Design and Evaluation of High Capacity Cathodes

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Annual Merit Review
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ES049

Vehicle Technologies Program

U.S. DEPARTMENT OF **ENERGY**

Overview

Timeline

- Start date: FY12
- End date: FY15
- Percent complete:
  - 25%

Budget

- Total project funding
  - 100% DOE
- Funding in FY12: $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, Kevin Gallagher, Donghan Kim, Roy Benedek
  - APS, Argonne: Mali Balasubramanian (XAS), Yang Ren (XRD)
  - EMC, Dean Miller, J.G. Wen (TEM)
  - ES, Argonne: Greg Krumdick, Young-Ho Shin
  - ABR 'Voltage fade' team
  - Industry: Envia, BASF, Toda, LG Chem

Objectives

- Design high capacity, high-power and low cost cathodes for PHEVs and EVs

  ➢ Improve the design, composition and electrochemical performance of Mn-based cathodes

  ➢ Explore new processing routes to prepare advanced electrodes and 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 (FY13)

- Identify promising, high capacity (200-250 mAh/g) $xLi_2MnO_3 \bullet (1-x)LiMO_2$ materials, and other composite structures, with a high Mn content using Li_2MnO_3 or other layered precursors, determine their structures and evaluate their electrochemical properties– *on going*

- Improve the surface stability of electrode materials at high charging potentials by coating/surface modification methodologies– *on going*

- Model coatings and interfacial phenomena at the surface of lithium-metal-oxide electrodes – *on going*

- Continue collaborative interactions with DOE's User Facilities and personnel. – *on going.*
  - X-ray absorption studies on BATT materials at Argonne's Advanced Photon Source (APS) and HR-TEM at Argonne's Electron Microscopy Center (EMC) continue to support the BATT materials effort.

Approach

- Exploit the concept and optimize the performance of *structurally-integrated ('composite') electrodes structures.*

- Explore new *processing routes* to prepare composite electrodes that provide 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

Lithium and Manganese Rich Composite Electrodes

- **Structure** – integrated nanodomains (C2/m, R-3m) yield complex structures

- **Energy** – cathode energy densities can reach ~900 Wh/kg

- **Surface stabilization**– "activation" leads to irreversible structural changes, surface damage, voltage fade, and hysteresis

- **Hysteresis** – energy efficiency, system management

- **Voltage Fade** – continuous decrease in energy output with cycling

Li_2MnO_3
(Mn^{4+})

$LiMO_2$ (M = Mn, Ni, Co)
(M^{3+} or M^{4+}/M^{2+})

← MO_6 octahedra

• = Li

The characteristic $LiMn_6$ unit of Li_2MnO_3

MO_2

$xLi_2MnO_3•(1-x)MO_2$ $-xLi_2O$ >4.5 V

y Li

Path of delithiation
$xLi_2M'O_3•(1-x)Li_yMO_2$
(4.2-3.0 V)

"inactive"
Li_2MnO_3

"active"
$LiMO_2$
(M=Mn, Ni, Co)

$xLi_2MnO_3•(1-x)LiMO_2$

U.S. Pat. 6,677,082 (2004); U.S. Pat. 6,680,143 (2004)
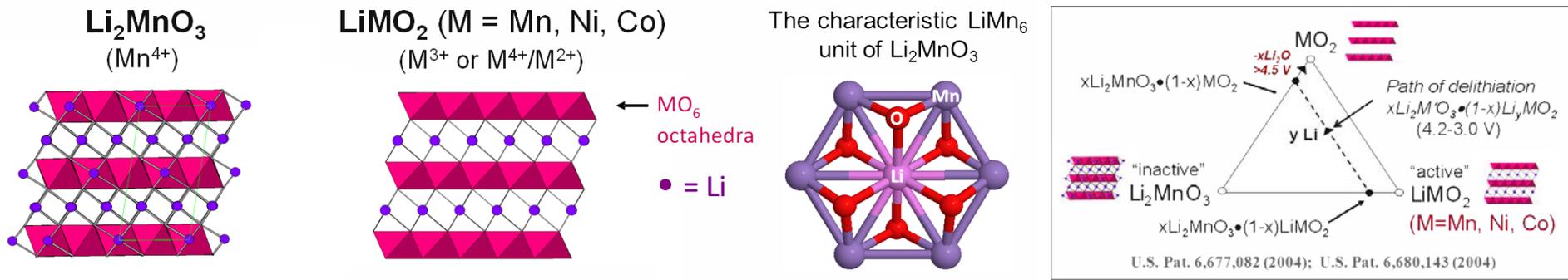
Charge Ordering During Synthesis of $xLi_2MnO_3(1-x)LiMO_2$

