathode following 100 cycles with a high cutoff voltage of 4.8 V



- (a, b) From a region with the well-preserved layered structure. (e, f) From disordered region
- (i, j) From heavily disordered region. Enlarged images from panels b, f, and j are shown in panels c, g, and k, respectively. Panels d and h are the corresponding crystal model for panels c and g
- (l) Illustrates tetrahedral site TM ion and lattice distortion in panel k. The scale bars are 1 nm As indicated by the black dashed line in panel b, the chemical shift of L-edge for both Ni and Co indicates the reduction of Ni and Co

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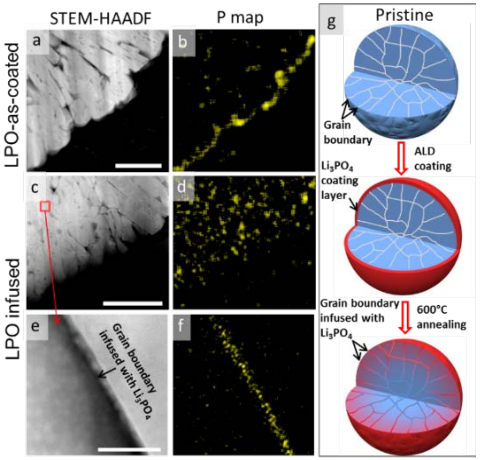
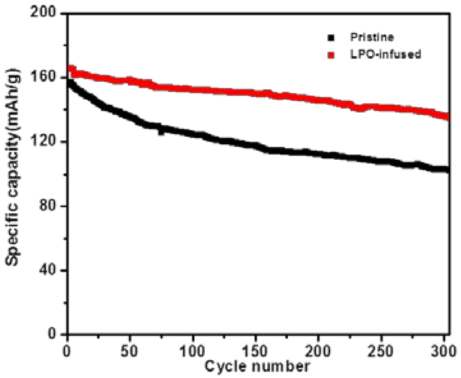
Pengfei Yan et al, Nano Lett., 17, 3946-3951(2017)

Technical Accomplishments

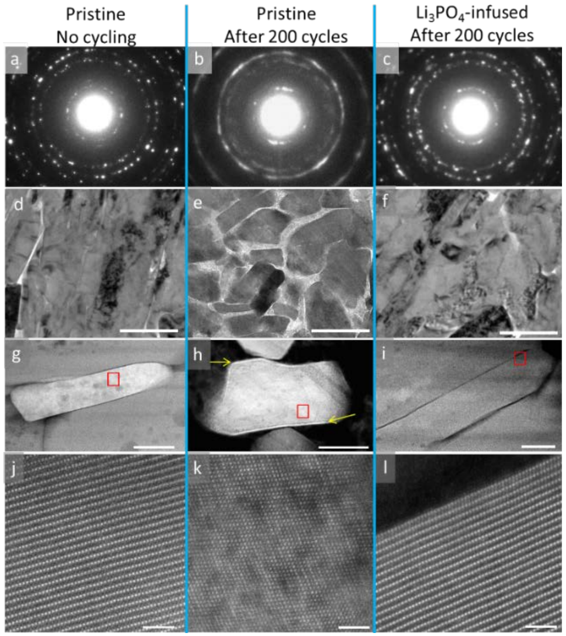
Direct demonstration of solid-liquid interfacial reaction to control the degradation of cathode performance



