Design and Evaluation of High Capacity Cathodes

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Argonne National Laboratory

Annual Merit Review
DOE Vehicle Technologies Program
Arlington, VA
8-12 June, 2015

ES049

Vehicle Technologies Program

Overview

Timeline

- Start date: FY12
- End date: FY15
- Percent complete:
  - 90%

Budget

- Total project funding
  - 100% DOE
- Funding in FY15: $500K

Barriers

- Low energy density
- Cost
- Abuse tolerance limitations

Partners

- Lead PI: Michael Thackeray, Co-PI: Jason R. Croy
- Collaborators:
  - CSE, Argonne: Brandon Long, Joong Sun Park, Eungje Lee, Roy Benedek, Jeff Elam
  - APS: Mali Balasubramanian (XAS)
  - EMC/CNM: Dean Miller, Jianguo Wen (TEM)
  - ES: Greg Krumdick, Young-Ho Shin
  - NUANCE, Northwestern University: Vinayak Dravid (TEM)
  - Industry: Argonne licensees and collaborators

Objectives

- Design and characterize high capacity, high-power and low cost cathodes for PHEVs and EVs
  - Improve the structural design, composition and electrochemical performance of Mn-based cathodes
  - Explore methodologies to engineer electrode surfaces with stable architectural designs
  - Use atomic-scale modeling as a guide to identify, design and understand the structural features and electrochemical properties of cathode materials

Milestones (FY14)

- Evaluate the stabilization and performance of near end-member, Li_2MnO_3-containing composite electrodes. Specifically, high and low Li_2MnO_3-content electrodes – *transferred to ABR's 'high-voltage' project.*
- Evaluate new synthetic routes using layered $LiMO_2$ (M = Mn, Ni, Co) precursors to prepare composite electrode materials – *in progress.*
- Synthesize and characterize unique surface architectures that enable >200 mAh/g at a >1C rate with complementary theoretical studies of surface structures – *in progress.*
- Identify structures and compositions, including surface and bulk, that can deliver ~220 mAh/g at an average discharge voltage of ~3.5 V on extended cycling – *in progress.*

Approach

- Exploit the concept and optimize the performance of *structurally-integrated ('composite') electrodes structures* with a focus on '*layered-layered-spinel*' materials.

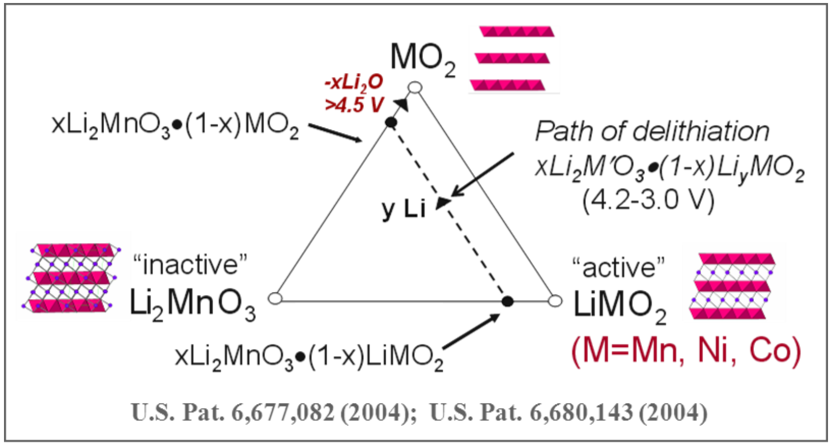
- Explore *processing routes* to fabricate electrodes with acceptable capacity, power, and life.

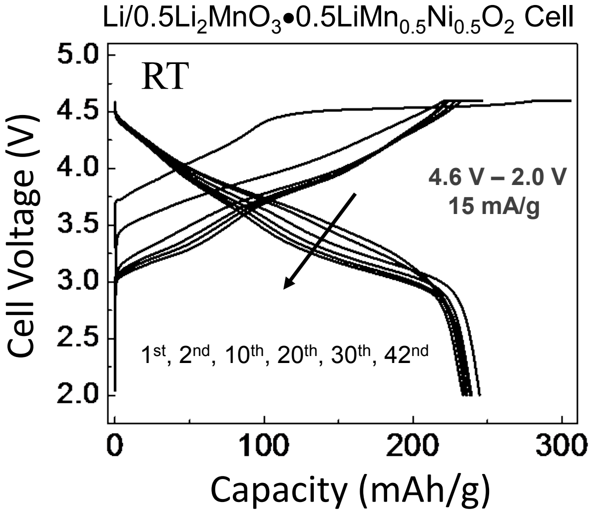
- Design effective *surface structures* to protect the underlying metal oxide particles from the electrolyte and to improve their rate capability when charged at high potentials.

- Use *first principles modeling* to aid the design of bulk and surface cathode structures and to understand electrochemical phenomena. (The theory component of this project was temporarily shifted to meet the needs of the ABR program at ANL.)

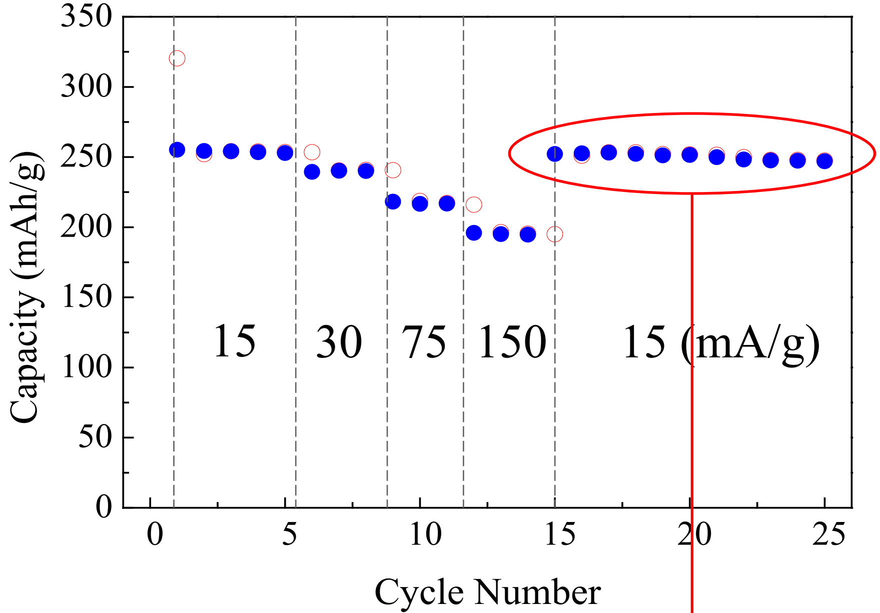
Lithium- and Manganese-Rich Composite Electrodes