(a) Mn-M ... Controlled / Uncontrolled / Quenched, Mn K

(b) Co-M ... Controlled / Uncontrolled / Quenched, Co K

$LiMn_6$

Mn, O, Li

Croy et al., *JES*, **161** A318 *(2014)*

(c) Mn-O, Mn-M, Mn K
x = 0
x = 0.1
x = 0.3
x = 0.5
Li_2MnO_3
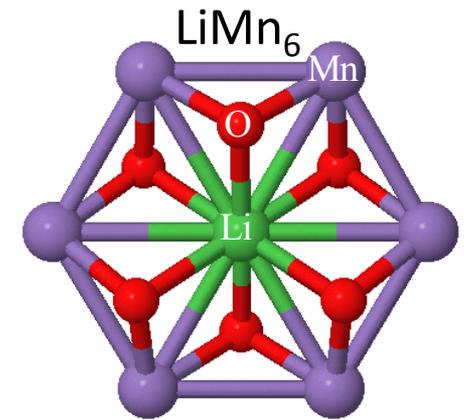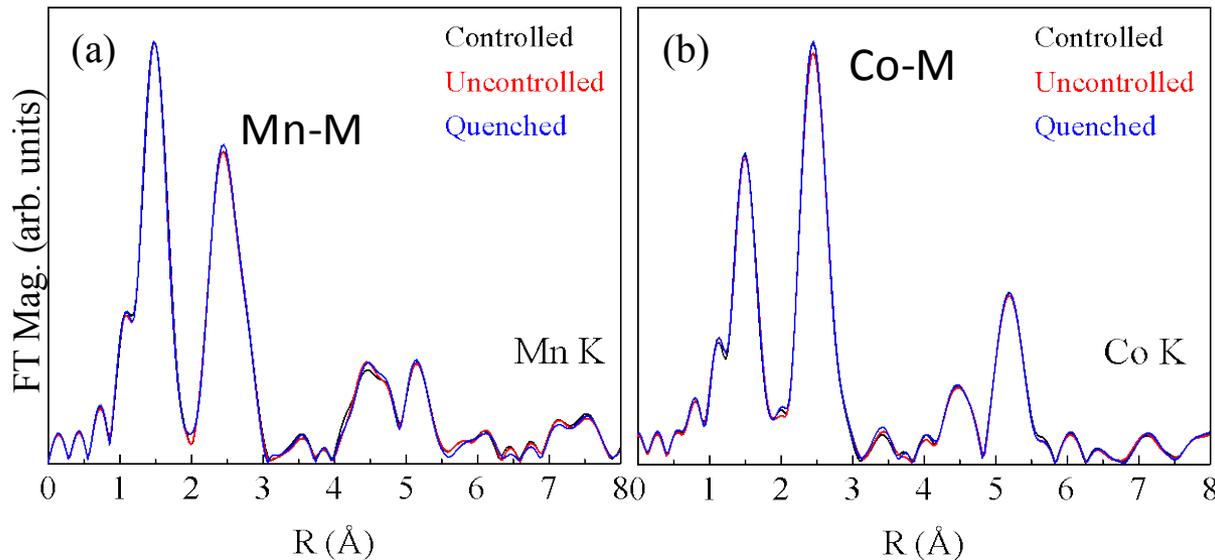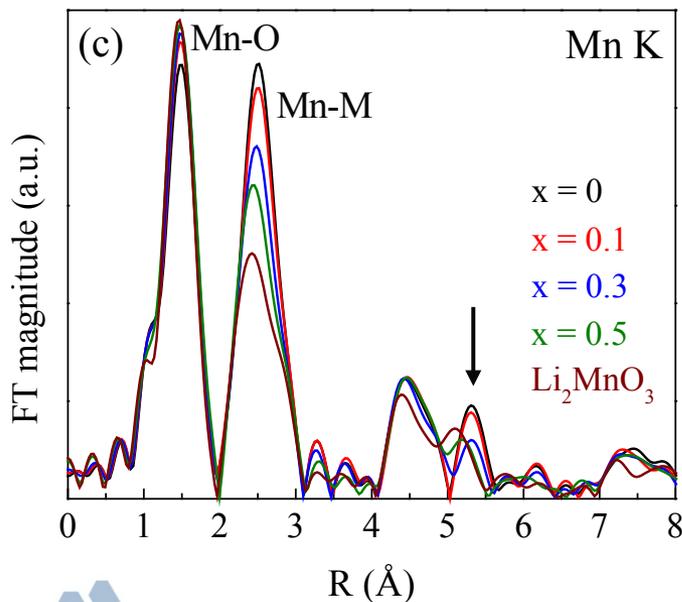
(a) Li and Mn ordering in $0.5Li_2MnO_3 \bullet 0.5LiCoO_2$ (e.g. $LiMn_6$ units) was similar for three cooling rates.

(b) Fully coordinated (6 metal neighbors) Co-M reveals $LiCoO_2$-like local structure.

(c) Increasing Li and Mn ordering as a function of x in $xLi_2MnO_3 \bullet (1-x)LiMn_{0.5}Ni_{0.5}O_2$.

Charge ordering at low temp (~400°C) during synthesis dictates the local composite nature of these materials.

