DOE Merit Review
February 25-28, 2008

Synthesis and Characterization of Cathode Materials

Marca M. Doeff
Materials Sciences Division
Lawrence Berkeley National Laboratory
Berkeley, CA 94720
email:mmdoeff@lbl.gov

Purpose of work/Barriers

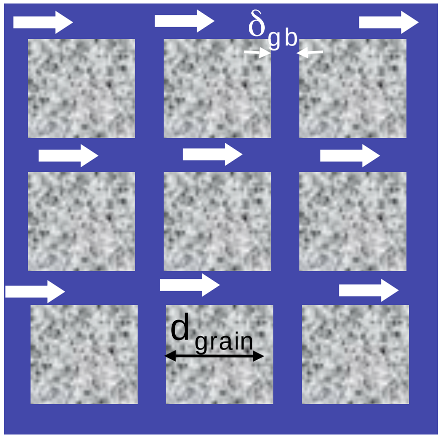
- Develop low-cost cathodes based on benign materials having electrochemical characteristics consistent with vehicular applications (EV, PHEV, HEV)
- High stability (olivines):
  - Barriers: rate capability/energy density ($LiMnPO_4$)
    - optimize carbon coatings-if more conductive, less carbon is needed
    - Less carbon=improved practical energy density (PHEVs)
- High energy (mixed transition metal oxides):
  - Barriers: high cost of Co, rate capability
    - Reduce Co content in $Li[Ni,Co, Mn]O_2$ by substitution
- High voltage (manganese oxides):
  - Barriers: compatibility with electrolyte, dissolution
    - Investigate compatibility with room temperature ionic liquids (RTILs) having stability windows in excess of 5V.

Approach-olivines

The bricklayer model

A composite material in a dense pellet

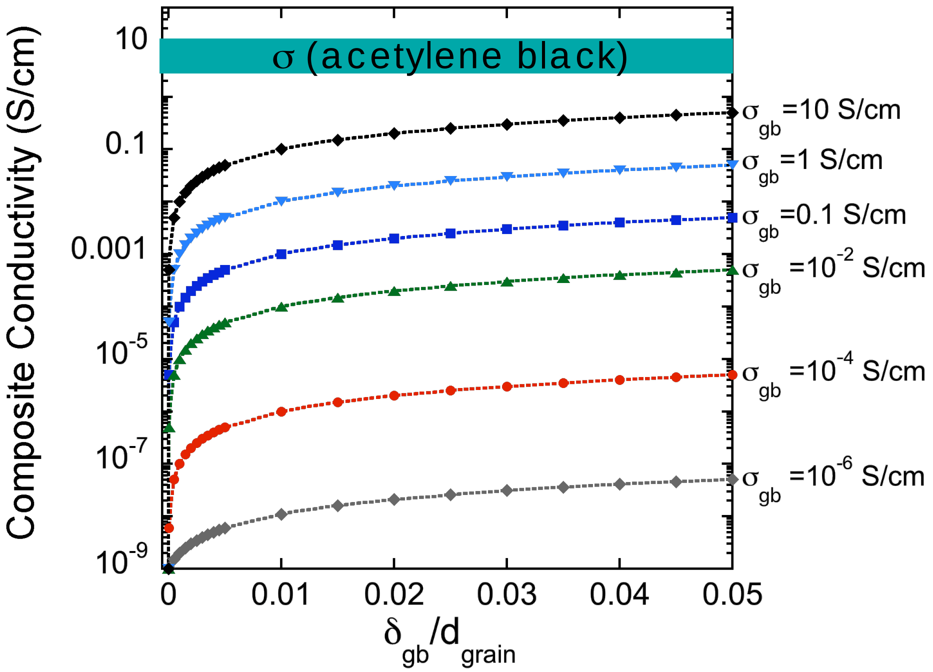
i



When $s_{gb} >> s_{bulk}$ and $d_{gb} << d_{grain}$:

$$\sigma_{composite} = (1 + \frac{\sigma_{gb}}{\sigma_{bulk}} \frac{\delta_{gb}}{d_{grain}})\sigma_{bulk}$$

For $\sigma_{bulk} = 10^{-9}$ S/cm



✳ **rapidly diminishing returns as g.b. phase amount is increased**

✳ increasing σ_{gb} has big impact!

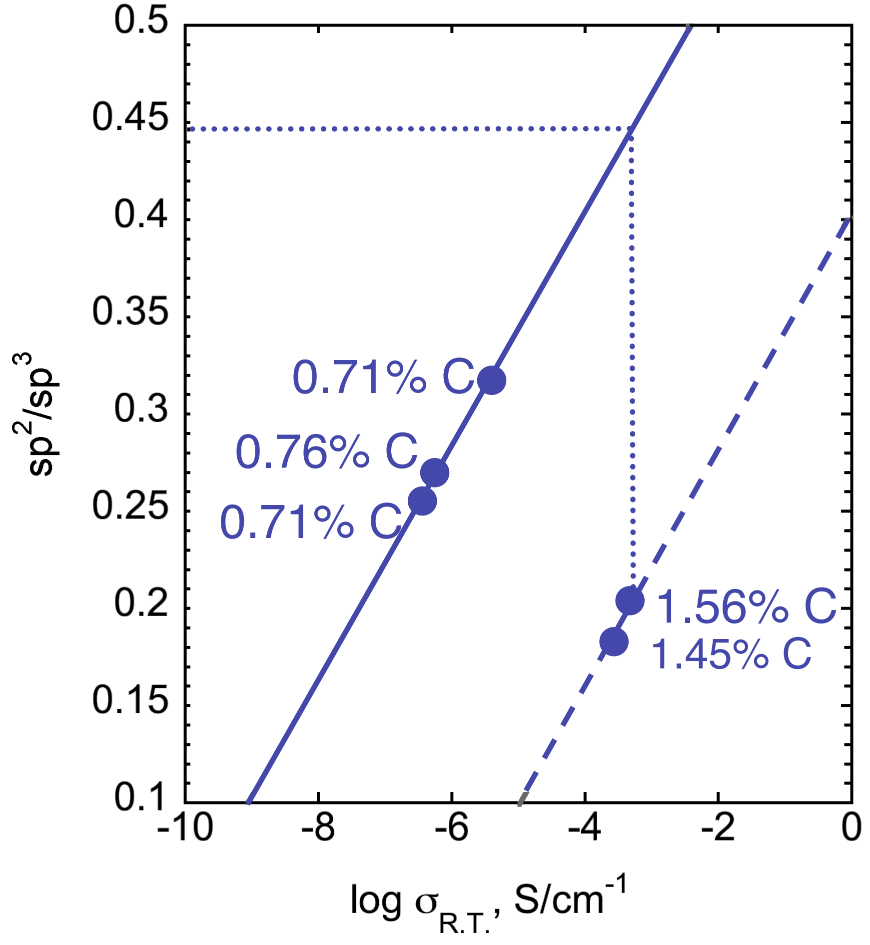
✳Use graphitization catalysts to improve structure of carbon in coatings (conductivity)

