Olivines and Substituted Layered Materials

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Overview

Timeline

- ongoing

Budget

- Total project funding
  - 100% DOE
- FY08 505k
- FY09 525k

Barriers

- Barriers addressed
  - Cost
  - Power/Energy Density
  - Cycle Life

Partners/Collaborations

- R. Kostecki, J. Kerr, T. Richardson, and G. Chen, J. Cabana, K. Persson (LBNL)
- E. Rodriguez (LANL)
- T. Hollenkamp (CSIRO, Australia)
- S. Patoux (CNRS, France)
- H. Gabrisch (UNO)
- S. Whittingham (SUNY), C. Grey (magnetic measurements)
- E. Cairns (LBNL), A. Deb (U. Michigan) EXAFS, S. Cramer (UC Davis)

Objectives

- To develop low-cost benign cathode materials having electrochemical characteristics (e.g., cycle life, energy and power densities) consistent with the goals of the USABC and/or FreedomCAR.
- Recent and ongoing work:
  - Lower cost of $Li[Ni_xCo_yMn_z]O_2$ electrodes by full or partial replacement of Co with other metals-maintain or improve electrochemical performance
  - Investigate feasibility of using $LiMnPO_4$ and related compounds in batteries for vehicular applications
  - New materials

Milestones

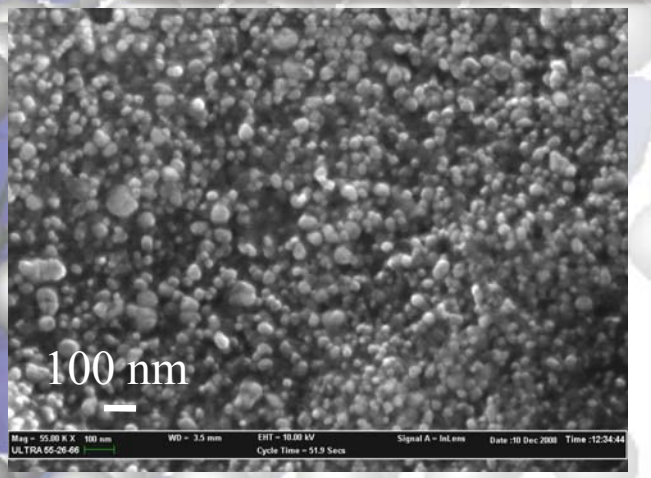
- **FY2008**
  - 4.3a Complete characterization of best-performing substituted transition metal oxides. (9/08). Postponed to 12/09 due to large amounts of data.
  - 4.3b Determine feasibility of synthesizing electrochemically active nano-
  - $LiMnPO_4$ and/or $Li(Mn,Fe)PO_4$ and other polyanionic compounds for use in the BATT program. (9/08). A go decision has been made, with plans to reassess during FY2009.
- **FY2009**
  - Finish characterization of $Li[Ni_xAl_yCo_{1-y}Mn_z]O_2$ (x+y+z=1) compounds (3/09) on schedule, decision is to continue investigating these materials
  - Develop spray pyrolysis method for synthesis of $LiMnPO_4$ and other polyanionic compounds (6/09). on schedule

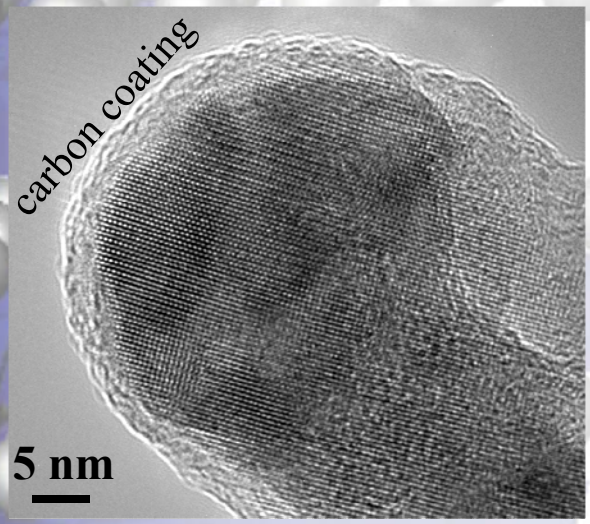
Approach

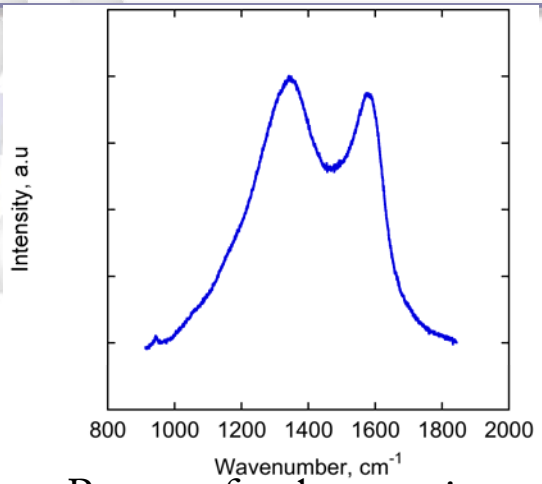
- Cathode materials are synthesized and characterized electrochemically. Relevant physical properties are measured in conjunction with the diagnostics teams. Emphasis is placed on reducing cost and improving electrochemical properties. Some work is directed towards surveying new materials with potential for increased energy density.
  - $Li[Ni_xCo_yMn_z]O_2$ (started in FY2007)
    - Synthesized $Li[Ni_{1/3}Co_{1/3-y}M_yMn_{1/3}]O_2$; M=Al, Ti, Fe and $Li[Ni_{0.4}Co_{0.2-y}M_yMn_{0.4}]O_2$; M=Al, Fe (FY2007-2008)
    - Electrochemical and preliminary structural characterization (FY2007-2008)
    - In-depth structural and spectroscopic characterization of $Li[Ni_{0.4}Co_{0.2-y}M_yMn_{0.4}]O_2$; M=Al, Fe (FY2008-2009)
  - $LiMnPO_4$ and variants (started in FY2008)
    - Synthesis of nanostructured $LiMnPO_4$/C composites
    - Electrochemical characterization
    - Evaluation of feasibility in batteries for vehicular applications
  - Application of synthesis techniques for $LiMnPO_4$ to new materials (start in latter half of FY2009).