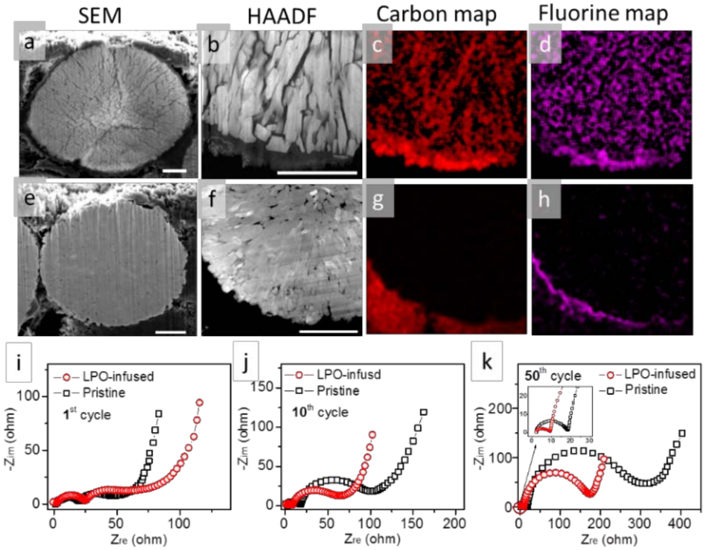
Grain boundary infusion of Li_3PO_4



Full cell cycling performance



Eliminating layer to spinel phase transition after the infusion of Li_3PO_4

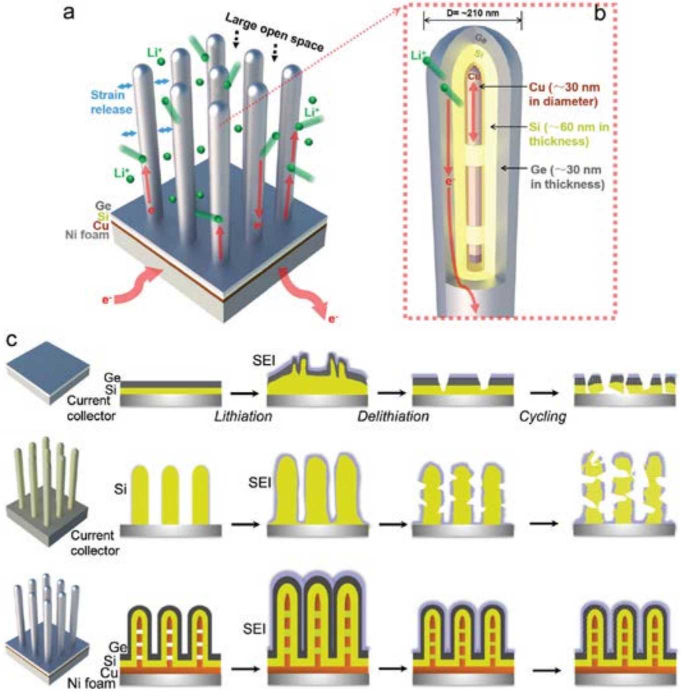


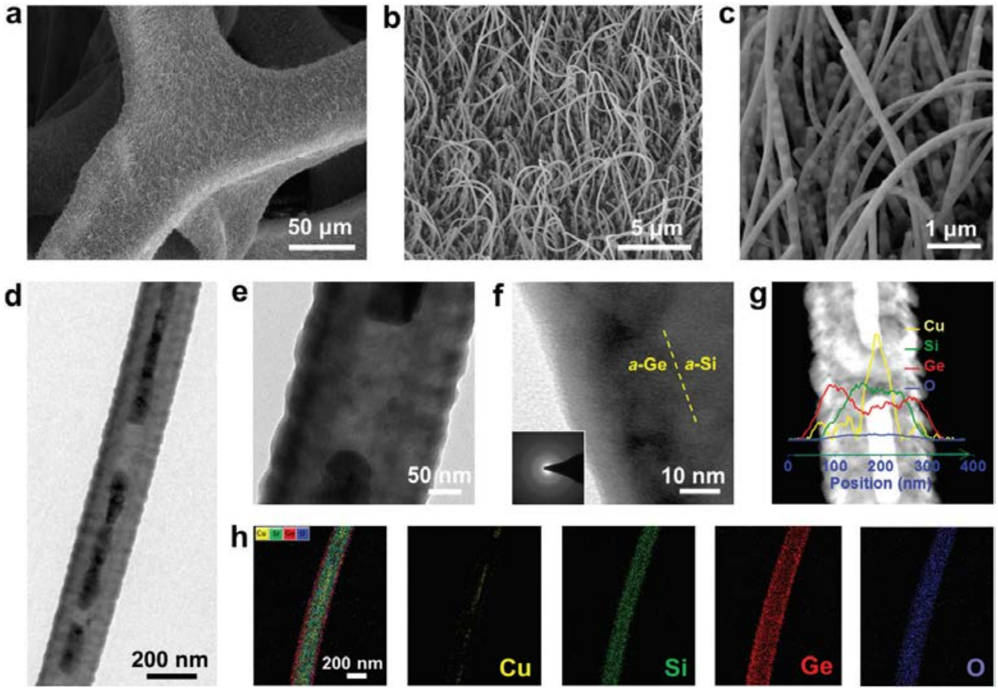
Eliminating intergranular cracking after the infusion of Li_3PO_4