✳More effective than increasing C amount

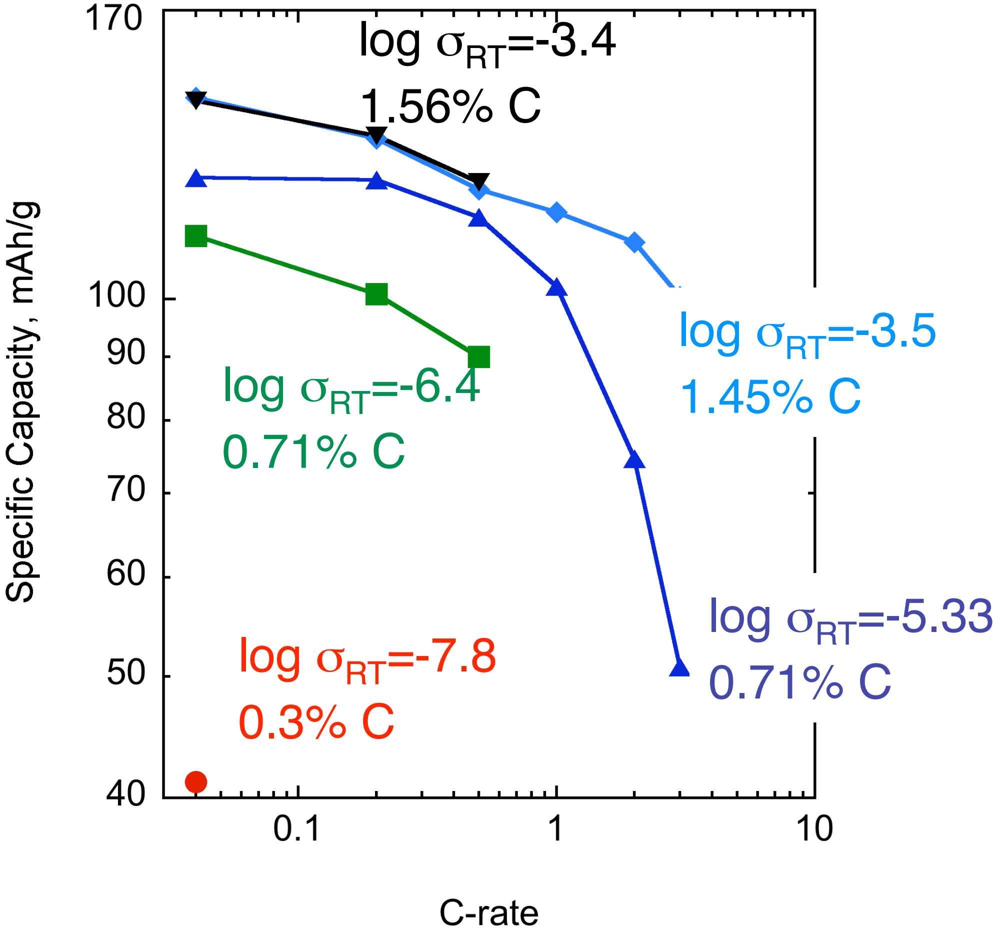
Results-olivines

DOE Merit Review
February 25-28, 2008

- Composite conductivity depends on C structure, not amount



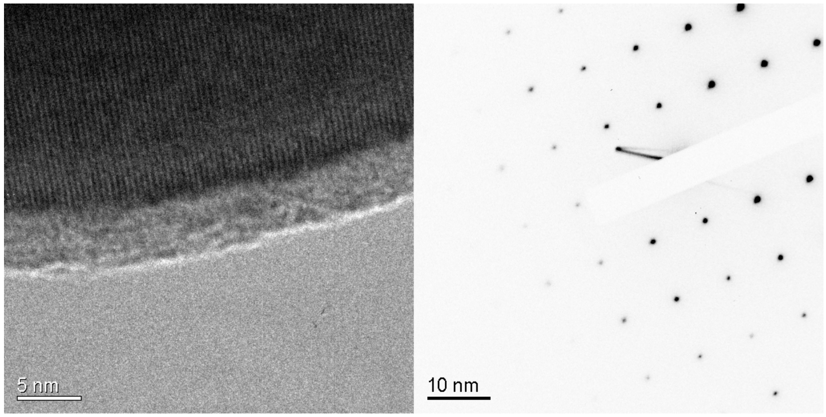
Rate capability in Li cells



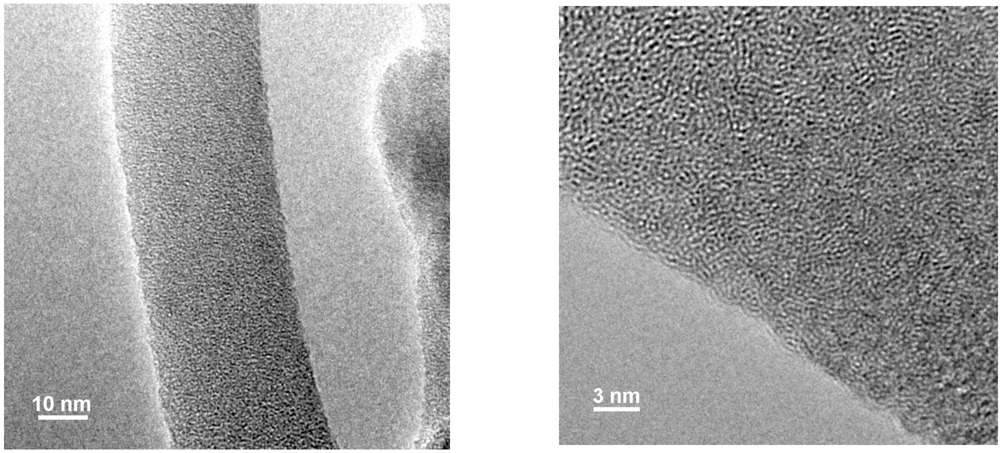
- performance in Li cells scales with composite conductivity

