Development of High-Capacity Cathode Materials with Integrated Structures

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ES019

Vehicle Technologies Program

Overview

Timeline

- Start date: FY09
- End date: On-going
- Percent complete:
  - project on-going

Budget

- Total project funding
  - 100% DOE
- Funding in FY11: $400K
- Funding in FY12: $300K

Barriers

- Low energy density
- Cost
- Abuse tolerance limitations

Partners

- Lead PI: Michael Thackeray
  (Previous PI: S.-H. Kang)
- Collaborators:
  - CSE, Argonne: **Donghan Kim**, Jason Croy, Kevin Gallagher, Giselle Sandi (materials design, synthesis and electrochemical characterization)
  - APS, Argonne: Peter Chupas, Karena Chapman, Matthew Suchomel (HR-XRD and PDF analyses)
  - MIT: Yang Shao-Horn, Chris Carlton (HR-TEM)

Objectives

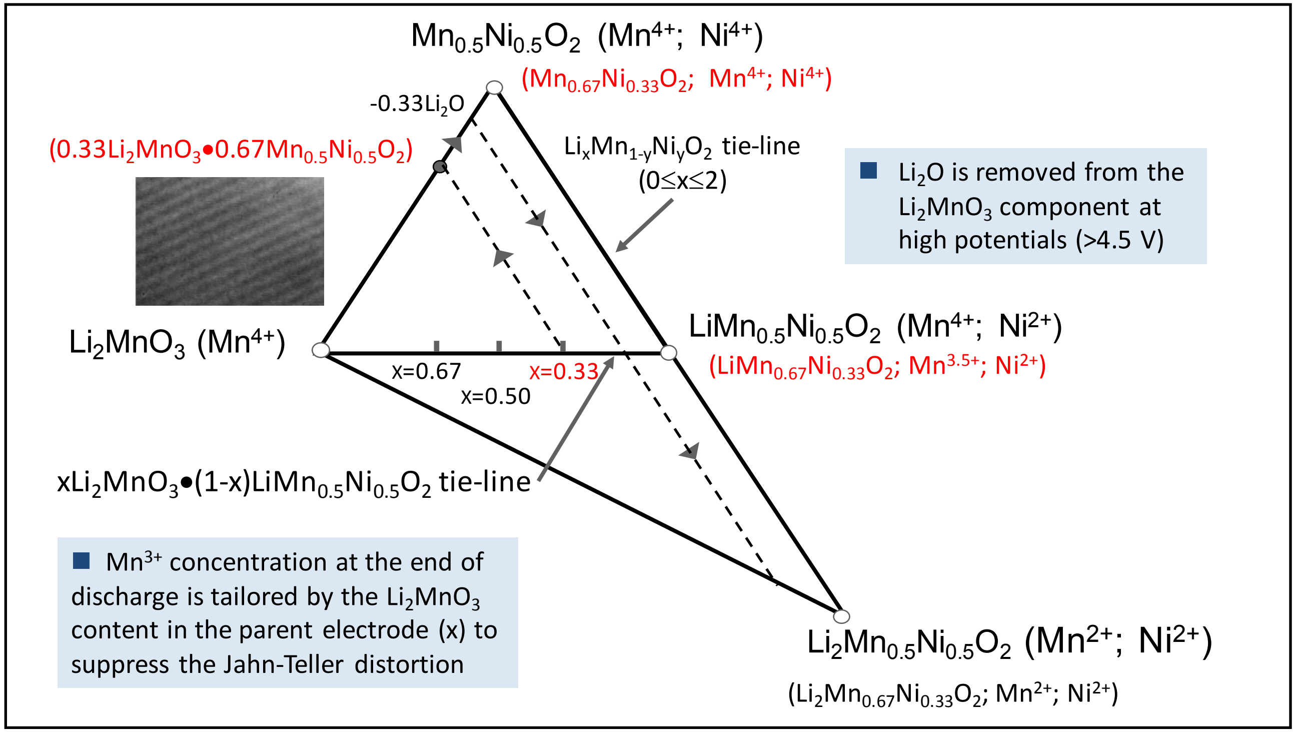
- Develop low cost, high-capacity cathode materials with good structural, electrochemical and thermal stability for PHEVs
  - Design and synthesize Li- and Mn-rich oxides with integrated structures, notably 'layered-spinel' materials, to *counter the voltage fade phenomenon* observed in 'layered-layered' electrode materials
  - Identify and overcome performance degradation issues
  - Exchange information and collaborate closely with others in ABR's 'voltage fade' team
  - Supply promising high-capacity cathode materials for PHEV cell build

Milestones FY12

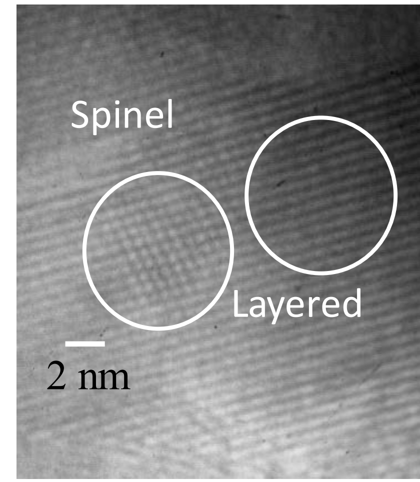
- Explore/optimize the electrode composition using phase diagrams as the guide – *on going*
- Evaluate electrochemical properties of ‘layered-spinel’ electrode materials in lithium half cells and a full Li-ion cell configuration with various anode materials – *on going*
- Investigate both bulk and surface effects – *on-going*
- Initiate detailed structural analyses of composite electrode structures at the Advanced Photon Source (APS) by X-ray diffraction, X-ray absorption and pair-distribution-function (pdf) analyses – *initiated October 2011*

Background: Integrated Cathode Structures

'Layered-Layered' Li_2MnO_3-$LiMO_2$-MO_2 (M=Mn, Ni) Phase Diagram



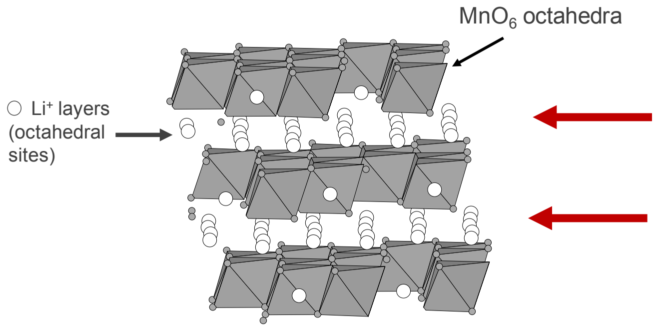
'Layered-Spinel'
$0.7Li_2MnO_3 \bullet 0.3Li_4Mn_5O_{12}$



- Compatibility of ccp planes in layered Li_2MnO_3 (C2/m, 001) with those in layered $LiMO_2$ (R-3m, 003) and spinel LiM_2O_4 (Fd3m, 111) allows structural integration of the two components
- Strategy: Use the 'layered-layered' component to provide high capacity and the spinel component to act as a stabilizer to counter voltage fade

