Development of High-Energy Cathode Materials

Ji-Guang Zhang and Jie Xiao

Pacific Northwest National Laboratory

2014 DOE Vehicle Technologies Program Review
June 16-20, 2014

Project ID #ES056

Overview

Timeline

- Start date: Oct. 2011
- End date: Sept. 2015
- Percent complete: 63%

Budget

- Total project funding
  - DOE share 100%
- Funding received in FY13: $300k
- Funding for FY14: $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 failure mechanism of LMR cathode.

- Develop electrolyte additives to improve cycling stability of LMR cathode.

Milestones

FY13

- ✓ Identify the key factors related to the oxygen release in layered composite (May 2013). ***Complete***
- ✓ Demonstrate the effects of different treatments on cathode. (Sept. 2013). ***Complete***
- ✓ Identify electrolyte additives that can improve the cycling stability of layered composite. (Sept. 2013). ***Complete***

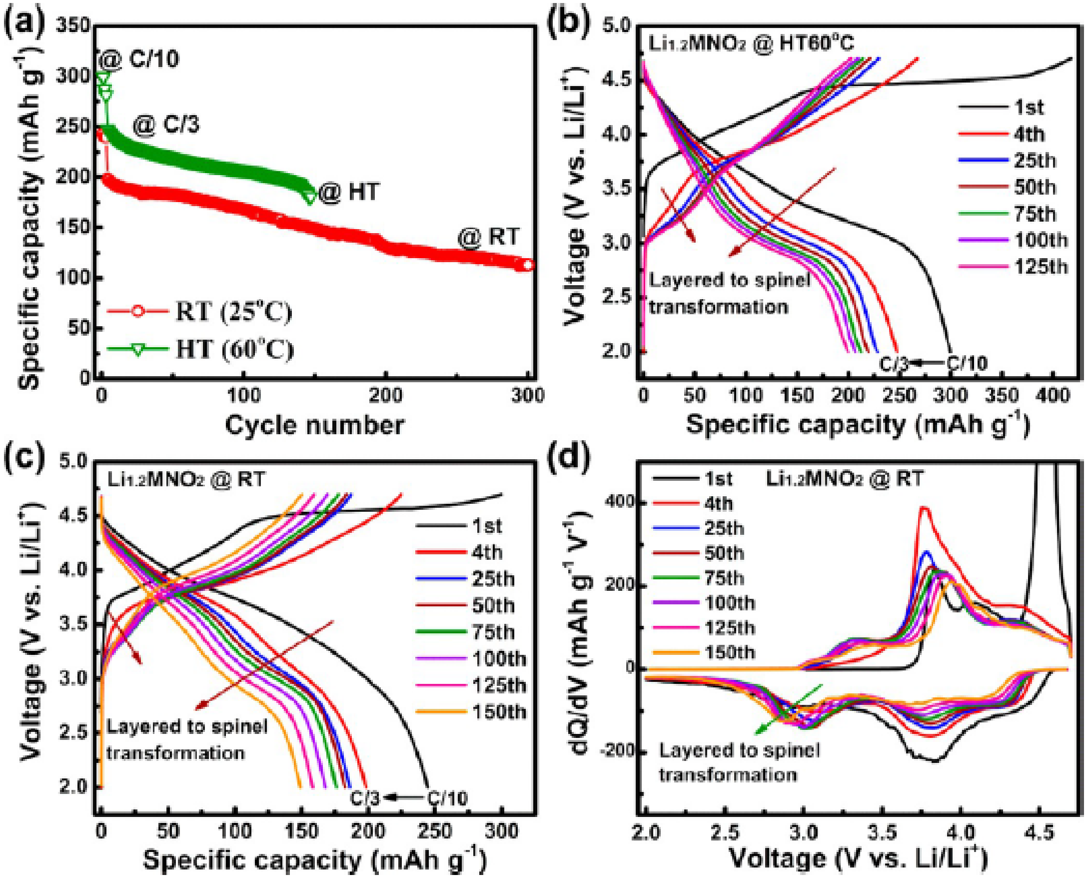
FY14

- ✓ Preparatory work on stable cycling of high energy LMR cathode. (Dec. 13) **Completed.**
- ✓ Stable cycling of 80% capacity retention after 150 cycles from LMR high energy cathode. (March 14) **Completed**
- ✓ 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. (Sep. 14) **On going**

Approach

1. Use advanced characterization techniques to understand the failure mechanism of LMR cathode.
2. Mitigate the voltage fading and capacity loss of LMR through modified synthesis route.
3. Utilize electrolyte additive to improve the interfacial reactions and improve cycling stability of cathode.

Technical Accomplishments
Typical Cycling and Charge/Discharge Profiles of LMR Cathode