- With grain boundary infusion of solid electrolyte, the capacity retention is enhanced both for half and full cell, eliminated the layer to spinel transition, intergranular cracking
- No CEI formation
- No dissolution

Technical Accomplishments

Revealed the interaction of Si with liquid electrolyte by coating of the Si surface with a thin layer of Ge





- Schematic illustration of a high-performance Cu/Si/Ge nanowire (NW) electrode. (a) The Cu/Si/Ge NW array was grown on a Ni foam substrate, and (b) each NW had a core of Cu segments and a Si/Ge bilayer shell No CEI formation
- (c) The favorable design features enable a long-cycle stability in the Cu/Si/Ge NW electrode, while the Si/Ge thin-film electrode and Si NW (or NT) electrode are prone to mechanical degradation in both active components and SEIs during cycling
- Characterization of the Cu/Si/Ge NW electrode (c) The favorable design features enable a long-cycle stability in the Cu/Si/Ge NW electrode, while the Si/Ge thin-film electrode and Si NW (or NT) electrode are prone to mechanical degradation in both active components and SEIs during cycling
- (a–c) SEM images of Cu/Si/Ge NW arrays grown on a Ni foam. (d and e) TEM image of a single Cu/Si/Ge NW, (f) HRTEM image of the Si/Ge bilayer with the corresponding SAED pattern (inset)
- (g) STEM image of a Cu/Si/Ge NW, with corresponding EDX spectra and (h) STEM image and corresponding Cu, Si, O and Ge EDX maps

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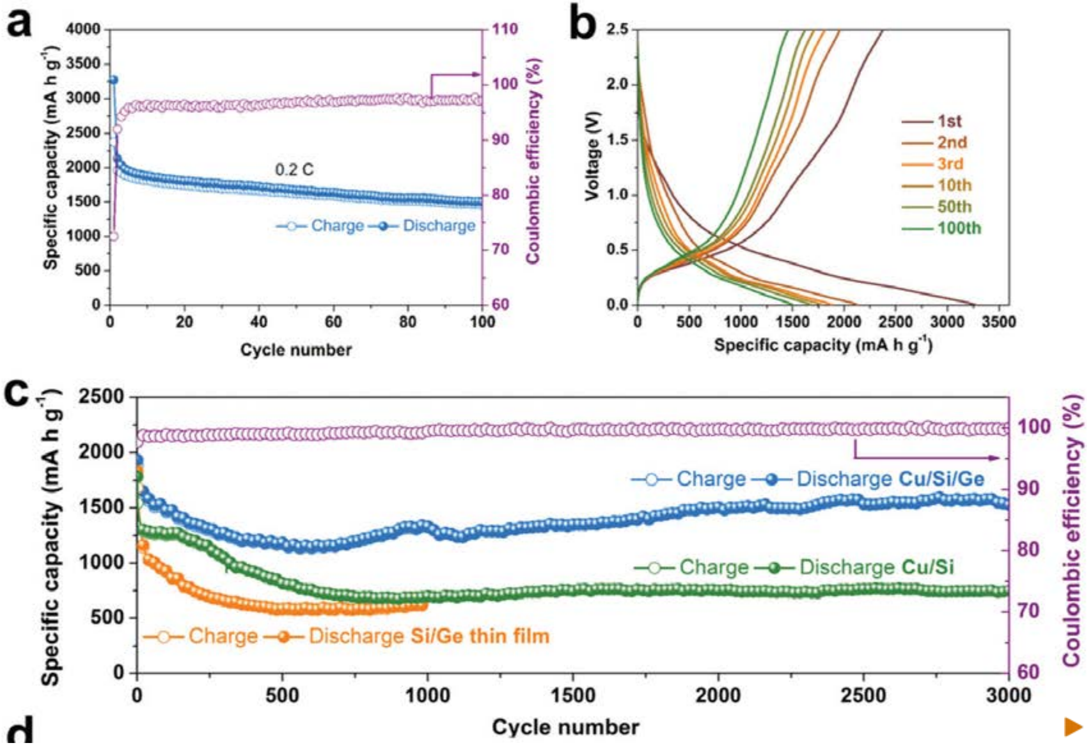
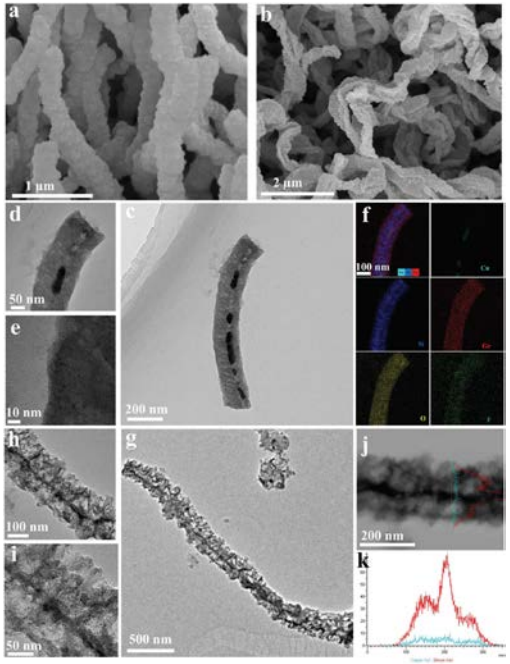
Zhang et al, Energy Environ. Sci. 2018 Online

