Development of High-Energy Cathode Materials

Ji-Guang Zhang and Jie Xiao

Pacific Northwest National Laboratory

2015 DOE Vehicle Technologies Program Review
June 8-12, 2015

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Pacific Northwest
NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*

Project ID #ES056

Overview

Timeline

- Start date: Oct. 2011
- End date: Sept. 2015
- Percent complete: 88%

Budget

- Total project funding
  - DOE share 100%
- Funding received in FY14: $400k
- Funding for FY15: $400k

Barriers addressed

- Low energy/low rate
- High cost
- Limited cycle life

Partners

- SUNY Binghamton
- Argonne National Laboratory
- Brookhaven National Laboratory
- Hydro-Québec
- Army Research Laboratory
- University of Rhode Island

Relevance/Objectives

- Synthesis of Li-Mn-rich (LMR) layered composite cathode material by cost-effective approaches.

- Use advanced characterization techniques to understand the voltage-fade related phase transformation pathway of LMR cathode.

- Develop surface treatment approaches to improve cycling stability of LMR cathode.

- Regulate the structural defects to understand the activation process of Li_2MnO_3 component in LMR cathode.

Milestones

FY14

- ✓ Stable cycling of 80% capacity retention after 150 cycles from LMR high energy cathode. (March 14) **Complete**

- ✓ Identify the fundamental mechanism responsible for electrolyte-additive-induced performance improvement of LMR cathode. (June 14) **Complete**

- ✓ Demonstrate the effects of elemental doping to improve the cycling stability of >200 cycles. (Sept. 14) **Complete**

FY15

- ✓ Identify the transition metal migration pathway in LMR during cycling. (Dec. 2014) **Complete**
- ✓ Identify appropriate synthesis step to enhance the homogeneous cation distribution in the lattice and demonstrate 200 cycling with less than 10% energy loss. (March 2015) **Complete**
- ✓ Develop the surface treatment approaches to improve the stability of high energy cathode at high voltage conditions. (June 2015) **Complete**
- ✓ Demonstrate high voltage operation of traditional NMC with 180 mAh/g capacity and less than 20% in100% cycling. (Sept. 2015) **On going**

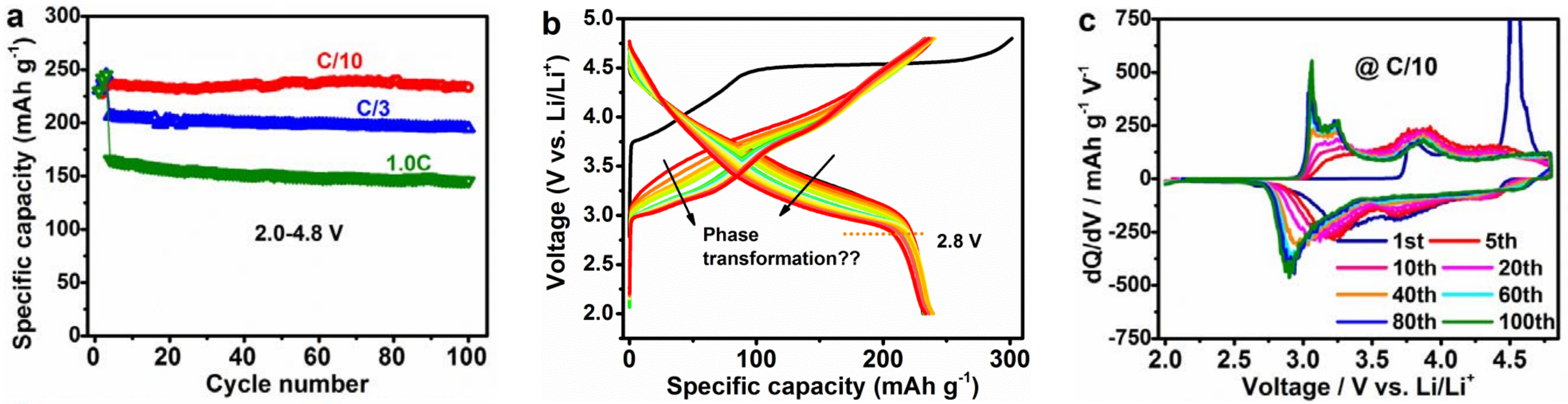
Approach

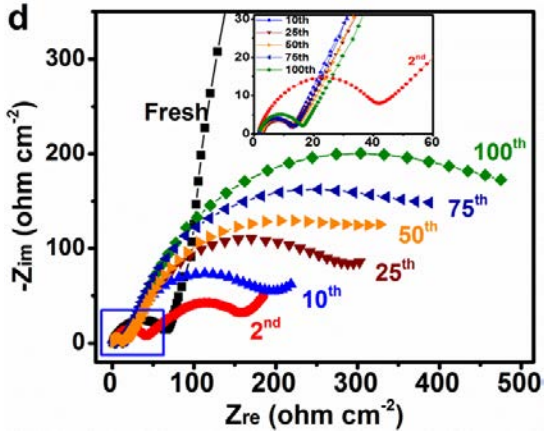
1. Fundamental understanding of LMR phase transition mechanism by using advanced characterization.
2. Surface modification on LMR to mitigate the side reactions between cathode and electrolyte.
3. Regulate the oxygen non-stoichiometry to improve the electrochemical properties of LMR.