Effect of Li$_2$MnO$_3$ Content on Electrochemical Performance

$xLi_2MnO_3 \bullet (1-x)LiMn_{0.5}Ni_{0.5}O_2$
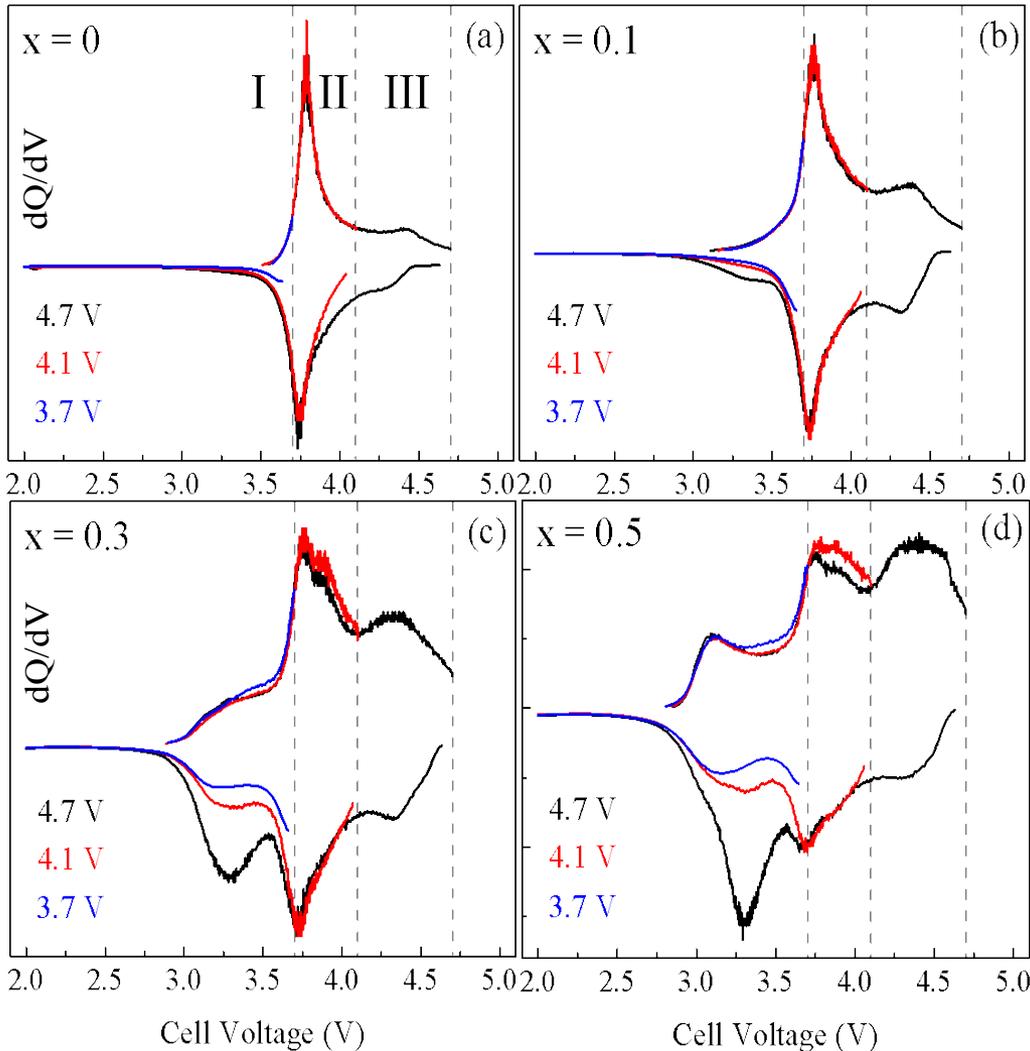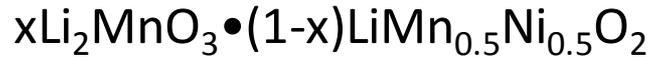
- Activation and cycling above ~4.0 V induces VF/hysteresis.

- New processes appear in the low voltage region I, indicating voltage fade.

- High voltage process in region III directly related to hysteresis.

- Voltage fade and hysteresis are both increasing functions of Li$_2$MnO$_3$ content (i.e., Li/Mn ordering).