Collaboration with R. Kostecki, LBNL

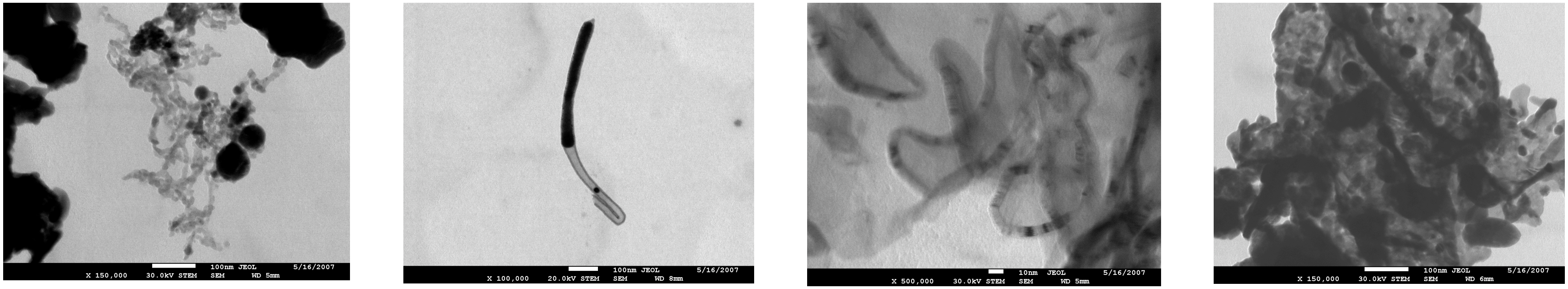
Results-olivines



Carbon coating on $LiFePO_4$ particle after 100 cycles



Amorphous carbon fibers in $LiFePO_4$ sample



Carbon nanotubes in $LiFePO_4$ sample

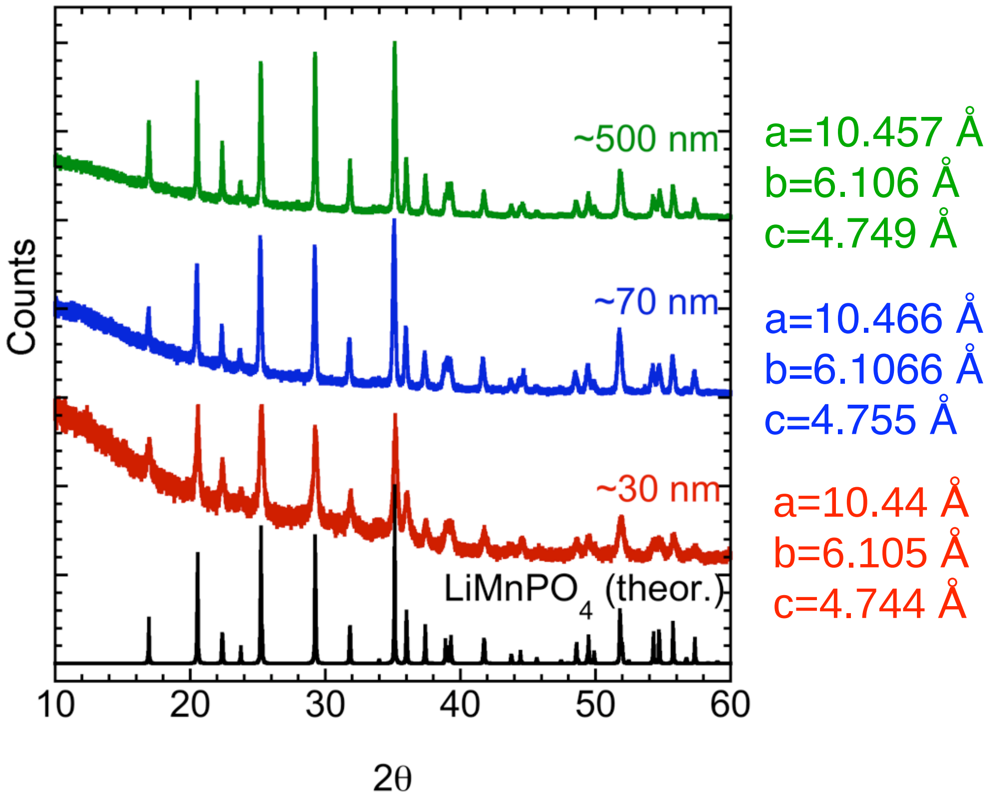
- Fibers and nanotubes enhance performance
- Coatings stay intact throughout cycling

Collaborations with H. Gabrisch (U. of New Orleans)
R. Yu (LBNL) and JEOL, USA, Pleasanton, CA

Technology transfer/Future work-olivines

- Tech transfer
  - Patent filed on carbon coating technology
  - In negotiations with Bay Area company for co-development agreement/ licensing

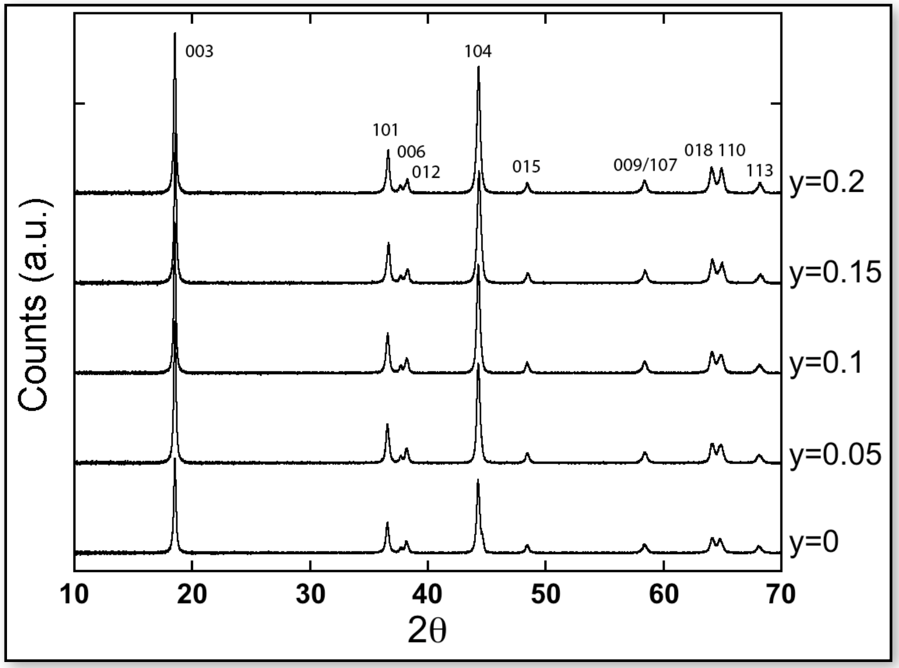
- Future Work-next fiscal year
  - successful synthesis of nano-$LiMnPO_4$
  - HPL $LiMnPO_4$ (35 nm)-100 mAh/g (C)
  - can't get much smaller!
  - use C-coating technology to improve performance