Voltage Fade: Relationship to other EERE projects

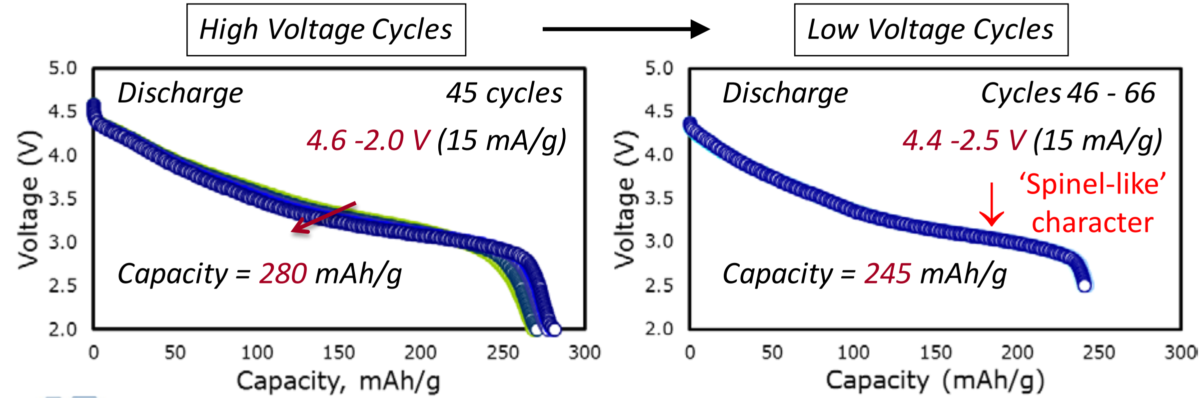
- Use Li_2MnO_3 as precursor to fabricate 'layered-layered' electrodes - see Croy et al., BATT Poster ES049
- Voltage decay due to internal phase transitions - migration of transition metal ions into Li layers provides 'spinel-like' character
- **Hypothesis:** Phase transitions may be arrested by introducing and controlling the number of stabilizing ions in Li layer via a Li_2MnO_3 precursor



New BATT process

Li⁺/M⁺/H⁺-ion exchange during acid treatment, followed by annealing step to complete M⁺ diffusion into the lithium and transition metal layers

$Li_2MnO_3 \bullet LiMn_{0.5}Ni_{0.5}O_2$ (Li_2MnO_3_Ni)

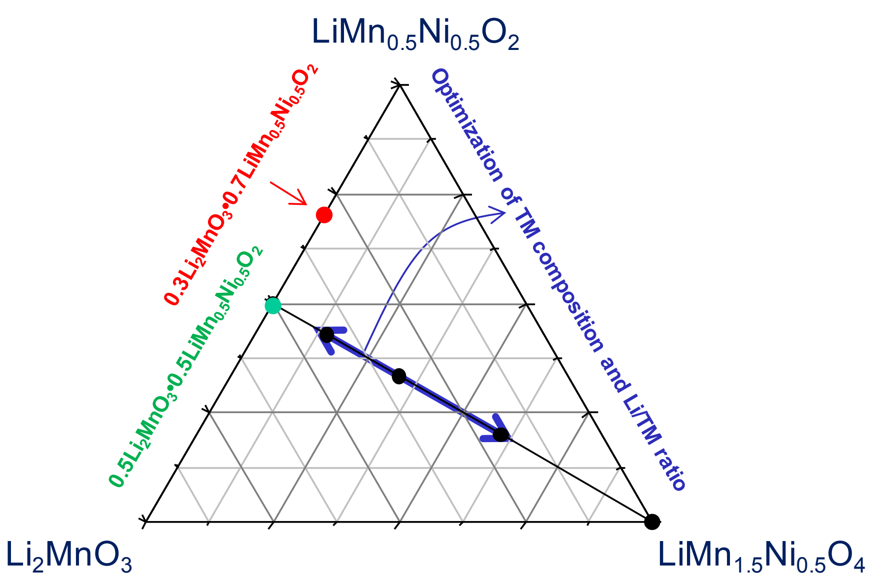


- **Strategy and Goal of ABR project: Fabricate (by standard industry processes, e.g., solid state reactions using mixed metal hydroxides /carbonate precursors) stabilized 'layered-layered-spinel' electrodes that do not exhibit voltage decay**

Approach

Initial strategy

- Embed a spinel component to stabilize 'layered-layered' composite structures
  - *Spinel domains can be created by controlling the lithium content in the composite electrode structure*
  - *Lower the Li : Transition Metal ratio relative to 'layered-layered' electrodes*



  - *Electrodes investigated on the tie-line $x\{0.5Li_2MnO_3•0.5LiMn_{0.5}Ni_{0.5}O_2\}•(1-x)LiMn_{1.5}Ni_{0.5}O_4$*
  - *Mn:Ni ratio in 'layered-layered' component = 75:25*

Recent approach

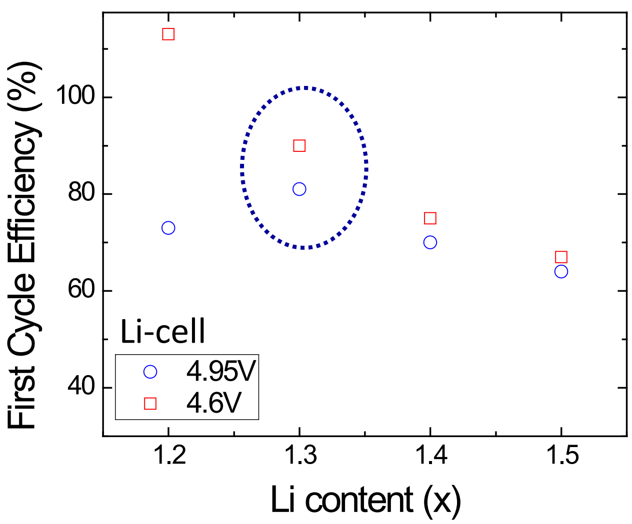
- Evaluate composite electrodes with a higher Ni content in the 'layered-layered' component to enhance structural stability during cycling
- Use a small amount of spinel stabilizer (5-10%) in $0.3Li_2MnO_3•0.7LiMn_{0.5}Ni_{0.5}O_2$ 'layered-layered' component in which the Mn:Ni ratio = 65:35
- Based on literature results, investigate the potential benefits of Mg substitution and surface stabilization with AlF_3
- Initiate structural analyses of 'layered-layered' and 'layered-layered-spinel' electrode structures at the Advanced Photon Source (APS), using a 'layered-layered' component $xLi_2MnO_3•(1-x)LiCoO_2$ as a baseline standard for simplicity

$Li_xMn_{0.75}Ni_{0.25}O_y$ 'Layered-Layered-Spinel' Compositions

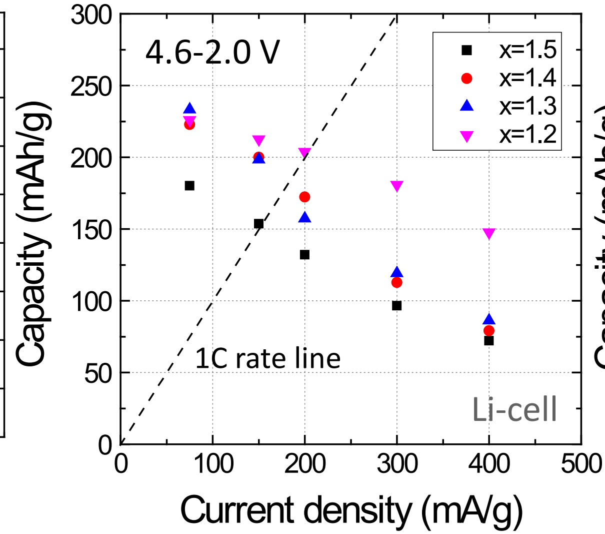
RECAP:

- $Li_xMn_{0.75}Ni_{0.25}O_y$ compositions fall on the tie line between $0.5Li_2MnO_3\bullet0.5LiMn_{0.5}Ni_{0.5}O_2$ ('layered-layered') and $LiMn_{1.5}Ni_{0.5}O_4$ (spinel) tie line with constant Mn:Ni ratio (3:1).
- $Li_{1.5}Mn_{0.75}Ni_{0.25}O_{2.5} = 0.5Li_2MnO_3\bullet0.5LiMn_{0.5}Ni_{0.5}O_2$; $Li_{0.5}Mn_{0.75}Ni_{0.25}O_2 = LiMn_{1.5}Ni_{0.5}O_4$
- Therefore, lowering the Li:Mn+Ni ratio from 1.5 :1 to 0.5:1 induces spinel formation in the 'layered-layered' structure