- *Structure* – integrated nanodomains yield complex structures
- *Surface stabilization* – electrochemical "activation" leads to irreversible structural changes, surface damage, voltage fade, and hysteresis
- *Hysteresis* – energy inefficiency
- *Voltage Fade* – continuous decrease in energy output with cycling – compromises battery management

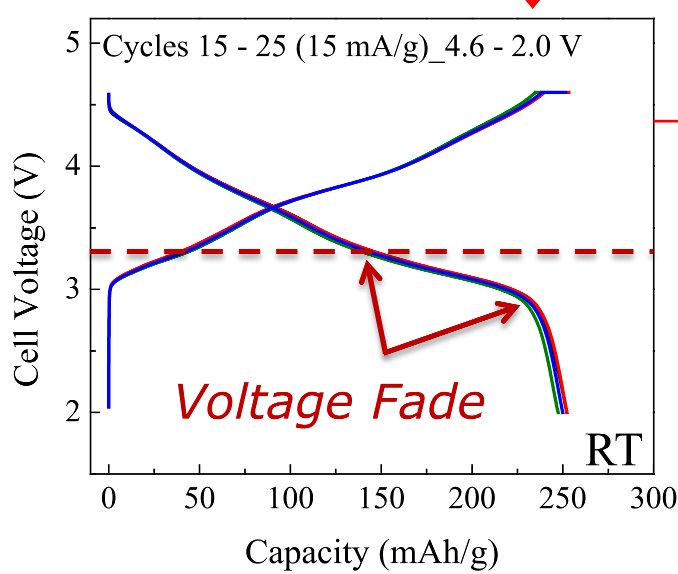


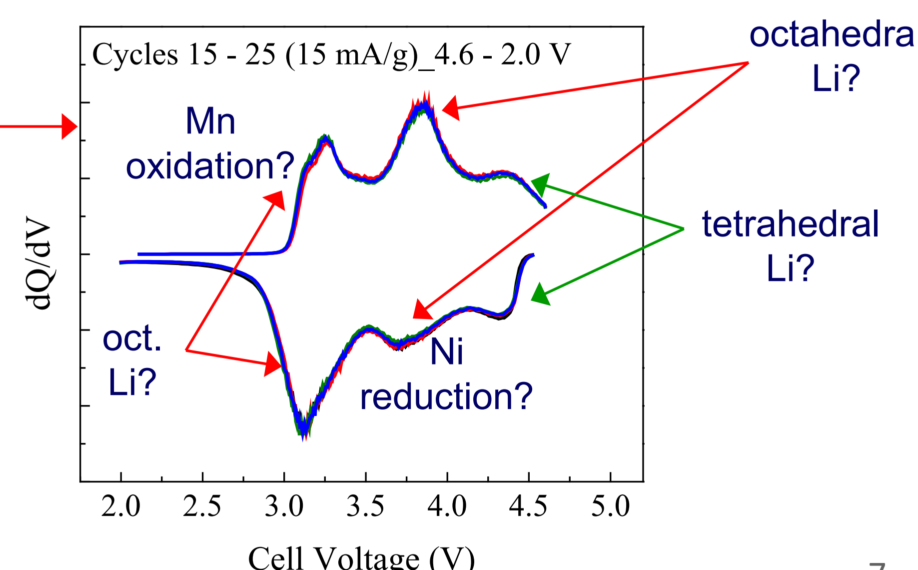


$Li/0.5Li_2MnO_3 \bullet 0.5LiMn_{0.5}Ni_{0.5}O_2$ Half Cells



- High capacity above 3 V (~225 mAh/g)
- 'Stable' profile and dQ/dV plot after ~10 cycles
- 'Reversible' reaction with hysteresis
- Discharge different to charge process $\Rightarrow$ cation migration affects reaction routes/rates?
- Composition of a fully activated discharged electrode is $LiMn_{0.75}Ni_{0.25}O_2$ or $Li_2Mn_{1.5}Ni_{0.5}O_4$, but profile more 'layered-like' than 'spinel'.

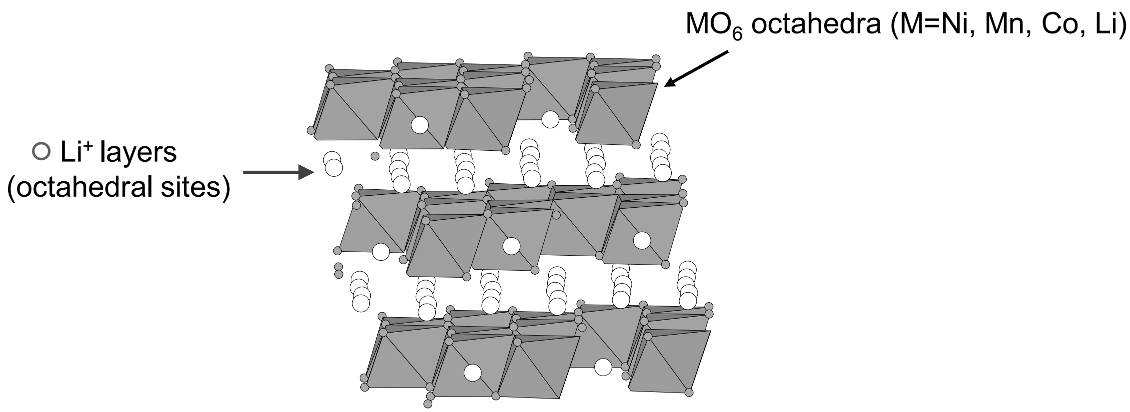




Mitigation of Voltage Fade in LL Electrodes

- Voltage fade attributed to internal phase transitions migration of transition metal ions into Li layers that provides 'spinel-like' character (cf. $Li_{1-x}MnO_2$ to $LiMn_2O_4$)

