

## 2008 DOE Peer Review Presentation

# First Principles Calculations and NMR Spectroscopy of Cathode Materials

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Feb 2008

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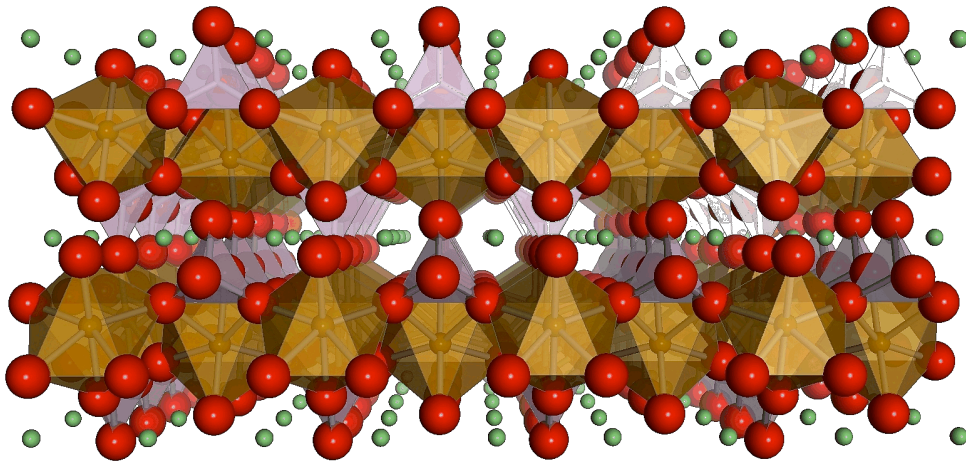
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# Objectives and Materials Focus

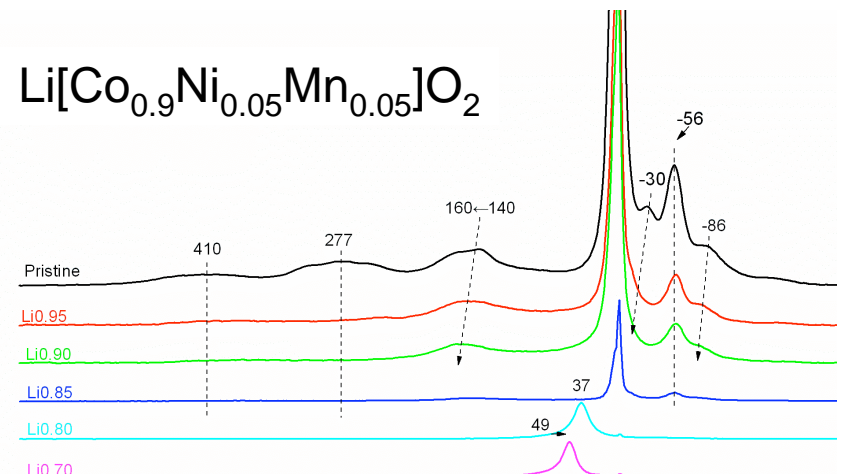
**OBJECTIVES:** Determine the effect of structure on stability of electrode materials. Explore rate limitations and relation to structure and particle size/morphology.

**APPROACH:** Use first-principles computations, NMR, and other characterization methods to characterize materials and relate to performance

## Atomic-level detail from modeling



## Local structure from experiment



**Phosphates** for low cost high performance ( $\text{LiMPO}_4$ ,  $M = \text{Fe}, \text{Mn}, \text{Co}, \text{Ni}, \text{etc.}$ )

- reasonable energy density
- high stability
- good rate achievable in  $\text{LiFePO}_4$  (not in others ?)

**Layered  $\text{Li}(\text{Ni}, \text{Mn}, \text{Co})\text{O}_2$**  with low Co content for high energy density and low cost

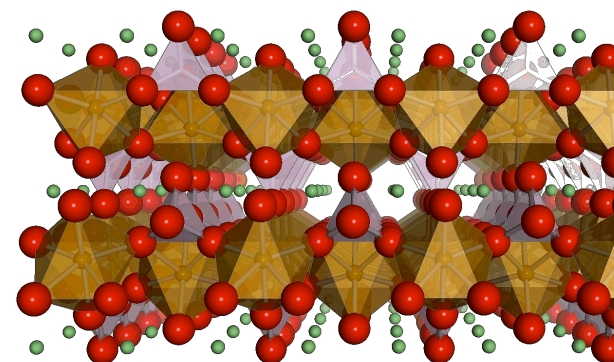
- $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$  has excellent thermal stability and  $> 200$  mAh/g capacity, but local structure key to rate performance
- Co addition has marked influence on structure and rate performance, but increases cost and reduces thermal stability