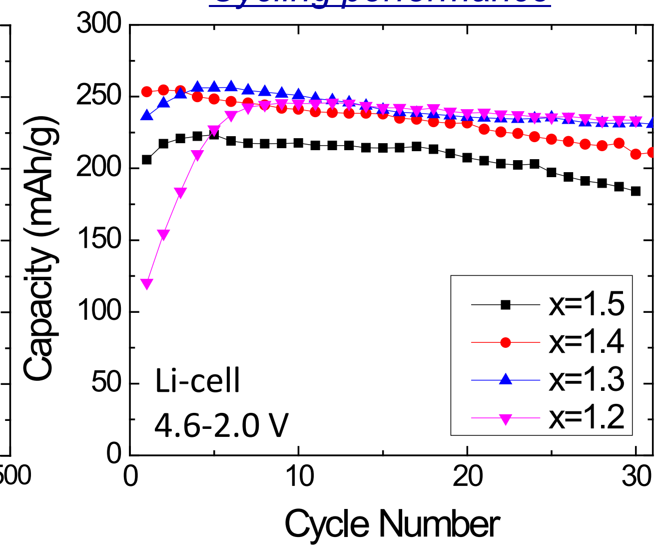
1st cycle efficiency



Rate capability



Cycling performance



- Improvement in the 1st-cycle efficiency was achieved by incorporating a spinel phase in the 'layered-layered' matrix. (e.g., 90% for $Li_{1.3}Mn_{0.75}Ni_{0.25}O_y$ when cycled at 4.6-2.0 V)
- 200 mAh/g at 1C rate was achieved for $Li_{1.2}Mn_{0.75}Ni_{0.25}O_y$
- But…… Mn concentration too high (cf. phase diagram)

Kang et al (2011)

The $Li_xMn_{0.65}Ni_{0.35}O_y$ System

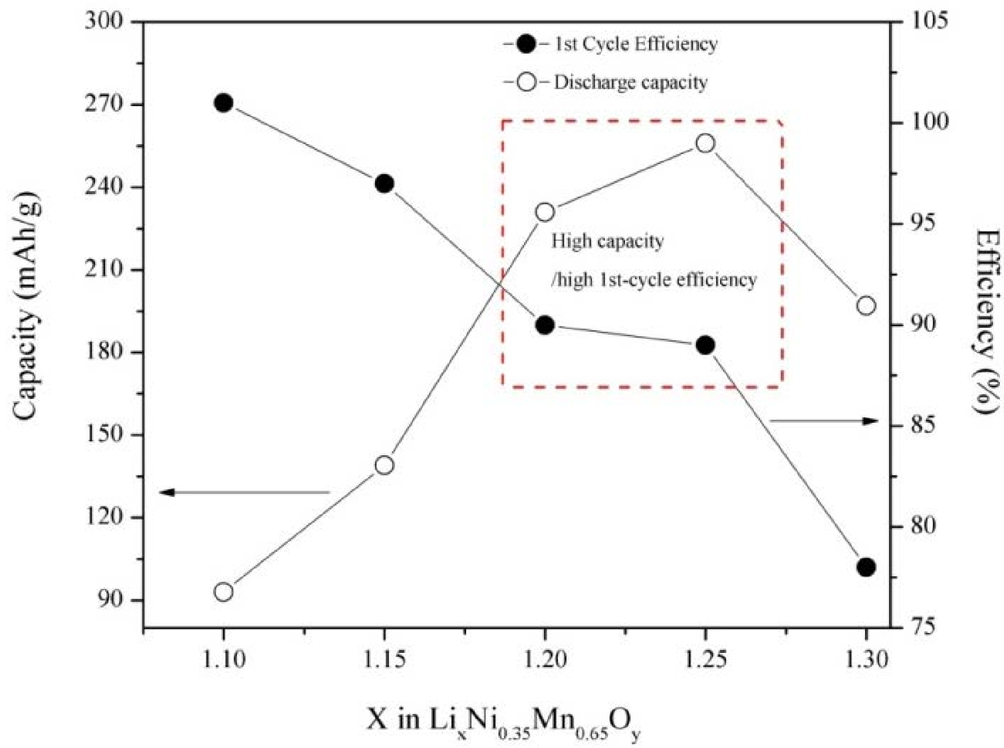
- $Li_xMn_{0.65}Ni_{0.35}O_y$ products were synthesized from Li_2CO_3 and $Mn_{0.65}Ni_{0.35}C_2O_4 \bullet 2H_2O$* (850 °C, 12 h, air, Mn:Ni ratio = 65:35)
- In this system, $Li_{1.3}Mn_{0.65}Ni_{0.35}O_{2.3}$ corresponds to the spinel-free, 'layered-layered' composition $0.3Li_2MnO_3 \bullet 0.7LiMn_{0.5}Ni_{0.5}O_2$
- Lowering the lithium content induces the formation of spinel in the layered structure

$Li_xNi_{0.35}Mn_{0.65}O_y$	$\delta(0.3Li_2MnO_3 \bullet 0.7LiNi_{0.5}Mn_{0.5}O_2)$	$(1-\delta)Li_{0.5}Ni_{0.25}Mn_{0.75}O_2$
(a) x= 1.3	$\delta = 1$ $0.3Li_2MnO_3 \bullet 0.7LiNi_{0.5}Mn_{0.5}O_2$	$(1-\delta) = 0$
(b) x = 1.25	$\delta = 0.94$ $0.28Li_2MnO_3 \bullet 0.66LiNi_{0.5}Mn_{0.5}O_2$	$(1-\delta) = 0.06$ $0.06Li_{0.5}Ni_{0.25}Mn_{0.75}O_2$
(c) x = 1.2	$\delta = 0.88$ $0.26Li_2MnO_3 \bullet 0.62LiNi_{0.5}Mn_{0.5}O_2$	$(1-\delta) = 0.12$ $0.12Li_{0.5}Ni_{0.25}Mn_{0.75}O_2$
(d) x = 1.15	$\delta = 0.81$ $0.24Li_2MnO_3 \bullet 0.57LiNi_{0.5}Mn_{0.5}O_2$	$(1-\delta) = 0.19$ $0.19Li_{0.5}Ni_{0.25}Mn_{0.75}O_2$
(e) x = 1.1	$\delta = 0.75$ $0.23Li_2MnO_3 \bullet 0.53LiNi_{0.5}Mn_{0.5}O_2$	$(1-\delta) = 0.25$ $0.25Li_{0.5}Ni_{0.25}Mn_{0.75}O_2$