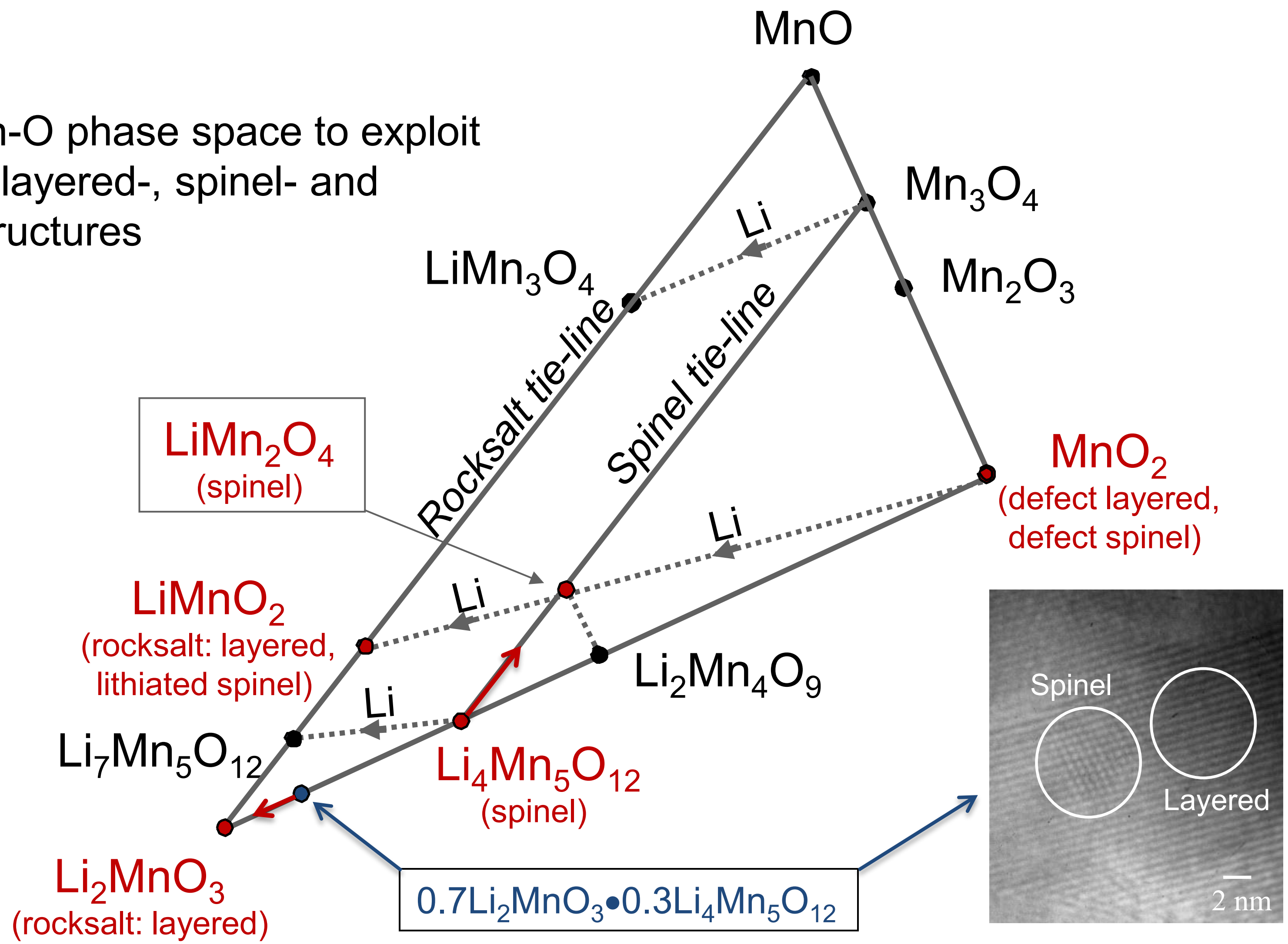
- Strategy: Arrest phase transitions by introducing/controlling the number of stabilizing transition metal (TM) ions in the Li layers



  - Ideal layered structure (R-3m symmetry): No TM ions in Li layers
  - Ideal spinel structure (Fd-3m symmetry): 25% TM ions in Li layers & vice-versa
  - Rocksalt structure (random – Fm3m symmetry): 50% TM and Li ions in layers
  - Embed pillars (spinel component) to stabilize 'layered-layered' NMC structures

Isothermal Slice of the Li-Mn-O Phase Diagram

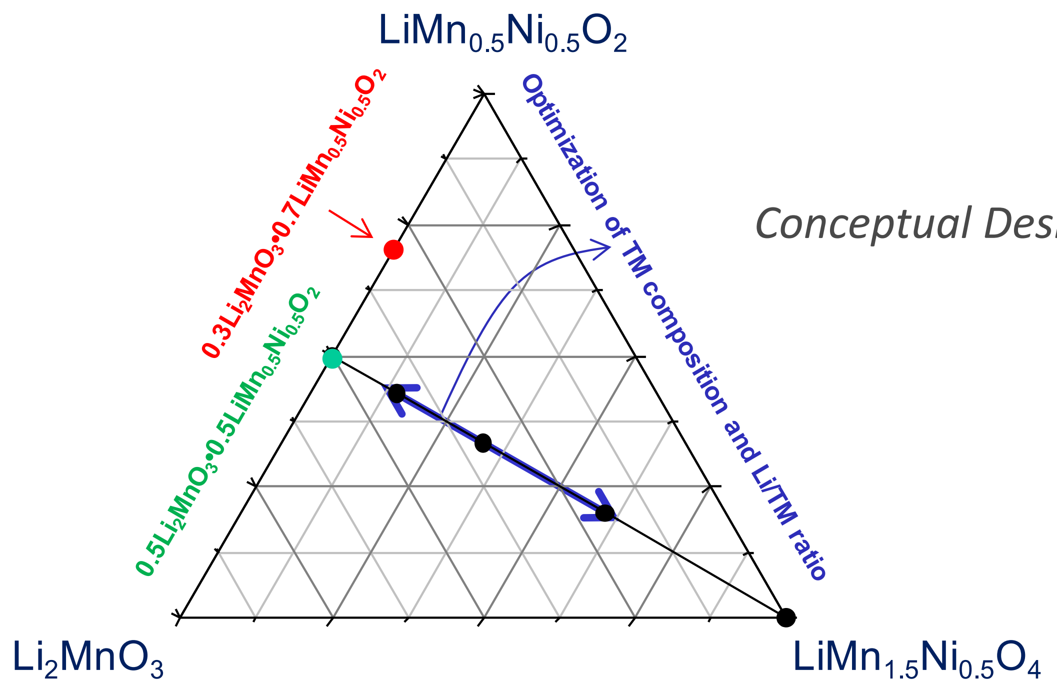
- Wide Li-Mn-O phase space to exploit integrated layered-, spinel- and rocksalt structures



Johnson et al., Electrochem. Comm. **7**, 528 (2006)

