Development of High-Energy Cathode Materials

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Pacific Northwest National Laboratory

2013 DOE Vehicle Technologies Program Review
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Project ID #**ES056**

Overview

Timeline

- Start date: Oct. 2011
- End date: Sept. 2015
- Percent complete: 38%

Barriers addressed

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

Budget

- Total project funding
  - DOE share 100%
- Funding received in FY12: $300k
- Funding for FY13: $300k

Partners

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

Objectives

- Systematically investigated high-voltage spinels with the key understandings transferrable to other high-energy cathodes.
- Improved the performance of Li-rich, Mn-rich layered composite cathode suitable for PHEV and EV applications.
- Developed electrolyte additives for high-energy battery systems.

Milestones (FY12-13)

FY12

- ✓ Rheological phase synthesis of layered composite cathode with 200 mAh/g capacity and stable cycling performance (Sept. 2012). ***Completed***
- ✓ Optimize the synthesis approach and inactive components for the high-voltage spinel and composite cathode (Sept. 2012). ***Completed***

FY13

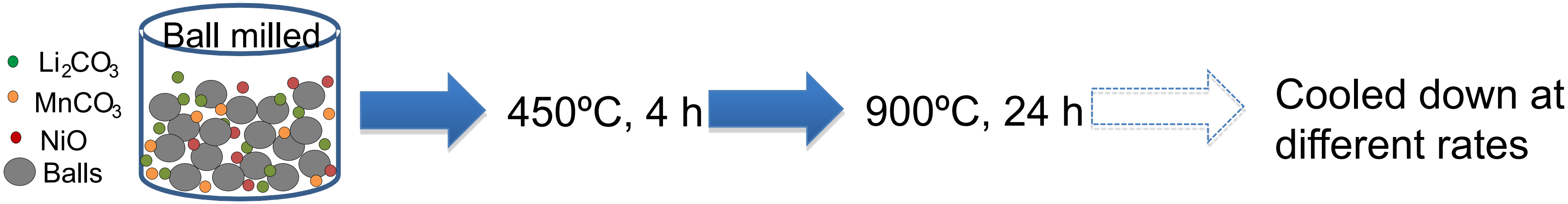
- ✓ Identify the key factors related to the oxygen release in layered composite (May 2013). ***Ongoing***
- ✓ Demonstrate the effects of different treatments on cathode. (Sept. 2013). ***Ongoing***
- ✓ Identify electrolyte additives that can improve the cycling stability of layered composite. (Sept.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

Approach

1. Tune the contents of disordered phase/lattice Mn^{3+} in spinel structure($LiNi_{0.5}Mn_{1.5}O_4$) by controlling the cooling rate, post-synthesis annealing, and elemental substitution/doping.
2. Investigate the relationship of synthesis, structure, and performance in spinel by advanced characterizations.
3. Improve the stability of layered composite cathodes by using novel electrolyte additives and/or surface treatment.

Technical Accomplishments

Facile Synthesis of Cathode Materials

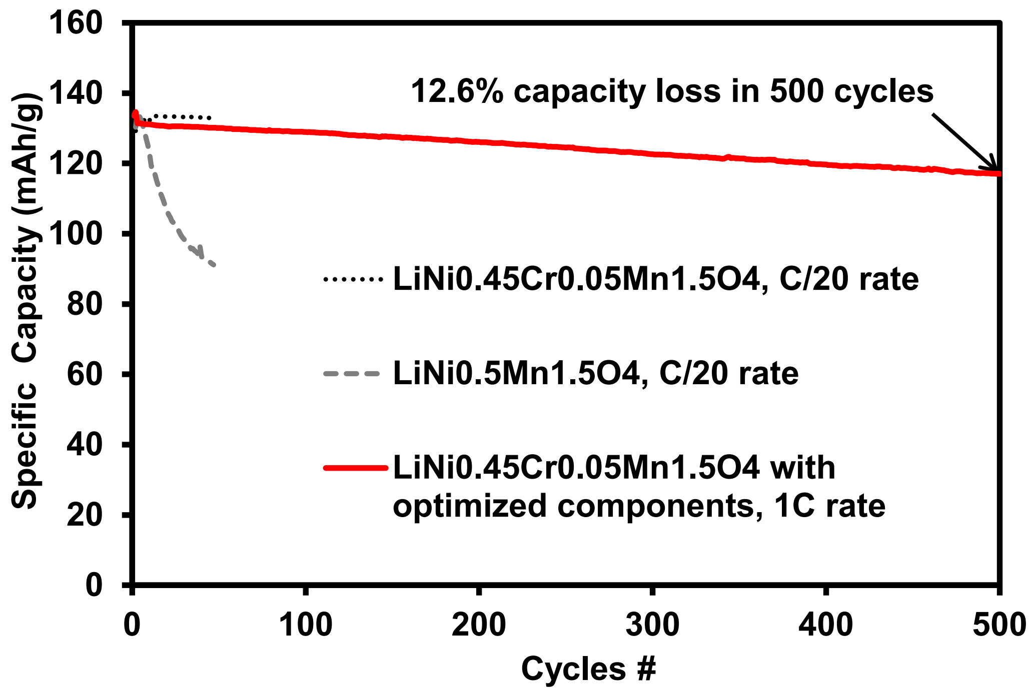


- ✓ Materials as well as synthesis approach are cost effective.

- ✓ Different cooling rates have been used to modulate the oxygen deficiency.
  - Oxygen defficiency is generated during high-temperature calcination.
  - Faster cooling yields more oxygen-deficient/disordered phase.