Technical Accomplishments/Progress/Results

nano-$LiMnPO_4$ /C composites and variants

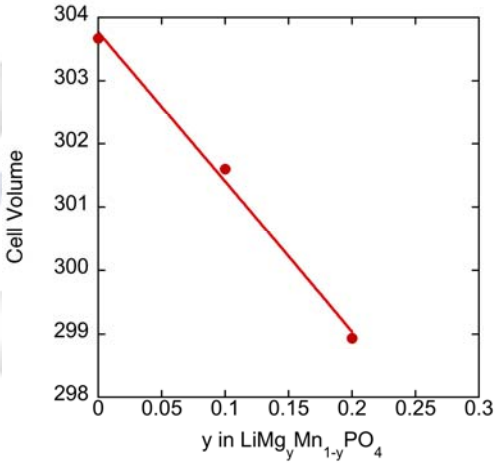




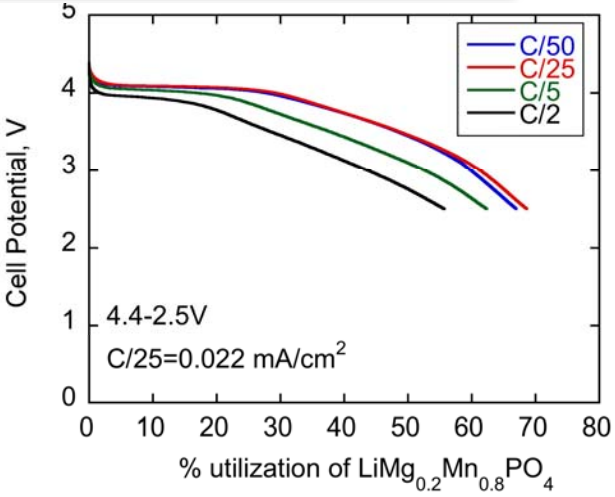


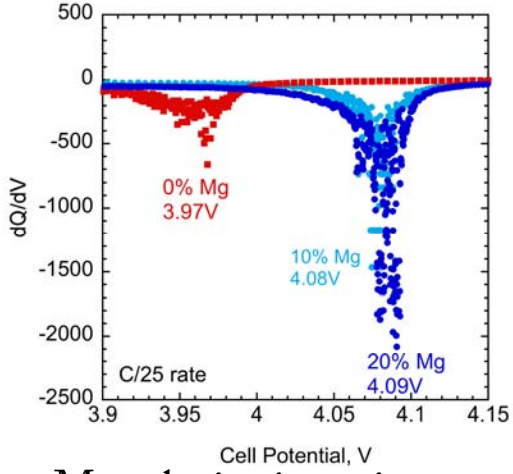
Raman of carbon coating

(R. Kostecki, LBNL)



Mg substitution reduces unit cell volume-relieves strain

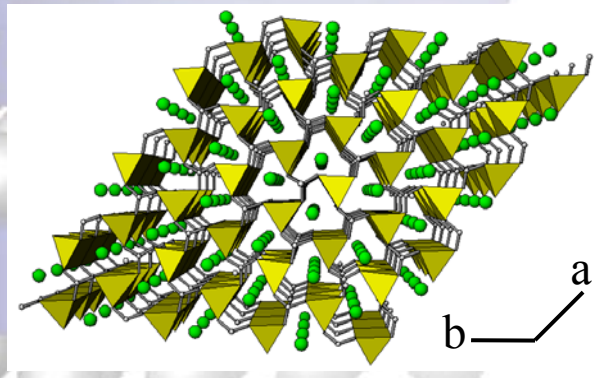




Mg substitution raises discharge potential

Summary and Future Work-$LiMnPO_4$

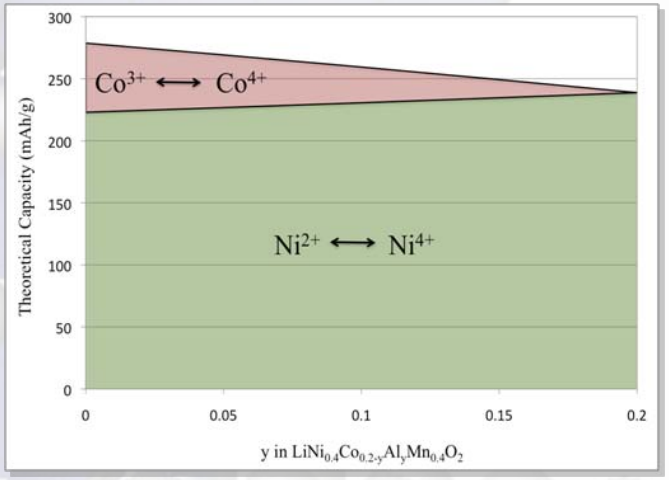
- Lack of sample homogeneity leads to lower than expected utilization at low rates
- Develop spray pyrolysis method to improve homogeneity (FY 2009)
- Reasonable rates can be achieved, but they come at the expense of energy density (Mg substitution, C coating)
- Go/no go decision on $LiMnPO_4$ for vehicular applications (FY 2009)
  - Most likely "no go" ($LiFePO_4$ and oxides are much better)
  - BUT apply synthesis knowledge to materials that don't work right now
  - Example: $LiMnBO_3$ 221 mAh/g-no electrochemical activity
  - compare $LiFeBO_3$ ~3Vvs Li (electroactive at low rates)