# Accomplishments

- Computationally investigated quaternary **phase diagram** of **Li-Fe-O-P** to understand synthesis and thermal stability
- Investigated effect of **surface** and **particle size** (underway) on electrochemical properties:  $\text{LiFePO}_4$  and  $\text{LiMnPO}_4$  (underway)
- Identified several **key physical processes** that affect **rate** in olivines
- Developed  $\text{LiFePO}_4$  capable up to **400 C rate** discharge through standard sintering process
- Investigated electrochemical behavior of metal oxide and metal sulfide **nanoparticles**, **nanostructures**, **nanotubes** and **nanowires** (underway)
- Developed methodology to **predict thermal stability** in charged cathodes
- Optimized **ion-exchanged methods** for “ideal”  $\text{Li}(\text{MnNi})_{0.5}\text{O}_2$
- Identified **high voltage processes** in “Li-excess” lithium nickel manganates
- Used a combination of pair-distribution function (**PDF**) and **NMR** methods to **determine structure** and explain the electrochemical processes in  $\text{Li}[\text{Co}_{1-2x}\text{Mn}_x\text{Ni}_x]\text{O}_2$
- Built and tested **in situ NMR probe** to allow **real-time studies** of batteries



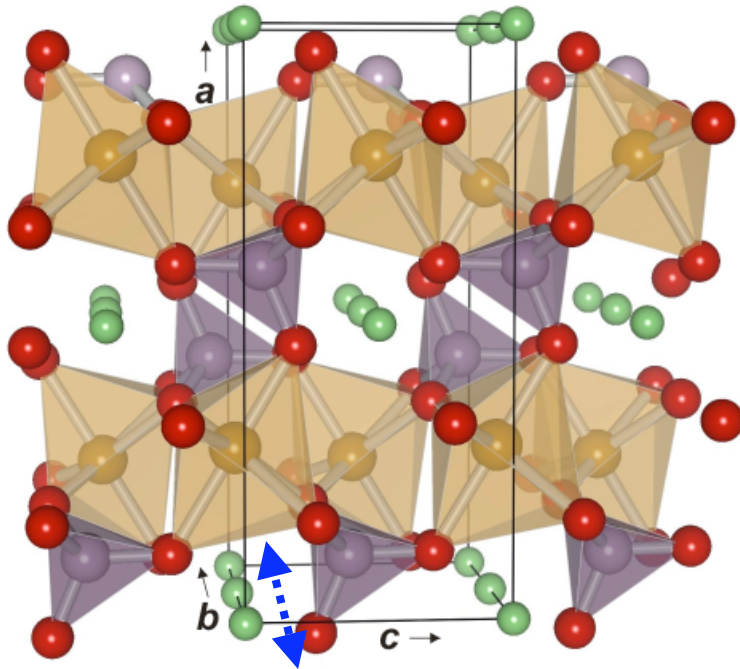
## Key questions



- What are the mechanisms that limit transport ?
- Why/how are the different phosphates (e.g., M = Fe and Mn) different ?
- How is nano different ?