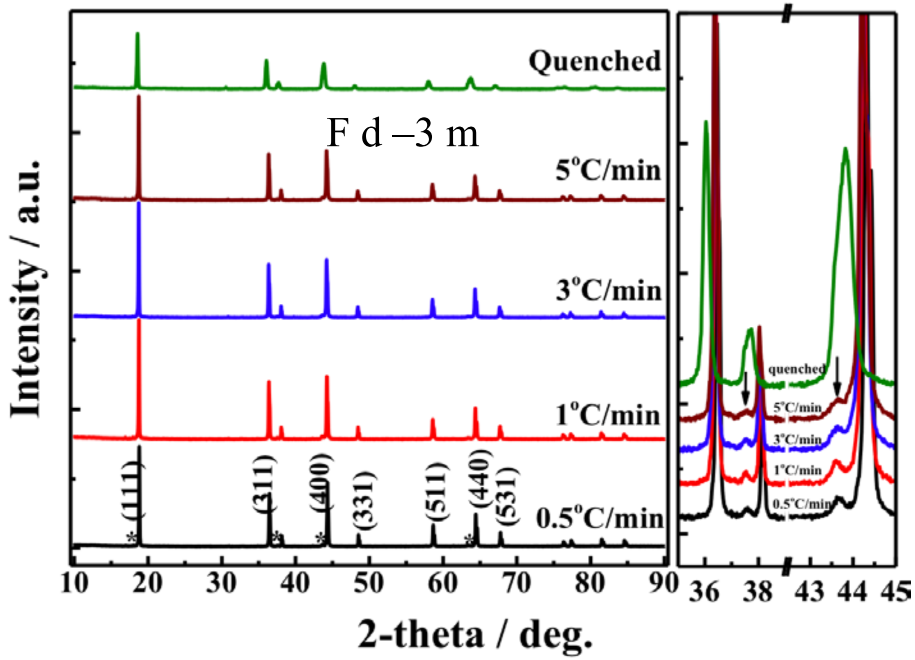
- ➢ This method was also used to control the synthesis of Li-, Mn-rich cathode materials.

Technical Accomplishments
Doping or Post-Synthesis Heating also Affects Cell Performance

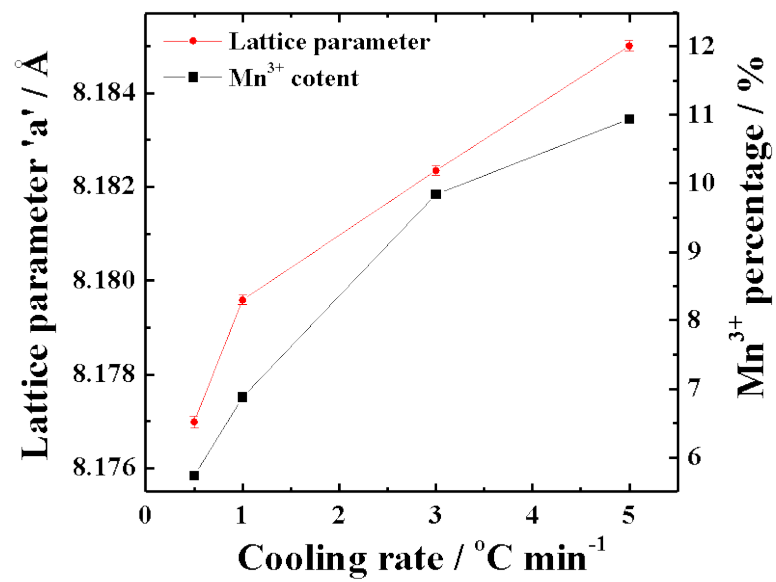


- ✓ Doping or reheating can also tune the content of the disordered phase.
- ✓ 12.6% capacity fading for 500 cycles is observed using optimized material and testing conditions.

Technical Accomplishments
Cooling Rate Controls Lattice Mn^{3+} Content



Higher cooling rate, more Mn^{3+}.

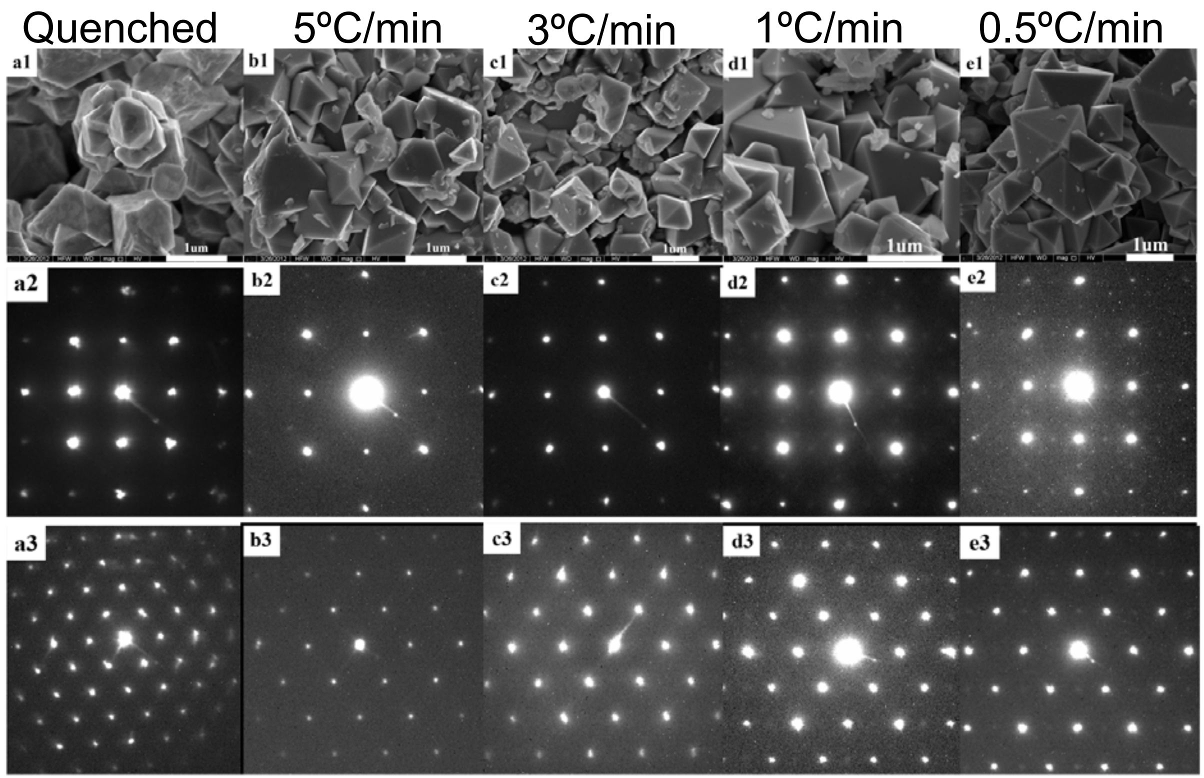


Peak shifts to lower angle systematically with increasing cooling rate.