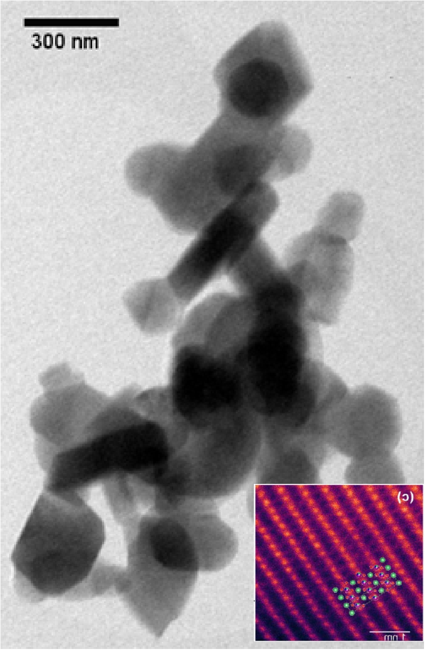


$Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$
2.0-4.7 V
1C=250 mA/g

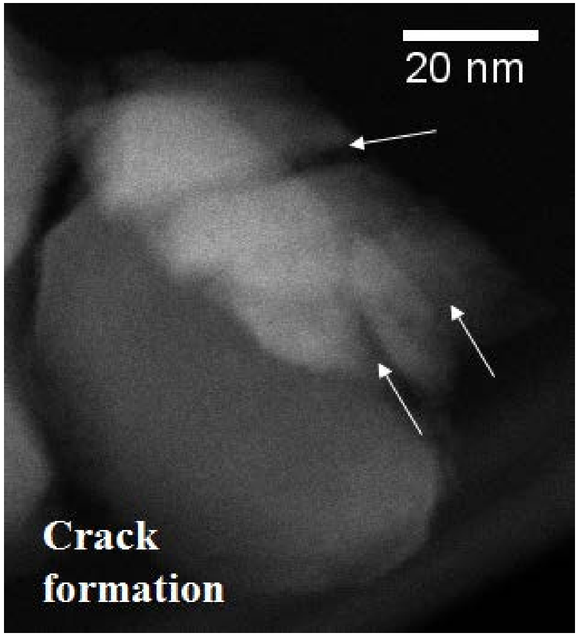
- ✓ Both capacity and voltage fades in LMR.
- ✓ Higher reversible capacity at elevated temperature but still degrades fast.

Technical Accomplishments

Fragmentation of LMR Particles after Cycling



Pristine LMR

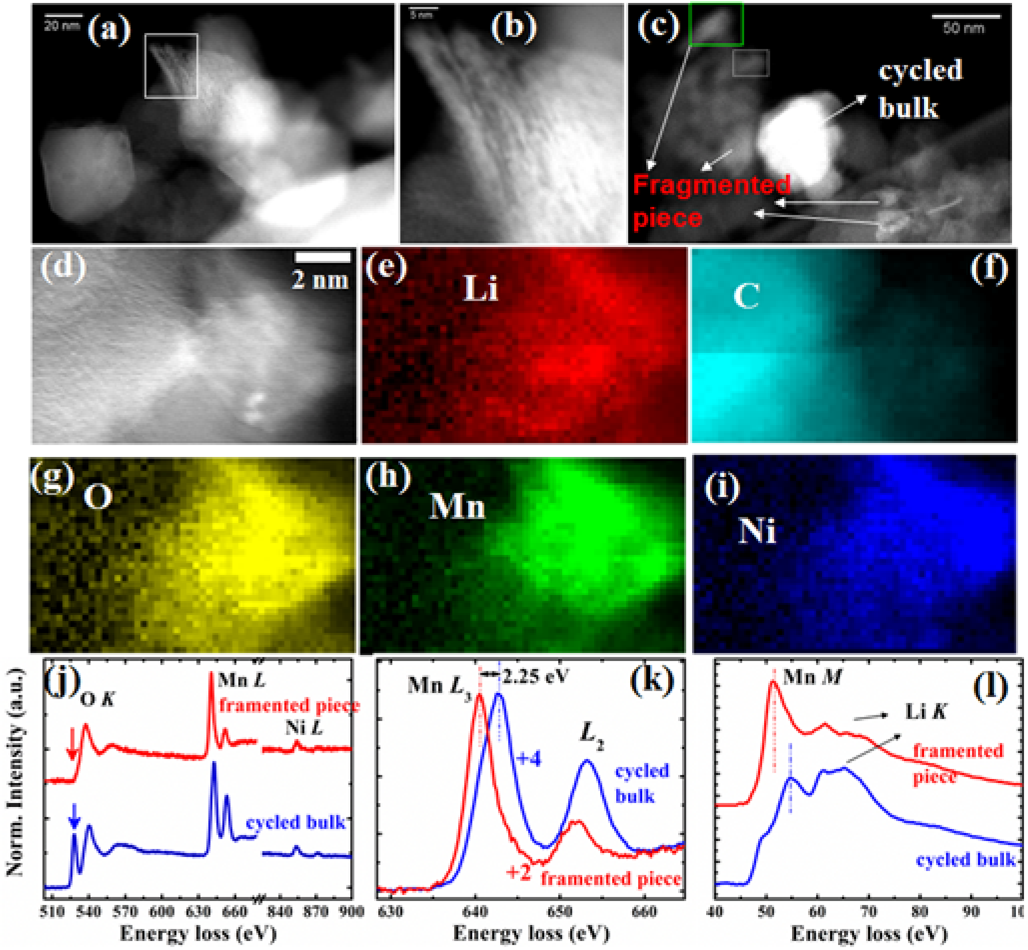


Cycled LMR

- ✓ Pristine LMR is ca.100 nm with well defined layered structure.
- ✓ Microcracks were identified on cycled LMR.