*coprecipitated in-house

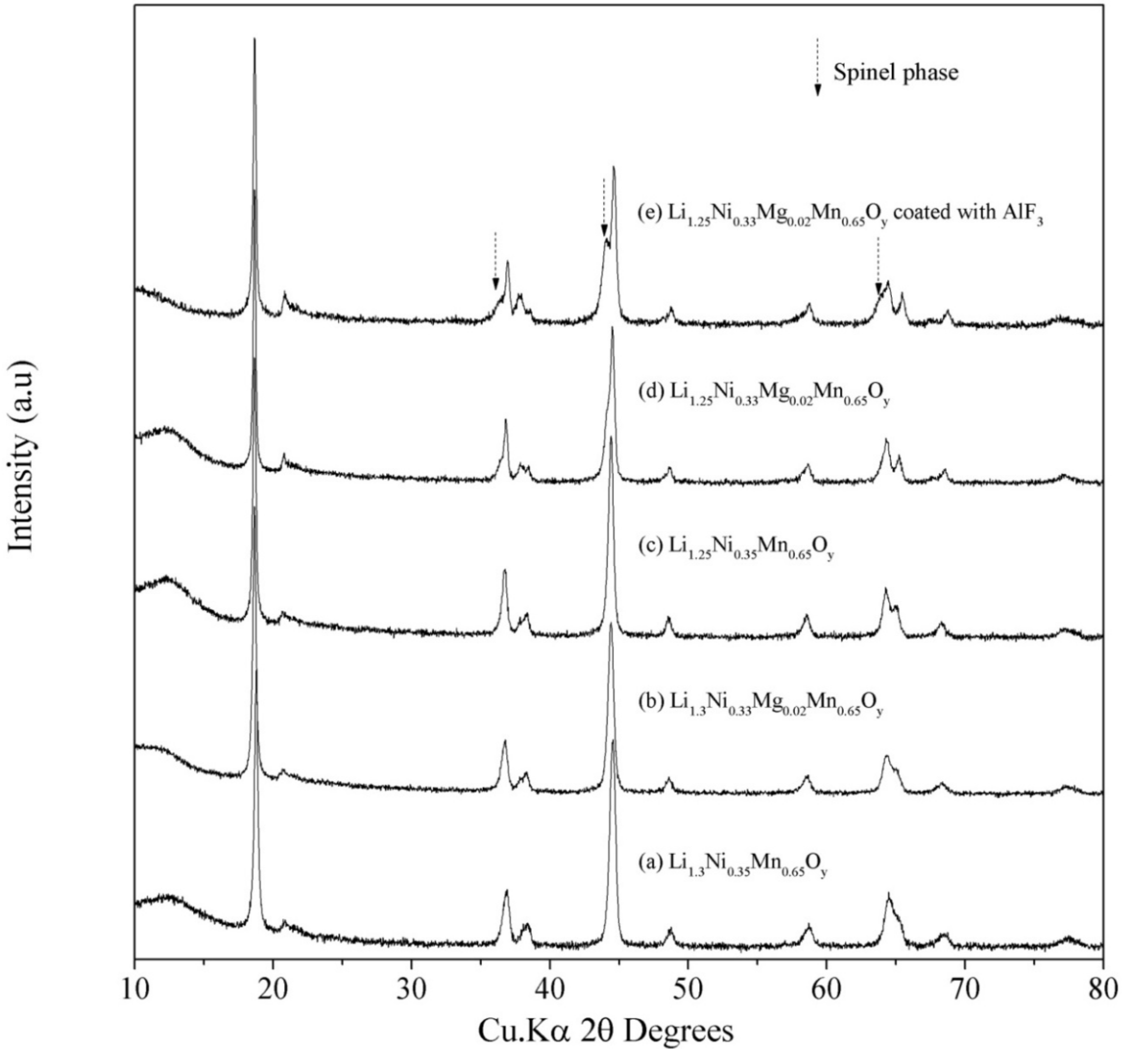
The Effect of Lithium Content in $Li_xMn_{0.65}Ni_{0.35}O_y$:

Optimizing capacity and first cycle efficiency



- Like the $Li_xMn_{0.75}Ni_{0.25}O_y$ system, the 1st cycle efficiency and rate capability were enhanced by introducing a spinel component into the 'layered-layered' structure.
- Based on the 1st-cycle efficiency and the rate capability, $Li_{1.25}Mn_{0.65}Ni_{0.35}O_y$ was selected for further study.

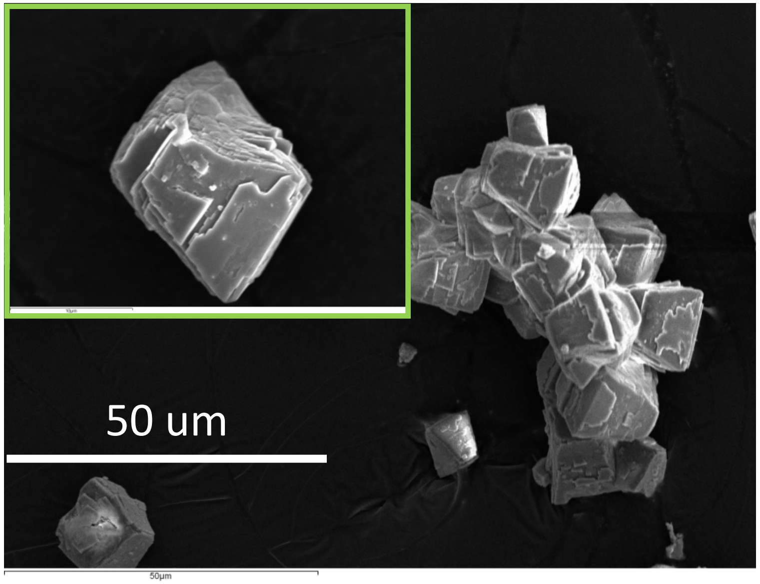
XRD patterns of $Li_xMn_{0.65}Ni_{0.35}O_y$ samples



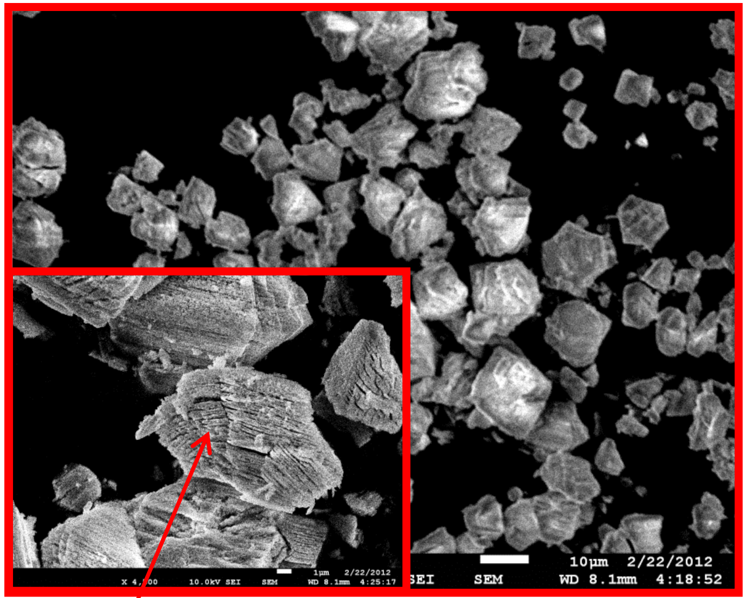
- Spinel component is detectable in samples with x = 1.25, but not x = 1.3, as expected
- AlF_3 treatment enhances the spinel content through Li removal (acid leaching) and annealing
- Provides a technique to simultaneously stabilize the surface and tailor the amount of stabilizing spinel in the bulk?

SEM/TEM Images of Precursor and Products

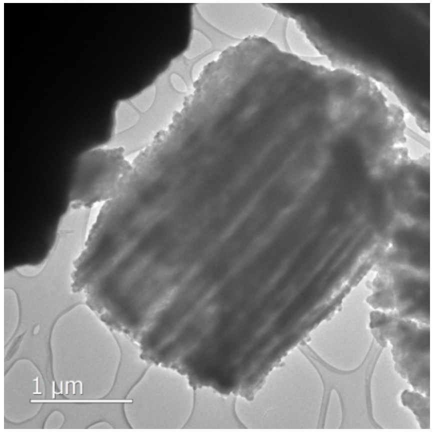
$Mn_{0.65}Ni_{0.33}Mg_{0.02}C_2O_4{\bullet}2H_2O$



$Li_{1.25}Ni_{0.33}Mg_{0.02}Mn_{0.65}O_y$

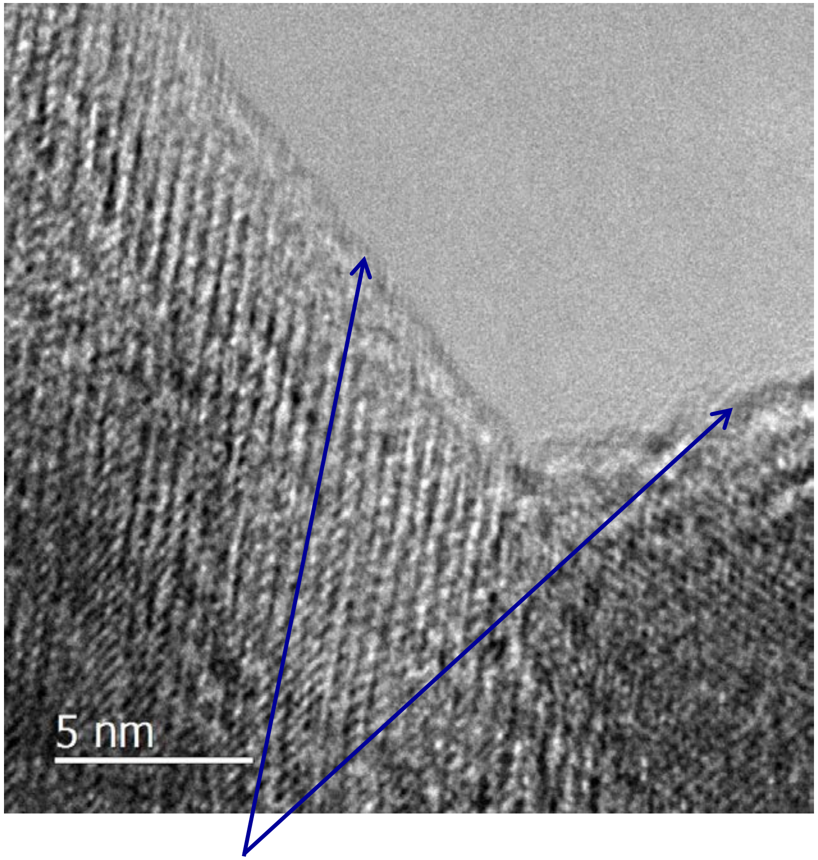


Cleaved crystallites, believed to be result of H_2O/CO_2 loss from oxalate precursor, contribute to the porosity of secondary particles