- Faster cooling generates more Mn^{3+} so lattice parameter increases.
- Lattice Mn^{3+} concentration can be used to estimate the relative amount of oxygen deficiency.

Technical Accomplishments

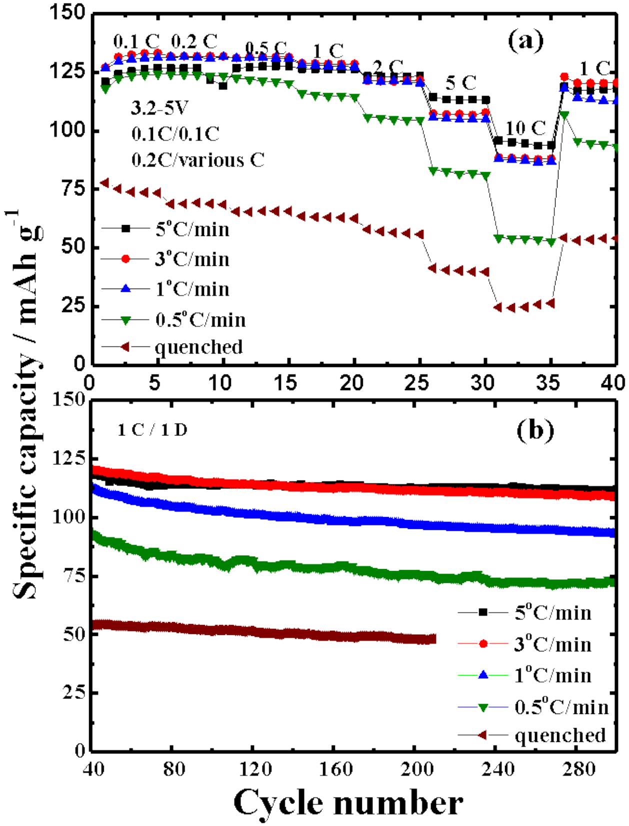
Superlattice Pattern (Ordered Phase) Occurs with Very Slow Cooling Rate

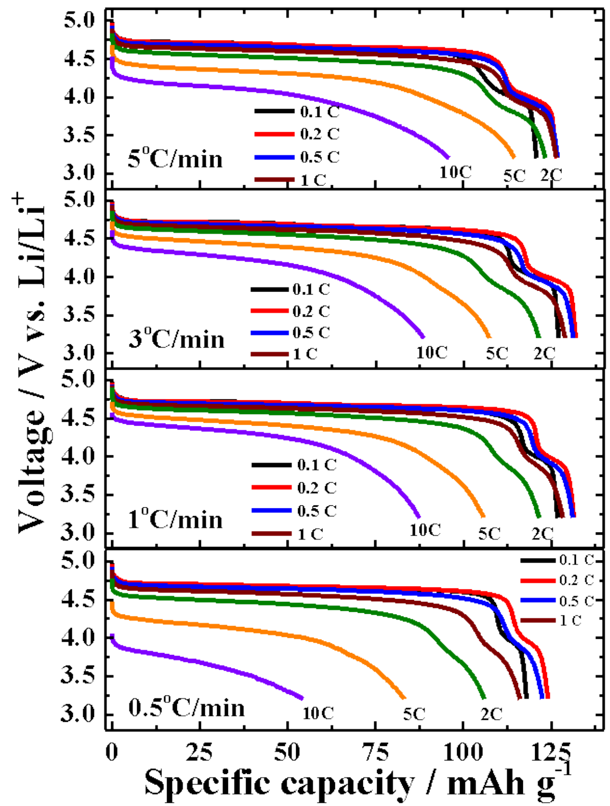


- Superlattice pattern occurs when cooling is slower than 3ºC/min.
- Faster cooling rate ⇒ more oxygen deficiency ⇒ more Mn^{3+}/disordered phase.
- Mn^{3+} is directly related to the relative amount of disordered phase in spinel.

Technical Accomplishments

Disordered Phase Accelerates Li^+ Transport





- ➢ Disordered phase leads to greatly improved rate capability.
- ➢ Disordered phase also improves the long-term cycling stability.