Technical Accomplishments

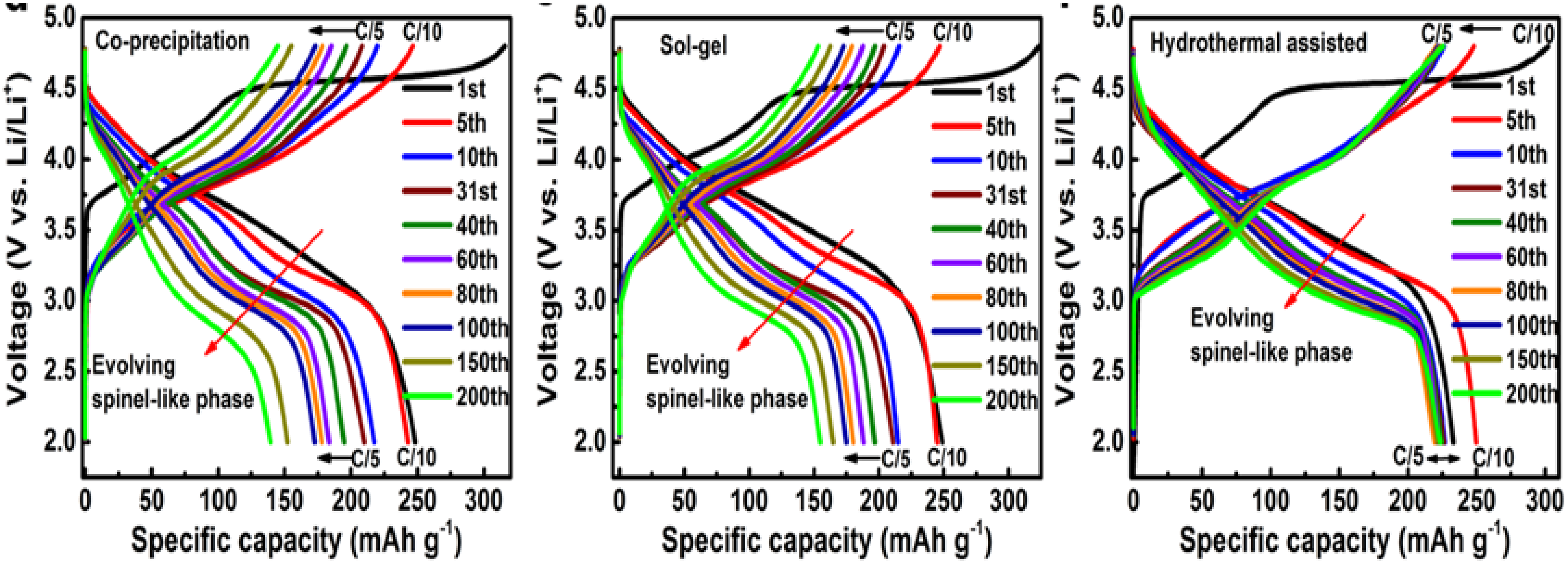
Elemental Mapping on Fragmented Pieces



- ✓ Mn valence in the fragmented pieces was quantified to be 2^+ (Fig. k), much lower than that in the bulk, and is consistent with the oxygen deficient environment in the fragments.
- ✓ Li K edge peak intensity in the fragmented particle was also lower than in the bulk region.
- ✓ Oxygen release and extensive removal of Li^+ generated large strain and led to the fragmented pieces.

Technical Accomplishments

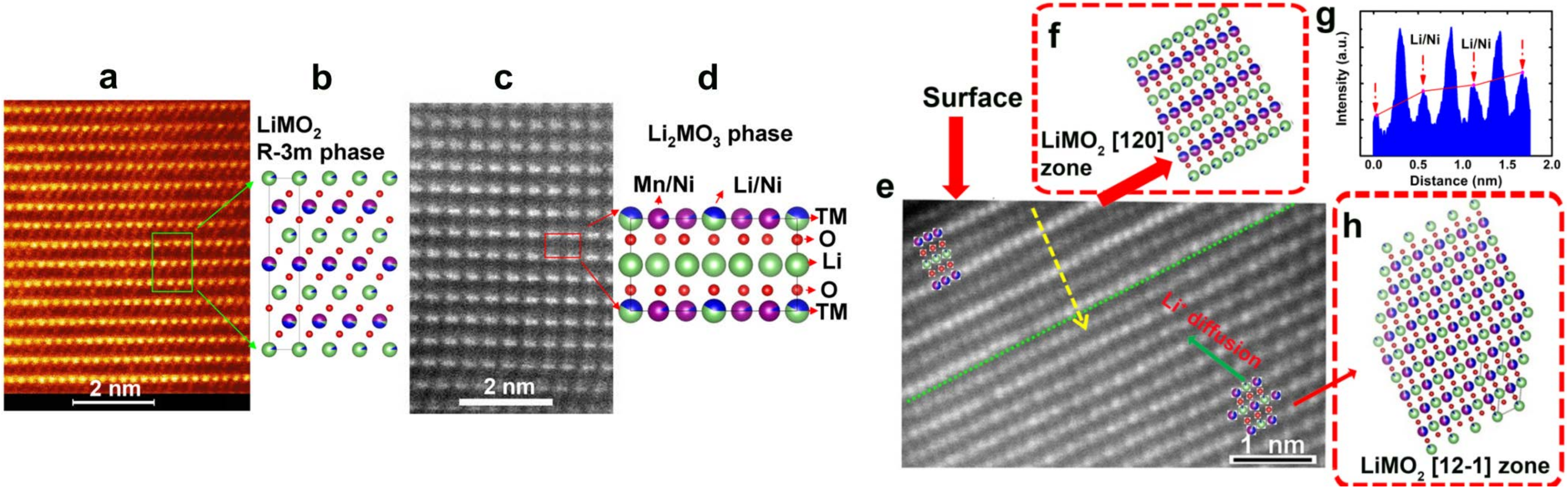
Hydrothermal-assisted Synthesis Mitigates Voltage Fading In LMR



- ➢ Voltage fading was observed in LMR prepared from three different methods: Layered-to-spinel phase transition still occurred.
- ➢ Voltage degradation was the least in LMR using hydrothermal assisted approach.
- ➢ Non-uniform Ni distribution in LMR could accelerate voltage degradation.