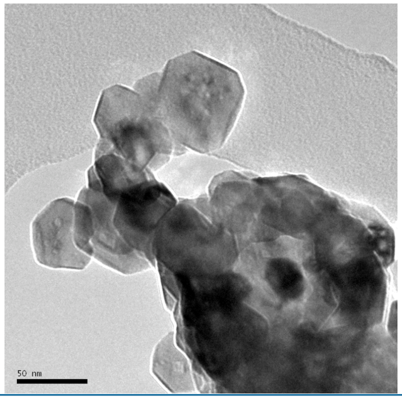
Approach-layered mixed transition metal oxides

- Rate capability of Li[Ni, Co, Mn]O_2 is better than $LiNi_{0.5}Mn_{0.5}O_2$ but Co is expensive
- For $Li_{1-x}[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$
  - $Co^{3+} \leftrightarrow Co^{4+}$ redox occurs mainly between $2/3 \leq x \leq 1$ (e.g., above 4.3V)
    - XANES study-Cairns et al., J. Electrochem. Soc. 154 A534 (2007).
  - Best cycling results below ~4.3V vs Li/Li^+ (electrolyte oxidation a concern)
- Replacing all or some Co with something cheaper may not impact capacity below 4.3V vs. Li
- In FY2007, survey of Li[Ni, Co, M, Mn]O_2 (M=Fe, Al) was carried out
  - most interesting results with $Li[Ni_{0.4}Co_{0.2-y}Al_yMn_{0.4}]O_2$ system
  - $Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2$-Whittingham et. al, J. Mater. Chem. 14 214 (2004).

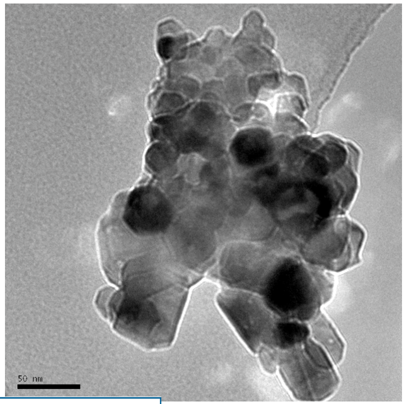
Results-$Li[Ni_{0.4}Co_{0.2-y}Al_yMn_{0.4}]O_2$