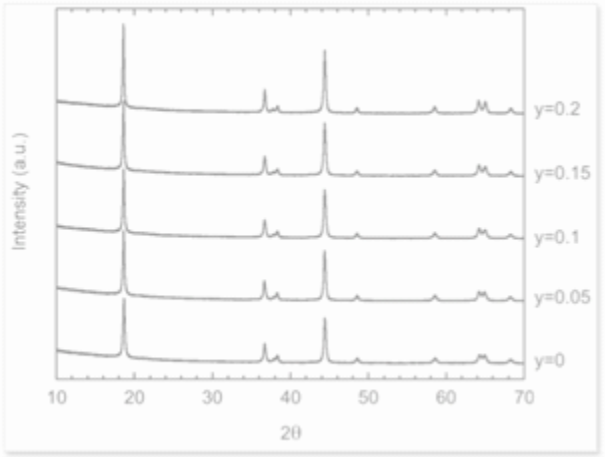
Guyomard et al., *SSI* 139, 37 (2001).
Allen et al., *Proc. Mat. Res. Soc.* 730, 9 (2002).

Technical Accomplishments/Progress/Results
$Li[Ni_xCo_{y-w}M_wMn_z]O_2$

- FY2007-2008: $Li[Ni_{0.4}Co_{0.2-y}Al_yMn_{0.4}]O_2$ and other systems
- Reduce materials cost by replacing some or all Co

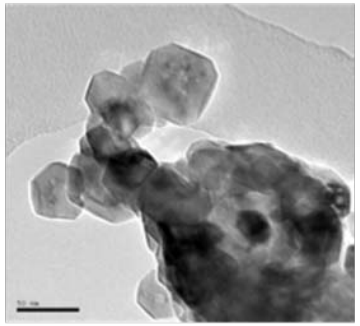


Co electroactive above 4.3V vs Li
Practical capacity not affected by replacing with inactive Al

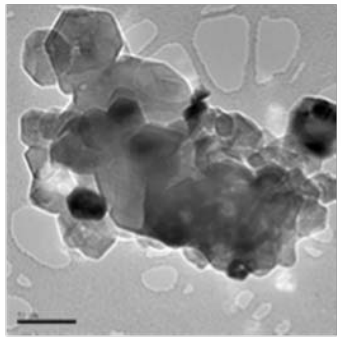


Solid solutions are formed for $0 \leq y \leq 0.2$

Particle morphology unaffected by substitution



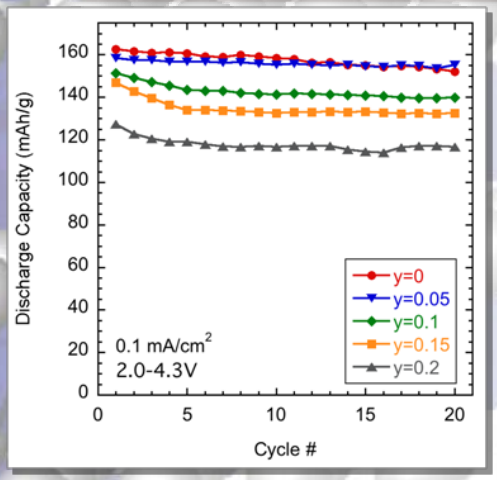
$Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2$