Technical Accomplishments

Structure of LMP material prepared by CP approach

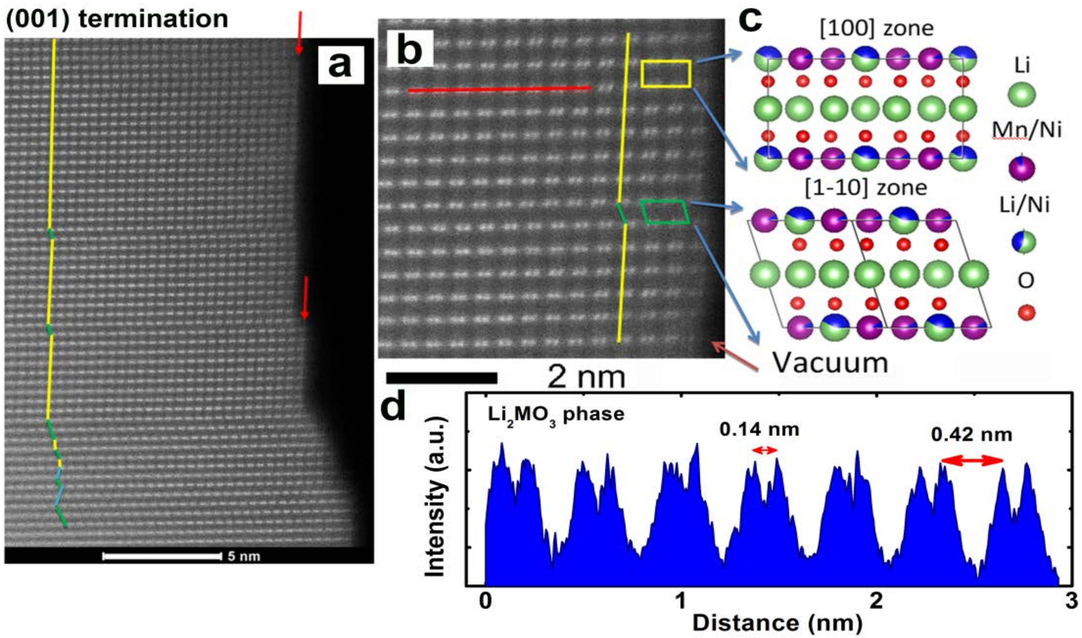


STEM imaging of fresh CP material. (a) Crystal structure of R-3m phase; (b) atomic model of the R-3m phase in the [100] zone projection, which corresponds to the green rectangle in panel (a); (c) crystal structure of C2/m phase; (d) atomic model of the C2/m phase in the [100] zone projection, which corresponds to the red rectangle in panel (c). (e) Atomic-scale Z-contrast image showing the Ni-rich induced surface modification. Note that the upper left region above the green dashed line is the Ni-rich region; its atomic model (f) corresponds to the [120] zone projection of the $LiMO_2$ R-3m phase and the intensity plot along the yellow arrow is shown in (g); the bottom right region corresponds to the [12-1] zone projection of the $LiMO_2$ R-3m phase, and the corresponding model is presented in (h).