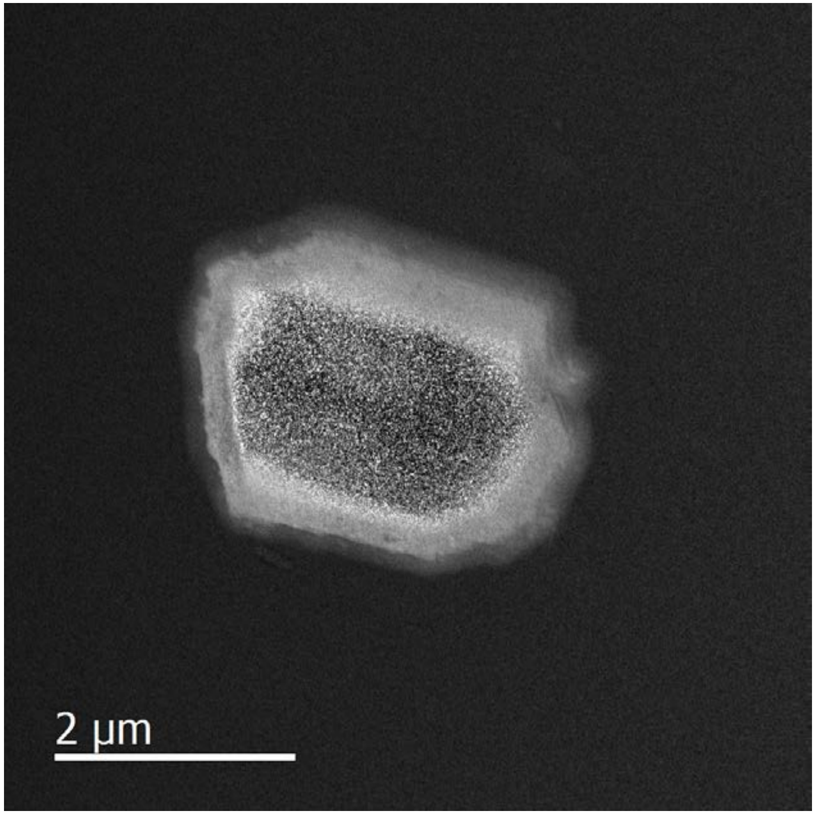
High resolution TEM/EELS images of AlF_3-coated $Li_{1.25}Ni_{0.33}Mg_{0.02}Mn_{0.65}O_y$ Samples

TEM



- ~1nm AlF_3 layer on particle surface

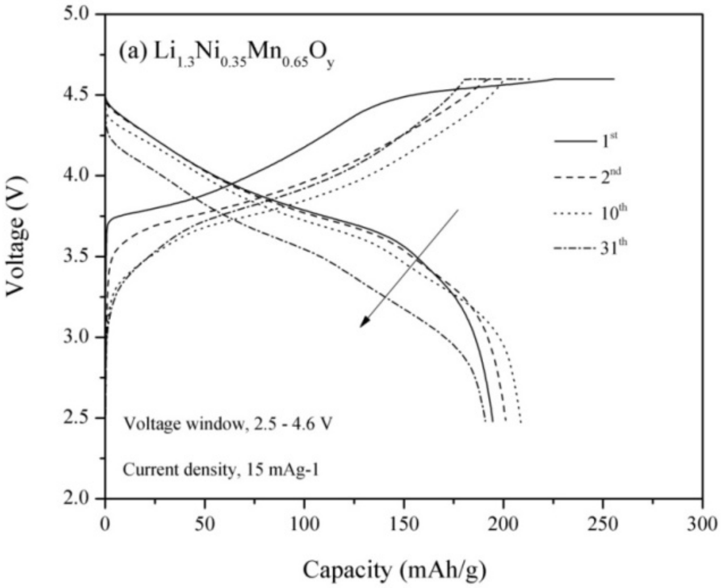
EELS



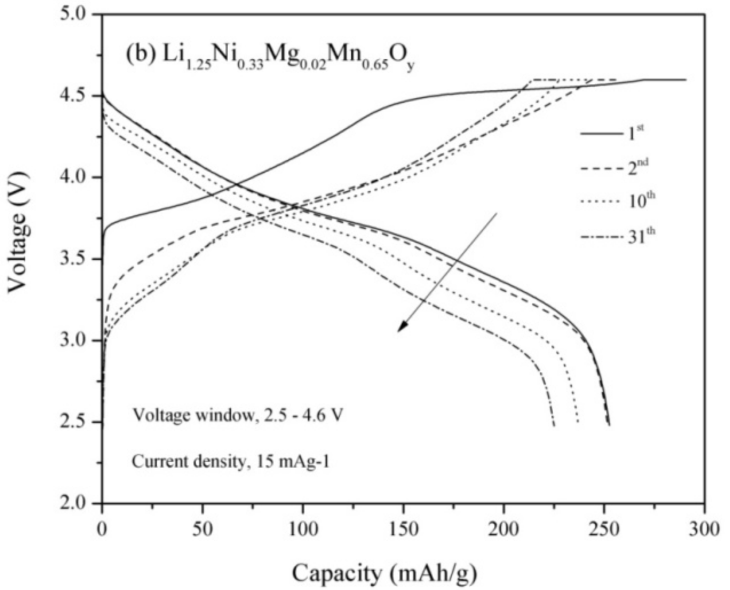
- EELS map shows uniform Al distribution (white dots) over particle surface

Electrochemistry of $Li_{1.3}Mn_{0.65}Ni_{0.35}O_{2.3}$ and $Li_{1.25}Ni_{0.33}Mg_{0.02}Mn_{0.65}O_y$ Electrodes