Technical Accomplishments

Electrochemical performances of LMR Cathode prepared by hydrothermal assisted method

LMR cathode $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$



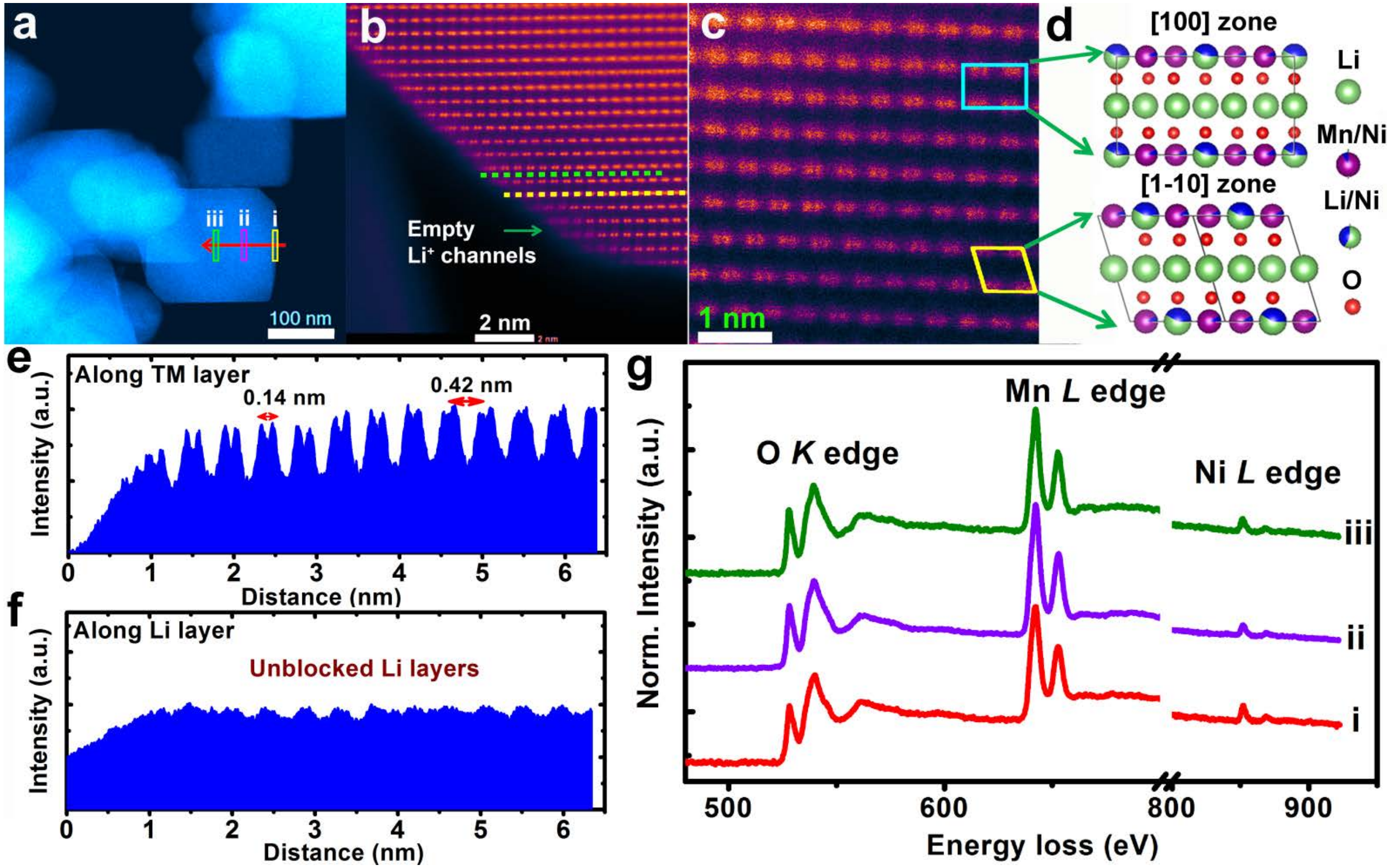


- ✓ Discharge capacity is stabilized but working voltage still fades.
- ✓ SEI layer resistance is relatively stable, while the charge transfer resistance increases considerably during cycling.

Pacific Northwest
NATIONAL LABORATORY

Technical Accomplishments

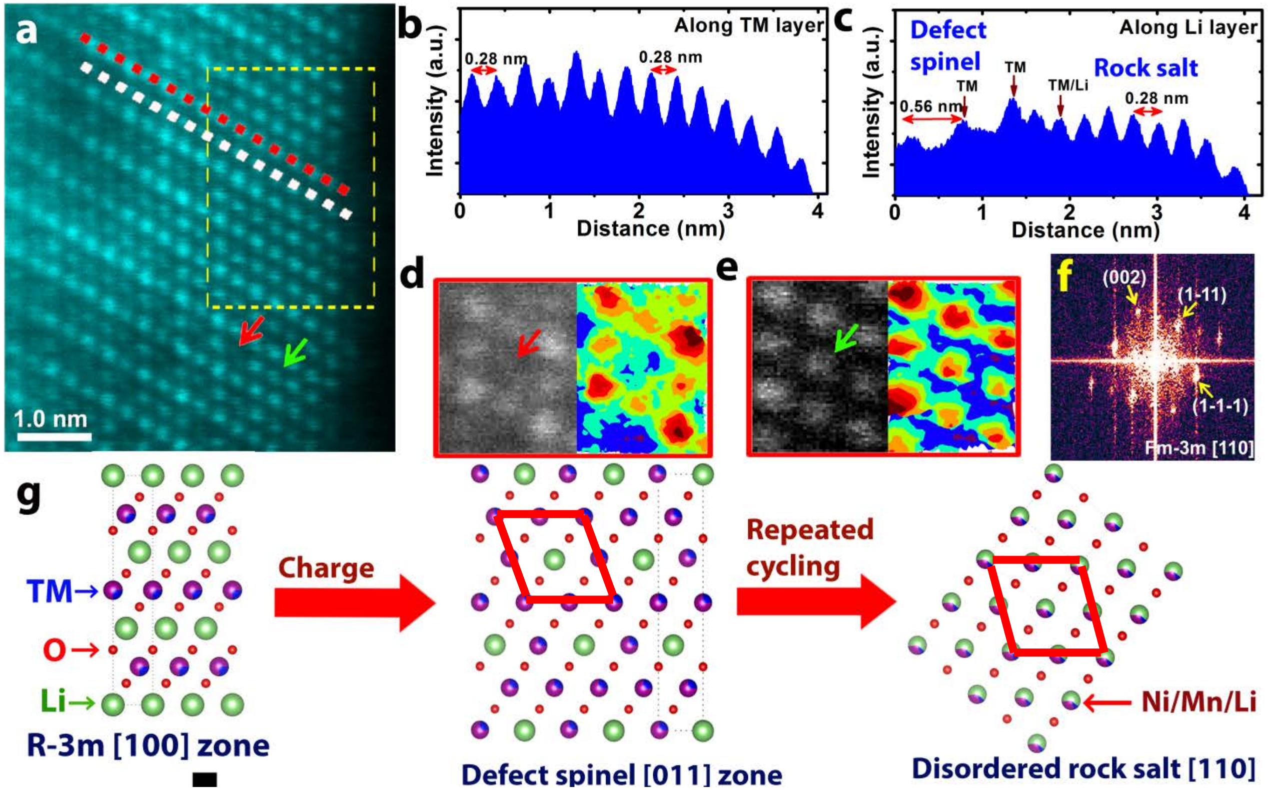
Layered Structure of Pristine LMR Particles