- As-prepared CP materials is dominated by $LiMO_2$ type R-3m phase

Technical Accomplishments

Structure of LMP material prepared by HA approach

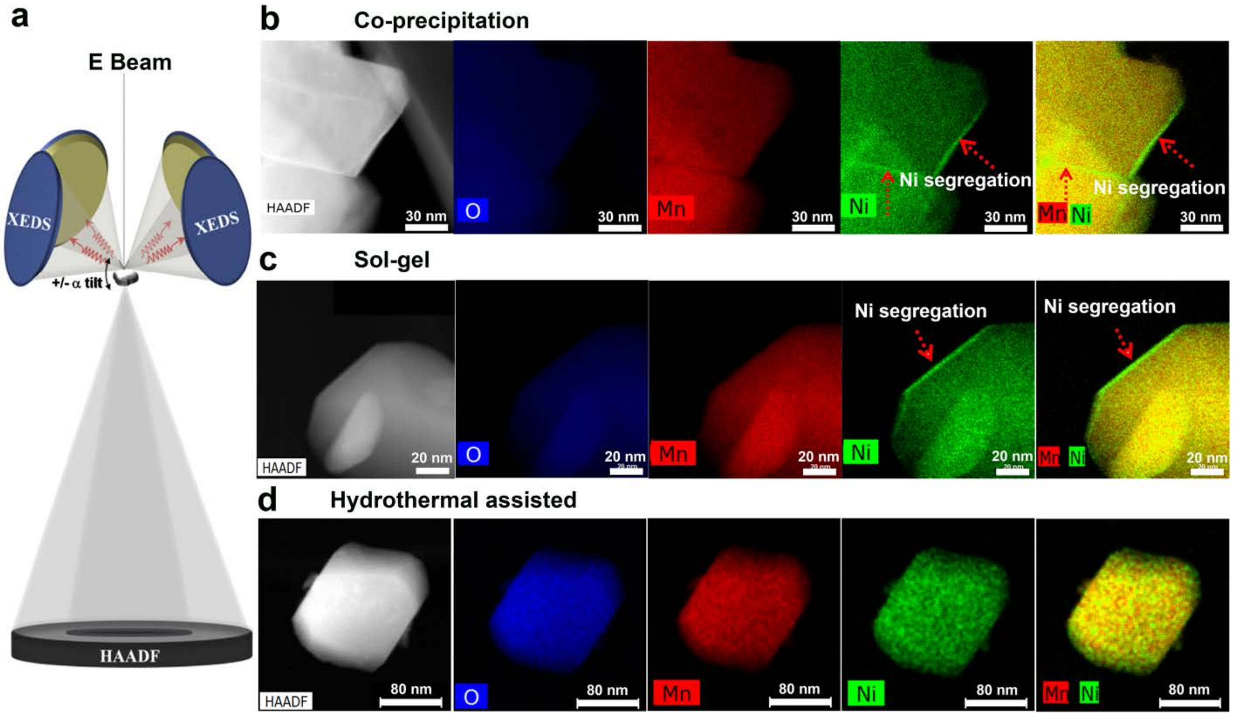


TEM imaging of the fresh HA material. (a) Atomic-scale Z-contrast image showing the mixed growth of different zone axes of the C2/m phase; (b) higher magnification Z-contrast image showing the mixed [100] (yellow) and [1-10] zone (green); (c) atomic model showing the atomic arrangement of the C2/m phase in [100] and [1-10] zone projections; (d) intensity plot along the red line shown in panel (b). Note that the termination plane of the crystal is indexed as (010) plane.

- As-prepared HA materials is dominated by Li_2MO_3 type C2/m phase

Technical Accomplishments

Hydrothermal-Aided Synthesis Improves the Atomic Level Uniformity of Elemental Distribution



Hydrothermal-assisted synthesis conditions:

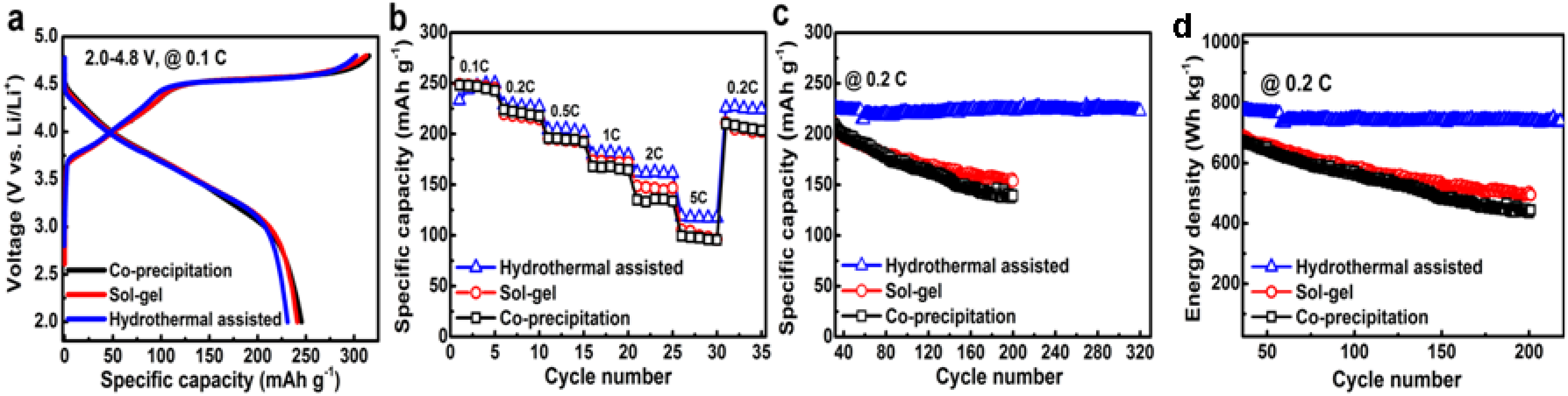
- Hydrothermal treatment: 200^{o}C, 10 hrs
- HT calcination: 900^{o}C, 24hrs.

- Ni segregation was found on LMR surfaces and boundaries: Impact Li$^+$ diffusivity (reported in last year's AMR meeting)
- Ni segregation was generally observed in LMR prepared by sol gel or co-precipitation method.

➢ Hydrothermal-assisted solid-state synthesis route homogenize cation distribution at the atomic level: no Ni segregated on LMR particle surface.

Technical Accomplishments

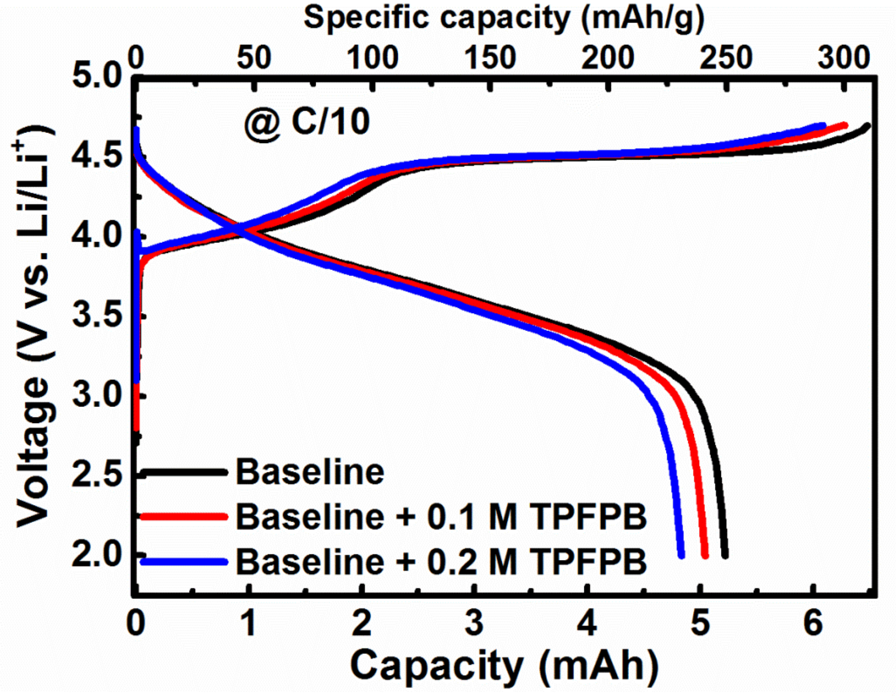
Atomic Level Uniformity of Elemental Distribution in Cathode Nano-particles can Mitigate its Voltage Fade