Strategy

- Embed a spinel component to stabilize ‘layered-layered’ composite structures
  - *Spinel domains created by reducing the lithium content in ‘layered-layered’ structures*

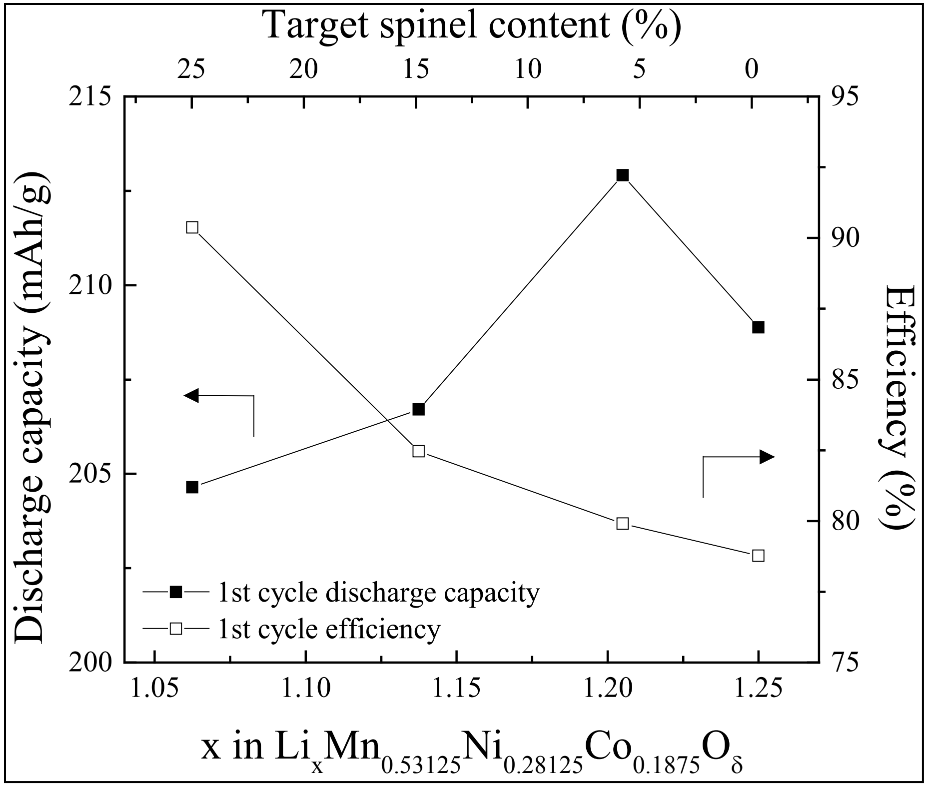


Conceptual Design Space

- Electrodes on ‘layered-layered-spinel’ tie-lines have a constant Mn:Ni ratio, e.g., 3:1 on the $0.5Li_2MnO_3\bullet0.5LiMn_{0.5}Ni_{0.5}O_2$ - $LiMn_{1.5}Ni_{0.5}O_4$ line

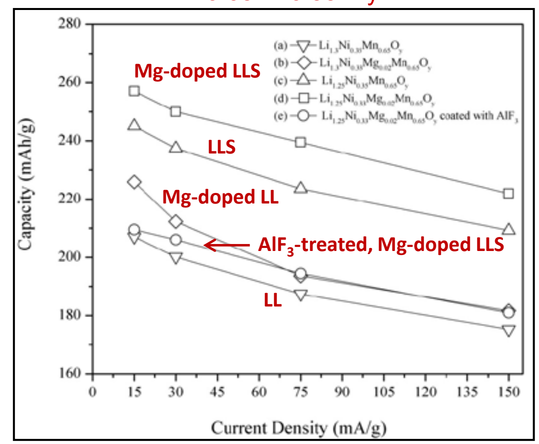
S.-H. Park, S.-H. Kang et al., Electrochem. Comm. (2007)
D. Kim, S-H. Kang et al., JES (2013)

The Effect of Lithium Content in NMC: $Li_xMn_{0.53}Ni_{0.28}Co_{0.19}O_\delta$



B. Long et al., JES (2014)

$Li_xMn_{0.65}Ni_{0.35}O_y$ system



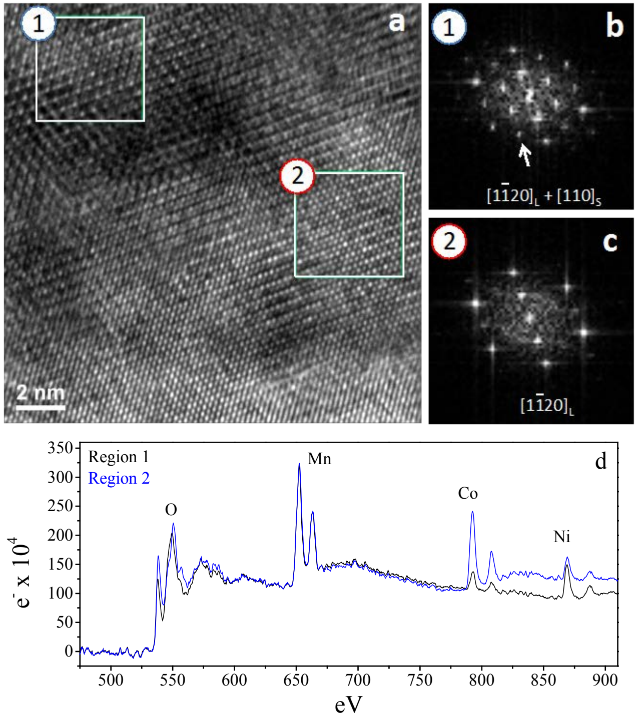
D. Kim, S-H. Kang et al., JES (2013)

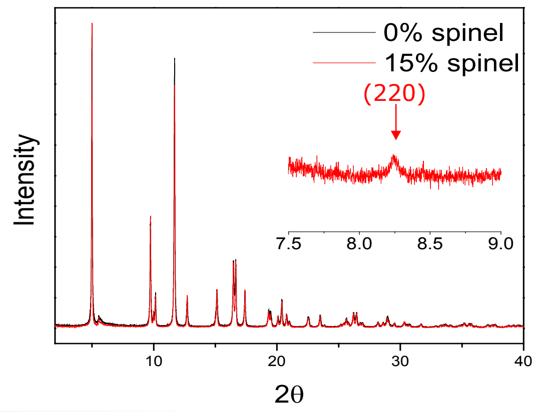
- LLS and Mg-doped LLS electrodes have a higher rate capability than the parent LL electrode