- ✓ Pristine LMR is ca.200 nm with well defined layered structure.
- ✓ The lithium ion diffusion pathways are not blocked.

Technical Accomplishments

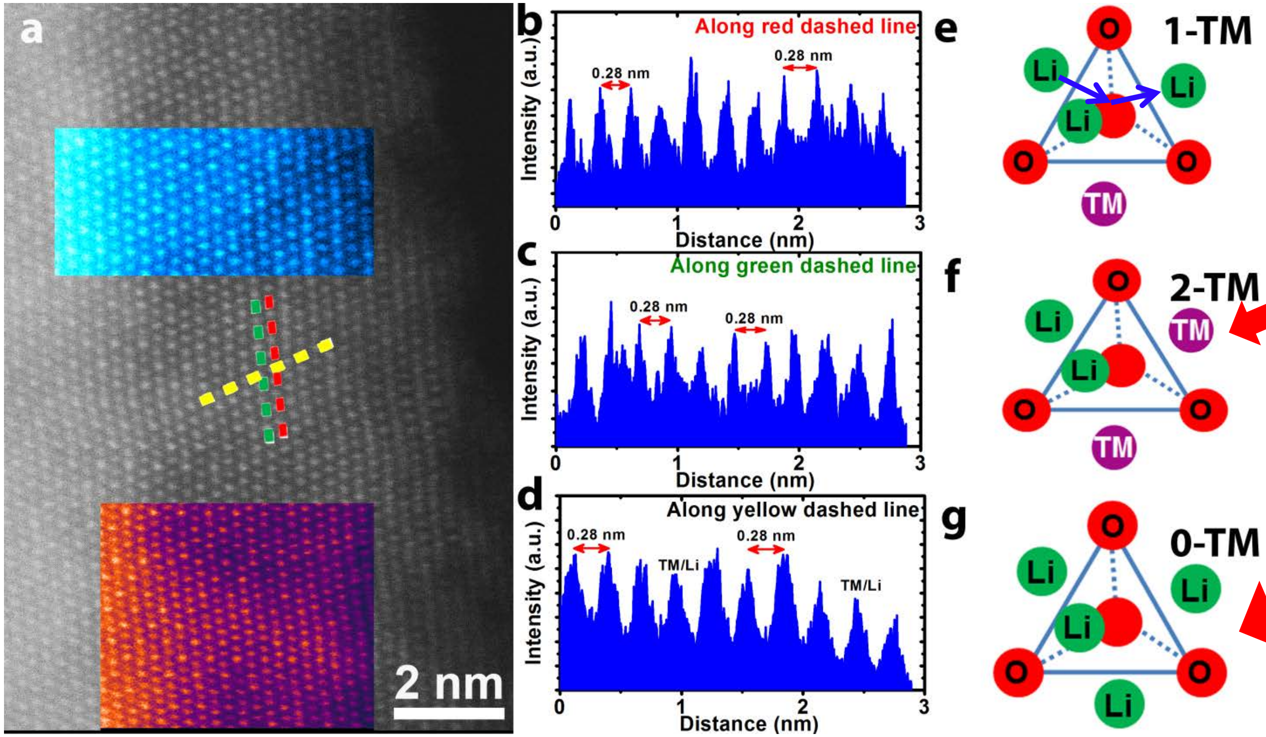
Direct Observation of LMR Lattice Structure Change



- ✓ Direct evidence of TM ions migration into Li layers via the adjacent tetrahedral sites, which is induced by the concurrent O and Li^+ ion removal.
- ✓ The outmost surface layer transforms to disordered rock-salt structure.
- ✓ Defect spinel structure forms as an intermediate layer between disordered rock-salt structure and the bulk layered structure.