# Effect of Li$_2$MnO$_3$ Content on Electrochemical Performance
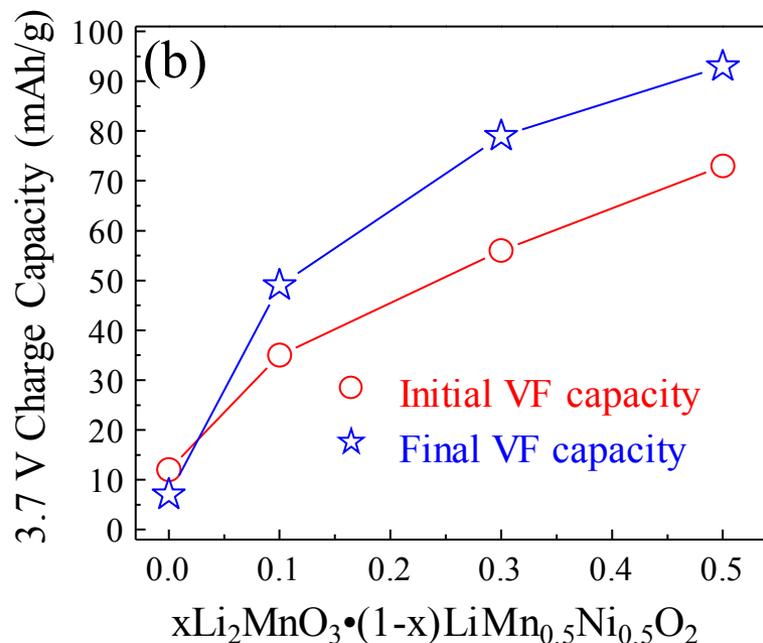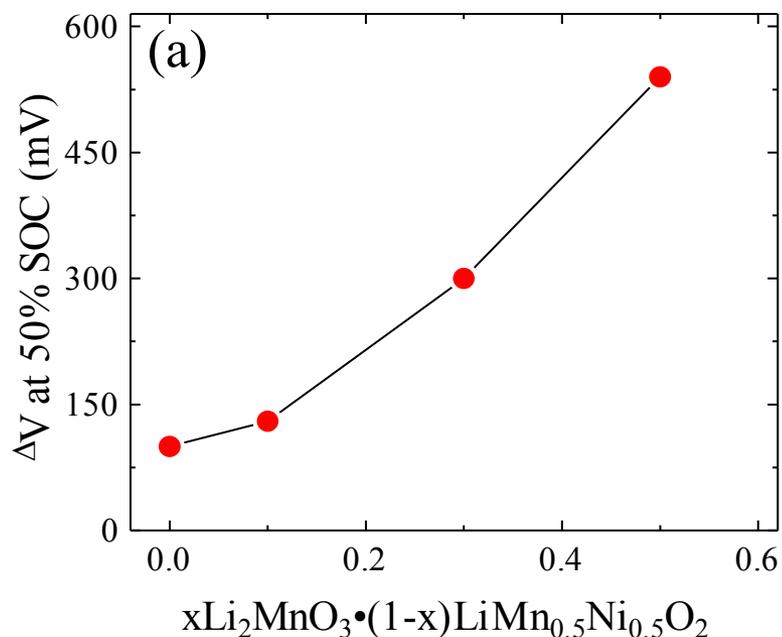
(a) Magnitude of the hysteresis at 50% SOC as a function of x in xLi$_2$MnO$_3$•(1-x)LiMn$_{0.5}$Ni$_{0.5}$O$_2$ electrodes.

(b) Magnitude of the voltage fade (in mAh/g, below 3.7 V) at 50% SOC as a function of x, after activation.

Croy et al., *JES*, **161** A318 *(2014)*

Stabilization of Li$_2$MnO$_3$ Component
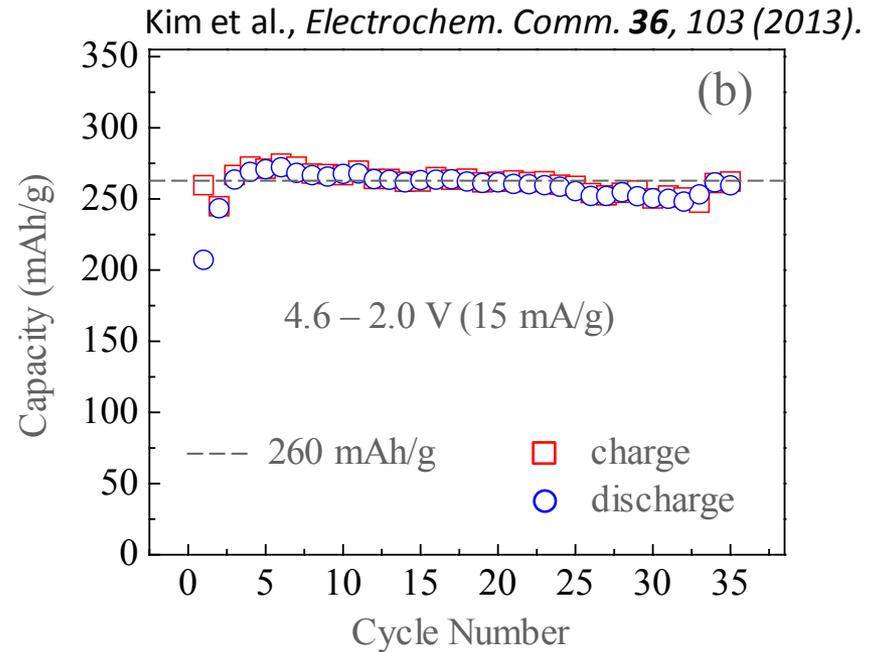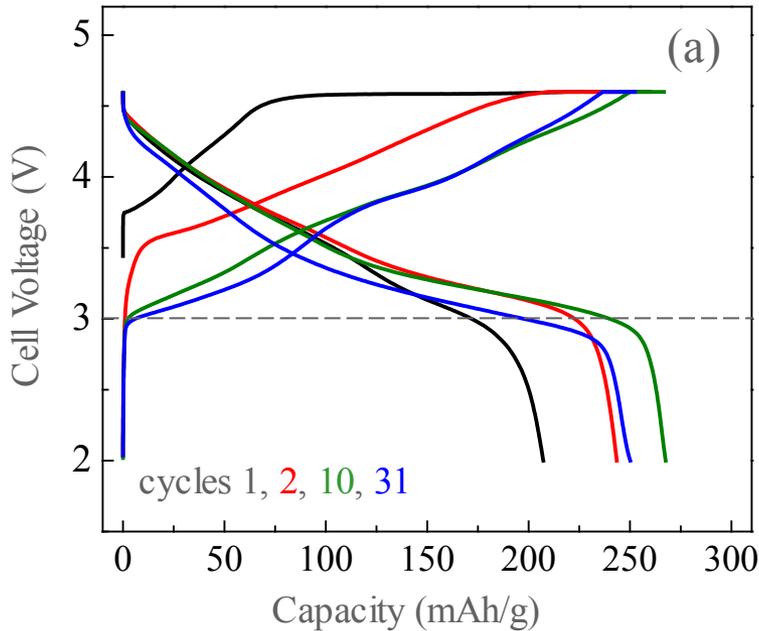
- Bulk Li$_2$MnO$_3$ shows very poor cycling performance.