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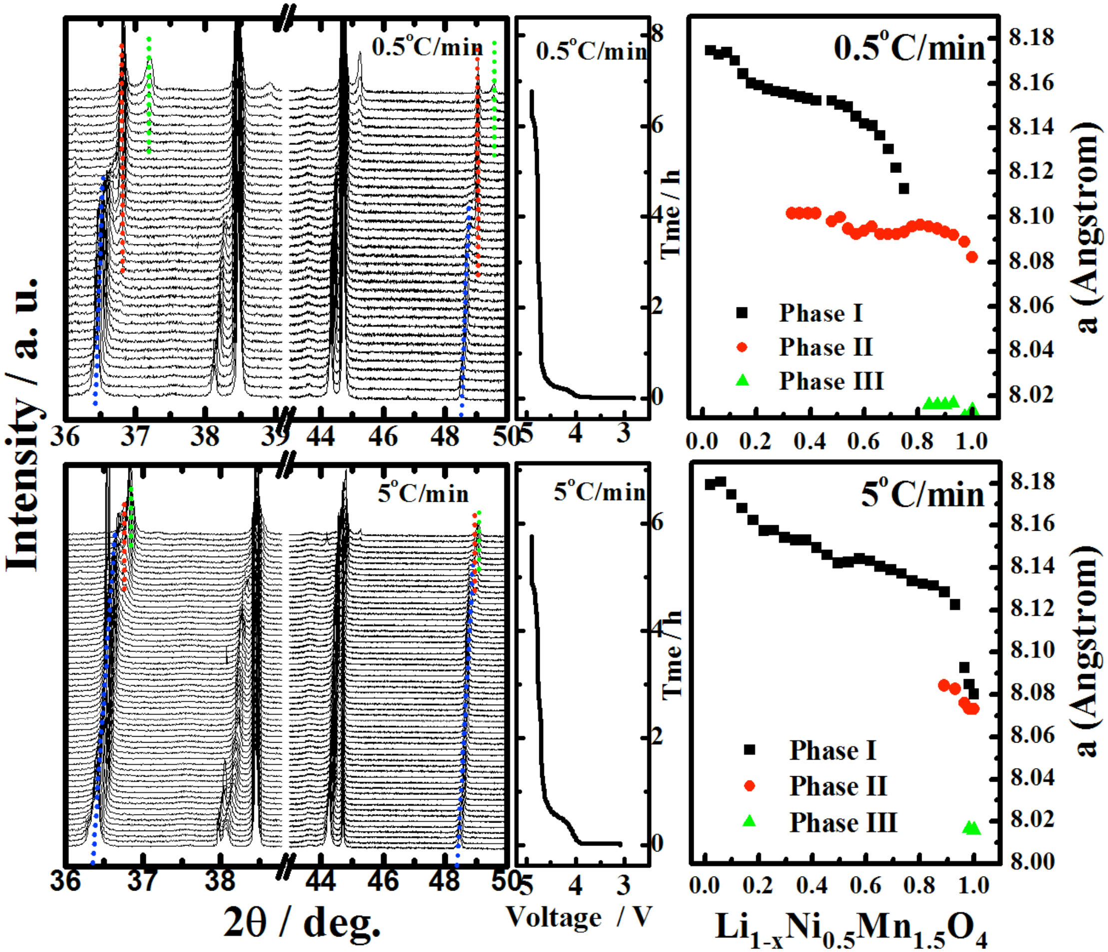
Technical Accomplishments
Disordered Phase Changes Reaction Pathway

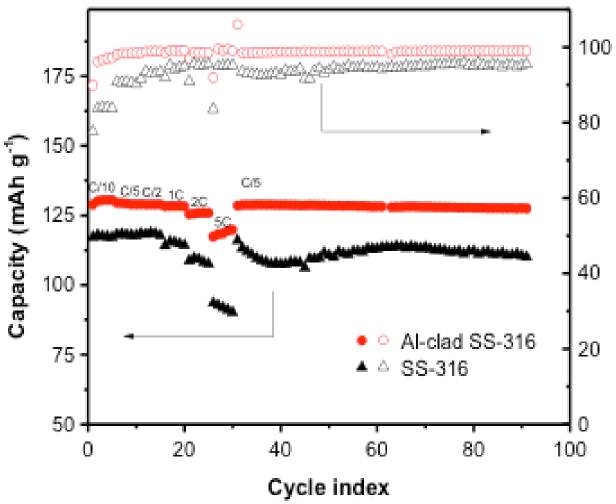


In collaboration with
Drs X. Yu and X-Q Yang at BNL.

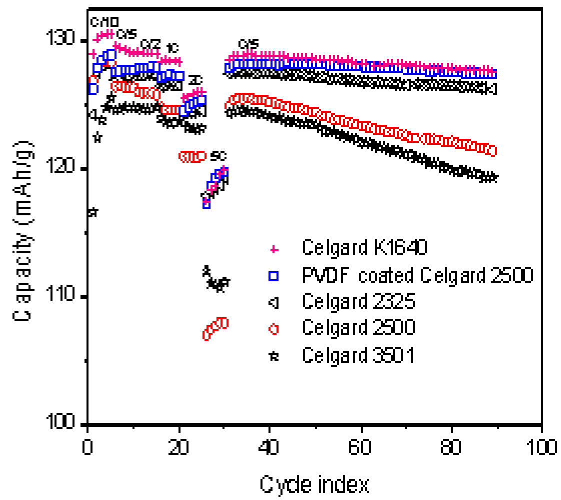
- 0.5ºC/min: more ordered phase, two successive two-phase reactions occur.
- 5ºC/min: more disordered phase, a solid-solution domain dominates until 75% SOC, benefiting Li^+ transport especially at high discharge rates.

Technical Accomplishments
"Inert" Components May Exhibit Side Reaction at High Voltage