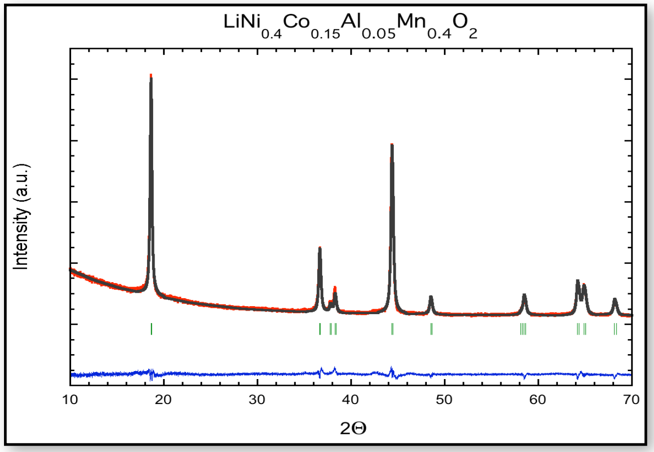
y=0

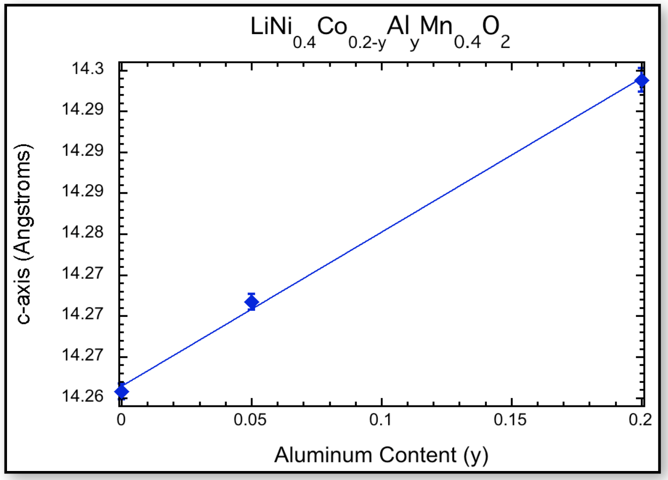


y=0.20

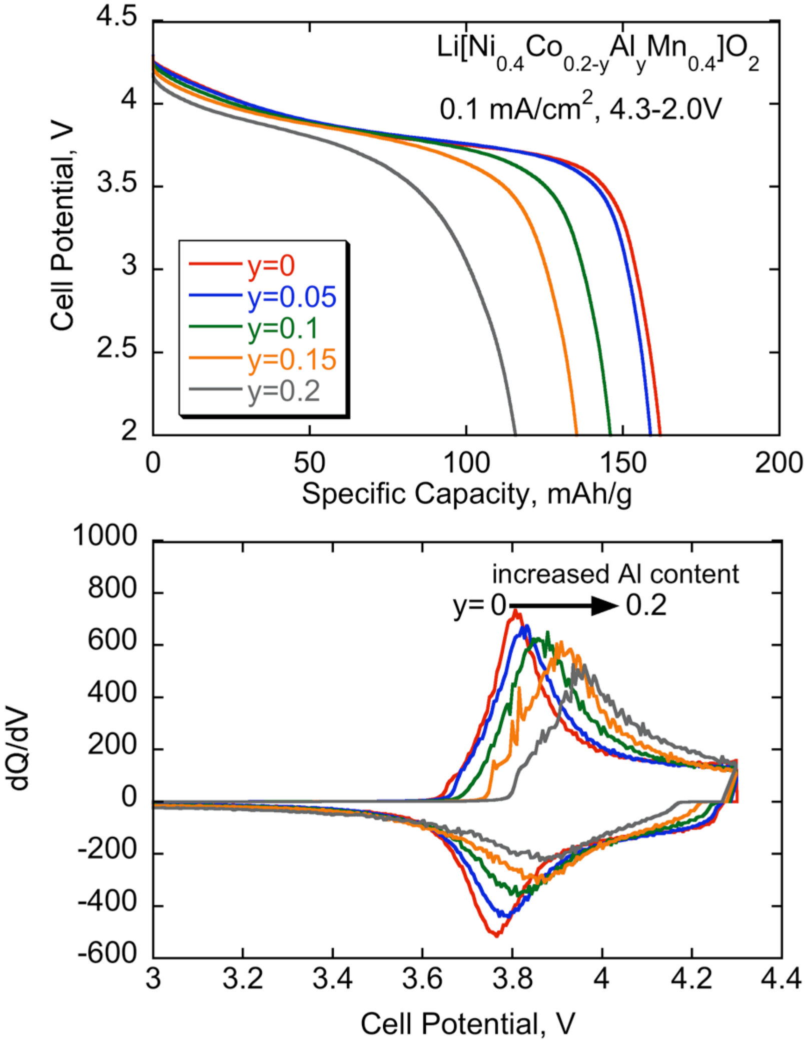


- Solid solutions are formed over entire range
- No changes in particle morphologies
- Cation mixing decreases from ~4% (y=0) to ~2.5% (y=0.2)
- c-axis increases with higher y
- lithium slab dimension increases with higher y

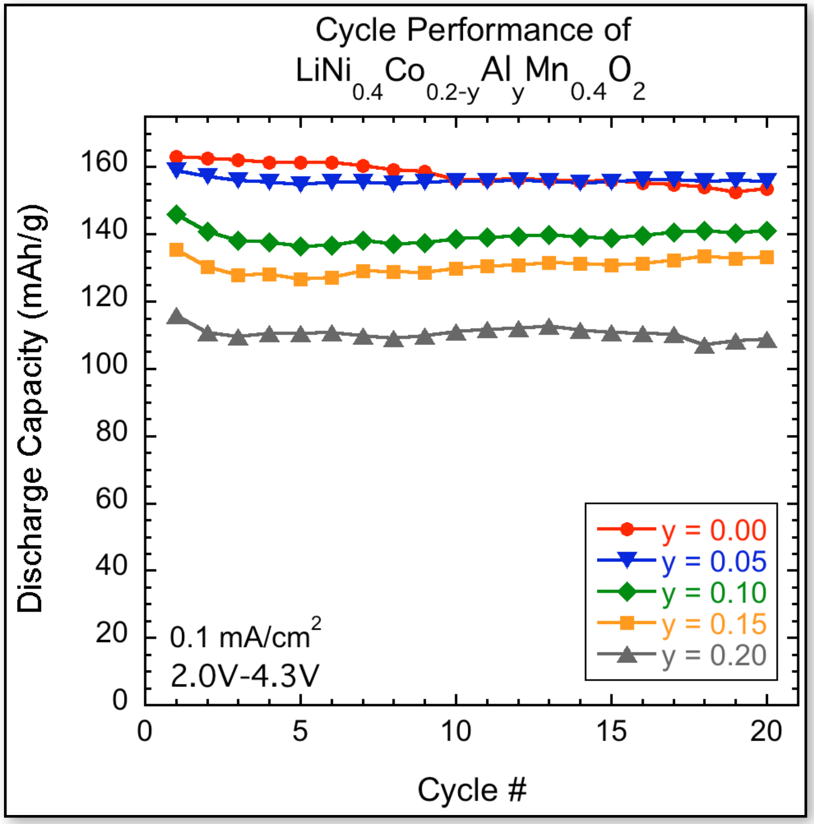




Results-Li[$Ni_{0.4}Co_{0.2-y}Al_yMn_{0.4}$]$O_2$

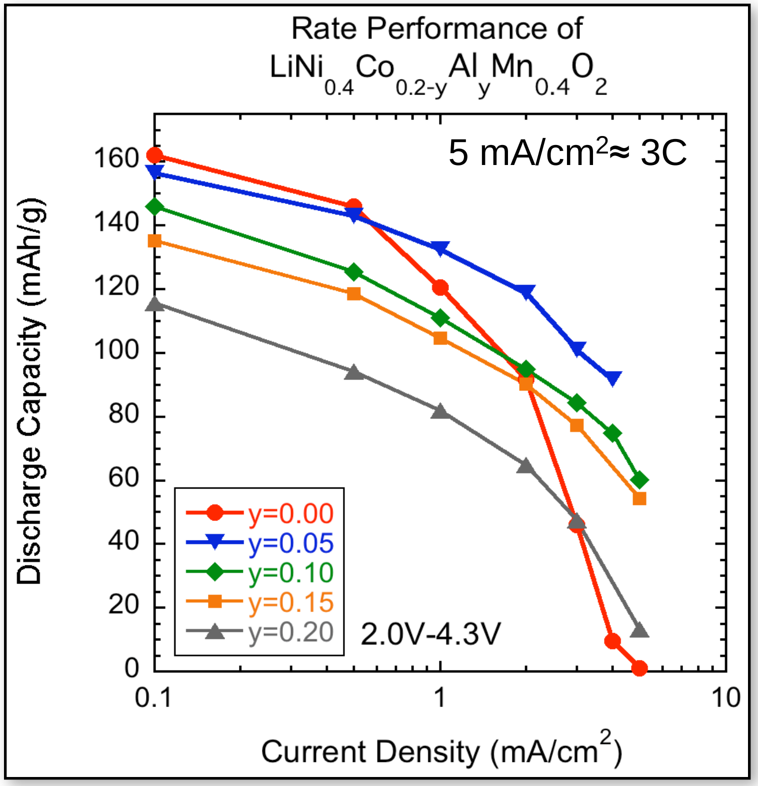


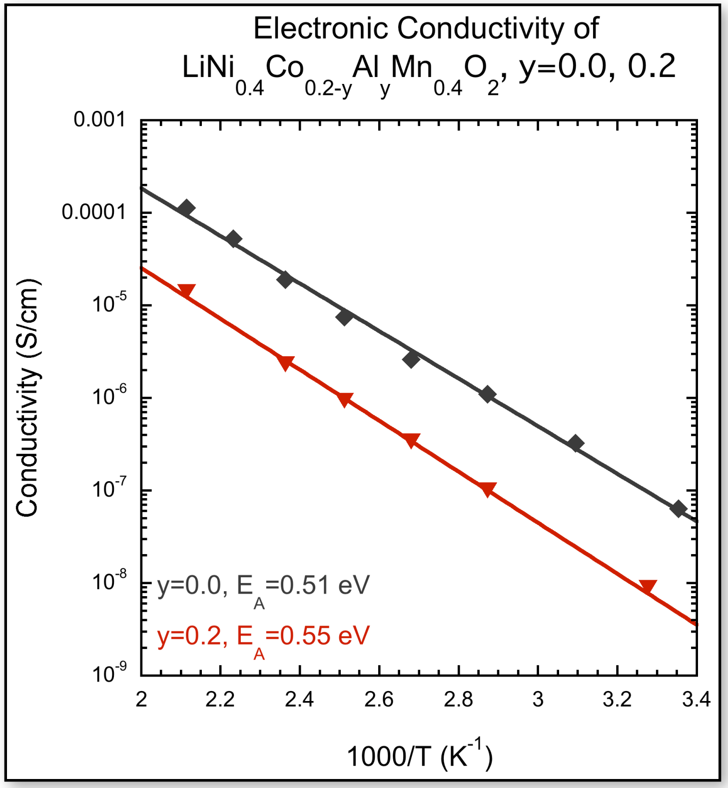
- •All samples cycle well between 2.0-4.3V
- •Capacity decreases with higher Al content
- •Al substitution shifts voltage profiles higher
- •Very little impact on capacity for y=0.05