- 0.7Li$_2$MnO$_3$•0.3LiMn$_{0.5}$Ni$_{0.5}$O$_2$ electrodes show high reversible capacities.

- Ni incorporation forms MnNi-rich LiMO$_2$ domains that 'stabilize' Mn in the Li and Mn rich Li$_2$MnO$_3$ component.

- Mn migration at boundaries can be stabilized via Ni interactions

Stabilization of Composite Bulk Structures

Li$_{1.2}$Mn$_{0.6}$Ni$_{0.2}$O$_2$

charge

discharge

1st cyc. eff. = 81%
cycling eff. = 99.6%

4.6 - 2.0 V (15 mA/g)
RT half-cell

Li$_{1.2}$Mn$_{0.6}$Ni$_{0.2}$O$_2$

charge

discharge

First Cycle
4.7 – 2.0 V
96 hour
12 hour
(a)

Second Cycle
4.1 – 2.0 V
96 hour
12 hour
(b)
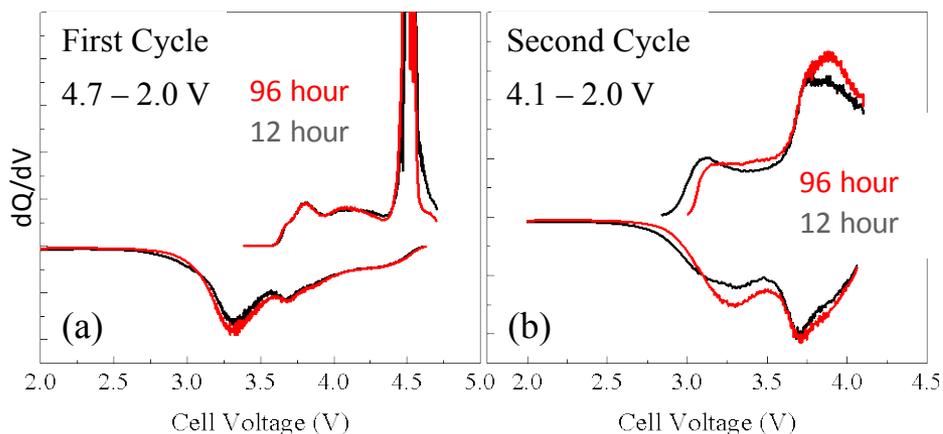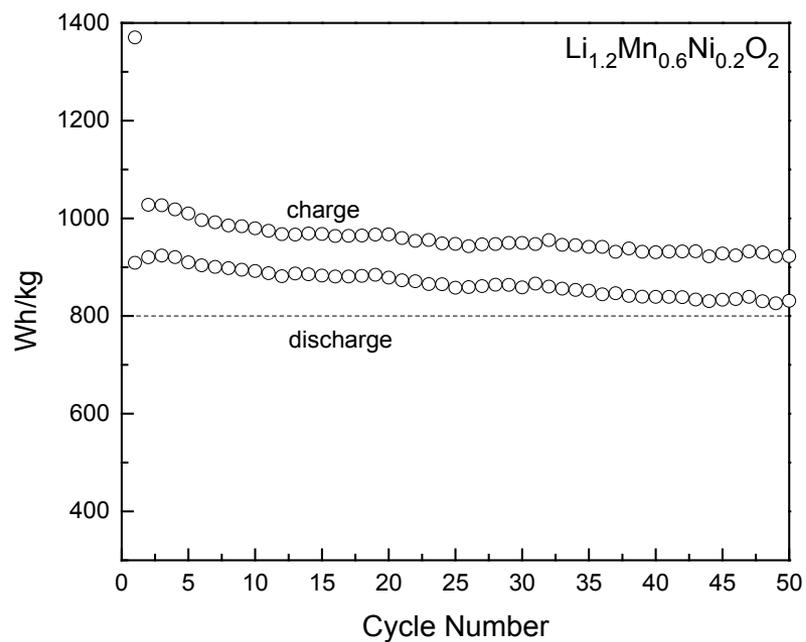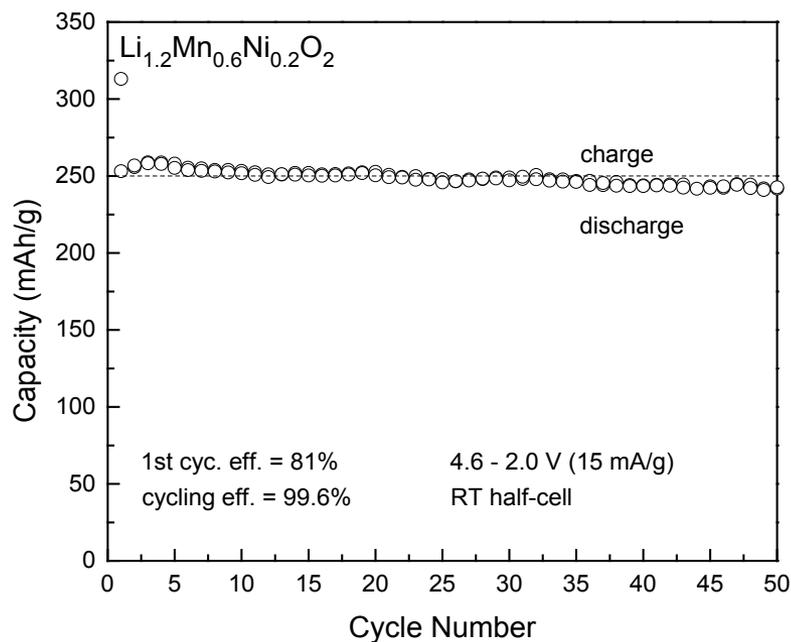
- Crystallinity and order can effect the short-term cycling behavior.

- Samples annealed for 96 hours, 850°C show greater low voltage stability in early cycles (b).

- Cells delivered >800 Wh/kg (cathode) for 50 cycles.

Stabilization of Composite Bulk Structures