$Li[Ni_{0.4}Al_{0.2}Mn_{0.4}]O_2$

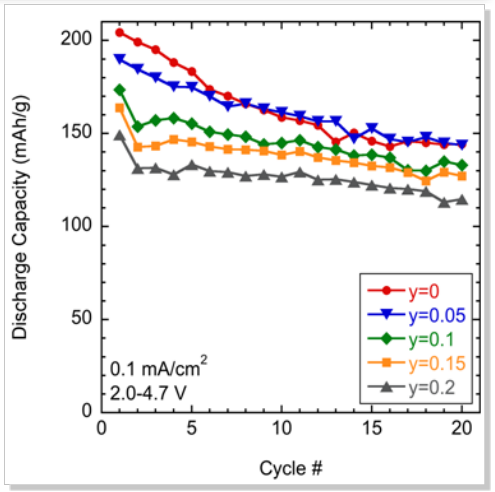
Electrochemical Results

$Li[Ni_{0.4}Co_{0.2-y}Al_yMn_{0.4}]O_2$

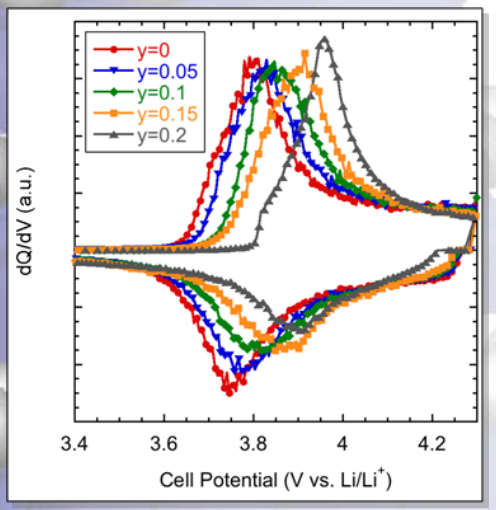


Al substitution reduces capacity below 4.3V

Higher capacities upon cycling to 4.7V, but increased fade rate

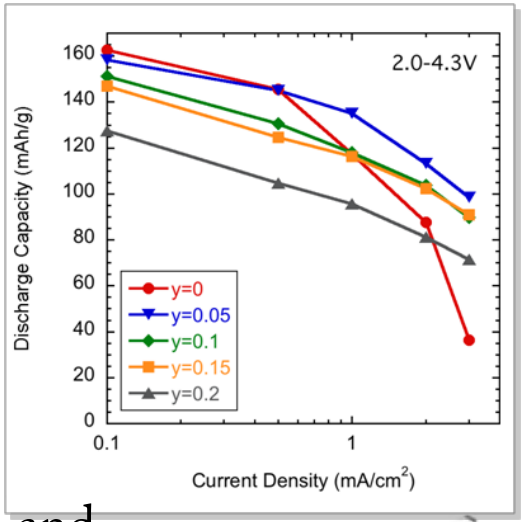


Better cycling with Al substituted compounds



Al substitution raises charge/discharge potentials

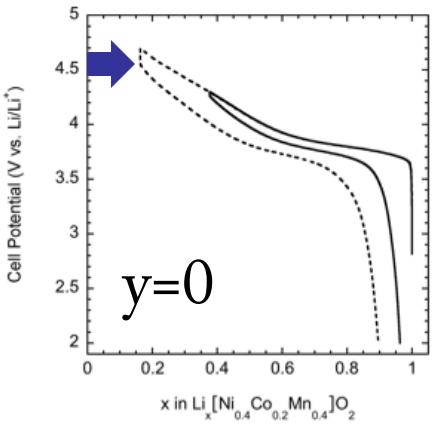
Better rate capability with Al-substituted compounds



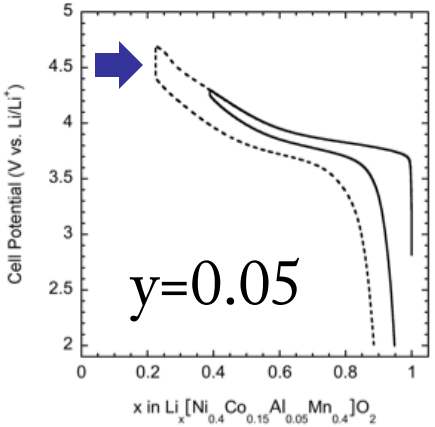
Best overall results with $Li[Ni_{0.4}Co_{0.15}Al_{0.05}Mn_{0.4}]O_2$

Goal this year -understand effect of Al on structure and electrochemistry

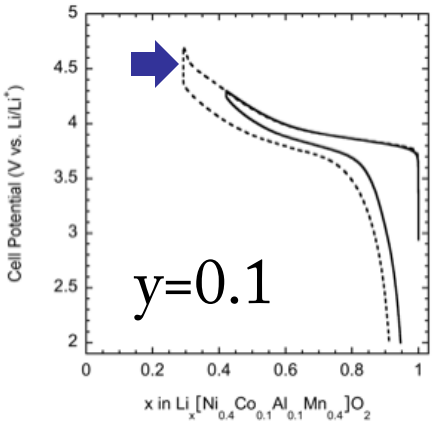
Cycling profiles of $Li/Li[Ni_{0.4}Co_{0.2-y}Al_yMn_{0.4}]O_2$ cells



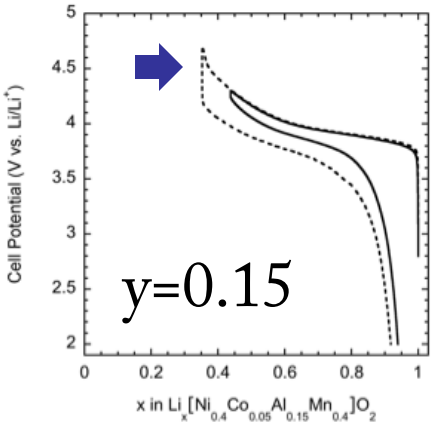
(a)



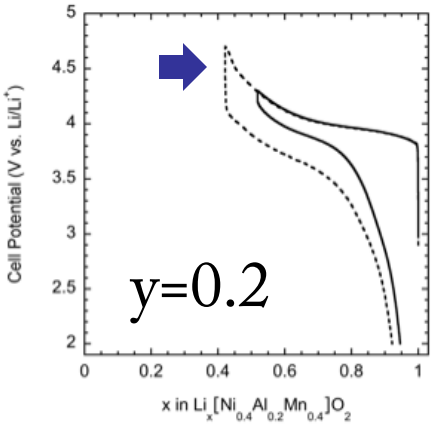
(b)



(c)



(d)



(e)

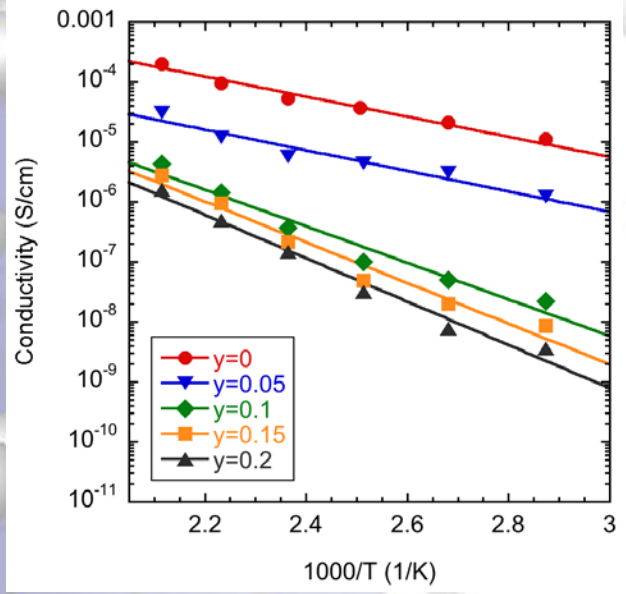
y	Irrev. Cap. Loss (%)	
	to 4.3V	to 4.7V
0	6.10±0.47	14.32±0.2
0.05	9.18±1.6	17.27±0.1
0.1	13.24±2.2	14.83±1.0
0.15	14.20±2.6	15.17±0.9
0.2	14.14±4.1	20.86±5.2