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

DOE Merit Review
February 25-28, 2008





Al-substitution greatly improves rate capability
Best results with y=0.05
Not a particle size effect
Al-substitution decreases electronic conductivity
Effect must involve Li ion diffusion rates (structural effects)

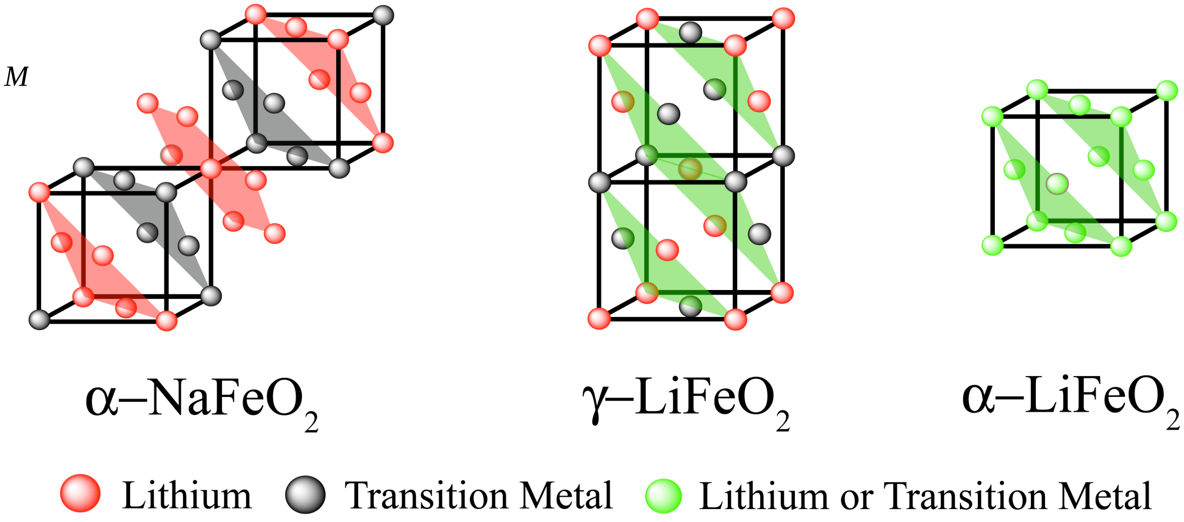
Relating Ionic Radius and Structure

Cation	Ionic Radius[1] (Å)	M^{3+}/Li^{+} Radius Ratio	Structure (Experimental)[2]
Er^{3+}	0.89	1.17	γ-$LiFeO_2$
Tm^{3+}	0.88	1.16	γ-$LiFeO_2$
Yb^{3+}	0.868	1.14	γ-$LiFeO_2$
Lu^{3+}	0.861	1.13	γ-$LiFeO_2$
In^{3+}	0.8	1.05	γ-$LiFeO_2$
Li^{+}	0.76	1.00	--
Sc^{3+}	0.745	0.98	γ-$LiFeO_2$
Mo^{3+}	0.69	0.91	α-$NaFeO_2$
Rh^{3+}	0.665	0.88	α-$NaFeO_2$
Fe^{3+}	0.645	0.85	γ-$LiFeO_2$
V^{3+}	0.64	0.84	α-$NaFeO_2$
Cr^{3+}	0.615	0.81	α-$NaFeO_2$
Ni^{3+}	0.6	0.79	α-$NaFeO_2$
Co^{3+}	0.545	0.72	α-$NaFeO_2$
Al^{3+}	0.535	0.70	α-$NaFeO_2$

Decreasing


Rock Salt

Layered



---

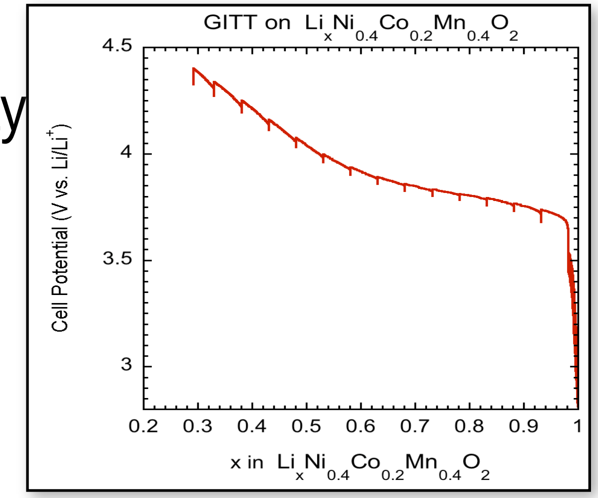
[1] R. D. Shannon, *Acta Crystallographica Section A*, **32**, 751 (1976).