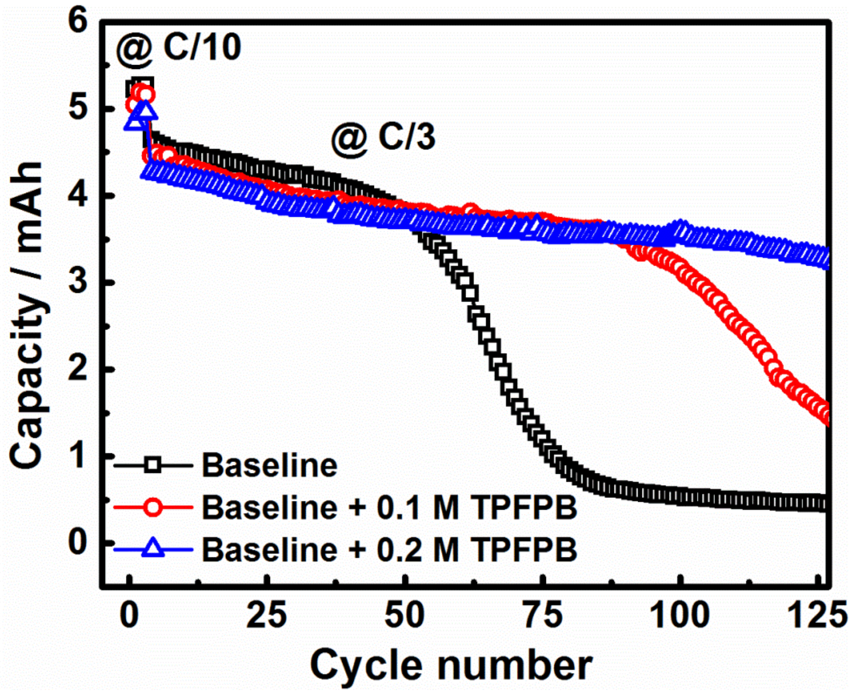


- ➢ Both Co-precipitation and Sol-gel materials display fast capacity degradation during cycling at C/5.
- ➢ Hydrothermal-assisted material shows excellent cycling stability at C/5. It demonstrates a discharge capacity of 226 mAh g^{-1} with no visible capacity fade after 320 cycles.
- ➢ Hydrothermal-assisted material also demonstrates much smaller voltage and energy loss.

Technical Accomplishments

Effects of TPFPB Additive by Using ANL Testing Protocol

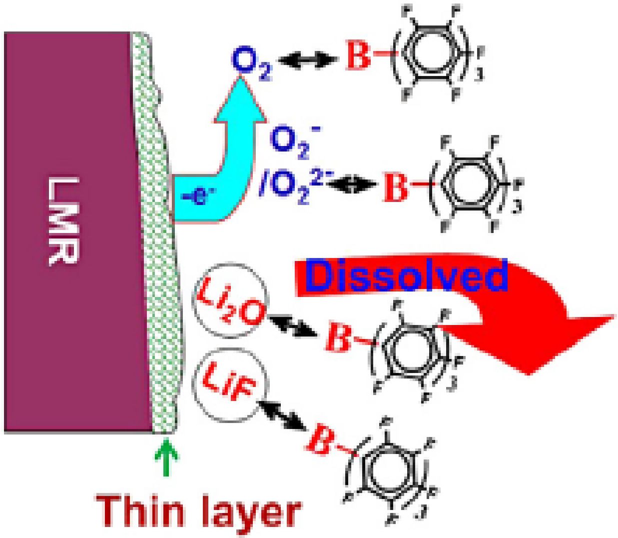


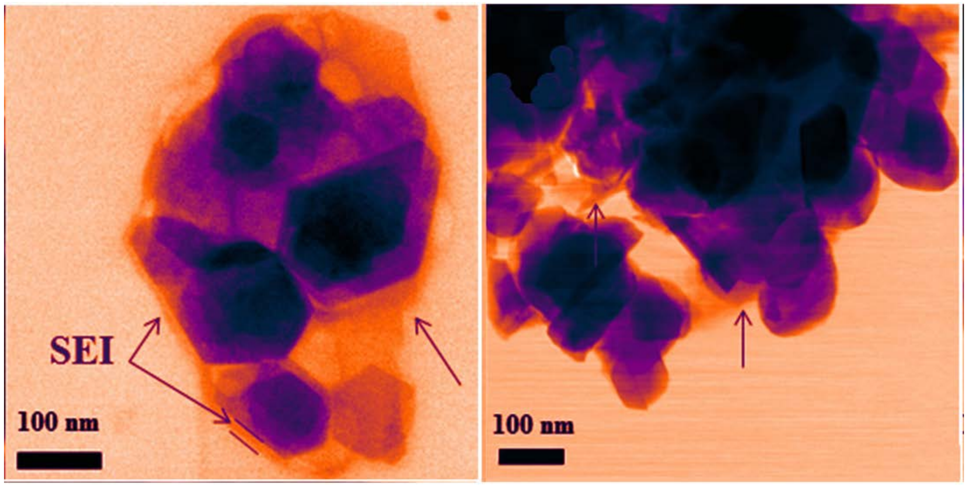


- ✓ ANL testing protocol:

  LMR Loading: 12.5 mg/cm^2; voltage range: 2.0-4.7 V; current: C/10 for 3 formation cycles and then C/3 for cycling (1C=250 mA/g= 3.13 mA/cm^2).
- ✓ TPFPB extends the cycling stability of thick LMR electrodes prepared by ANL under ANL testing protocol.
  - ✓ Lithium metal deteriorate fast under high current charging (C/3= 1.04 mA/cm^2) and also contributes to the fast capacity decaying.

Technical Accomplishments
Proposed Mechanism of TPFPB Additive




LMR after 300 cycles without TPFPB

LMR after 300 cycles With TPFPB

- ✓ TPFPB captures the intermediate oxygen anions or radicals released from LMR lattice before forming O_2.
- ✓ The increased oxygen solubility in TPFPB prevents O_2 from direct contact with electrolyte, greatly suppressing the side reactions.
- ✓ Byproducts such as Li_2CO_3 and LiF etc formed at high voltages are also partially soluble in TPFPB: thinner SEI layer on cathode lead to smaller polarization.

➢ Voltage fading may be a combined result of internal structure change and cell impedance increase.

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

Future Work - FY2014/15

- Identify the key factors during synthesis to mitigate the layered-to-spinel phase transition.
- Continue to use advanced characterization techniques (especially operando TEM using liquid electrolyte) to investigate the interface and bulk properties of LMR for both pristine and cycled samples
- Modulate the Ni/Mn ratio in LMR to balance the cycling stability and specific energy of the composite based on the better understanding on the fading mechanism in LMR.

Summary

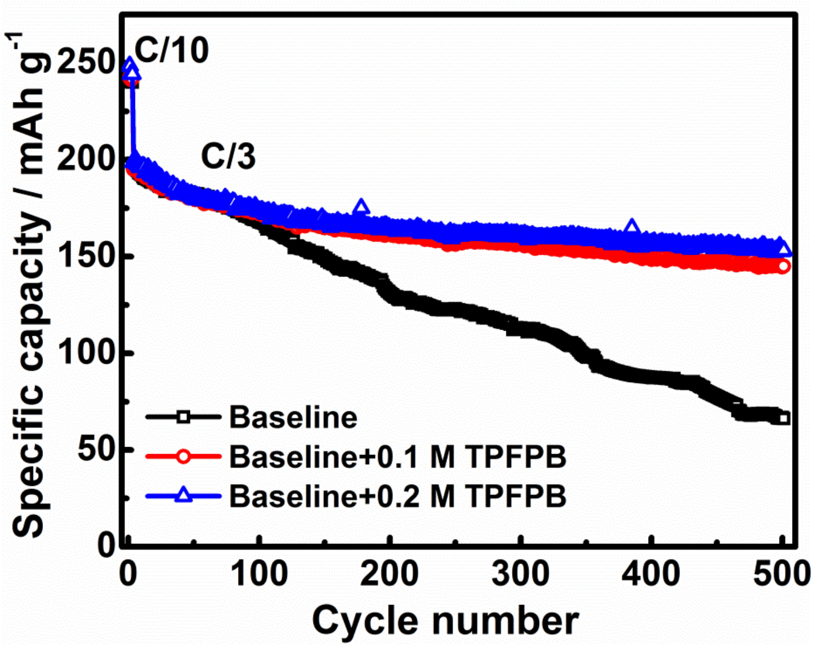
1. Investigated the failure mechanism of LMR
    - Surface corrosion and fragmentation were identified in cycled LMR.
    - Oxygen release and extensive removal of Li^+ led to LMR fragmentation.
2. Identified the mechanism for the improved performance of LMR cathode when TPFPB was used as additive
    - $O_2^-/O_2^{\bullet}/O_2$ were partially captured by TPFPB and had less side reactions with electrolytes.
    - Byproducts such as LiF and Li_2CO_3 were also partially soluble in TPFPB.
    - Thinner SEI on LMR in the presence of TPFPB thus reduced cell impedances: improved cycling and mitigated voltage fading.
3. Mitigated voltage fade in cathode material by improving its atomic level uniformity of elemental distribution
    - The hydrothermal pretreatment of starting materials before calcination homogenizes the cation distribution of LMR at the atomic level: less Ni segregation that impacts Li^+ diffusion.
    - Improved cycling stability and alleviated voltage fading during cycling.
    - Provide clues to mitigate voltage degradation from synthesis control.