- Data consistent with the $Li_xMn_{0.65}Ni_{0.35}O_y$ system (ANL data – 2013)
- Maximum capacity at ~6% targeted spinel content

'Layered-Layered-Spinel' Characterization
$Li_xMn_{0.53}Ni_{0.28}Co_{0.19}O_\delta$

- HR-TEM shows spinel domains integrated with layered domains (region 1)
- Electron energy loss spectroscopy indicates compositional differences between spinel and layered regions
  - Spinel domains show relatively high Ni content (Mn normalized)
  - Layered domains show relatively high Co content (Mn normalized)
- HR-XRD shows weak (220) spinel peak in composite structure (15% target spinel) indicating tetrahedral site occupancy





B. Long et al., JES (2014)

Composite LL NMC Electrodes

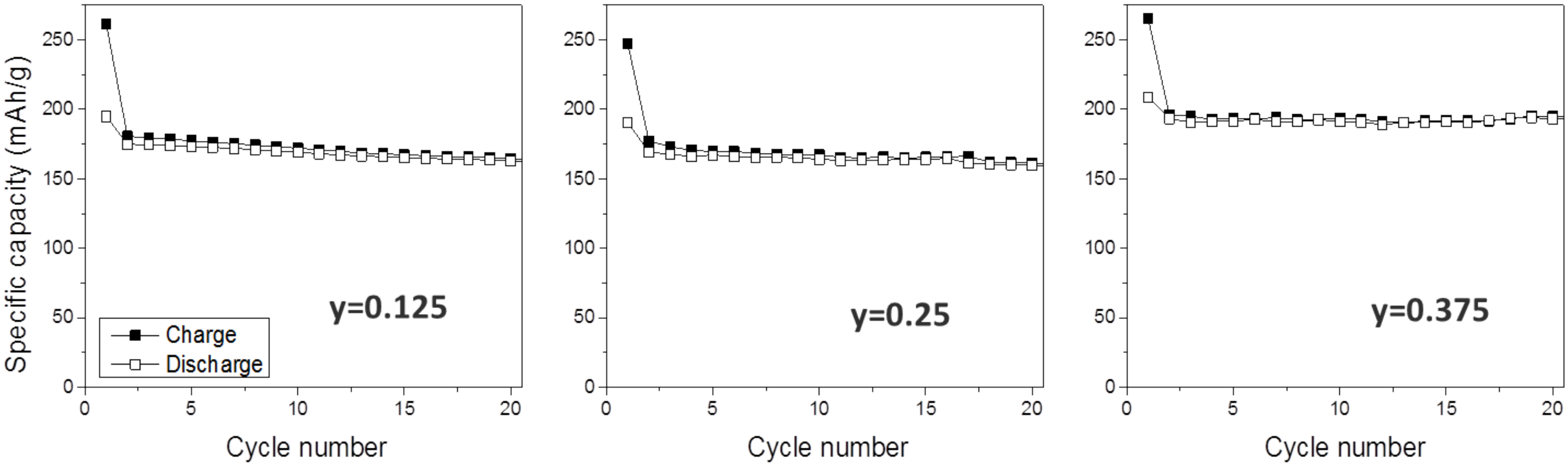
$0.25Li_2MnO_3 \bullet 0.75LiMn_yNi_yCo_{1-2y}O_2$

- Echem:
  - First cycle activation 2-4.6 V
  - Subsequent cycling 2-4.45 V
  - Sacrifice some voltage and capacity to gain structural and electrochemical stability
- Lower Co content improves capacity and cycling stability

$0.25Li_2MnO_3 \bullet 0.75LiMn_{0.125}Ni_{0.125}Co_{0.75}O_2$

$0.25Li_2MnO_3 \bullet 0.75LiMn_{0.25}Ni_{0.25}Co_{0.50}O_2$

$0.25Li_2MnO_3 \bullet 0.75LiMn_{0.375}Ni_{0.375}Co_{0.25}O_2$



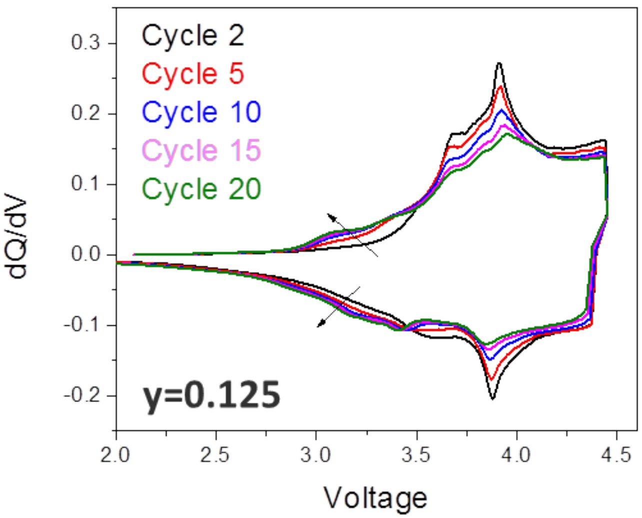
B. Long et al., JES (2014)

Composite LL NMC Electrodes: dQ/dV Plots

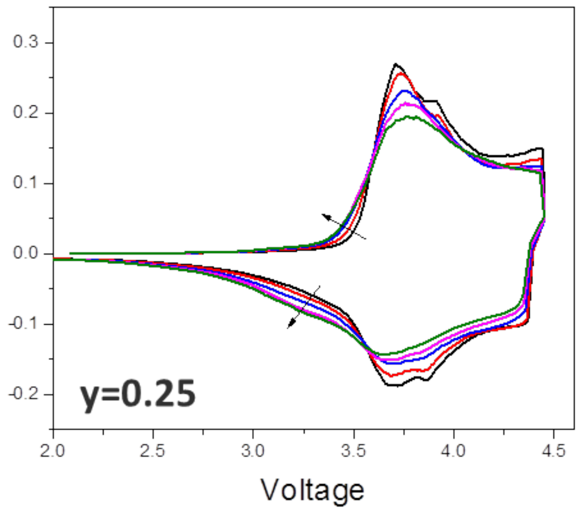
$0.25Li_2MnO_3 \bullet 0.75LiMn_yNi_yCo_{1-2y}O_2$

- All ‘layered-layered’ electrodes show voltage decay (3 – 3.5 V) on cycling
- $0.25Li_2MnO_3 \bullet 0.75LiMn_{0.375}Ni_{0.375}Co_{0.25}O_2$ (y=0.375) electrodes with low Co content provide the greatest electrode stability