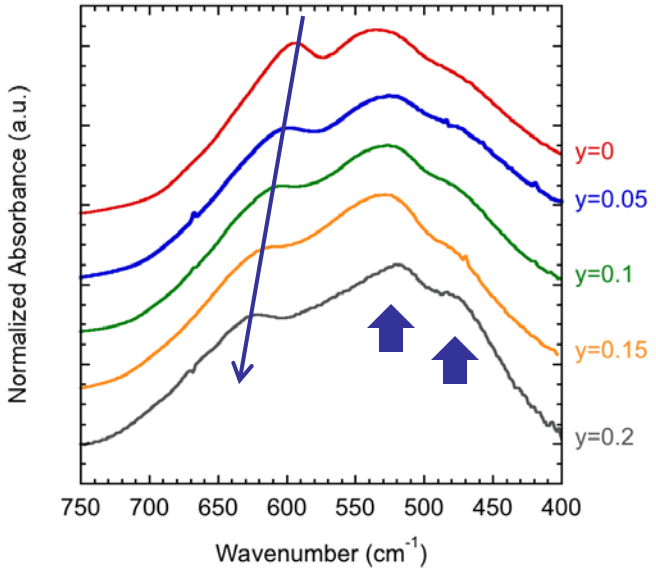
Increased polarization at end of charge-overcharge protection

Increased first cycle irreversible capacity to 4.3V, no effect to 4.7V

Characterization of $Li[Ni_{0.4}Co_{0.2-y}Al_yMn_{0.4}]O_2$

conductivity and FTIR





Pressed pellet conductivities

σ decreases as Al content increases

y=0: 1.1×10^{-5} S/cm at 75°C

y=0.05: 1.2×10^{-6} S/cm at 75°C

(compare to $LiCoO_2$: 10^{-3} S/cm at RT)

activation energies rise with higher Al content-increased ionicity

FTIR: M-O vibration/bending region

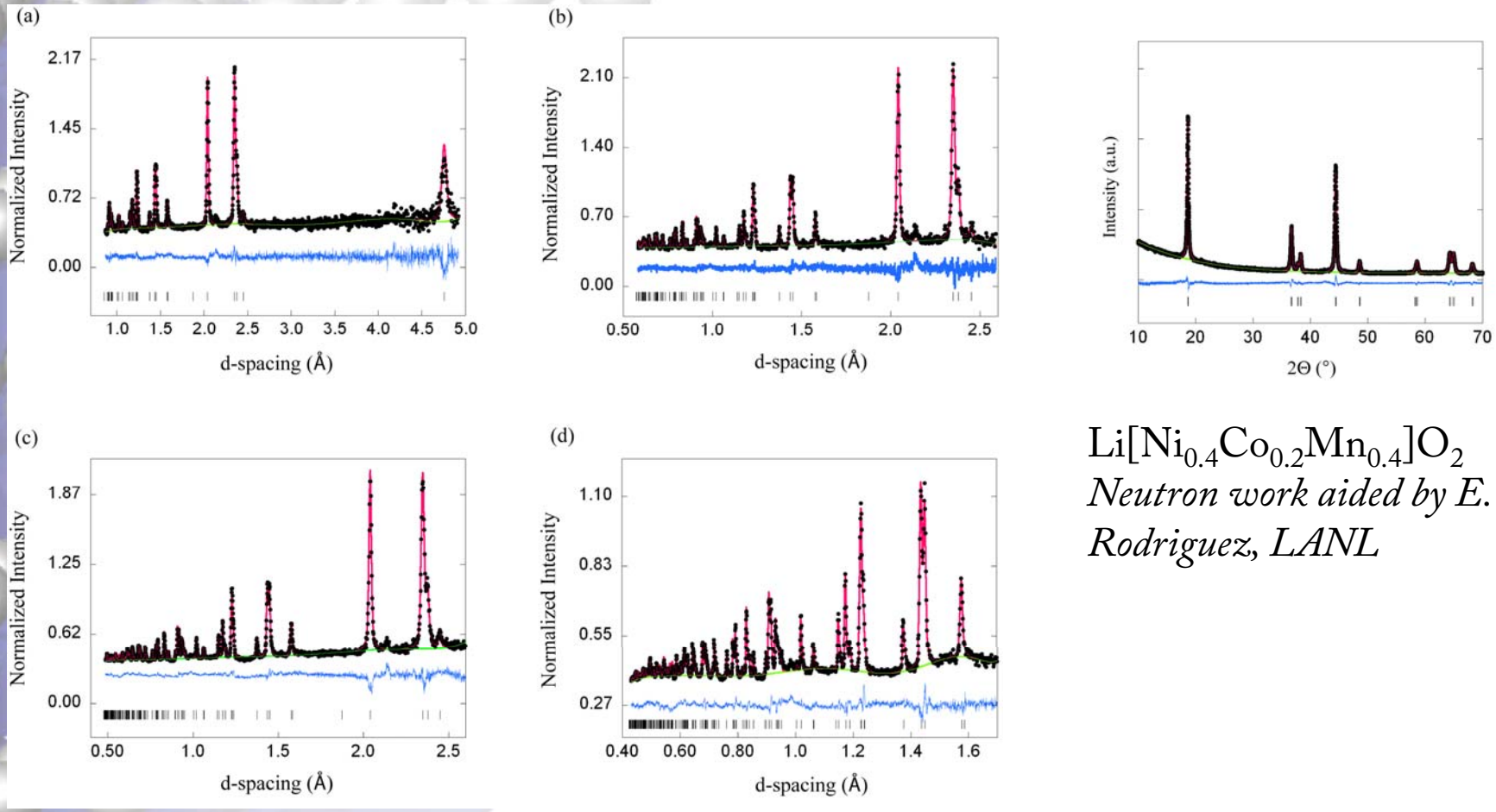
3 modes are predicted

M-O stretch shifts to higher cm^{-1} as Al content increases

O-M-O bends intensify

consistent with changes in unit cell and decreased bond covalency

Combined XRD/Neutron Rietveld Refinements



$Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2$

Neutron work aided by E. Rodriguez, LANL

Structural Parameters

$Li[Ni_{0.4}Co_{0.2-y}Al_yMn_{0.4}]O_2$

Al Content (y)	Unit Cell Parameters a (Å)	Unit Cell Parameters c (Å)	z_{Ox}	Unit Cell Volume (Å^3)	Ni_{3a}	I (LiO_2) (Å)	R_{wp} (%)
0	2.87238(2)	14.2688(2)	0.24165(3)	101.954(2)	0.066(1)	2.616(1)	4.26
0.05	2.87242(2)	14.2729(2)	0.24153(3)	101.987(2)	0.073(1)	2.621(1)	4.46
0.1	2.87169(3)	14.2854(2)	0.24168(3)	102.024(2)	0.075(1)	2.619(1)	4.92
0.15	2.86970(3)	14.2896(3)	0.24159(3)	101.913(2)	0.074(1)	2.622(1)	4.98
0.2	2.86900(2)	14.2993(2)	0.24159(3)	101.932(2)	0.074(1)	2.624(1)	5.35