Technical Accomplishments

Crystal structure of LMR after 100 cycles



Lithium ion diffusion
Octahedral-tetrahedral-Octahedral

TM ion migration to Li layer

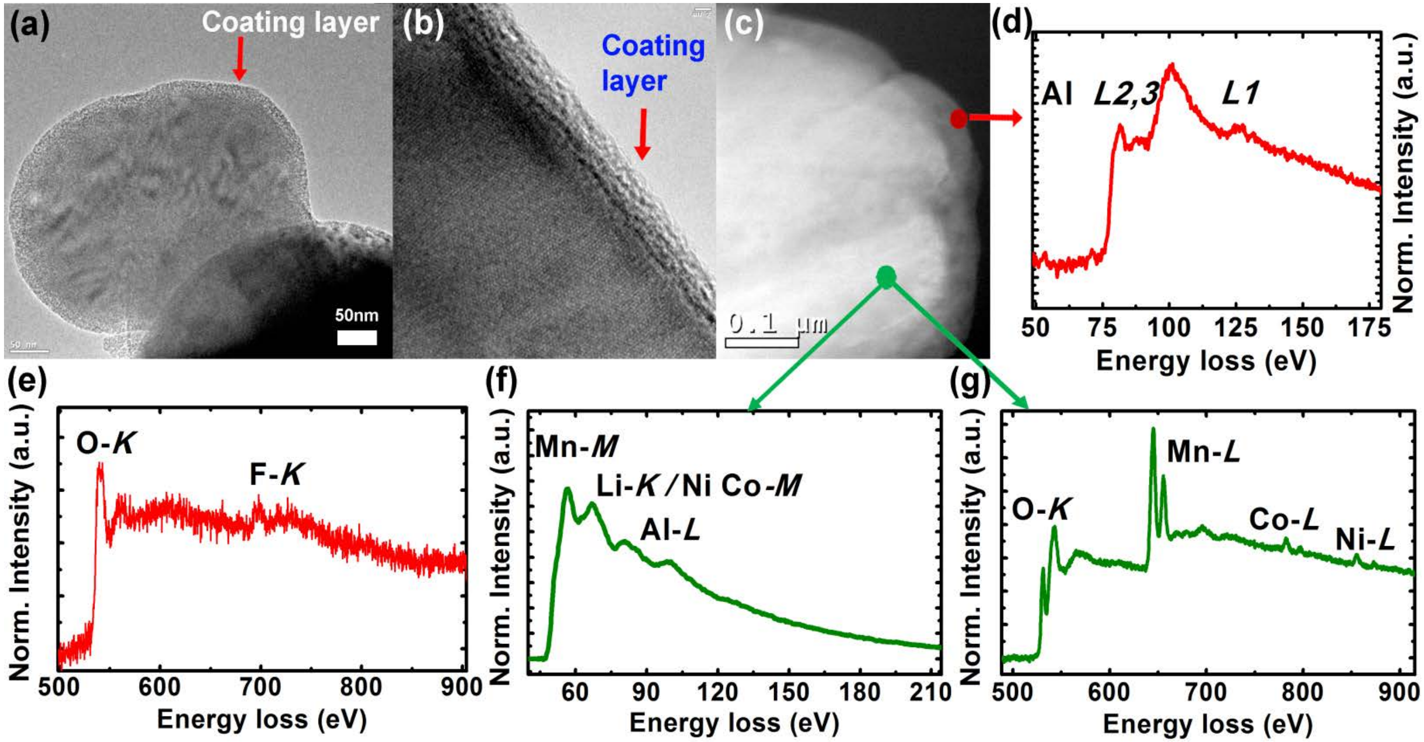
Excess Li environment

- ✓ After 100 cycles about 10 nm of LMR surface layer has been converted to the disordered rock-salt structure.
- ✓ The reversible Li transportation in the disordered rock-salt structure is ascribed to the **Li excess environment** that can satisfy the reversible Li percolation in the disordered rock-salt structure despite the increased kinetic barrier.

Technical Accomplishments

Protection Mechanism of AlF_3 Coating on LMR

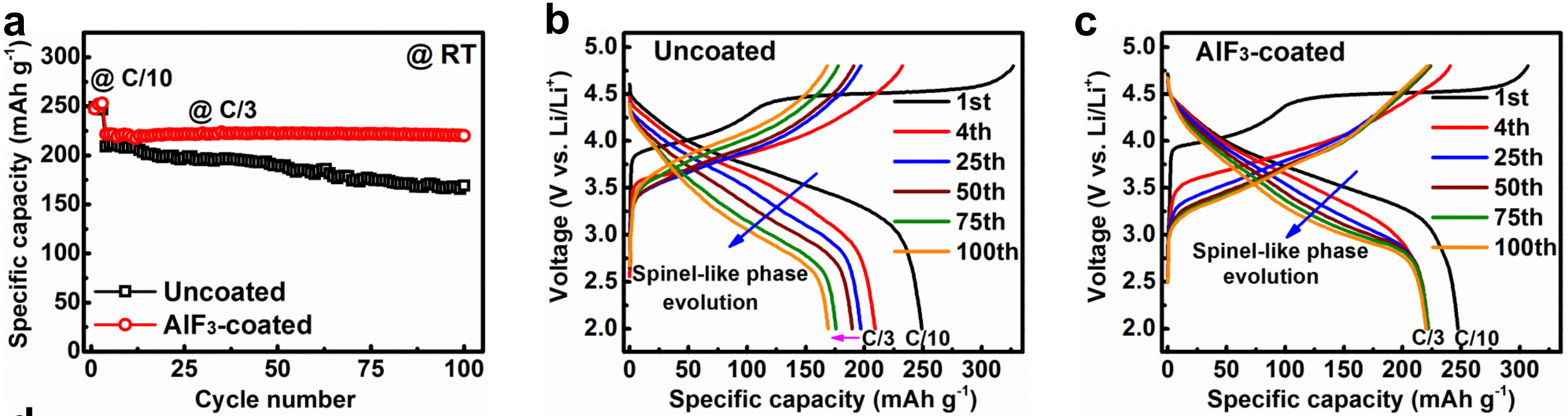
HE5050 LMR cathode : $Li_{1.2}Ni_{0.15}Co_{0.10}Mn_{0.55}O_2$

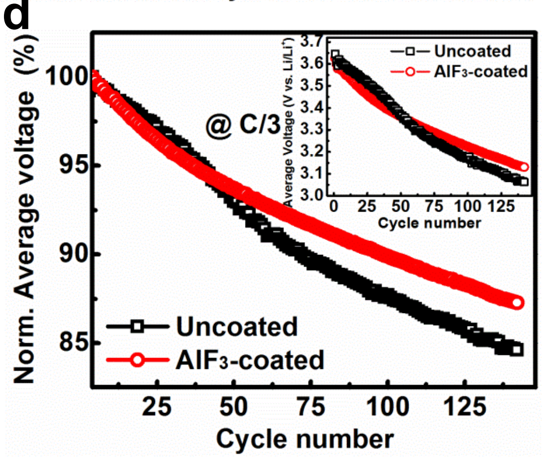


- The bulk material is uniformly covered with an AlF_3 coating layer with a thickness of ca. 10 nm.
- In the surface region, the coating layer shows a signal of O as well as Al and F, indicating the formation of AlO_xF_y on the surface as a protecting layer.