Technical Accomplishments

Revealed that coating of Si with Ge leads to enhanced electrochemical performance





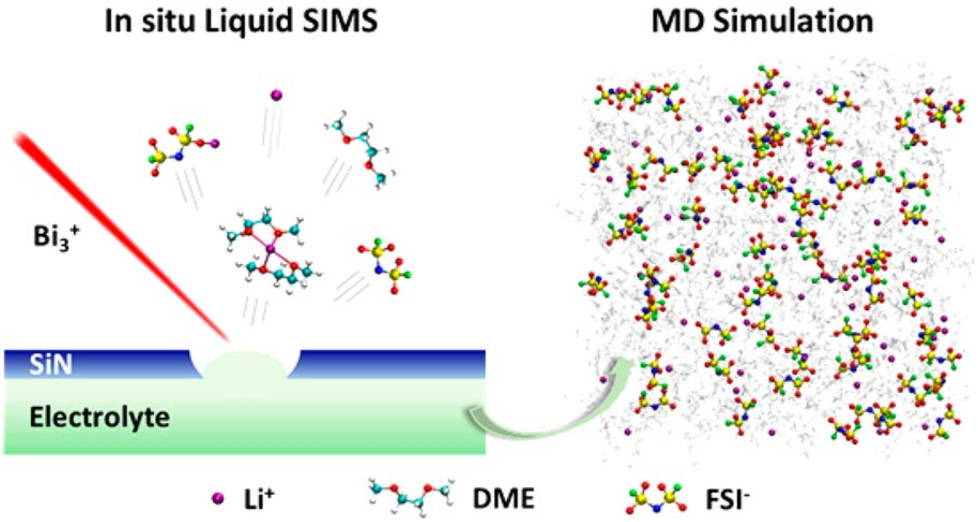
- Electrochemical performance of the Cu/Si/Ge NW electrode
- (a) Capacity performance at a low rate of 0.2C
- (b) Corresponding galvanostatic charge–discharge profiles at different cycles
- (c) Long-cycle performance for Cu/Si/Ge NW, Cu/Si NW and Si/Ge thin-film electrodes at 2C