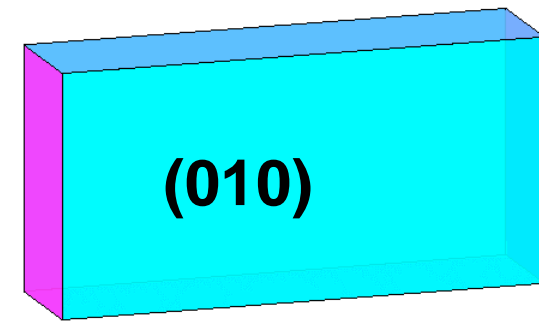
# Olivine Phosphates: Transport Issues

Diffusion is one-dimensional in all olivines

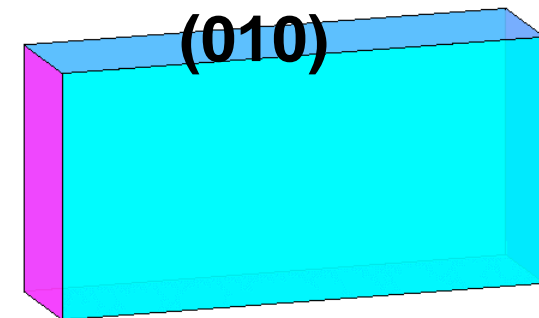


Consequences for Crystal Morphology effect on rate

Good



Bad



Result from first principles calculations

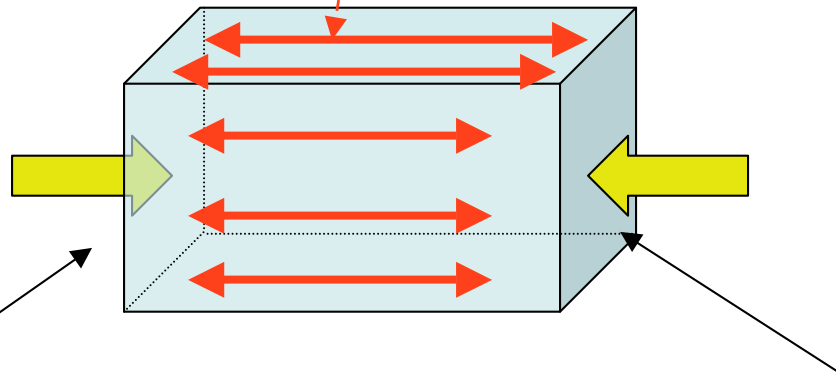
Along the  $a$ -axis:  $E_a > 1$  eV

Along the  $c$ -axis:  $E_a > 1$  eV

Along the  $b$ -axis:  $E_a$  is low (200-300 meV)

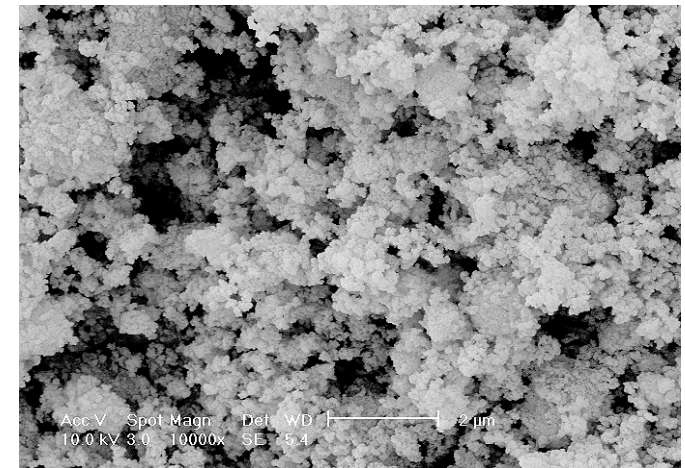
**migration time to go 50 nm  $\approx$  1 ms**