Technical Accomplishments

AlF_3 Surface Modification Improves Capacity Retention and Mitigates Voltage Fade



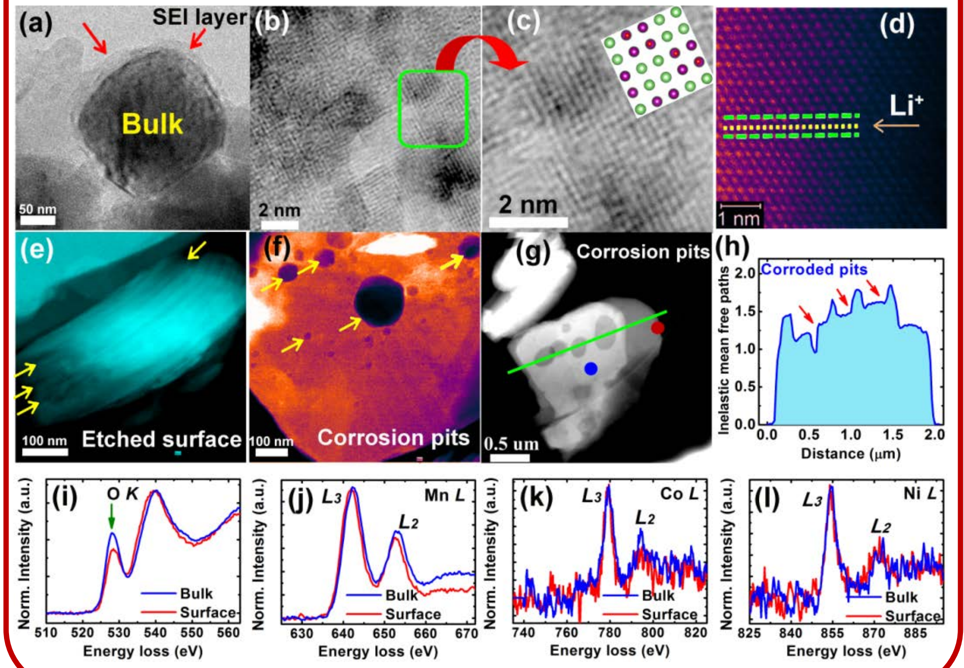


- AlF_3 coating decreases the interactions between LMR cathode material and the electrolyte.
- AlF_3 coating extends the cycle life of LMR cathode, demonstrating 100 stable cycling without visible capacity loss.
- AlF_3 coating also stabilizes the electrode structure and mitigates the voltage fade of LMR cathode.