Slight decrease in a lattice parameter

Slight increase in c lattice parameter

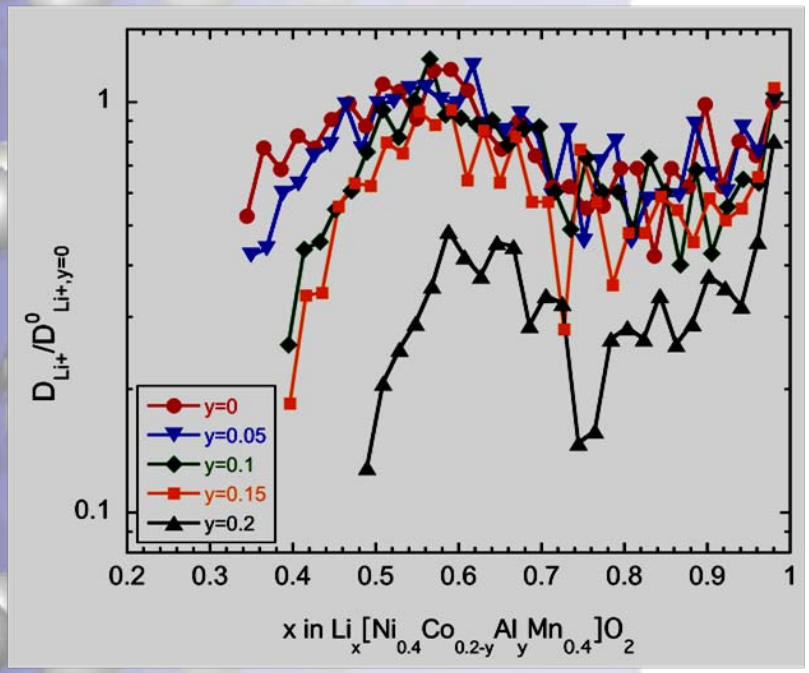
Slight increase in anti-site mixing

Increase in LiO_2 slab spacing

Decreased covalency in T.M plane with Al substitution-shortens M-M distances, weakens LiO bonds, increases c and I(LiO_2)

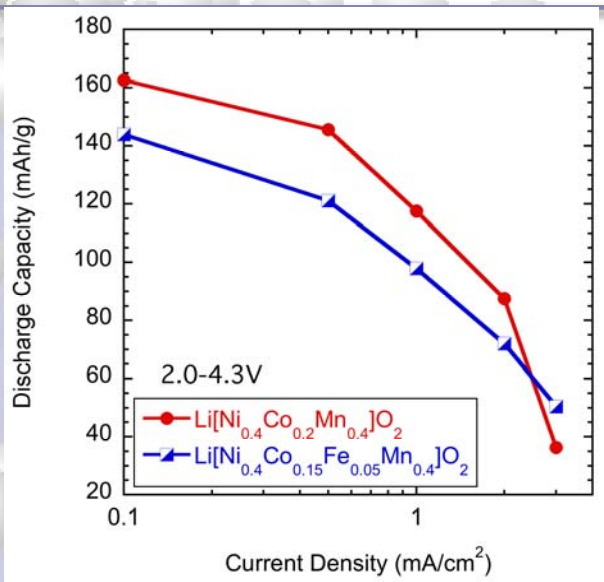
Relative Diffusion Coefficients (GITT)

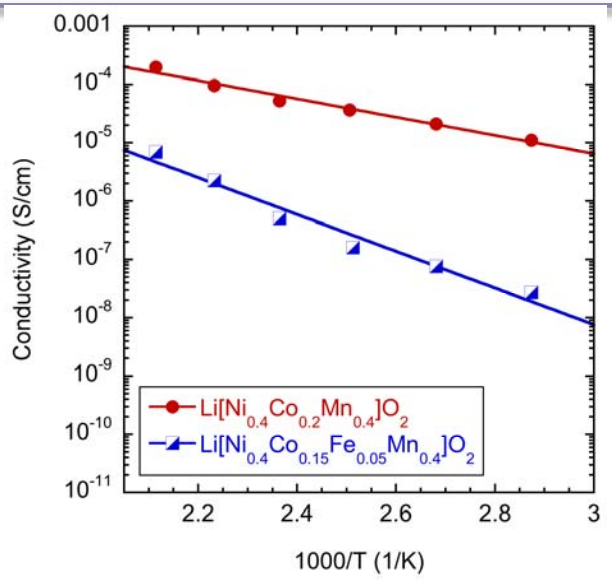
$Li/Li[Ni_{0.4}Co_{0.2-y}Al_yMn_{0.4}]O_2$ cells



- Experiments are ONLY to compare diffusion behavior as function of state-of-charge (x) in $Li_x[Ni_{0.4}Co_{0.2-y}Al_yMn_{0.4}]O_2$
  - Absolute diffusion coefficients not possible to determine with composite electrodes
  - Data normalized w.r.t. parent material, $Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2$
- Materials all exhibit similar behavior
  - Decrease in diffusion rates at low x
  - GITT experiments are slow, deintercalation proceeds further than in constant i charging to 4.3V for Al substituted materials
  - In constant i experiments, Al substitution causes discharge to be limited to compositions with fast Li diffusion