- Comparison of microstructural changes in the Cu/Si NW and Cu/Si/Ge NW electrodes after 3000 cycles at 2C
- (a) SEM image of a Cu/Si/Ge NW array. (b) SEM image of a Cu/Si NW array. (c–e) TEM image of a single Cu/Si/Ge NW. (f) STEM image of a single Cu/Si/Ge NW and corresponding Cu, Si, Ge, F and O X-ray maps
- (g–i) TEM image of a single Cu/Si NW. (j)STEM image of a single Cu/Si NW, with corresponding EDX spectra and (k) corresponding enlarged EDX spectra

Zhang et al, Energy Environ. Sci. 2018 Online

Technical Accomplishments

Reveal the solvation shell around Li^+ at different electrolyte concentration using in-situ liquid SIMS



- In situ liquid SIMS was used to examine ion-solvent interactions in three representative electrolytes
- LiPF6 at 1.0 M in EC-DMC and LiFSI at both low 1.0 M and high 4.0 M in DME
- In the positive ion mode, solid molecular evidence strongly supports the preferential solvation of Li+ by EC
- From the negative spectra, $PF6^-$ forms association with EC, which has been neglected by previous studies due to the relatively weak interaction
- In both LiFSI in DME electrolytes, however, no evidence shows that FSI^- is associated with DME
- Strong salt ion cluster signals were observed in the 1.0 M LiPF6 in EC-DMC electrolyte, suggesting that a significant amount of Li+ ions stay in the vicinity of anions
- In sharp comparison, weak ion cluster signals were detected in dilute LiFSI in DME electrolyte, suggesting most ions are well separated, in agreement with our molecular dynamics simulation results

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

Responses to Previous Year Reviewers' Comments

The reviewers comments are very positive:

... *in situ* and in-operando HRTEM is a unique and effective tool to study atomic scale structure and morphology of electrodes …; …the general approach is excellent…;

…discovery of intergranular cracking as a function of the charging potential range is very important…; …pronounced the collaborations to be excellent…; …The reviewer was hugely impressed and looking forward to this future work…;…the mechanism of cathode impedance growth is of great importance to DOE objectives…

Comment: The reviewer would like to encourage the group to develop collaboration with institutes where characterization techniques are complementary to EM, such as synchrotron X-rays.

Response: We are collaborating with Lawrence Berkeley National Laboratory group to access beam line to get complimentary result for XAS and TEM.

Comment: It would be important to see the effects of preconditioning of the electrode by restructuring the surface as shown by Kostecki in this year's review to see if there are beneficial effects on particle cracking.

Response: We are conditioning the electrode surface and investigate such an effect.

Collaboration and Coordination with Other Institutions

Partners:

- Argonne National Lab: Preparation of cathode materials, ALD coating
- Lawrence Berkeley National Lab: 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
- UC San Diego: Preparation of cathode
- 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

Remaining Challenges and Barriers

- Needs new capability to probe fine structural features of SEI layer at atomic level resolution

- 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

- For SEI and Li dendrite studies using liquid cell TEM, building of a half cell or a full cell battery is always a challenge. More develop is needed based on deposition or microchip techniques

- Minimizing the liquid layer thickness to gain a better resolution in liquid cell. This can be achieved by designing of the liquid window geometry to minimize the bulging effect

Proposed Future Work

FY2018

- Solid-liquid interfacial reaction induced bulk lattice effect
- Atomic view of charge and discharge rate on the structural degradation of cathode
- Using in-situ TEM to gain atomic view on the intragranular crack formation process, because we have found that even following one cycling, intragranular crack forms

FY2019

- Cryo-TEM study of detailed structure of solid-liquid interphase layer and this will be combined with in-situ liquid SIMS work
- Strategy of mitigating the cathode-liquid electrolyte reaction: some new concepts have been demonstrated and this will be extended to lithium rich materials
- Detailed structure of SEI layers on anode: direct visualization of electrical double layer using in-situ liquid SIMS
- Identification of dopant to stabilize the lattice in cathode, answering why Al play a critical role on cycle life