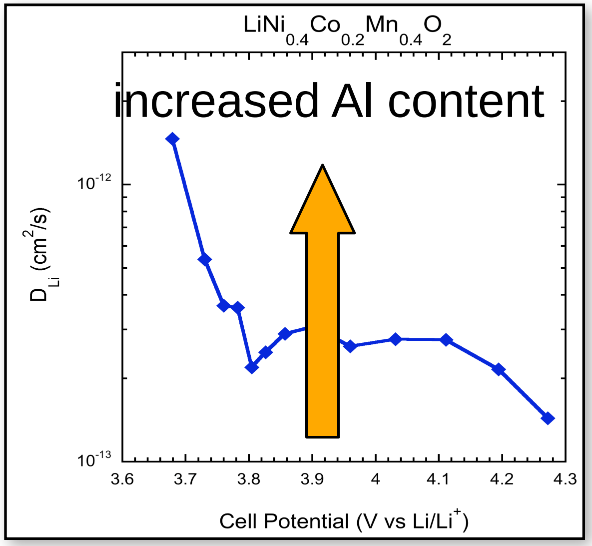
[2] E. J. Wu, P. D. Tepesch and G. Ceder, *Philos. Mag. B-Phys. Condens. M*

BERKELEY LAB
75 Years of World-Class Science 1931-2006

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

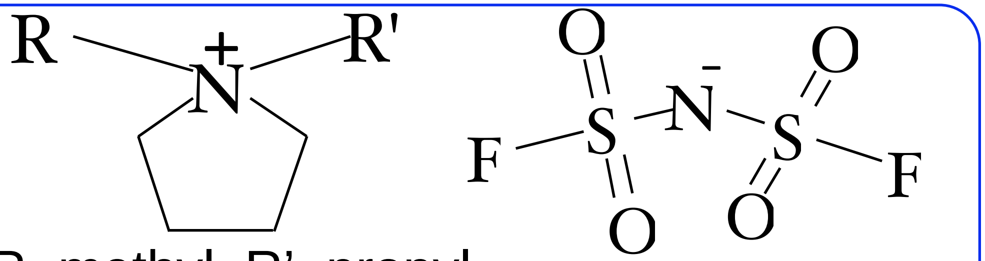
- Elucidate origin of rate enhancement (w. V. Srinivasan, LBNL)
  - GITT experiments-diffusion rates
  - Chronopotentiometry-ionic vs electronic conductivity
    - ion-blocking electrodes (Ti)
    - electron-blocking electrodes (LiI/Li)
- Further Structural Characterization
  - neutron diffraction
  - EXAFS/XANES (w. E. Cairns, LBNL)
- Thermal characterization ?
  - does Al improve thermal stability?





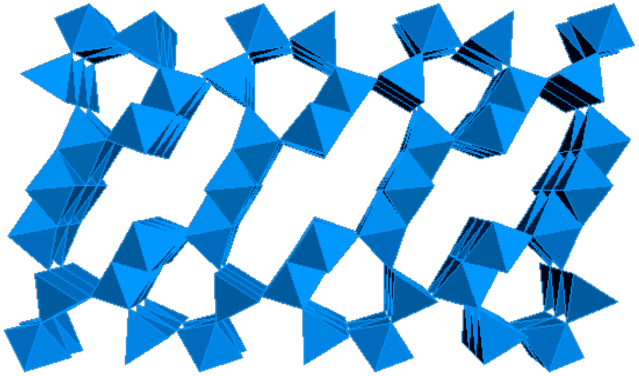
Approach-high voltage electrodes

- High voltage electrodes cannot be utilized fully due to incompatibility with conventional electrolytes
- Room temperature ionic liquids (RTILs) a possible solution?
- P_{13}FSI (K. Zaghib, HQ)
  - >5V stability window
  - stable vs. Li (half cell possible)
  - highly conductive, can operate cells at R.T. at moderate currents

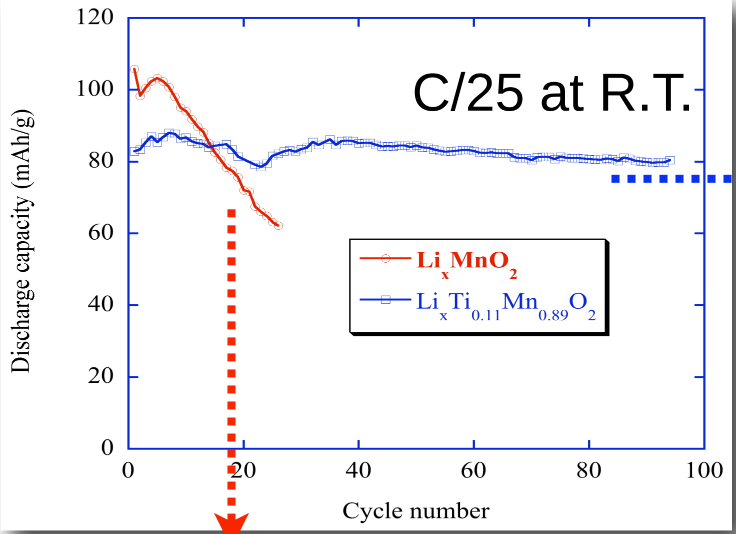


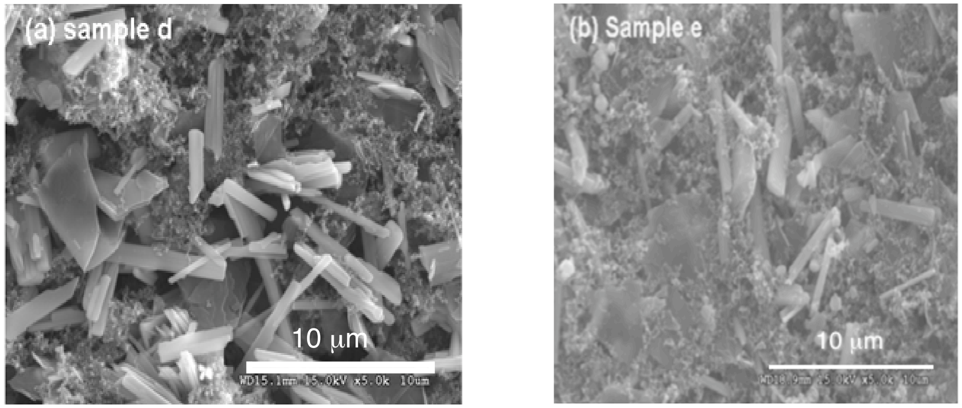
R=methyl, R'=propyl

- Choose cathodes carefully (cointercalation into layered materials)
  - tunnel Li_xMnO_2
  - theor. cap. 193 mAh/g
  - ~60 mAh/g above 4V
  - v. stable cycling in conventional electrolytes and polymer electrolytes