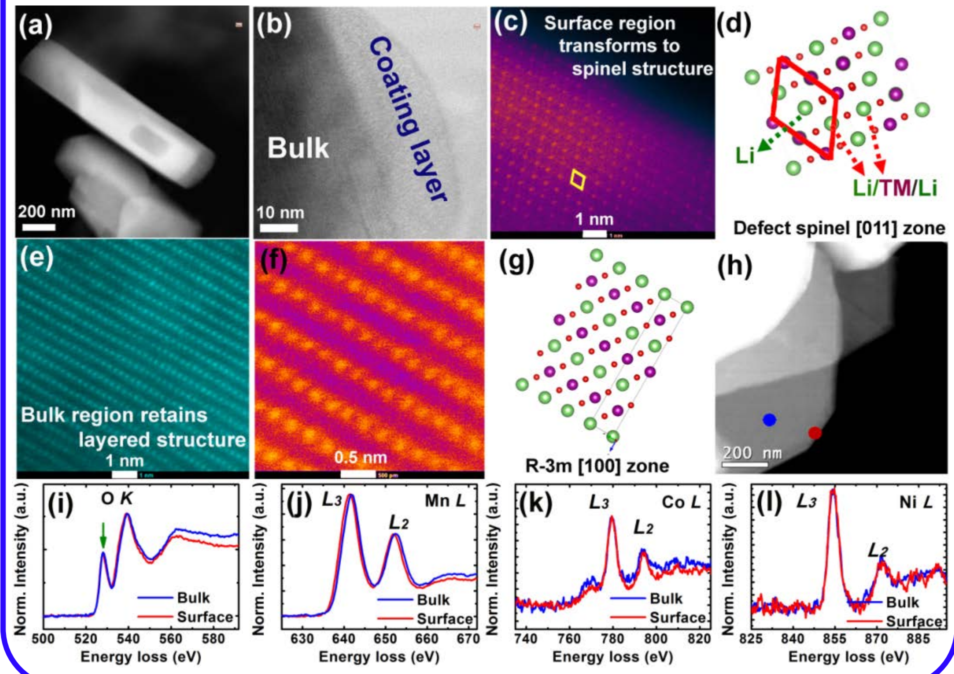
Technical Accomplishments

Structure of LMR material after 100 cycles at C/3

Uncoated



AlF_3-coated

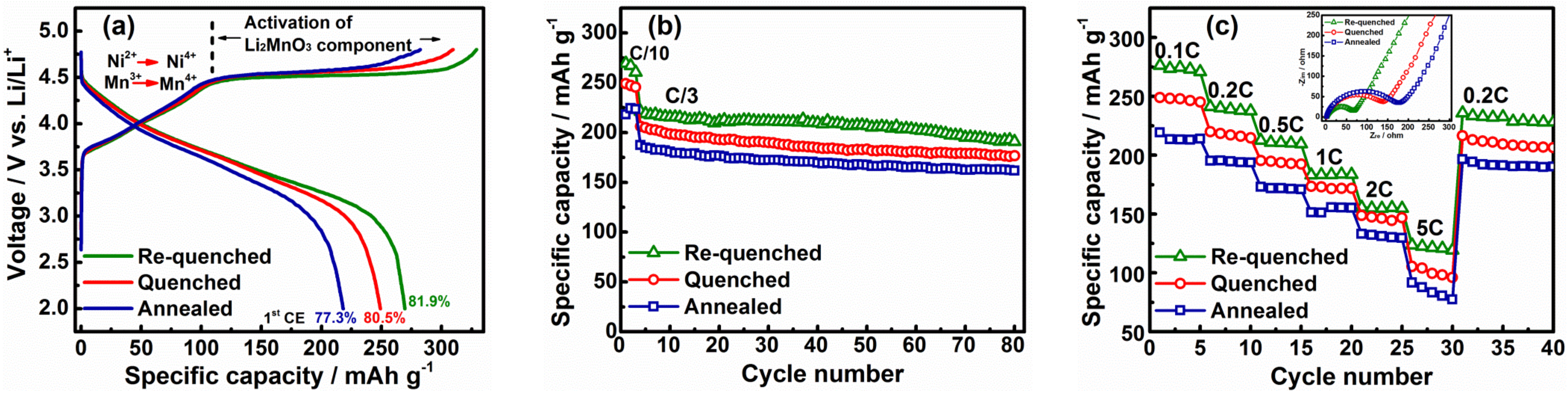


- Surface coating reduces the side reactions and suppresses the formation of thick SEI layer, etched particles and corrosion pits.
- Surface coating mitigates the phase transition from layered to Spinel-like/rock-salt structure during cycling.
- Mn oxidation state is much more stable at the surface region.

Technical Accomplishments

Effects of oxygen non-stoichiometry on the performance of LMR cathode

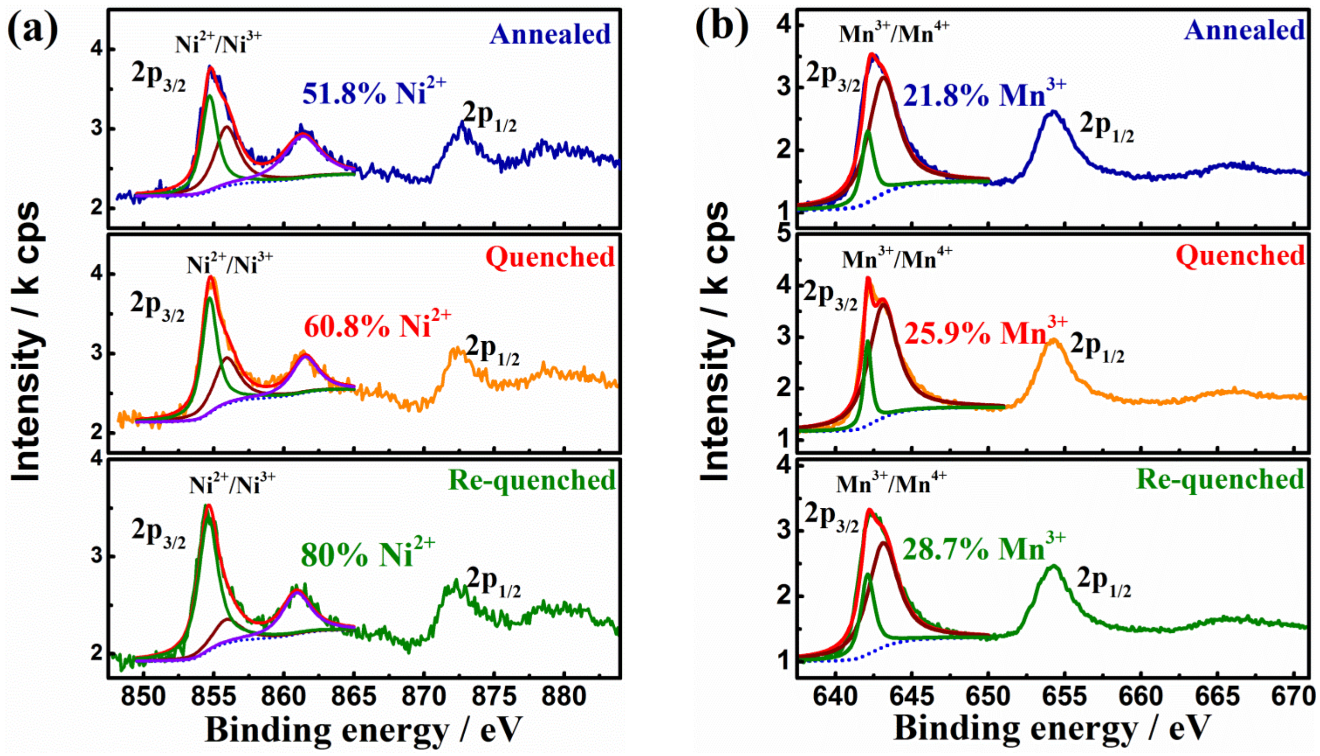
LMR material $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_{2-\delta}$



- ✓ Increased oxygen non-stoichiometry facilitates the activation of Li_2MnO_3 component and thus improves the rate capability of LMR cathode.