- Voltage decay due to internal phase transitions - migration of transition metal ions into Li layers that provides 'spinel-like' character

- Hypothesis: Phase transitions may be arrested by introducing and controlling the number of stabilizing ions in Li layer via a Li_2MnO_3 precursor

MnO_6 octahedra

○ Li^+ layers (octahedral sites)
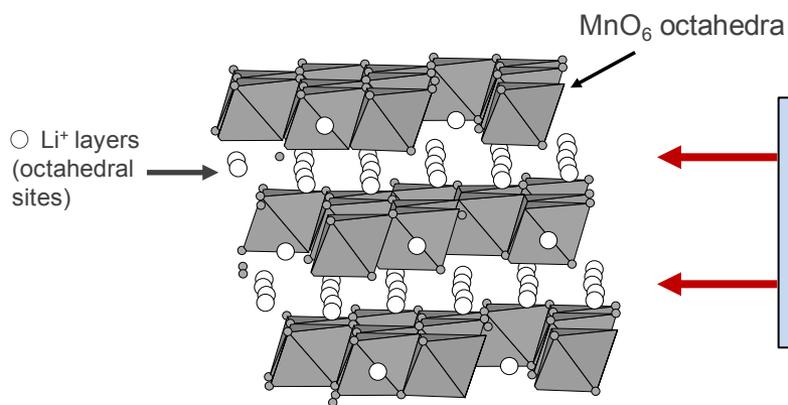
$Li^+/M^+/H^+$-ion exchange during acid treatment, followed by annealing step to complete M^+ diffusion into the lithium and transition metal layers

- Ideal 'layered-layered':   No transition metal ions in Li layers
- Ideal 'layered-layered-spinel':   25% transition metal ions in Li layers of spinel domains & vice-versa
- Ideal 'layered-layered-rocksalt':   No Li layers in rocksalt domains

Croy et al., JES 2012

$x[Li_{1.2}Mn_{0.6}Ni_{0.2}O_2] \bullet (1-x)LiMn_{1.5}Ni_{0.5}O_4$

$x[Li_{1.2}Mn_{0.55}Ni_{0.15}Co_{0.1}O_2] \bullet (1-x)LiMn_{1.5}Ni_{0.5}O_4$

x=0

x=0.50

x=0.75

x=1.00

2θ (deg)