On other surfaces Li has to move over surface to the sides

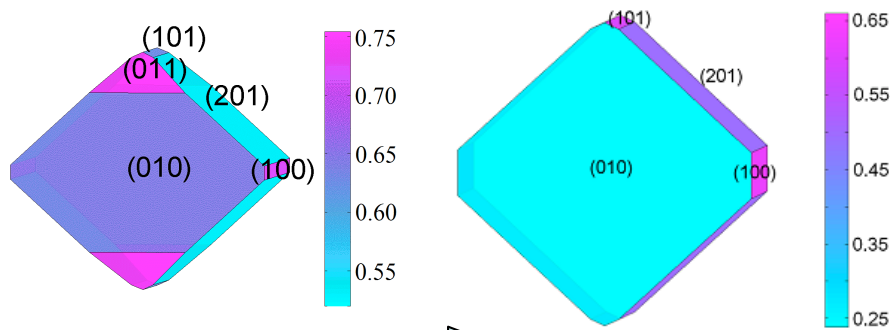


Li can only penetrate particle through these sides

Make nanoparticles

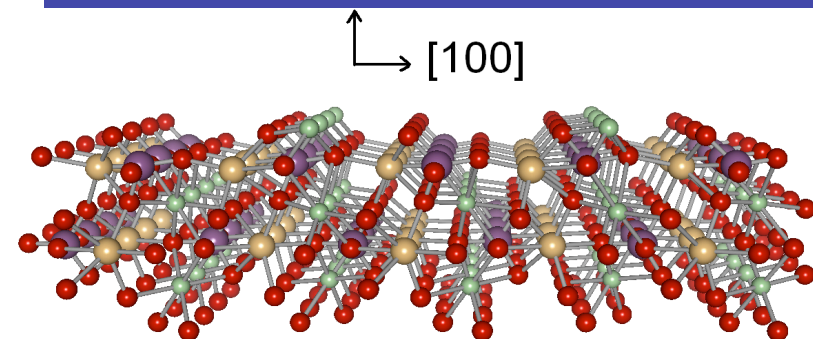