Results-Li_xMnO_2 +$P_{13}FSI$

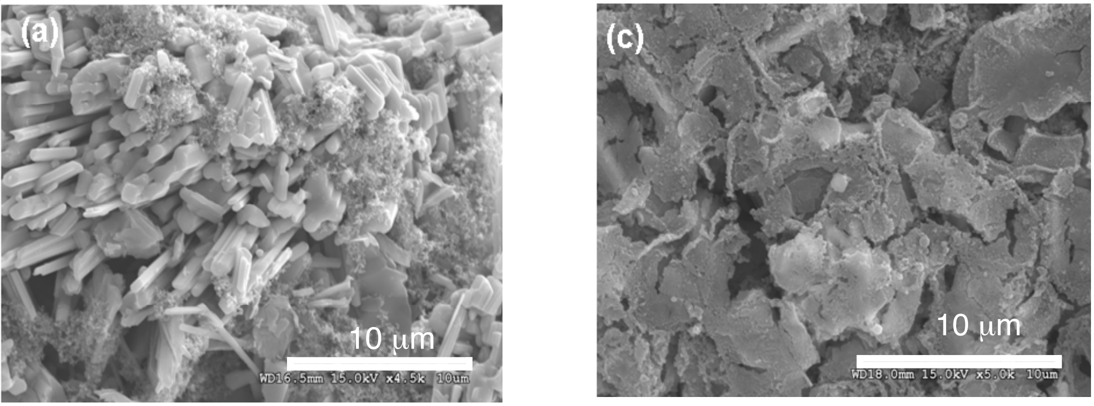




Fresh electrode

Cycled 450 hours

$Li_xTi_{0.11}Mn_{0.89}O_2$



Fresh electrode

Cycled 450 hours

Li_xMnO_2

- Li_xMnO_2 undergoes a dissolution/precipitation process during cycling in cells containing RTILs, causing capacity fading
- Partial Ti-substitution prevents dissolution in RTIL
- $Li_xTi_{0.11}Mn_{0.89}O_2$ cycles stably

Collaboration with J. Kerr (LBNL)
and A. Hollenkamp (CSIRO, Australia)

Future work-Li_xMnO_2 +P_{13}FSI

- No future plans for further cell development
- Raman and FTIR investigations of cycled electrodes (with R. Kostecki, LBNL)
  - What is the origin of protective effect of Ti?
    - Ti substitution also prevents Mn dissolution in $LiPF_6$ electrolyte solutions at elevated temperatures
  - What happens to P_{13}FSI upon cycling?

Publications, Presentations, Patents

- Selected Publications (mid-2006-2008)

1. “Electrode Materials with the $Na_{0.44}MnO_2$ Structure: Effect of Titanium Substitution on Physical and Electrochemical Properties”, J.A. Saint, J.D. Wilcox and M.M. Doeff, Chem. Mater. submitted (2008).
2. "TEM Study of Fracturing in Spherical and Plate-Like $LiFePO_4$ Particles", H. Gabrisch, J. Wilcox and M. M. Doeff, Electrochem. and Sol. State Lett., 11, A25 (2008).
3. "Compatibility of $Li_xTi_yMn_{1-y}O_2$ (y=0, 0.11) Electrode Materials with Pyrrolidinium-based Ionic Liquid Electrolyte Systems", Juliette Saint, A.S. Best, A. F. Hollenkamp, J. Kerr, J.-H. Shin, and M. M. Doeff, J. Electrochem. Soc. 155, A172 (2008).
4. "Impact of Carbon Structure and Morphology on the Electrochemical Performance of $LiFePO_4$ Composites", Marca M. Doeff, James D. Wilcox, Rong Yu, Albert Aumentado, Marek Marcinek, and Robert Kostecki, J. Solid State Electrochem. in press (2007).
5. "Synthesis and Electrochemistry of Li_3MnO_4: Mn in the +5 Oxidation State", Juliette A. Saint, Marca M. Doeff, and John Reed, J. Power Sources, 172, 189 (2007).
6. “Factors Influencing the Quality of Carbon Coatings on $LiFePO_4$”, James D. Wilcox, Marca M. Doeff, Marek Marcinek, and Robert Kostecki, J. Electrochem. Soc., 154, A389 (2007).
7. “Effect of Structure on the Storage Characteristics of Manganese Oxide Electrode Materials” Yong Joon Park and Marca M. Doeff, J. Power Sources, 165, 573, (2007).
8. “Carbon Surface Layers on a High-Rate $LiFePO_4$” Heike Gabrisch, James D. Wilcox, and Marca M. Doeff, Electrochem. and Sol. State Lett., 9, A360 (2006).
9. “Synthesis and Characterization of $M_2Mn_3O_8$ (M=Ca, Cu) Compounds and Derivatives” Yong Joon Park and Marca M. Doeff, Solid State Ionics, 177, 893 (2006).
10. “Optimization of Carbon Coatings on $LiFePO_4$”, Marca M. Doeff, James D. Wilcox, Robert Kostecki and Grace Lau, J. Power Sources, 163, 180 (2006).

Publications, Presentations, Patents

- Selected Presentations (mid 2006-2007)
  - "Batteries for Vehicular Applications: The Materials Challenge", given at the University of New Orleans Advanced Materials Research Institute, New Orleans, LA, October 12, 2007.
  - "The Impact of Carbon Structure and Morphology on the Electrochemical Performance of $LiFePO_4$/C Composites" International Conference on Materials For Advanced Technologies, July 2007, Singapore.
  - “Co-synthesis of $LiFePO_4$ and Carbon Nanotubes” 2006 Joint International Meeting of the Electrochemical Society (ECS) and Sociedad Iberoamericana de Electroquimica, Cancun, Mexico, October, 2006, Vol 2006-2 Abstract 230.
- Patents
  - “Optimization of Carbon Coatings on $LiFePO_4$” M. M. Doeff, J. D. Wilcox, R. Kostecki, G. Y. Lau. IB2289P, provisional filed June 13, 2006. Full patent application filed June 12, 2007.

Summary

- Olivines
  - amount of C in $LiMPO_4$/C composites can be reduced by optimization of carbon structure, reducing energy density penalty
  - Technology transfer of carbon coating technology to Bay Area company
  - Can't reduce $LiMnPO_4$ particle size further, must improve C to realize improved rate capability
- Layered mixed transition metal oxides
  - Co content was reduced by partial Al substitution, lowering cost
  - $Li[Ni_{0.4}Co_{0.15}Al_{0.05}Mn_{0.4}]O_2$ performance is comparable to $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ but Co content is less than 1/2
  - Rate capability is enhanced due to reduced ion-mixing
- High Voltage Manganese Oxides/RTILs
  - used Ti substitution to improve dissolution resistance

Acknowledgments

- DOE-BATT
- James Wilcox, graduate student (olivines, layered T. M. oxides)
- Juliette Saint, postdoc 2006-2007 (high voltage cathodes +RTILs)
- Jack Chen, postdoc 2007-current ($LiMnPO_4$)
- Albert Aumentado, undergraduate student (olivines)
- Collaborators
  - R. Kostecki, J. Kerr, V. Srinivasan, R. Yu, E. Cairns (LBNL)
  - H. Gabrisch (UNO)
  - T. Hollenkamp (CSIRO)
  - K. Zaghib (HQ)