$0.3Li_2MnO_3 \bullet 0.7LiNi_{0.5}Mn_{0.5}O_2$



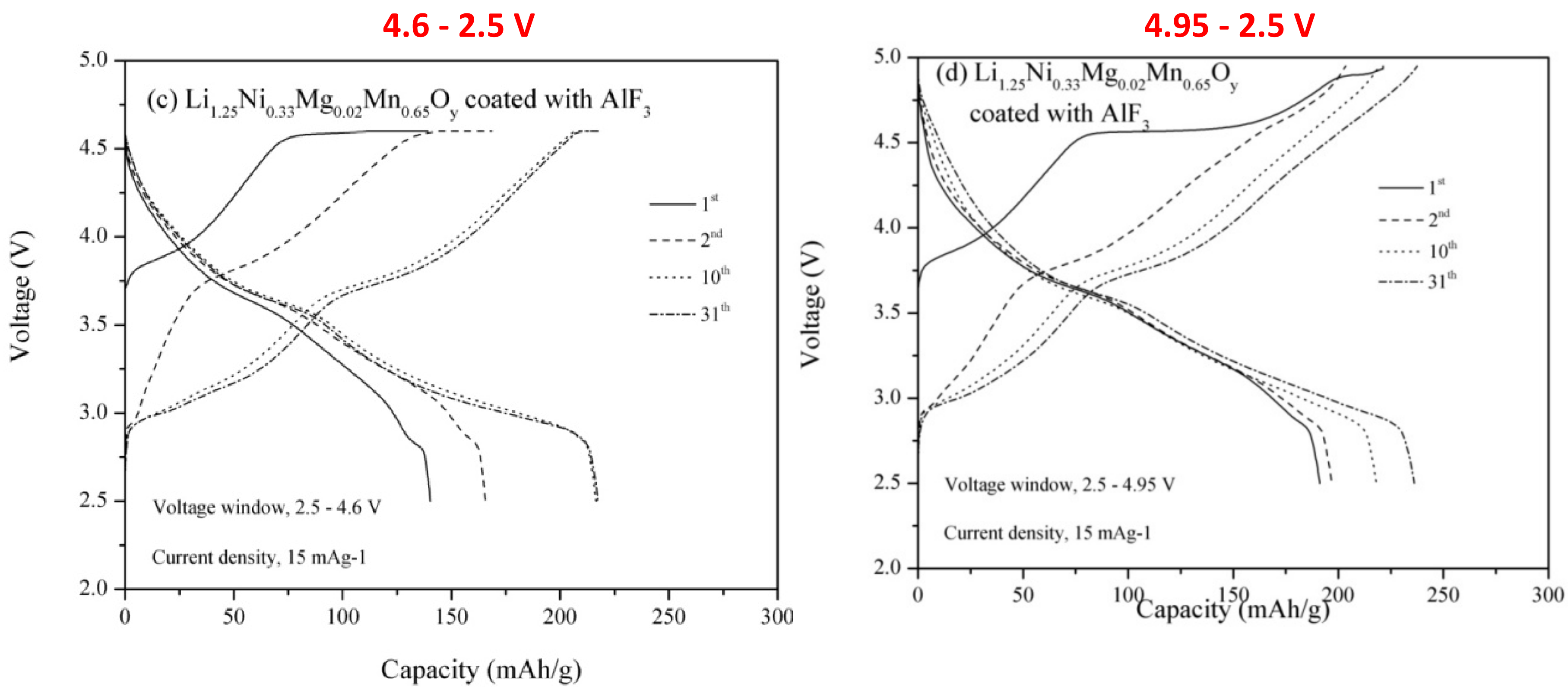
Mg-doped, Li deficient $0.3Li_2MnO_3 \bullet 0.7LiNi_{0.5}Mn_{0.5}O_2$



- First cycle efficiency = 78%
- Typical behavior for a 'layered-layered' electrode

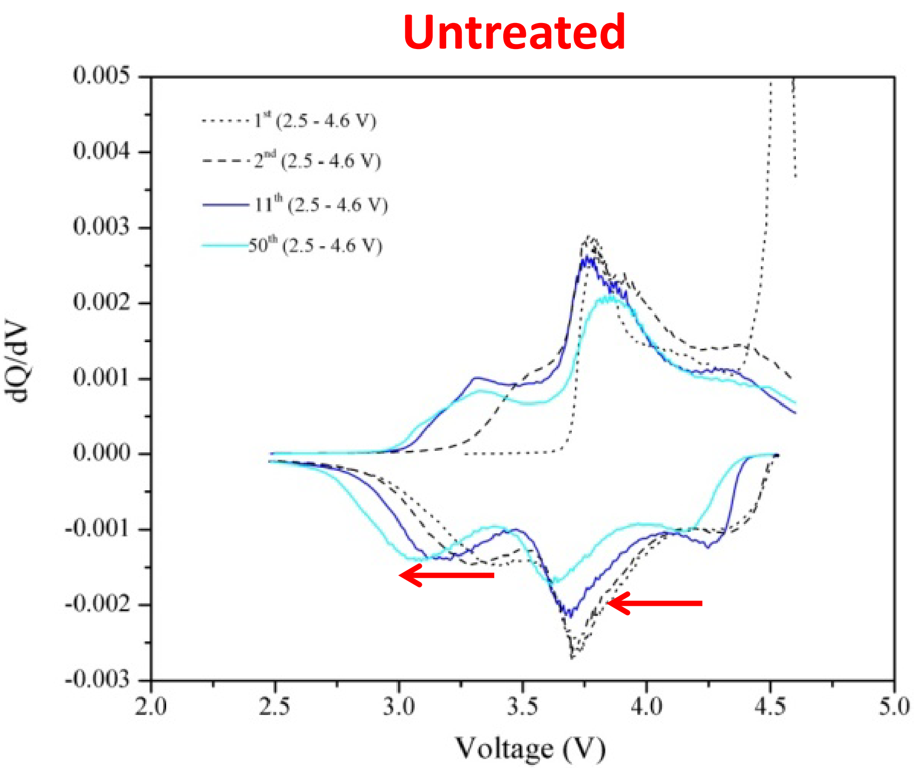
- First-cycle efficiency = 89% (spinel phase can accommodate surplus Li)
- Mg doping improves capacity (consistent with Sun et al, J. Mater. Chem. (2003))
- Voltage fade on discharge still significant $\Rightarrow$ stabilizing spinel concentration too low? (~6%)

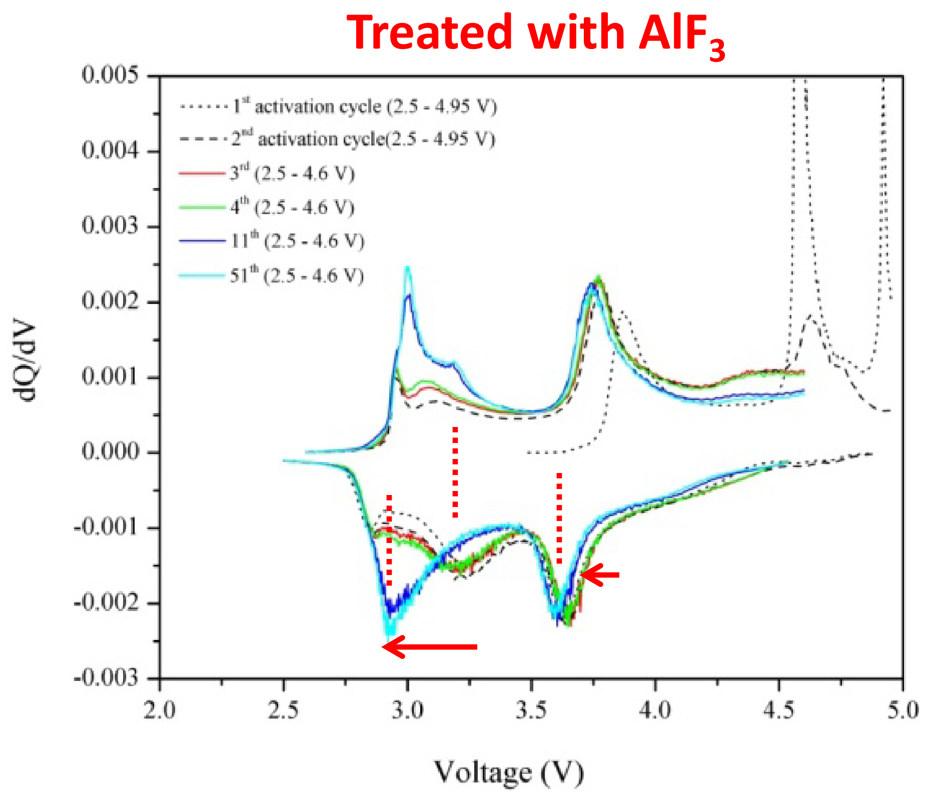
AlF_3-treated $Li_{1.25}Ni_{0.33}Mg_{0.02}Mn_{0.65}O_y$ Electrodes