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

Summary

- Ni and Co selectively segregate at different crystallographic surface
- At pristine state, the tendency of migrating to Li layer decreases from Ni, Co to Mn
- Upon battery cycling, Ni preferentially migrate to Li layer, followed by Co, and Mn is stable
- Discovered that the electrode-electrolyte reaction is far more beyond the general SEI or CEI layer
- For the case of cathode, a strategy has been identified to mitigate the soli-liquid reaction induced fading, that is the grain boundary infusion with solid electrolyte, leading to new ideas to mitigate capacity fading with cathode
- For the case of silicon anode, the Si-electrolyte reaction appears to be a serious problem, which is beyond the SEI layer, and leads to the continuous degradation of Si. We have demonstrated a strategy for dealing with this problem, pointing to new ways to mitigate the capacity fading

Technical Back-Up Slides

Patents/Publications/Presentations

1. 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).**

2. Pengfei Yan, Jianming Zheng, Meng Gu, Jie Xiao, Ji-Guang Zhang, Chongmin Wang, “Intragranular cracking as a critical barrier for high-voltage usage of layer-structured cathode for lithium-ion batteries”, **Nat. Commun. 8, 14101 (2017).**

3. Langli Luo, Bin Liu, Shidong Song, Wu Xu, Ji-Guang Zhang and Chongmin Wang, “Revealing the reaction mechanisms of Li–O_2 batteries using environmental transmission electron microscopy”, **Nature Nanotechnology, 12, 535-539 (2017).**

4. Pengfei Yan, Jianming Zheng, Ji-Guang Zhang, and Chong-Min Wang, “Atomic Resolution Structural and Chemical Imaging Revealing the Sequential Migration of Ni, Co, and Mn upon the Battery Cycling of Layered Cathode”, **Nano Lett., 17, 3946−3951 (2017).**

5. Hanlei Zhang, Fredrick Omenya, Pengfei Yan, Langli Luo, M. Stanley Whittingham, Chongmin Wang, and Guangwen Zhou, “Rock-Salt Growth-Induced (003) Cracking in a Layered Positive Electrode for Li-Ion Batteries”, **ACS Energy Lett. 2, 2607-2615 (2017).**

6. Hanlei Zhang, Fredrick Omenya, M. Stanley Whittingham, Chongmin Wang, and Guangwen Zhou, “Formation of an Anti-Core−Shell Structure in Layered Oxide Cathodes for Li-Ion Batteries”, **ACS Energy Lett. 2, 2598-2606 (2017).**

7. Won-Jin Kwak, Langli Luo, Hun-Gi Jung, Chongmin Wang, and Yang-Kook Sun, “Revealing the Reaction Mechanism of Na−O_2 Batteries using Environmental Transmission Electron Microscopy”, **ACS Energy Lett. 2, 2607-2615 (2017).**

8. Zelang Jian, Clement Bommier, Langli Luo, Zhifei Li, Wentao Wang, Chongmin Wang, P. Alex Greaney, and Xiulei Ji, “Insights on the Mechanism of Na-Ion Storage in Soft Carbon Anode”, **Chem. Mater. 29, 2314−2320 (2017).**

9. Xiaolin Li, Pengfei Yan, Xingcheng Xiao, Jae Ha Woo, Chongmin Wang, Jun Liu and Ji-Guang Zhang, “Design of porous Si/C–graphite electrodes with long cycle stability and controlled swelling”, **Energy Environ. Sci., 10, 1427(2017).**

10. Junhua Songa, Pengfei Yan, Langli Luo, Xingguo Qi, Xiaohui Rong, Jianming Zheng, Biwei Xiao, Shuo Feng, Chongmin Wang, Yong-Sheng Hu, Yuehe Lin, Vincent L. Sprenkle, Xiaolin Li, “Yolk-shell structured Sb@C anodes for high energy Na-ion batteries”, **Nano Energy 40, 504–511(2017)**.

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Acknowledgements

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- ✓ Team Members:
  Lianfeng Zou, Pengfei Yan, Langli Luo, Jianming Zheng, Wu Xu, Xiaolin Li, Jie Xiao, Jun Liu, and Ji-Guang Zhang

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