Optimize particle shape (surface energies !)



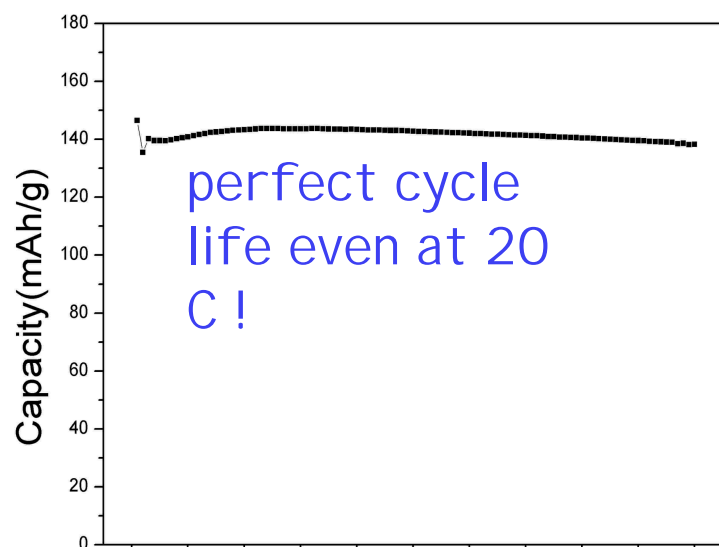
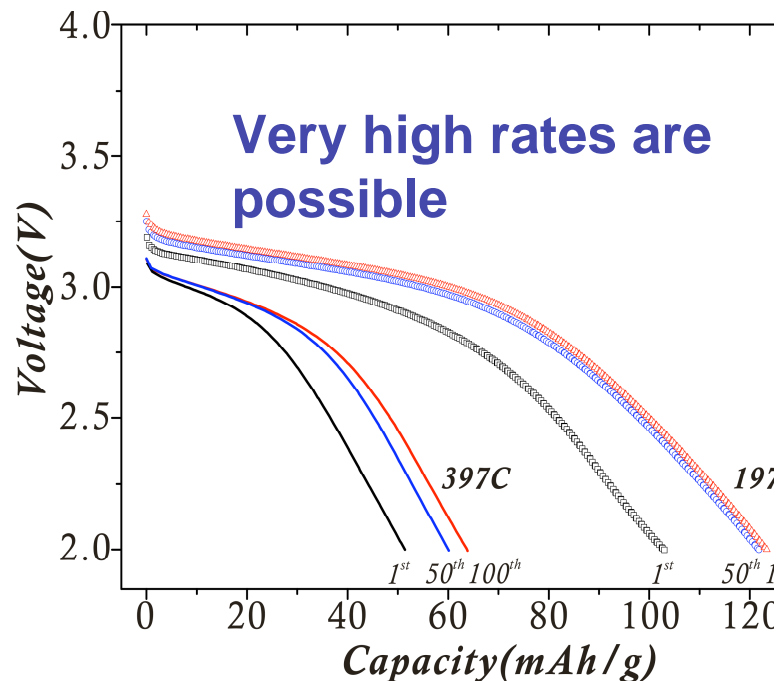
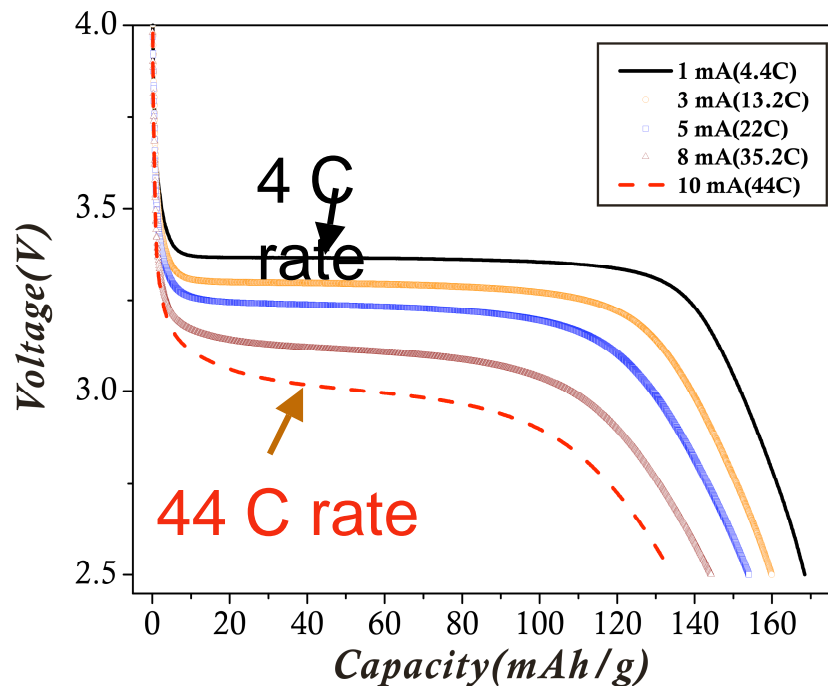
Platelet shape