- AlF_3 treatment enhances the cycling stability and provides cells with an apparent 'built-in' voltage decay $\Rightarrow$ increased spinel component in the acid-treated electrode?
- AlF_3-treated electrodes provides inferior capacity (higher surface impedance) relative to uncoated samples

dQ/dV Plots of $Li_{1.25}Ni_{0.33}Mg_{0.02}Mn_{0.65}O_y$ Electrodes



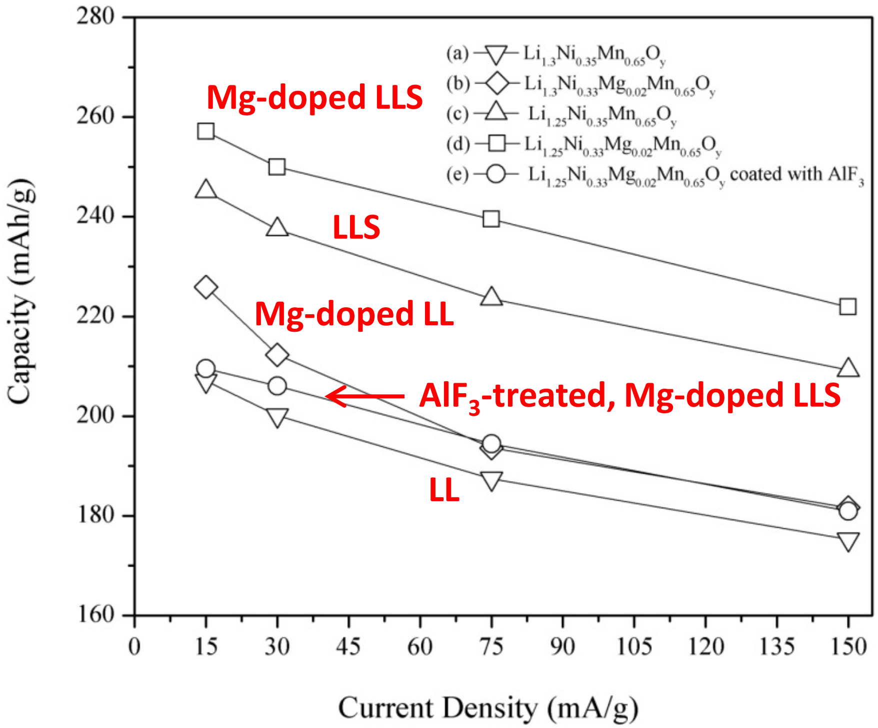


- Untreated electrodes with low spinel concentration (~6%) show typical voltage fade
- Ni reduction peak at ~3.7 V weakens on cycling

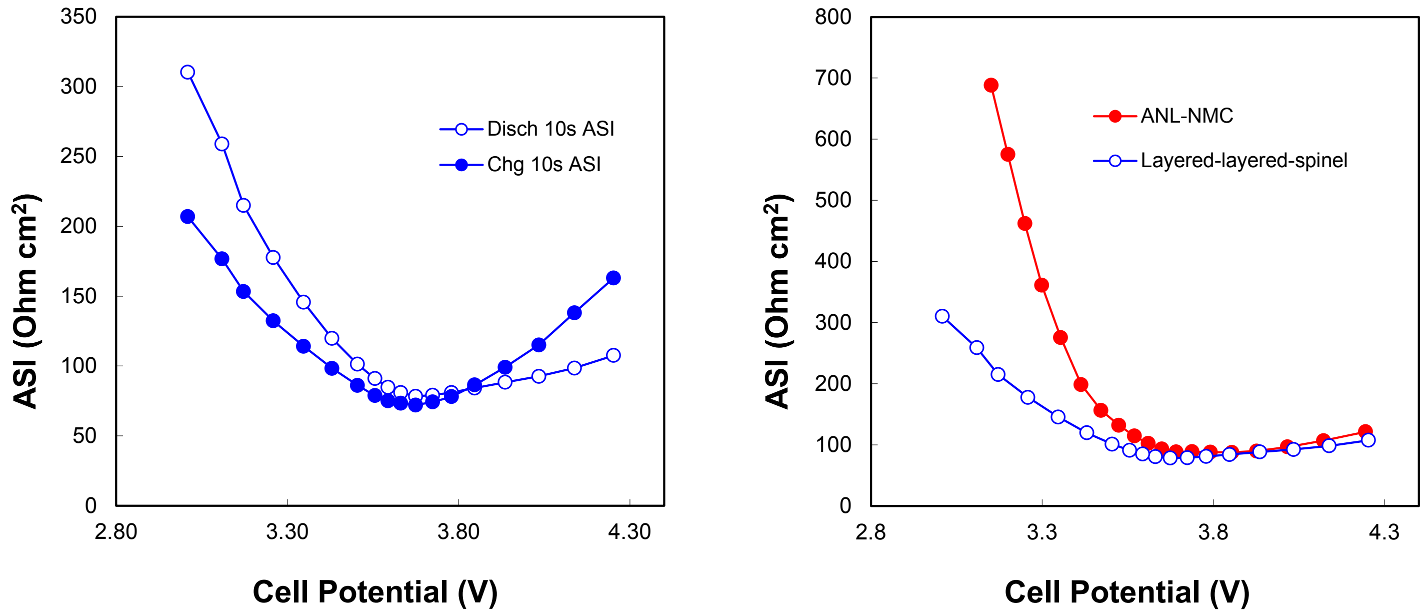
- AlF_3-treated electrodes show greater cycling stability at ~3.7 V
- Surface treatment influences bulk processes
- Spinel-like phase (~2.95 V) becomes dominant

Rate Capability of $Li_xMn_{0.65}Ni_{0.35}O_y$ Electrodes

- Discharge capacities measured at 15, 30, 75, and 150 mA/g
- 'Layered-layered-spinel' (LLS) composite electrodes provide higher capacity than 'layered-layered' (LL) electrodes
- AlF_3 surface treatment reduces the rate capability of 'layered-layered-spinel 'electrodes
- High rate performance tentatively attributed to the stabilizing effects of spinel at the surface as well as in the bulk