A

$[1\bar{1}20]_L$

B

$[1\bar{1}0]_S$

C

$[1\bar{1}20]_L$

2 nm
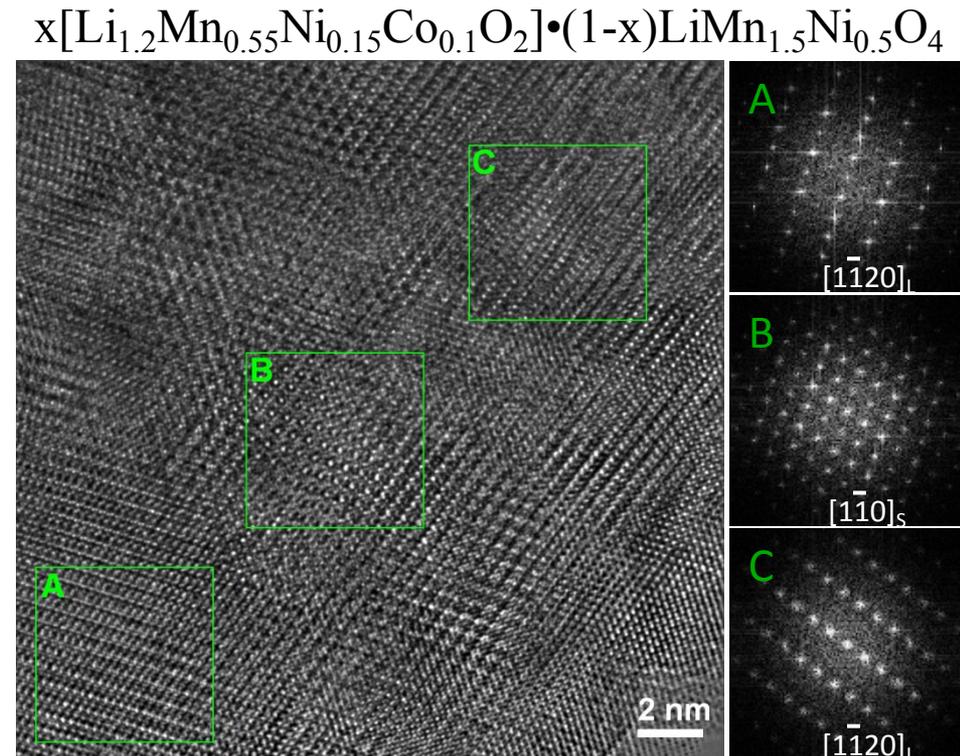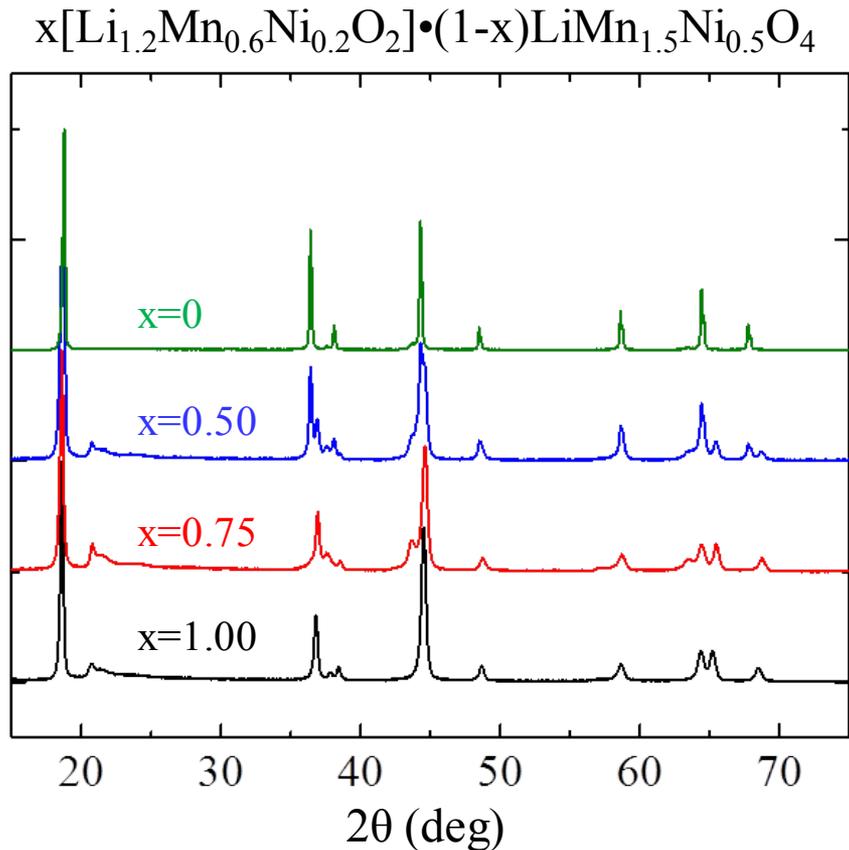
D. Miller, J.G. Wen - ANL

- XRD shows the evolution from layered (x=1) to spinel (x=0).