Technical Accomplishments

Oxygen deficiency comparison in different LMRs

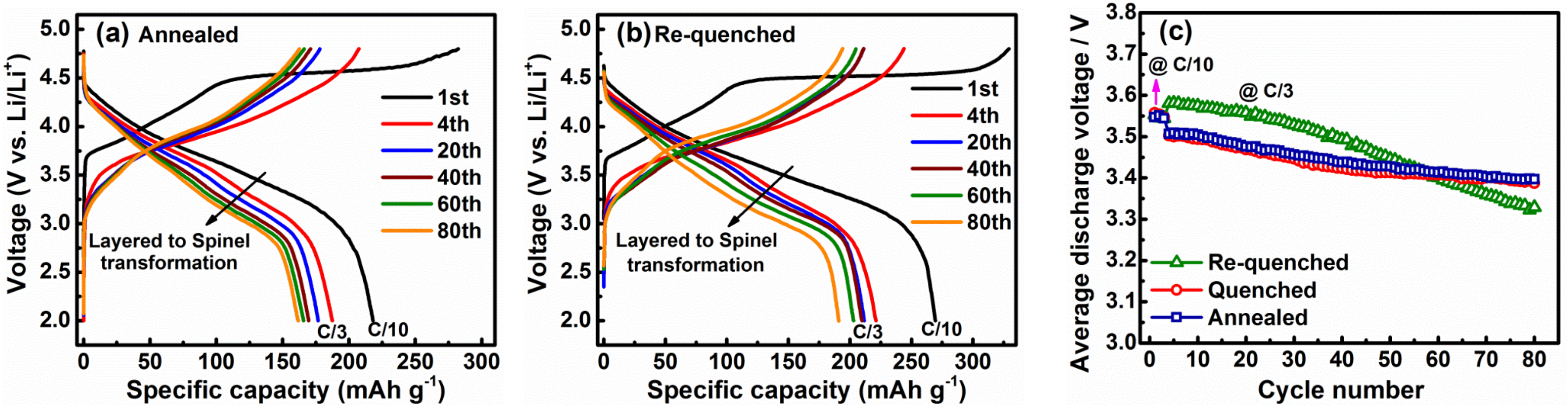


- The oxygen non-stoichiometry is estimated to be $\delta = 0.017$, $\delta = 0.039$ and $\delta = 0.066$ for annealed, quenched and re-quenched materials $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_{2-\delta}$.

Technical Accomplishments

Effects of oxygen non-stoichiometry on the performance of LMR cathodes

LMR material $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_{2-\delta}$



- ➢ The extensive activation of Li_2MnO_3 component accelerates the layered-to-spinel/rock-salt phase transformation, thus leading to fast voltage fade.
- ➢ There is a trade-off between long-term cycling stability/voltage fade and the rate capability.

Response to Reviewers' Comments

- 1. Comment: "The reviewer observed that the data indicates that synthesis routes or use of additives, although appearing beneficial to some degree, are some temporary measures to retard the eventual evolution of voltage decay or poor cycle-life."
  - **Response:** Voltage fade could be a combined result of intrinsic structural change and SEI layer accumulation. Therefore, the first step is to decouple these two factors when studying LMR cathode. Work has been done along the direction to enhance the structural stability by improving the atomic level uniformity of elemental distribution, or to reduce the accumulation of SEI layer on cathode surface using electrolyte additive. It is revealed that the intrinsic structural change of LMR at high voltages is very difficult to be completely eliminated. Although the voltage fade issue is not completely solved, the fundamental findings provided valuable clues on how to further mitigate voltage fade and enhance long-term cycle life.
- 2. Comment: "The reviewer asserted that the improvements were good, but this person was not sure they will hold at elevated temperatures or in the course of long-term cycling. The project person praised that the analytical work the authors have carried out to identify the failure mechanism was quite good."
  - **Response:** During the synthesis optimization, we cycled the CP/SG materials to 200 cycles and the HA material to 300 cycles at room temperature. Meanwhile, the performance of the CP/HA materials were also evaluated at 60^{o}C (slide 24). The long-term cycling for LMR/NCM cathodes will be further pursued after optimizing the electrode thickness and preferably to be done in full cells in the near future.
- 3. Comment: "The reviewer requested that the cathode loadings adopted here should be included (example on Slide 9). The reviewer noted that the LMR-LLC cycle life looks impressive, but only at low loadings. The reviewer expressed that it would be better to have this project coordinated through ANL for better synergy, based on the substantial effort being undertaken at ANL on various aspects of the LMR-LLC cathodes."
  - **Response:** For evaluating the performances of as-prepared LMR materials, the cathode loadings were controlled to be 3-4 mg cm^{-2} to insure the uniformity of the electrode prepared in small coaters. For electrolyte additive study, we used the high loading LMR electrodes (12.5 mg/cm^{2}) supplied by ANL. High loading electrode will be used in our future studies on cathode materials by using the newly established pouch cell line in PNNL.

Collaboration and Coordination with Other Institutions

Partners:

- Argonne National Laboratory (Federal Laboratory): Provide LMR cathode and standard anode materials for testing.

- Brookhaven National Laboratory (Federal Laboratory): *In situ* XRD on electrode materials.

- Army Research Laboratory (Federal Laboratory): Supply of treated cell cans and electrolytes.

- SUNY Binghamton (University): Materials characterizations.

- Hydro-Québec (Industry): Materials modifications.

Remaining Challenges and Barriers

- Voltage fade was mitigated but not completely eliminated.
- Both interfacial reactions and internal phase transition need to be considered to enable stable cycling of LMR cathodes without voltage fade.

Future Work - FY2015/16

- Use advanced characterization techniques (especially operando TEM using liquid electrolyte) to investigate the interface and bulk properties of both pristine and cycled $LiNi_xCo_yMn_zO_2$ (NCM) cathode and understand the factors affecting their intrinsic stabilities.

- Utilize the fundamental understanding obtained in microscopic and electrochemical studies to tailor the synthesis process and prepare the NCM with the desired compositions and structures.

- Optimize the composition and surface of NCM cathodes to enable their high discharge capacity ($\geq$200 mAh g^{-1}) at elevated cut-off voltages and enhance their long-term cycle life.

Summary

1. Investigated the phase transformation pathway of LMR
    - LMR experienced a phase transformation from a layered structure to a LT-$LiCoO_2$ type defect spinel and then to a disordered rock-salt structure.
    - Li excess environment enables the reversible Li percolation in the disordered rock-salt structure despite the increased kinetic barrier.
2. Identified the functioning mechanism of AlF_3 coating for the improved performance of LMR cathode
    - AlF_3 coating layer prevented direct contact between LMR and the electrolyte, thus greatly minimizing SEI layer thickness formed at high voltages.
    - AlF_3 coating enhanced surface structure stability of LMR by mitigating the layered-to-spinel-like structure phase conversion, largely stabilizing the voltage profiles during cycling.
3. Investigated the effects of oxygen non-stoichiometry on the performance of LMR cathode
    - Increased oxygen non-stoichiometry in LMR cathode material $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_{2-\delta}$ facilitated the activation of Li_2MnO_3 component, improving the rate capability of LMR cathode.
    - Extensive activation of Li_2MnO_3 component accelerates the layered-to-defect spinel/rock-salt phase transformation, leading to fast voltage fade.