$Li[Ni_{0.4}Co_{0.15}Fe_{0.05}Mn_{0.4}]O_2$





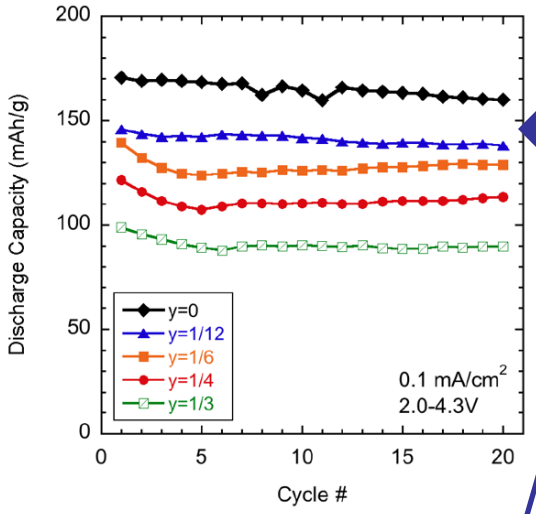
Fe substitution decreases conductivity, reduces capacity, does not improve rate capability, increases first cycle irreversible capacity, has negative impact on cycling behavior

	Ni (3a)	I (LiO_2), Å
$Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2$	0.066(1)	2.616
$Li[Ni_{0.4}Co_{0.15}Fe_{0.05}Mn_{0.4}]O_2$	0.072(1)	2.617

Increase in antisite defects
Li slab dimension unchanged

$Li[Ni_{1/3}Co_{1/3-y}Al_yMn_{1/3}]O_2$

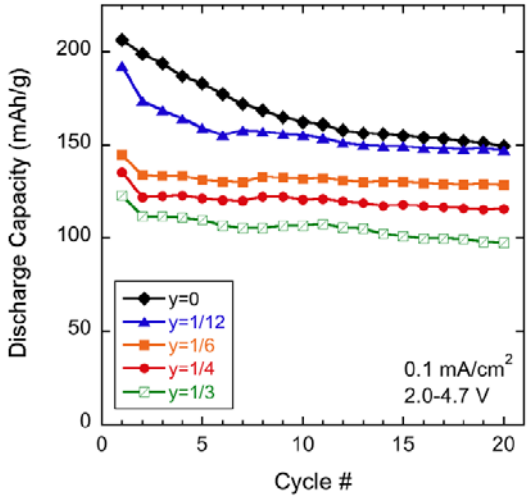
Solid solutions below about y=1/4

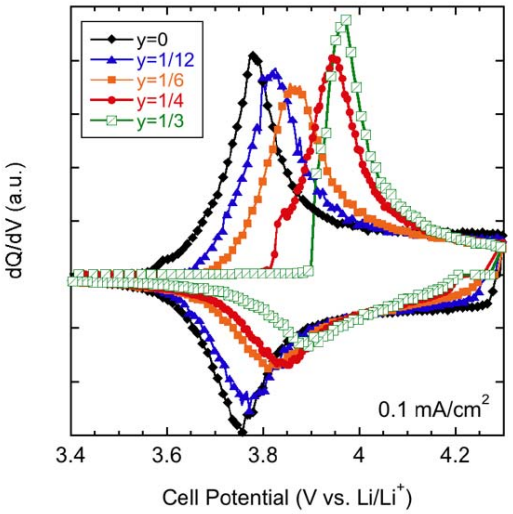


Al substitution reduces capacity

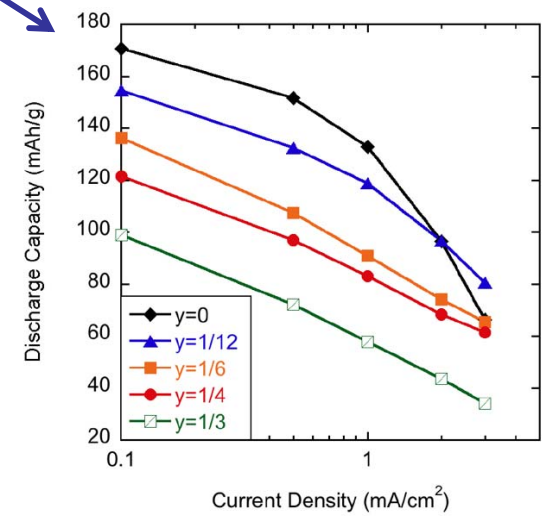
Al shifts potentials positive

Modest improvement in rate capability (rate capability of 3x1/3 is better than 442)