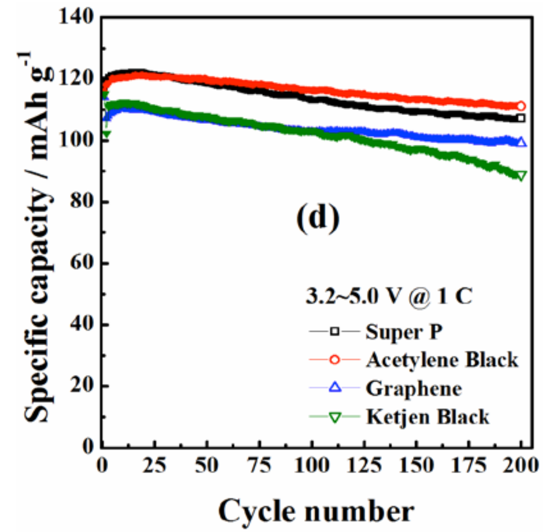
Cell Cans



Separators



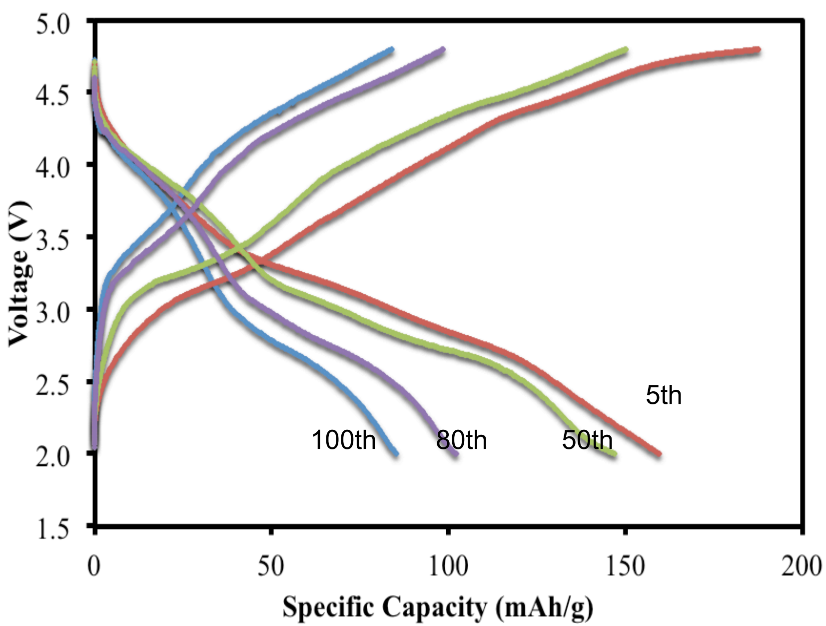
Carbon Additives

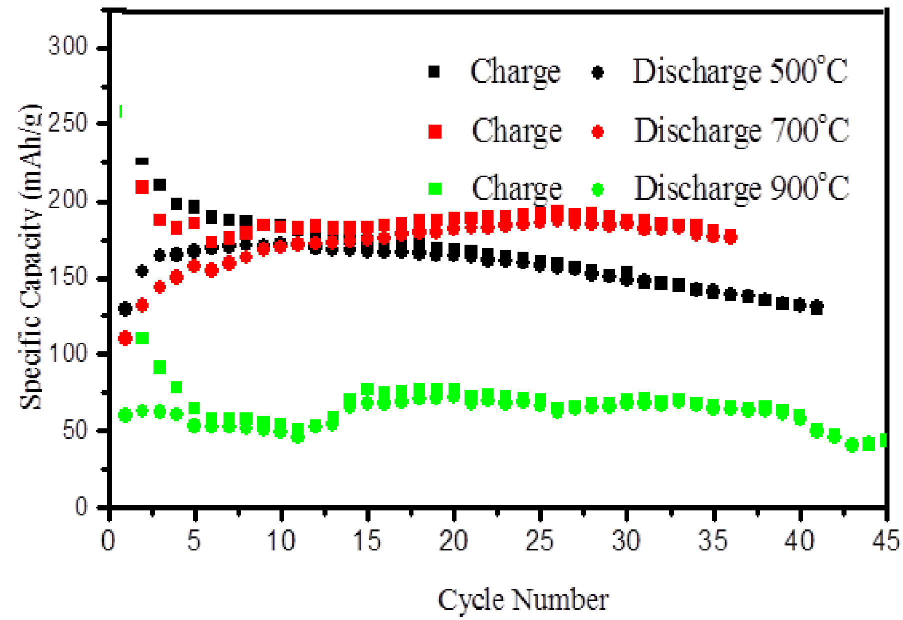


- S.S. can exhibits side reaction at high voltage (>4.8V).
- Polypropylene-based separator is unstable, especially when surfactants exist. (PP is oxidized and interacts with electrolytes, thus generating undesired deposits).

- ➢ Al-coated cell can is suitable for high-voltage cathodes.
- ➢ Polyethylene-based separators (such as Celgard K1640) are stable at high V.