Acknowledgments

- ✓ Support from the DOE/OVT/BATT program is greatly appreciated.

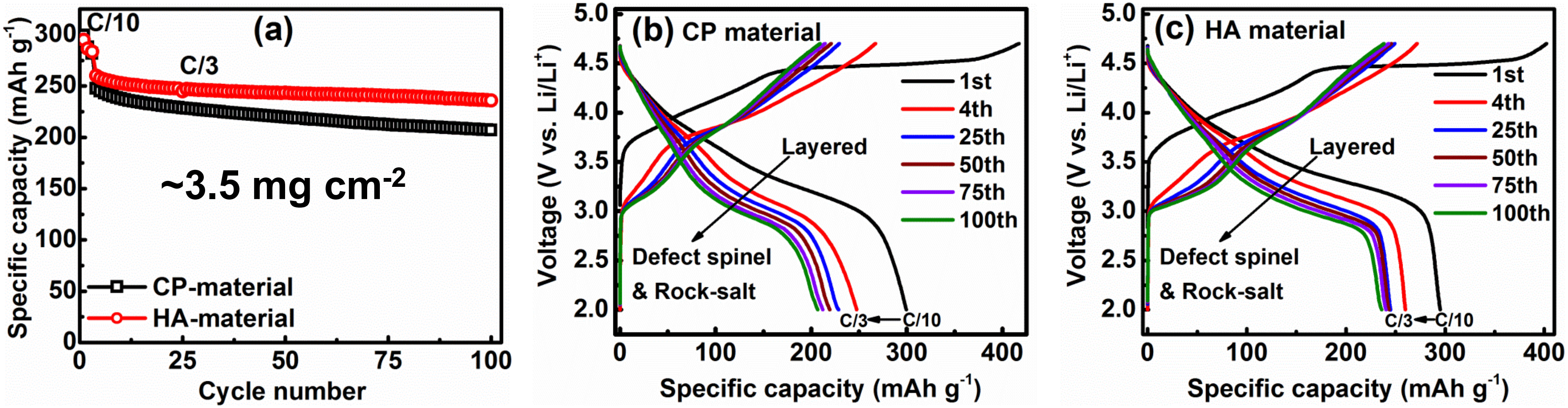
- ✓ Team Members: Jianming Zheng, Pengfei Yan, Liang Xiao, Wu Xu, Sookyung Jeong, Meng Gu, Chongmin Wang, Jun Liu

Technical Backup Slides

Technical Accomplishments

Atomic Level Uniformity of Elemental Distribution in LMR Improves High Temperature performance

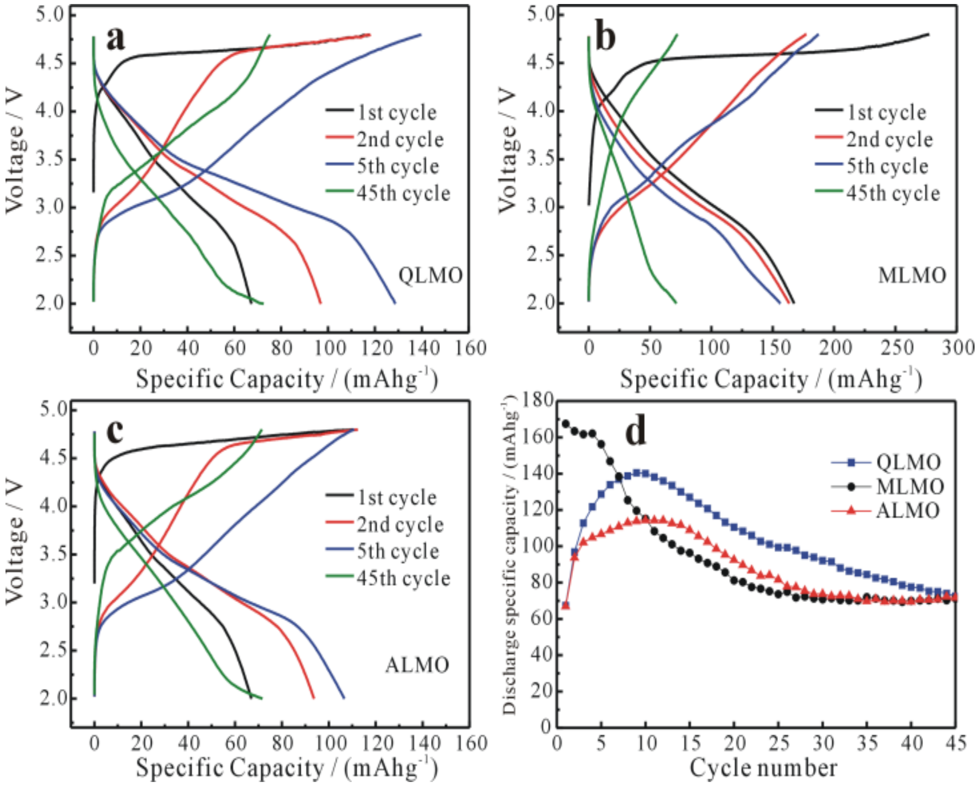
LMR material $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ at 60°C



- LMR materials exhibit much higher discharge capacity, indicating an increase of electrical conductivity at elevated temperature of 60°C.
- HA material shows superior cycling stability during cycling at elevated temperature of 60°C.

Technical Accomplishments

Effects of Oxygen non-stoichiometry on the performance of Li_2MnO_3



Heat treatment: 900°C 12 hr

ALMO: Annealed Li_2MnO_3

QLMO: Quenched Li_2MnO_3

MLMO: Quenched Li_2MnO_3 milled with 5% super P.

- MLMO with the largest amount of Mn^{3+} (9.7%) delivers the highest initial discharge specific capacity among all the three samples.
- Accelerated activation of Li_2MnO_3 gives rise to faster structural transformation from layered to spinel-like phase, leading to rapid capacity fading.