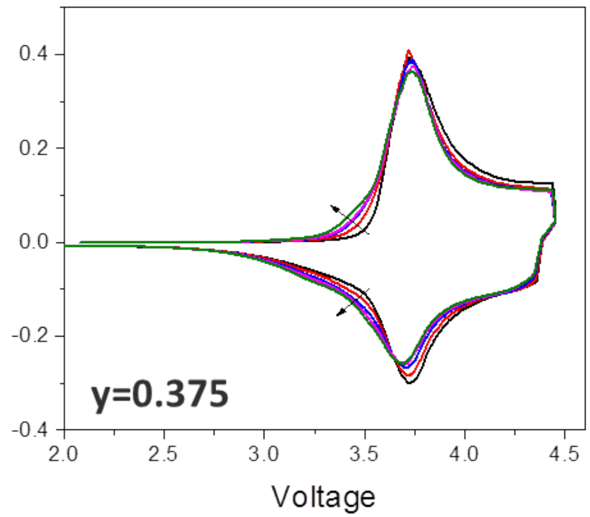
$0.25Li_2MnO_3 \bullet$
$0.75LiMn_{0.125}Ni_{0.125}Co_{0.75}O_2$



$0.25Li_2MnO_3 \bullet$
$0.75LiMn_{0.25}Ni_{0.25}Co_{0.50}O_2$



$0.25Li_2MnO_3 \bullet$
$0.75LiMn_{0.375}Ni_{0.375}Co_{0.25}O_2$

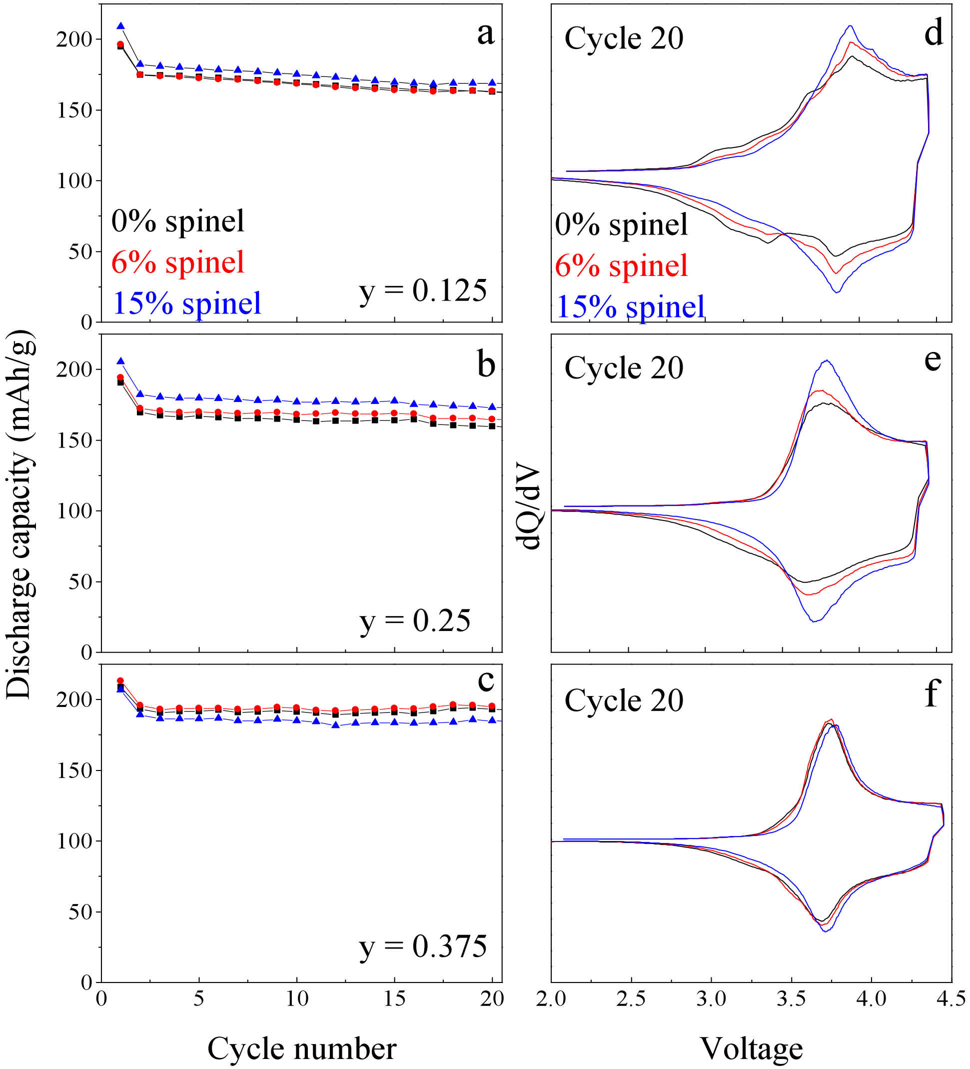


B. Long et al., JES (2014)

Composite LLS NMC Electrodes

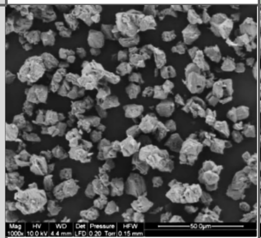
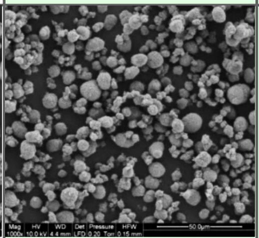
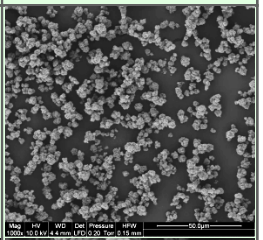
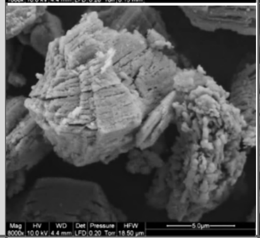
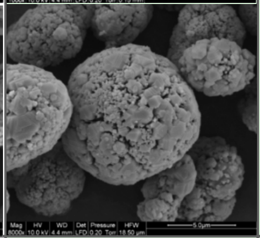
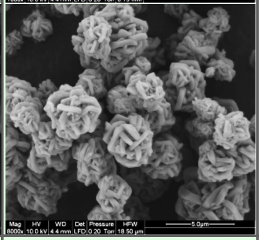
$0.25Li_2MnO_3 \bullet 0.75LiMn_yNi_yCo_{1-2y}O_2$