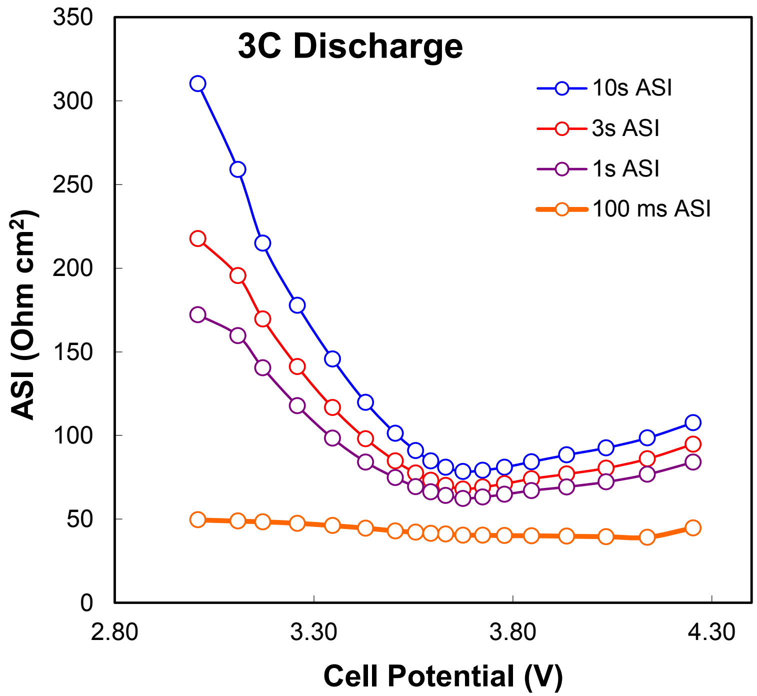


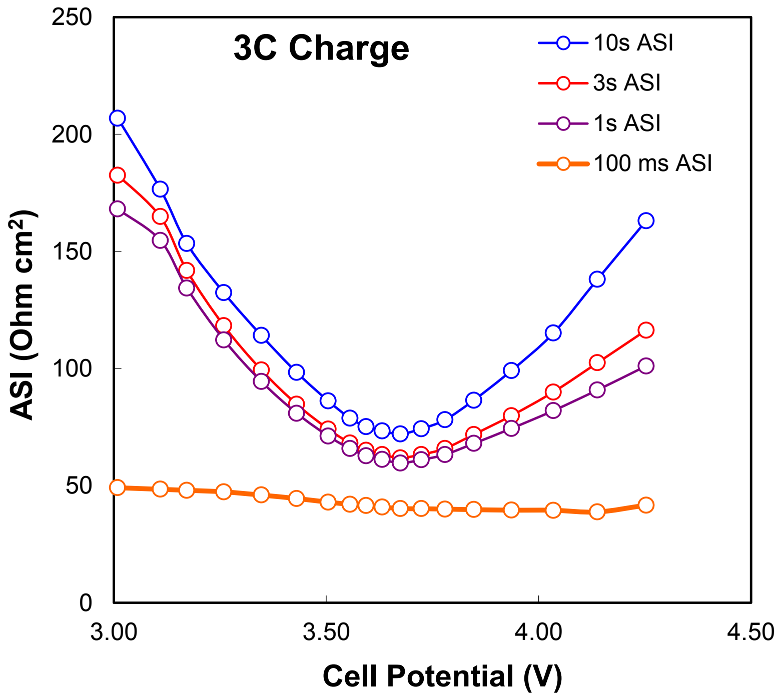
Pulse Power Performance of $Li_{1.25}Ni_{0.33}Mg_{0.02}Mn_{0.65}O_y$



- Impedance measured with DC pulses
  - Measured at 5% SOC increments
  - 10 sec 3C discharge, 60 minute rest, 10 sec 3C charge
- Layered-layered spinel / graphite full cell
  - $Li_{1.25}Ni_{0.33}Mg_{0.02}Mn_{0.65}O_y$ vs. MAG10 Li_xC_6 (1.2M $LiPF_6$ in 3:7 EC:EMC)
- Better impedance than ANL-NMC electrodes
  - Influence of spinel component unknown at this stage

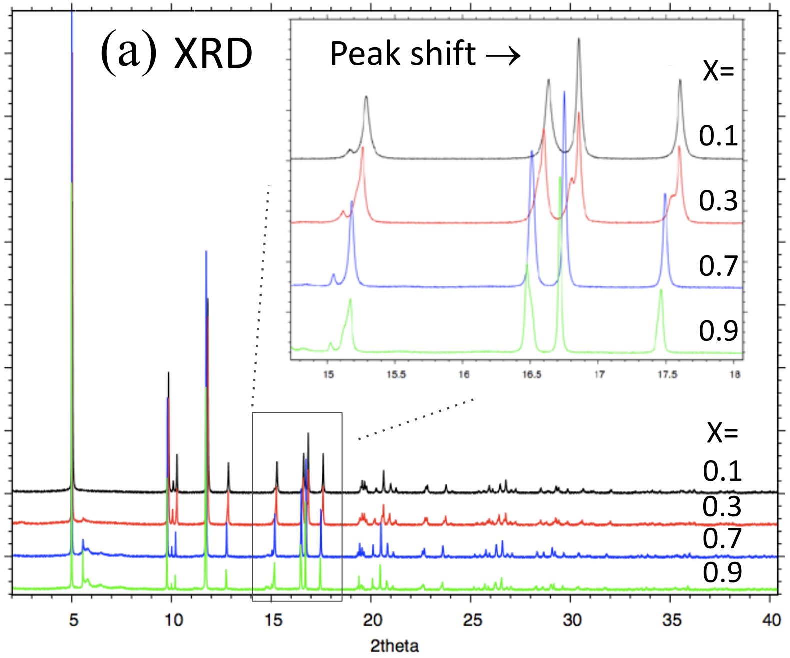
Area Specific Impedance of $Li_{1.25}Ni_{0.33}Mg_{0.02}Mn_{0.65}O_y$

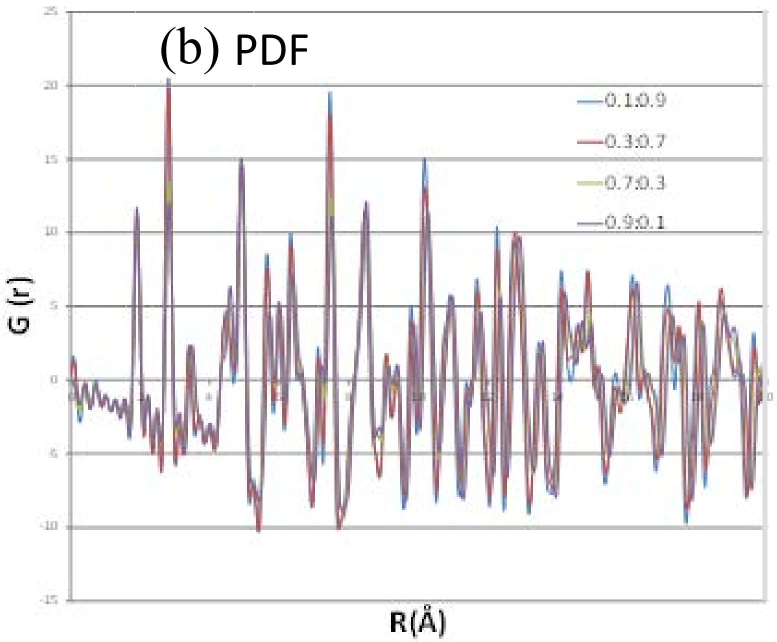




- Breakdown of measured ASI
  - Interfacial processes very significant (<1-3 seconds)
  - Diffusional impedance becomes most important at high and low SOC

XRD Patterns and PDF Spectra of xLi_2MnO_3•$(1-x)LiCoO_2$
(x=0.1, 0.3, 0.7, and 0.9 annealed at 850°C)





- Use a “simple” baseline system, xLi_2MnO_3•$(1-x)LiCoO_2$ to initiate in-depth studies of the voltage decay phenomenon in ‘layered-layered’ electrodes
- TEM data show a composite structure composed of Li_2MnO_3 and $LiCoO_2$ nanodomains
(J. Bareno, Chem Mater. (2011))
- XRD data indicate solid-solution behavior of a composite “Li_2MnO_3 + $LiCoO_2$” matrix as a function of x
- PDF data show short range environment of Mn, Co remains constant as a function of x (to R ≈ 15Å)
(M-M correlations: CN = 3 for Mn in Li_2MnO_3 layers; CN = 6 for Co in $LiCoO_2$ layers)

Future work

- Composition optimization
  - Continue to screen 'layered-layered-spinel' electrodes to determine optimized composition and the spinel content to circumvent voltage fade;
  - Select two most promising compositions/chemistries for exhaustive electrochemical evaluation and characterization of their chemical, physical and thermal properties;
  - Evaluate electrodes in a full lithium-ion cell configuration.
- Collaboration
  - Collaborate with other ABR participants, academic and industrial partners to understand and combat voltage fade phenomena and the cause thereof.

    For example, explore detailed structure-electrochemical relationships of relatively simple 'layered-layered' baseline materials (e.g., $xLi_2MnO_3{\bullet}(1-x)LiCoO_2$) and 'layered-layered-spinel' derivatives by XRD, XAS and PDF analyses with collaborators at the Advanced Photon Source.

Summary

- ‘Layered-layered’ composite electrode structures, stabilized by a spinel component, hold promise for countering voltage fade;
- Mg-doping of ‘layered-layered’ and ‘layered-layered-spinel’ electrodes enhances capacity;
- Mg-doped ‘layered-layered-spinel’ electrodes offer enhanced rate capacity over ‘layered-layered’ electrodes;
- ‘Layered-layered-spinel’ electrodes counter the first-cycle irreversible capacity loss of ‘layered-layered’ electrodes;
- AlF_3 surface treatment increases the spinel component in the structure and enhances cycling stability, but reduces the rate capability of the electrode (increased surface impedance); and
- Many questions are still to be answered: Further work is required 1) to obtain a detailed understanding of the reasons for voltage fade phenomena, 2) identify optimized ‘layered-layered-spinel’ compositions to best counter these effects (a basis for collaborative studies with academia and industry)

Acknowledgment

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- Peter Faguy