Technical Accomplishments
Electrochemical Behavior of Li_2MnO_3

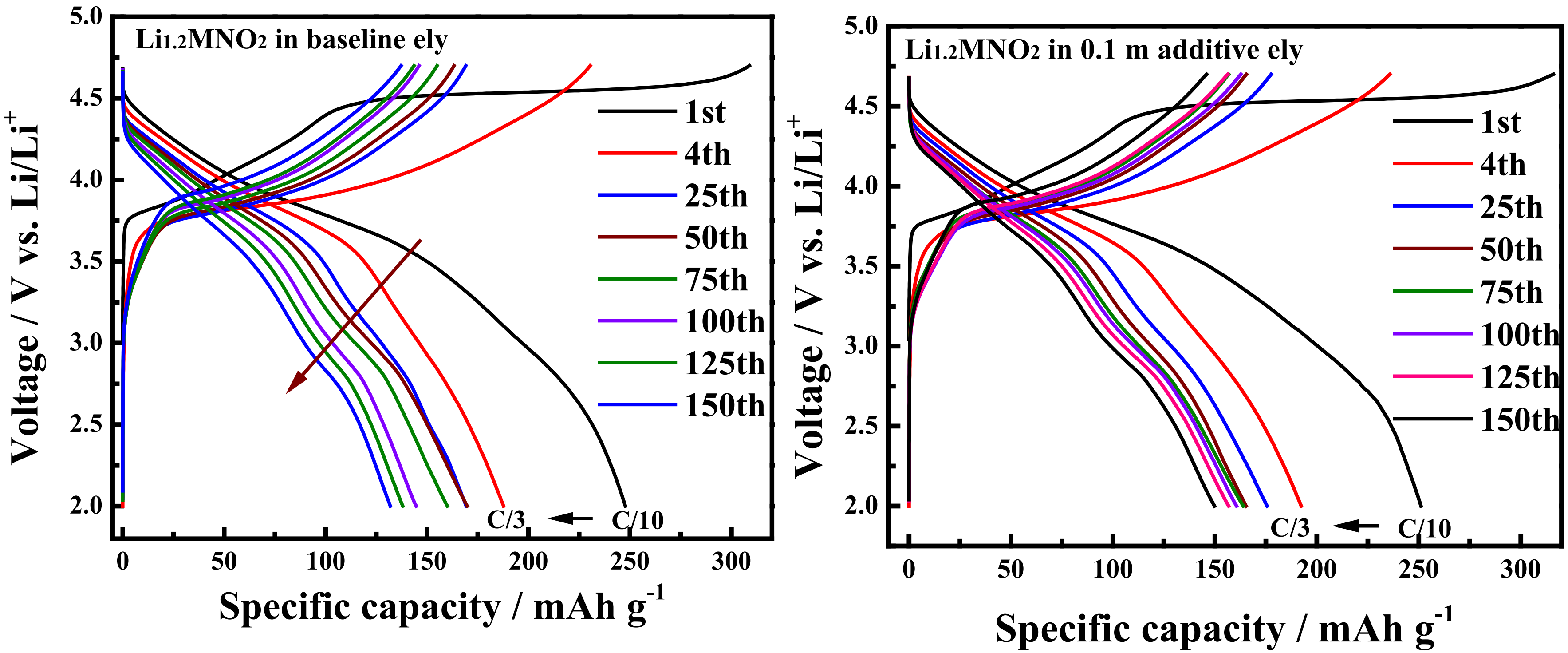




- ✓ Study on Li_2MnO_3 itself helps to understand the key issues in the composite.
- ✓ Gas release and voltage fading are observed to be similar to those in layered composite.

Technical Accomplishments
Electrolyte Additive Alleviates Voltage Fading

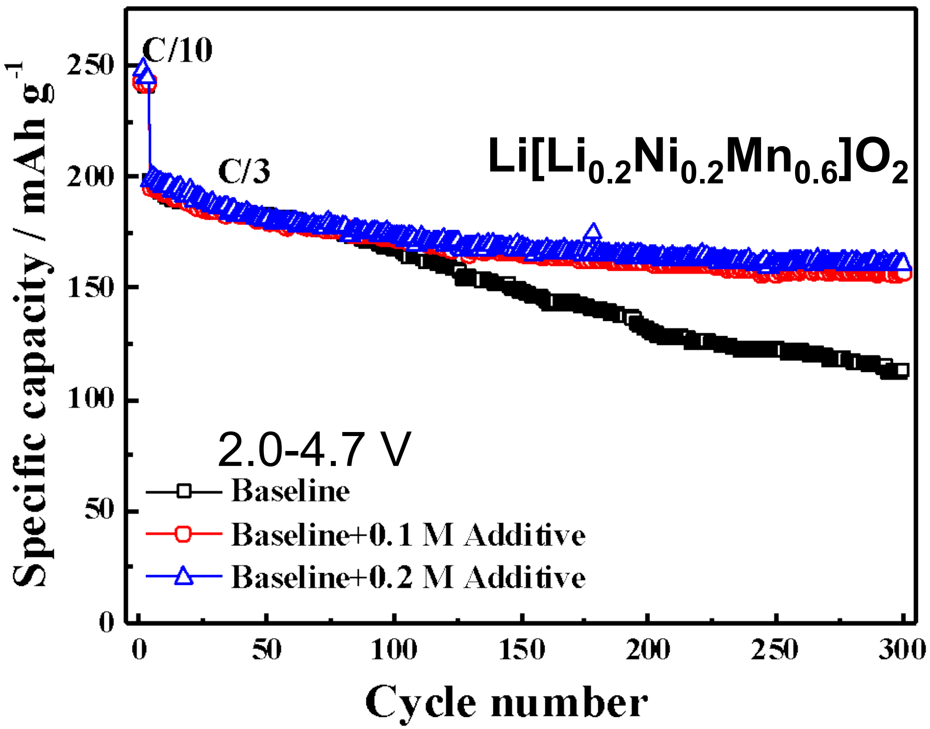
$Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$

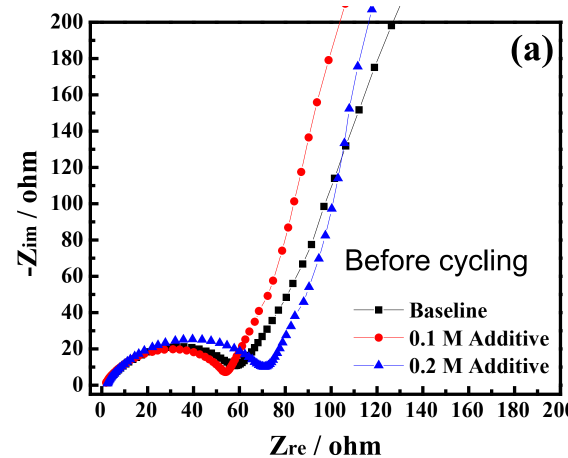


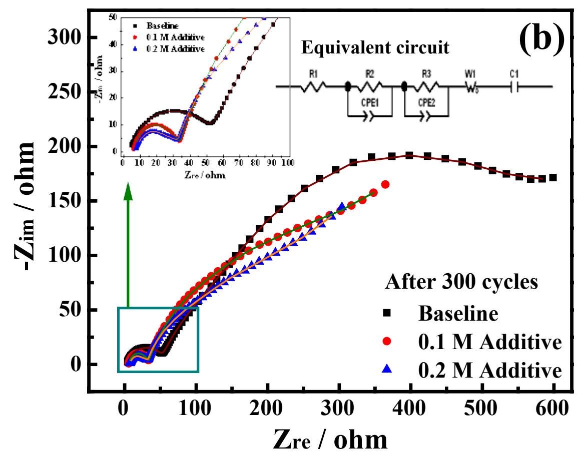
C/10 was used for the first three cycles, followed by C/3.