- Spinels incorporated into 'layered-layered' compositions
  - 6%
  - 15%
- First-cycle efficiency improves with increasing spinel content
- Targeted 6% spinel, low cobalt samples show least 'voltage fade' behavior (f)



B. Long et al., JES (2014)

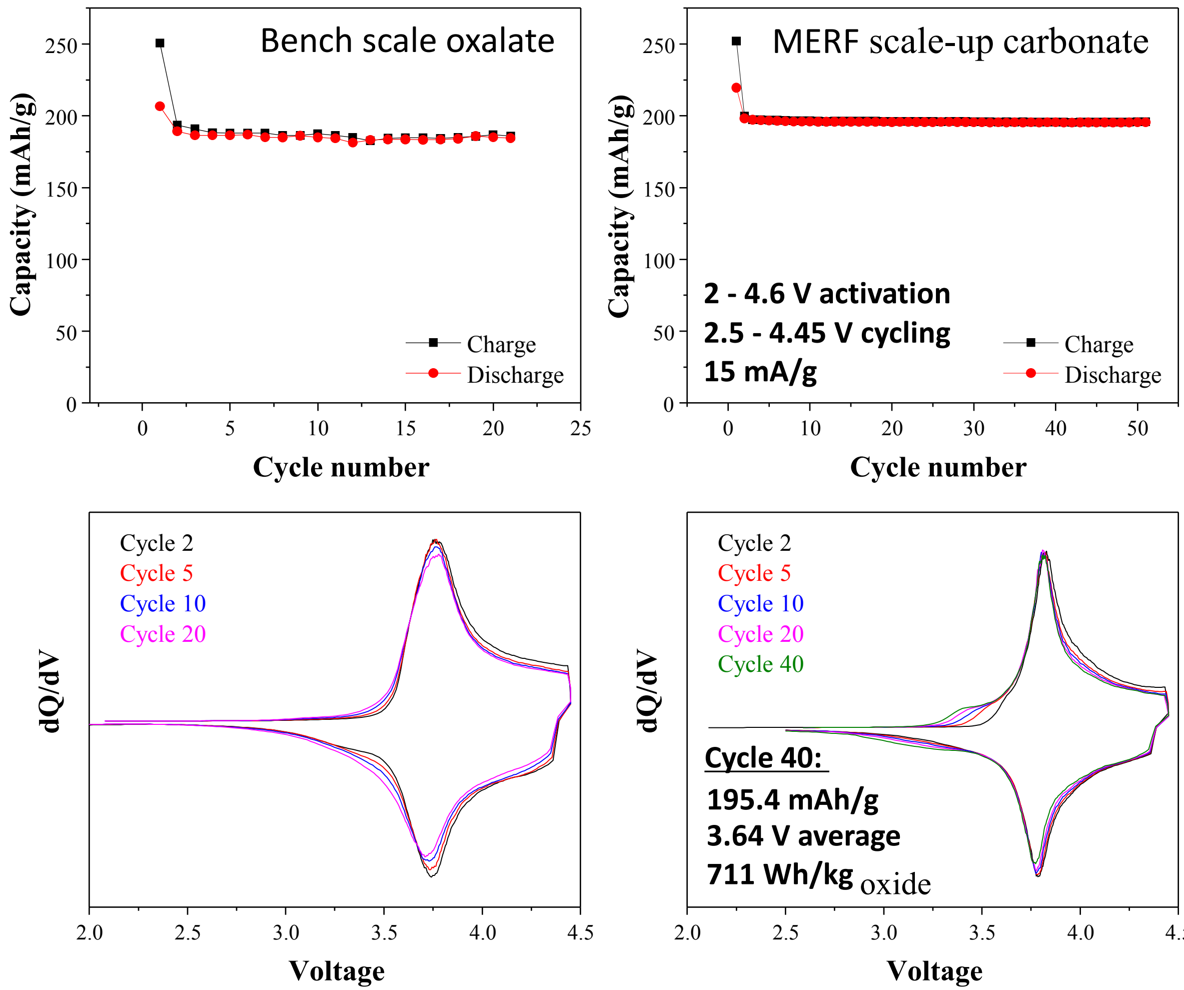
Comparison of Bench and Scaled-Up LLS Electrodes

	CSE LLS Oxalate	ES20140402 Scale-up Carbonate	ES20140710 Scale-up Hydroxide
	Bench scale	Pre-pilot Preliminary	Pre-pilot Preliminary
Composition (by ICP-MS)	$Li_{1.057}Ni_{0.286}Mn_{0.519}Co_{0.195}O_y$	$Li_{1.063}Ni_{0.265}Mn_{0.542}Co_{0.193}O_y$	$Li_{1.206}Ni_{0.274}Mn_{0.534}Co_{0.191}O_y$
SEM x1,000			
SEM x8,000			
$D_{10}/D_{50}/D_{90}$ [μm]	6.3 / 12.3 / 22.3	5.2 / 9.6 / 16.8	2.4 / 4.8 / 8.8
Tap density [g/cc]	1.70	1.80	1.51
Initial disch. cap. @10mA/g	193	218	202

- Preliminary data from MERF (ANL's Materials Engineering Research Facility)

Courtesy of Y. Shin and G. Krumdick

Comparison of Bench and Scaled-Up LLS Electrodes (ctd)