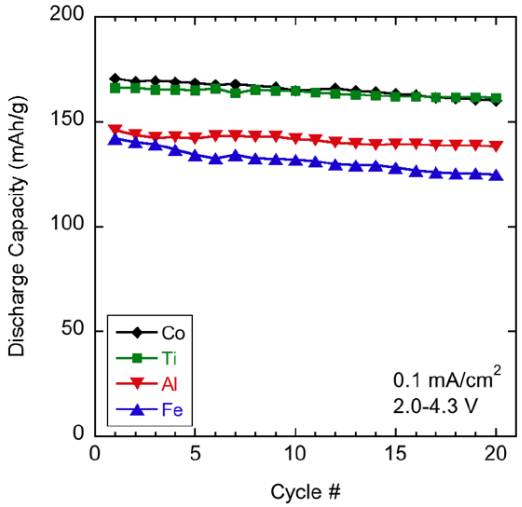


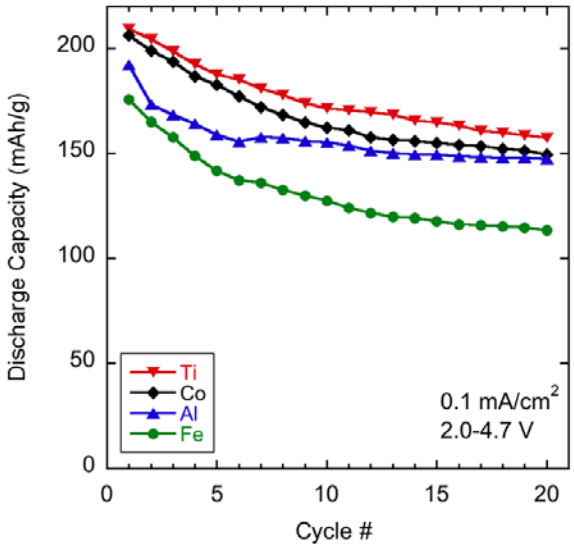


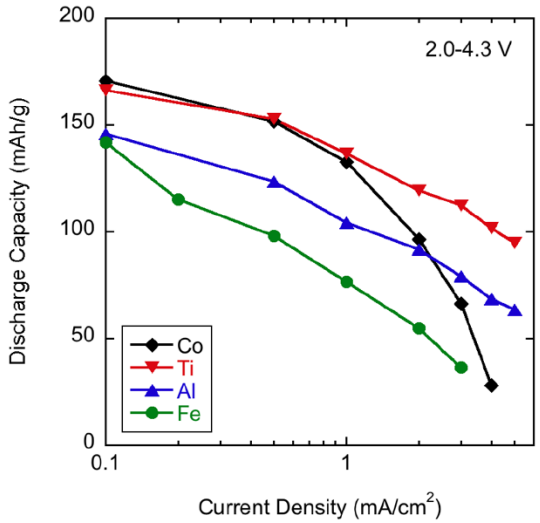
y	I(LiO_2), Å
0	2.59
1/12	2.66
1/6	2.65
1/4	2.64



$Li[Ni_{1/3}Co_{1/4}M_{1/12}Mn_{1/3}]O_2$; M=Al, Ti, Fe







Capacity to 4.7V:Ti>Co>Al>Fe; Capacity to 4.3V: Co≈Ti>Al>Fe

Rate: Ti>Al>Co>Fe; capacity retention: Fe is inferior

Ti^{4+} aliovalent substitution➔electroactive Mn^{3+} adds capacity back in

M	c/3a
Co	1.660
Ti	1.661
Al	1.663
Fe	1.656

c/3a is a measure of lamellarity:
contributions from Ni(3a) and other structural effects

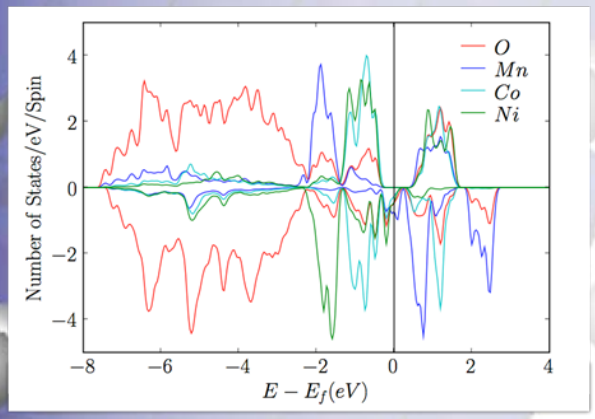
Increase for Ti, Al

Decrease for Fe

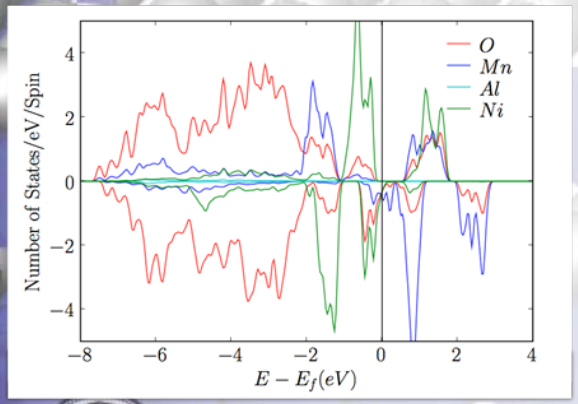
Computational work on Al substitution in $LiMO_2$ systems (K. Persson, M. Kocher)

Density of States Calculations

$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$



$LiNi_{1/3}Al_{1/3}Mn_{1/3}O_2$



As Al is substituted for Co…

- The number of occupied states near the Fermi level decreases.
- This decreases the electrical conductivity…
- and decreases the covalency of the bonding
- The pDOS show no Al occupied states, suggesting ionic Al^{3+}.
- The Bader analysis reveals an increase in the number of electrons associated with O in $LiMn_{1/3}Ni_{1/3}Al_{1/3}O_2$, relative to $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$.
- Oxygen is becoming more ionic (i.e., closer to O^{2-})

Summary and Future Work

$Li[Ni_xCo_{y-w}M_wMn_z]O_2$

- Co content in mixed transition metal oxides can be reduced through judicious substitution (Al, Ti)
  - Substituent need not be electroactive (Fe made things worse!)
  - Changes in electrostatic landscape are influential for structure and diffusivity
    - $I(LiO_2)$ is affected by Ni(3a) amount as well as bonding (degree of covalency)
    - It may not always be necessary to minimize anti-site defects below a certain level
    - Theoretical work by K. Persson and M. Kocher corroborates these results
- Many unanswered questions
  - Effect of state-of-charge on conductivity, $I(LiO_2)$, does Al migrate?
  - How are metals arranged in the transition metal layer?
  - Effect of synthesis parameters
  - Is low level Ti substitution worth pursuing?
- Plan is to continue work on these materials-goal is to reduce Co as much as possible and to achieve an understanding of how best to do that
- Collaborations planned or underway
  - Magnetic measurements (Whittingham, Grey), computation K. Persson
  - NMR (Cabana, Grey), EXAFS (Cairns, Deb, Cramer)