- HRTEM shows intimate integration of layered (A, C) and spinel (B) domains.

- Li_2MnO_3 precursor template can be used to create novel structural and elemental compositions.

$$x[Li_{1.2}Mn_{0.6}Ni_{0.2}O_2] \cdot (1-x)LiMn_{1.5}Ni_{0.5}O_4$$
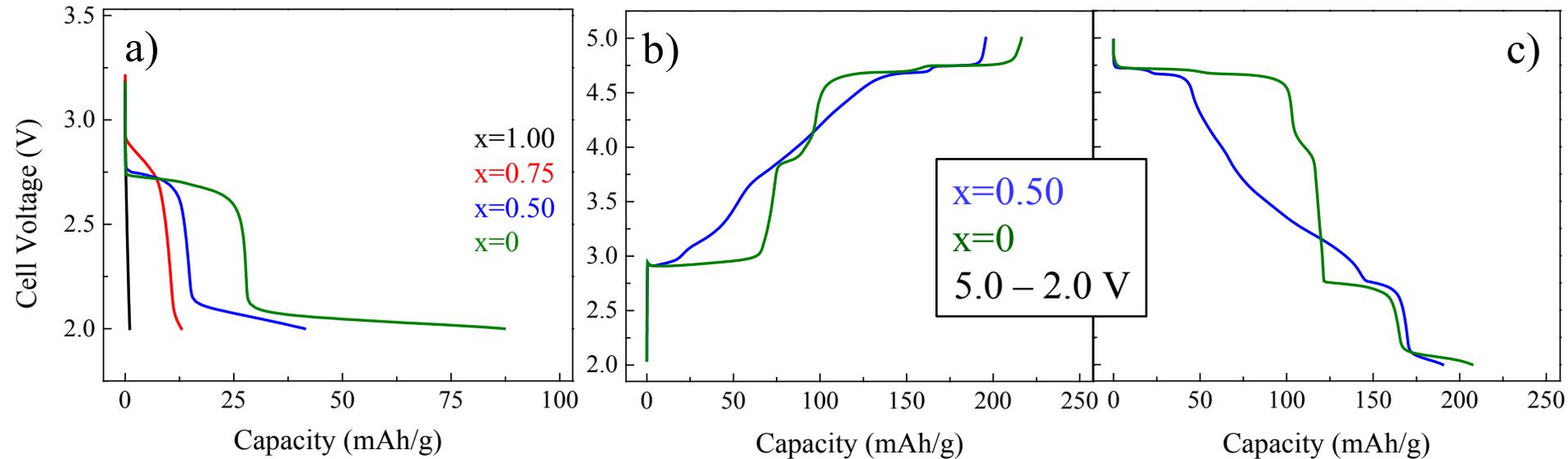
- First-cycle *discharge* capacities (a) confirm the trend of increasing lithium uptake in octahedral sites of the pristine samples on decreasing x.

- b) and c) compare cycle 5 charge and discharge curves, respectively, for pure (x=0) and 50% (x=0.50) spinel revealing the synergy between layered and spinel components.

Future Work - FY2014/FY2015

- The concept of using Li_2MnO_3, and other layered precursors, for fabricating composite electrodes with enhanced structural and electrochemical stability is extremely versatile and shows considerable promise. These efforts will therefore continue in FY2014/FY2015 with the goal of reaching/exceeding the energy and power goals required for 40-mile PHEVs and EVs.

- Low Li_2MnO_3-content composite structures, with and without stabilizing spinel components, will be explored. Special emphasis will be given to layering (e.g., mitigation of Li/Ni exchange) and rate capability, composition, and structural integration.

- Information on charge ordering and Mn mobility will be used to design stable compositions that resist voltage fade and deliver high energies.

- Efforts to fabricate stable surface architectures will be continued using sonication and ALD techniques. New precursors for use with ALD will be developed as well sputtering targets for direct deposition on laminated cathode materials in order to create unique surfaces.

Summary

- Important information on charge ordering during the synthesis of composite structures was obtained through a variety of synchrotron techniques at Argonne's Advanced Photon Source. This information will be used going forward to create composite structures with enhanced local ordering and stability.

- Efforts to understand the important role of the Li_2MnO_3 component in composite materials were continued with considerable success. It was also shown that Ni interactions, via Ni^{2+} incorporation in Li_2MnO_3, can act to stabilize Mn, even in high Li_2MnO_3-content composites.

- Continued progress in developing a new synthesis technique that utilizes layered precursor templates (e.g., Li_2MnO_3) was realized through the synthesis of structurally integrated layered-layered-spinel composite cathodes. These materials were confirmed by XRD, HRTEM, and electrochemical cycling.

- The theory component of this work was temporarily shifted to meet the needs of the ABR voltage fade program at Argonne National Laboratory.

Acknowledgment