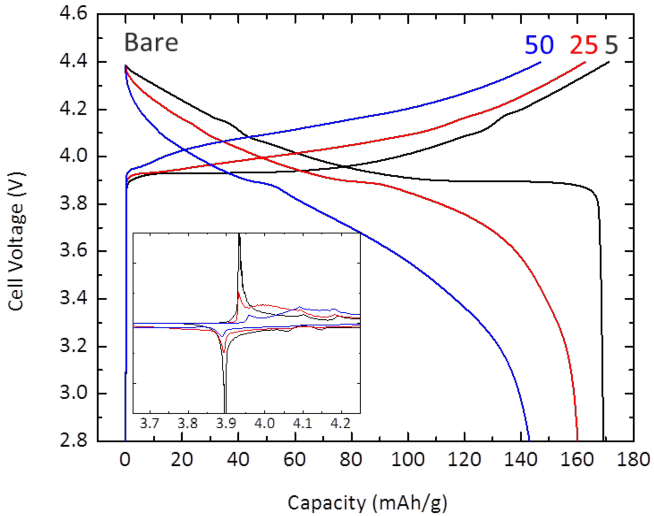


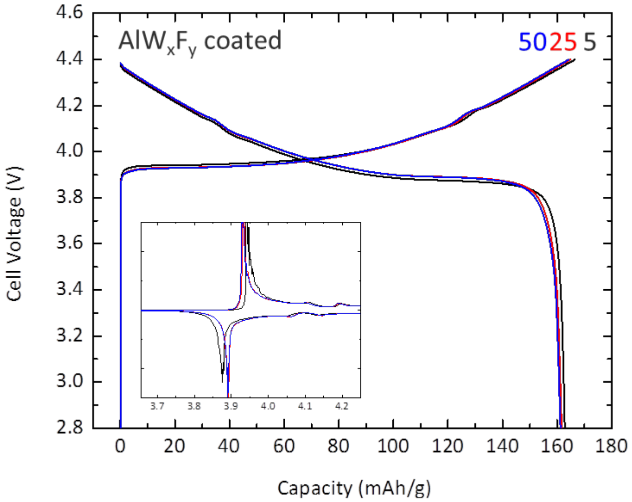
- Voltage fade is almost entirely suppressed in scaled up electrode, if capacity is restricted to ~200 mAh/g

Courtesy of Y. Shin and G. Krumdick

Coating Studies - 1

- ALD – Amorphous AlW_xF_y thin films (~1 nm)
  - Deposited on laminated $LiCoO_2$ electrodes
  - Tri-methyl aluminum (TMA) and tungsten hexafluoride (WF_6) precursors
  - 200 °C



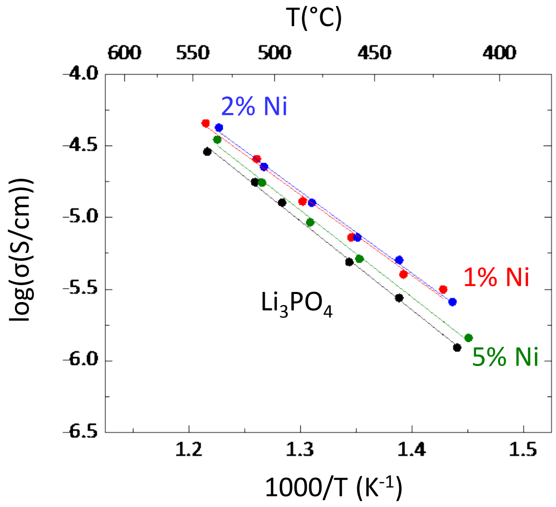


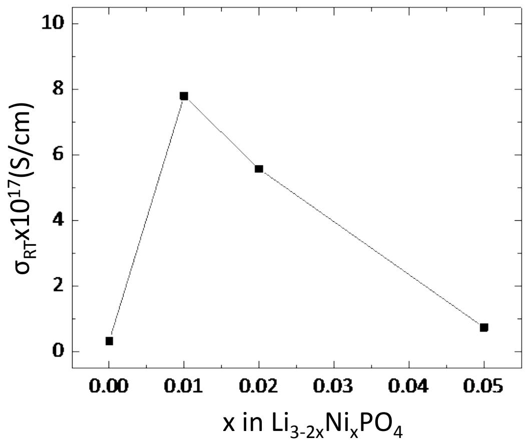
- XPS analyses revealed that the AlW_xF_y films are composed of W, C, Al and F as AlF_3, W, and WC
- Coated electrodes significantly improve electrochemical stability
- Rate capability improved: 95% capacity retention at 400mA/g vs. ~50% for uncoated electrodes
- Films not as effective on Li-rich NMC electrode compositions (work in progress)

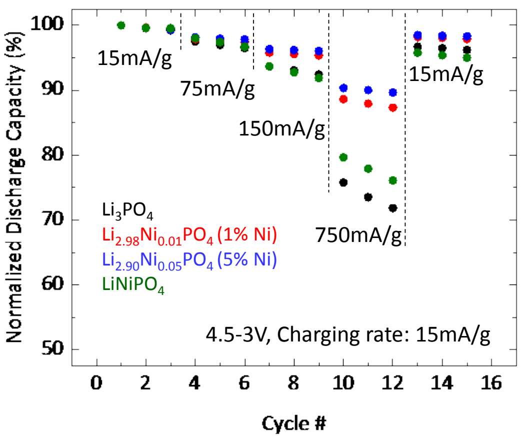
J. S. Park, A. U. Mane, J. W. Elam, and J. R. Croy, Chem. Mater., **27**, 1917 (2015)

Coating Studies - 2

- Substituted $Li_{3-2x}Ni_xPO_4$ coatings on $LiCoO_2$







- RT conductivity (σ) from AC EIS extrapolated from Arrhenius plots
- σ Li_3PO_4 increases by about an order of magnitude with 1% Ni doping, but still very low
- Ni-doped Li_3PO_4 coatings (e.g., 5%) enhance rate capability, consistent with our earlier findings on Li-Ni-PO_4 coated electrodes (Kang and Thackeray, Electrochem. Comm. (2009))

- Low ionic conductivity of Ni-doped Li_3PO_4 samples does not explain higher rate capability
- Studies of NMC-coated electrodes with compositionally modified coatings in progress.

Future Work - FY2015/FY2016

- Good momentum has been gathered and progress made in advancing the performance of 'layered-layered-spinel' cathode materials and stabilizing their surfaces through compositional control. For the remainder of FY2015 and in FY2016, efforts will focused on optimizing the capacity and electrochemical stability of this class of compounds.

- Characterization methods and facilities will be expanded to complement currently used techniques, e.g., the use of Raman spectroscopy that will aid the understanding of both surface and bulk structure and electrochemical phenomena. *(cf. Jason Croy presentation, ES235, Thursday 1:45pm)*

- Theoretical modeling of electrode materials (structures and surfaces) will be reintroduced into the project to complement experimental efforts.

Summary

- Despite the unwanted voltage fade phenomenon in high-capacity lithium- and manganese-rich 'layered-layered' electrodes, structurally integrated materials offer a vast compositional space for exploitation.

- The introduction of a minor amount of spinel in compositionally-modified 'layered-layered' electrodes:
  - improves structural stability
  - suppresses voltage decay (with restriction on upper voltage)
  - improves rate

- Use a 'bottom-up' approach to increase the capacity of 'layered-layered' electrodes from ~170 mAh/g upwards, rather than by reducing the capacity from ~250 mAh/g downwards, to a targeted 200-220 mAh/g.

Acknowledgments

Support for this work from the BMR Program, Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged – Tien Duong, David Howell