➢ **Voltage fading was alleviated with 0.1 M additive in the electrolyte.**

Technical Accomplishments
Working Mechanism of Electrolyte Additive



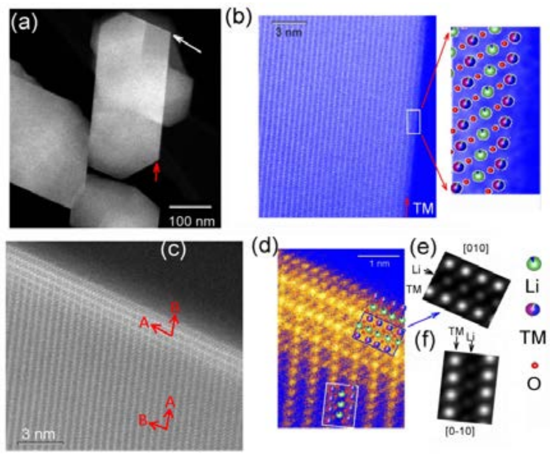


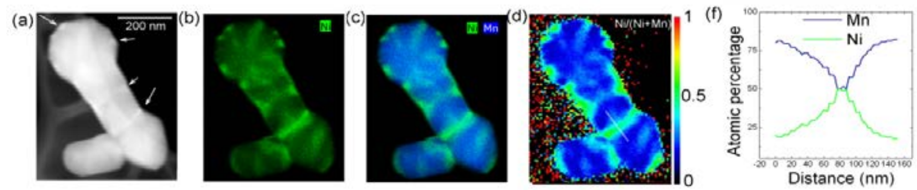


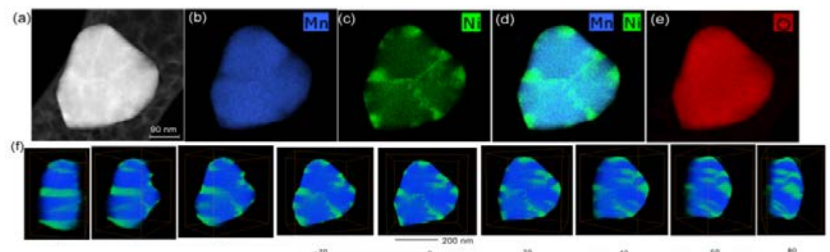
- The additive stabilized the electrode/ electrolyte interface and thus improved the long-term reversibility of the lithium-rich cathode $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$.
- The fast increase of R_{SEI} and R_{ct} during cycling is also slowed down in the presence of the additive.

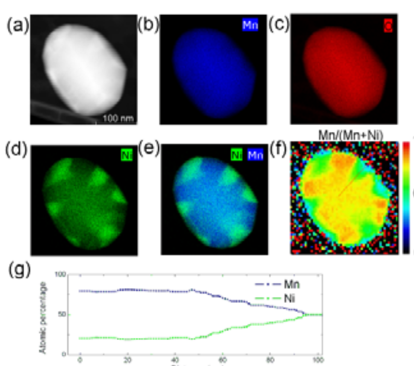
Technical Accomplishments

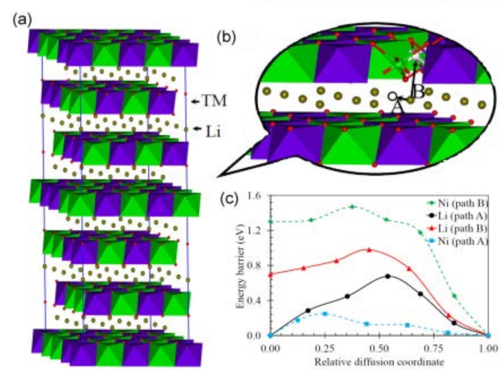
Surface Segregation of Ni in $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ Particles
(In collaboration with Ilias Belharouak and Khalil Amine of ANL)