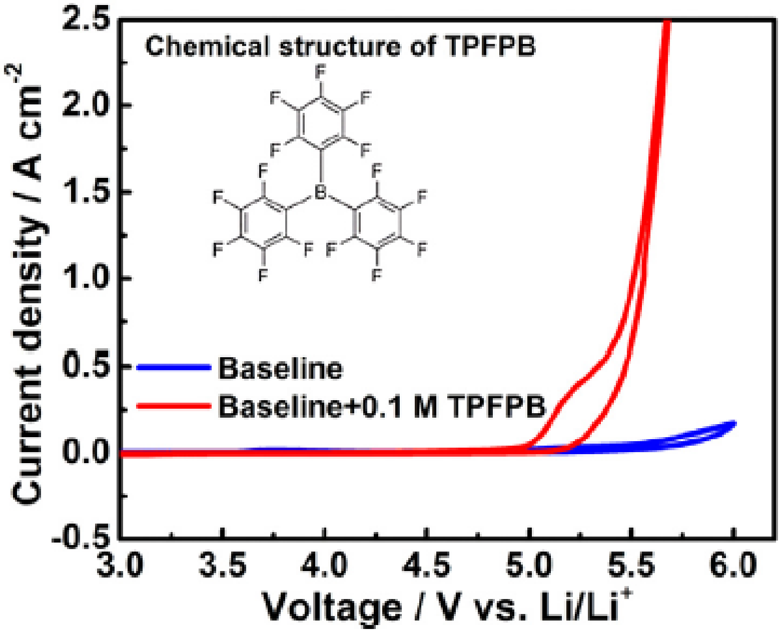
Acknowledgments

- ✓ Support from the DOE/OVT/BATT program is greatly appreciated.
- ✓ Team Members: Jianming Zheng, Liang Xiao, Wu Xu, Meng Gu, Pengfei Yan, Chongmin Wang, Jun Liu

Technical Backup Slides

Technical Accomplishments
TPFPB Additive to Modify Interfacial Reactions

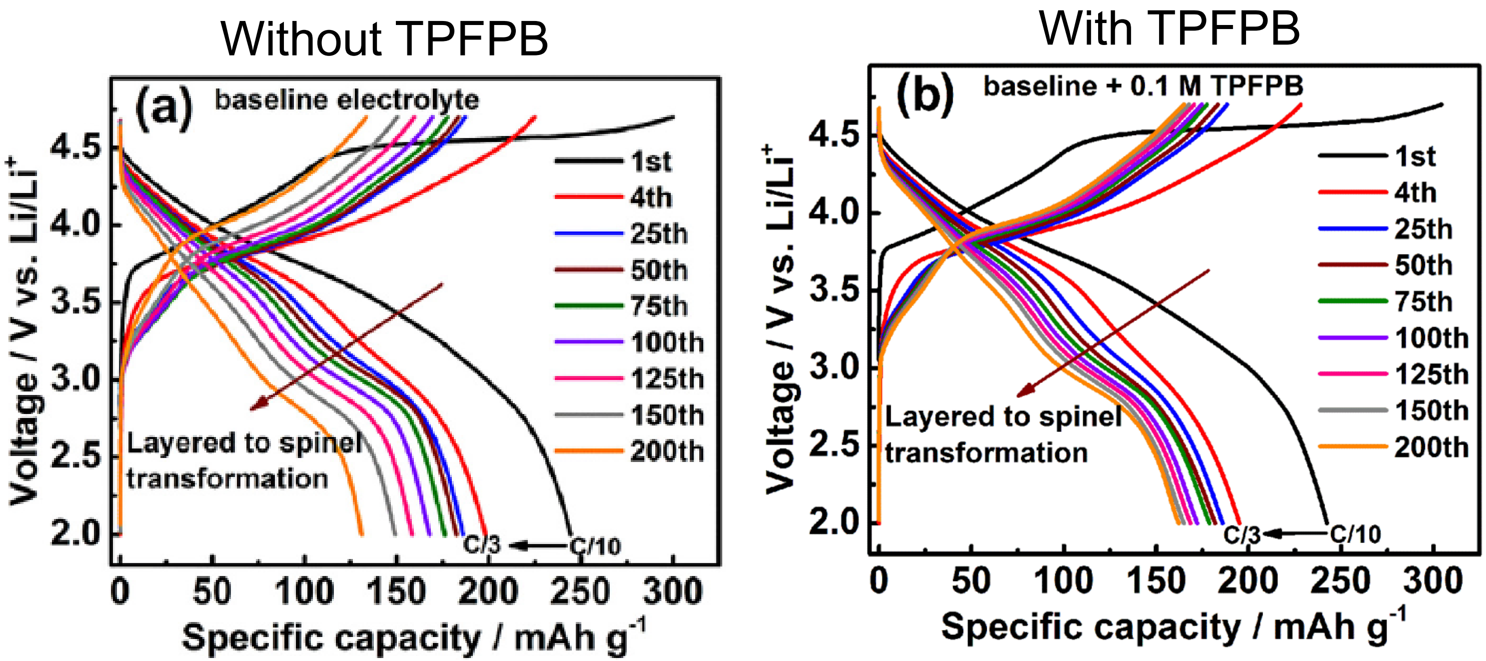




✓Tris(pentafluorophenyl)borane (($C_6F_5)_3B$, TPFPB) increases the cycling stability of LMR.

✓ TPFPB itself is stable up to ca.5 V and will not be oxidized during charge.

Technical Accomplishments
TPFPB also Alleviates Voltage Fading of LMR



Without TPFPB

With TPFPB

✧ LMR operates at high voltages and the electrolyte instability is worsened in the presence of O_2^{2-} and O_2 released from cathode: SEI built up cell impedance.

✧ Polarization was increased and accelerated the voltage fading.

✧ The addition of TPFPB mitigated the parasitic reactions (thinner SEI).

➢ Voltage fading may be a combined result of internal structure change and cell impedance increase.