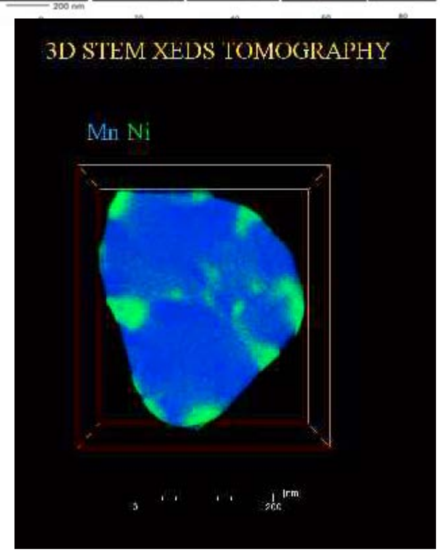








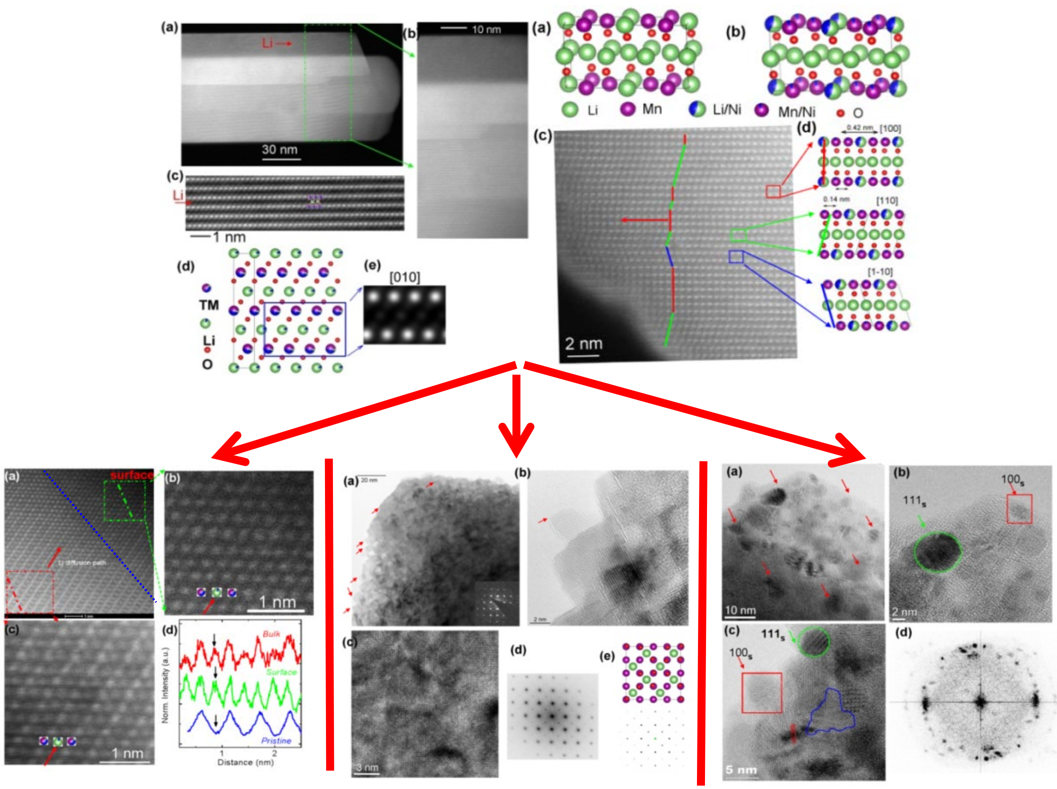


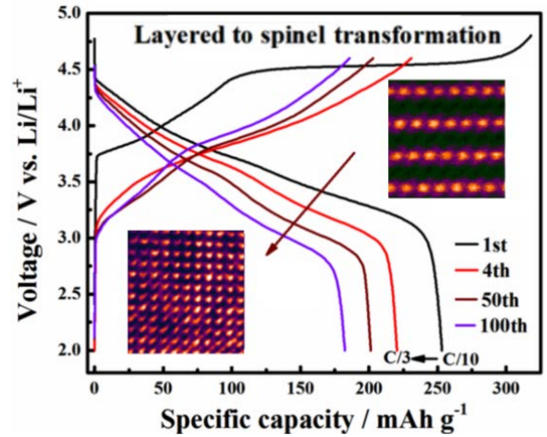


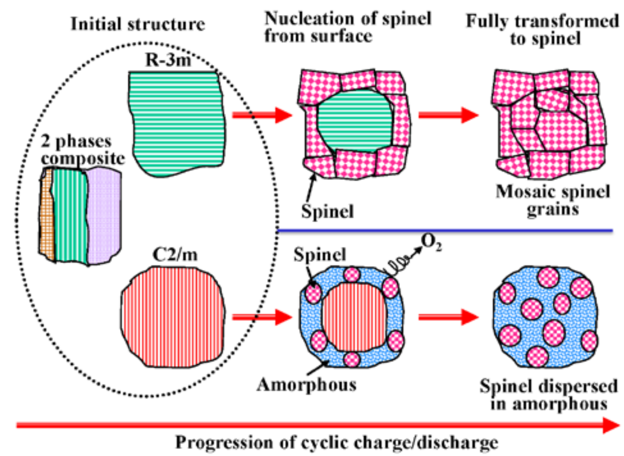
- Ni segregates to surfaces and boundaries
- Ni segregation will impact the Li diffusivity

Technical Accomplishments

New Finding on the Phase Transitions in LMR Cathode







- $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ exist both $LiMO_2$ R-3m and Li_2MO_3 C2/m phases.
  - ➢ After cycling, both phases gradually transform to spinel structures.
  - ➢ $LiMO_2$ R-3m to spinel: formation of mosaic of spinel grains in the parental particle.
  - ➢ Li_2MO_3 C2/m to spinel: random spinel grains within the same parental particle.

Collaboration and Coordination with Other Institutions

Partners:

- SUNY Binghamton (Academic): Characterization of high voltage spinels.
- University of Rhode Island (Academic): Electrolyte tests.
- Argonne National Laboratory (Federal Laboratory): Provide standard cathode and 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.
- Hydro-Québec (Industry): Surface coating on spinel and layered composites.

Future Work - FY2013/14

- Understand the capacity degradation and voltage fading mechanism of Li-Mn-rich layered composite cathode.
- Continue to develop electrolyte additives compatible with high-voltage environment.
- Combine advanced characterization techniques to investigate the interfacial properties between the electrode and electrolyte.
- Direct synthesis of the stable cathode structures observed in the cycled samples.

Summary

1. Systematically investigated high-voltage spinel cathode for Li-ion batteries
   - Control of cooling rate, annealing or substitution changed the content of Ni/Mn disordered phase in the lattice, which was the key to determining spinel performance.
2. "Inactive" cell components may exhibit side reaction at high voltage
   - Optimization of cell cans and separators has been completed for effective lab evaluation of high-voltage cathode materials.
   - Information obtained from high-voltage spinel system has been further applied in layered composite to accelerate the development of high-energy cathode materials.
3. Identified novel electrolyte additives that can improve the performance of high-energy LMR composite cathode
   - Baseline composite cathode $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ was built for further modification.
   - New electrolyte additive was identified to mitigate the continuous side reaction on the electrode/electrolyte interface at high voltages.
   - Discovered direct evidence of Ni segregation and layered-to-spinel transition correlated with the electrochemical behaviors of LMR cathodes.

Acknowledgments

- ✓ Support from the DOE/OVT/BATT program is greatly appreciated.
- ✓ Team Members: Jianming Zheng, Maria Sushko, Pengjian Zuo, Wu Xu, Meng Gu, Libor Kovarik, Chongmin Wang, Gordon L. Graff, Jun Liu