Modify surface chemistry so that Li ions can move rapidly over surface



# Olivine Phosphates: Surface Modification ( $\text{LiFePO}_4$ )

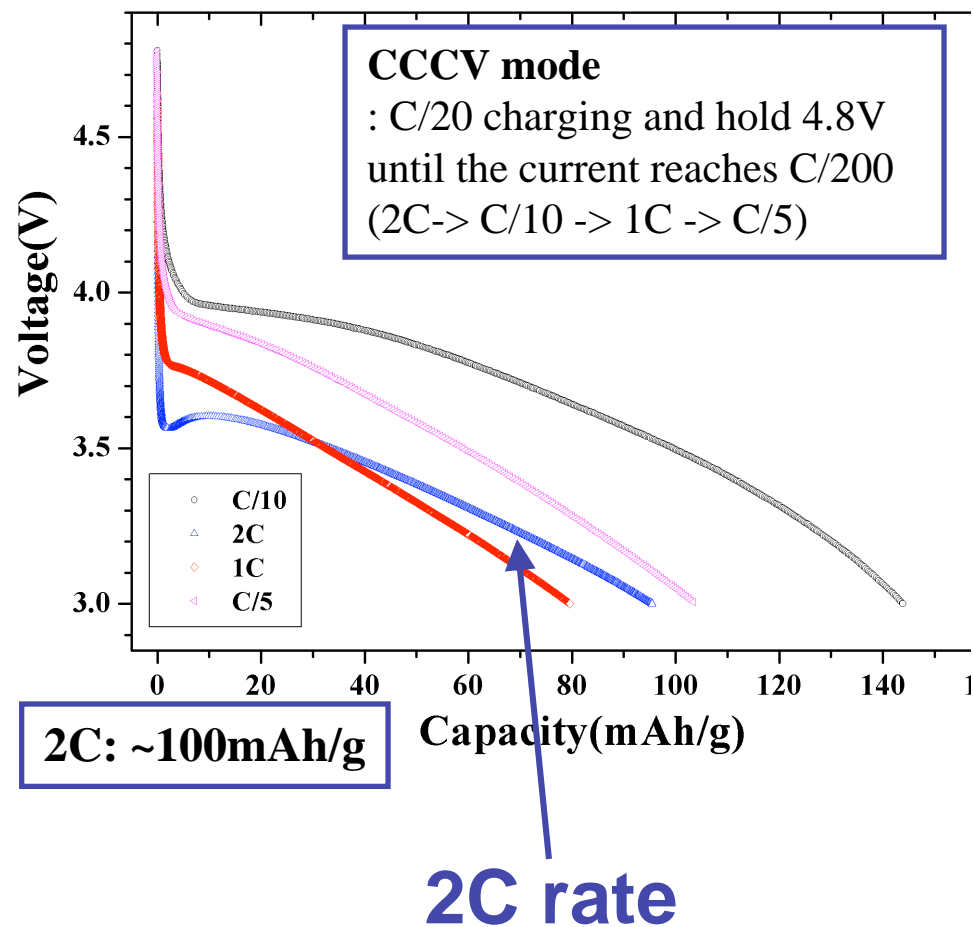
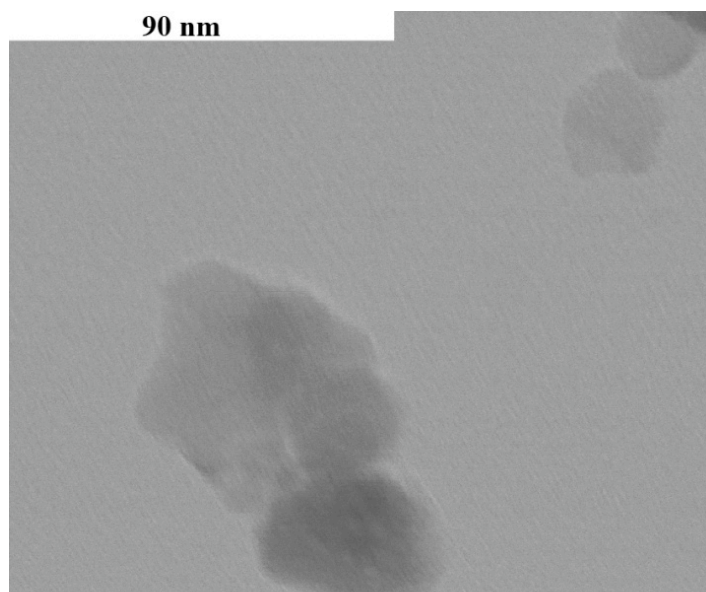
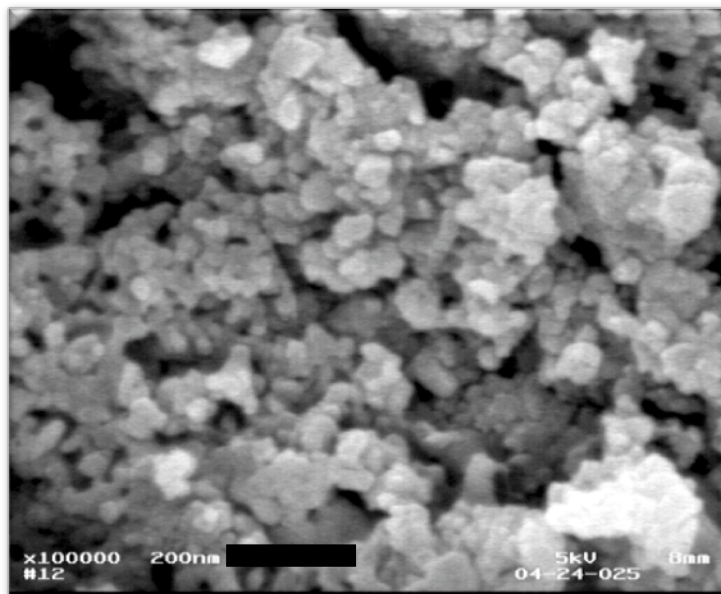
2008 DOE



B Kang and G. Ceder. submitted for publication

# Olivine Phosphates: Surface Modification ( $\text{LiMnPO}_4$ )

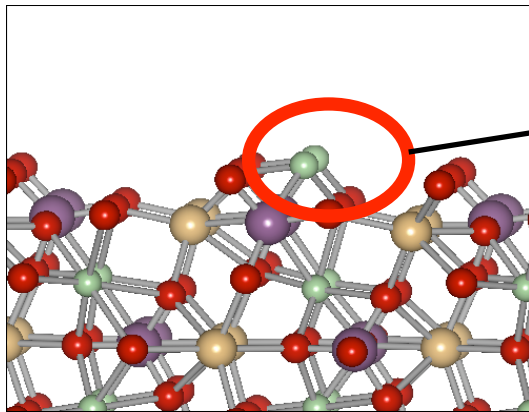
2008 DOE



# Understanding nano in Olivine Phosphates: Role of surfaces

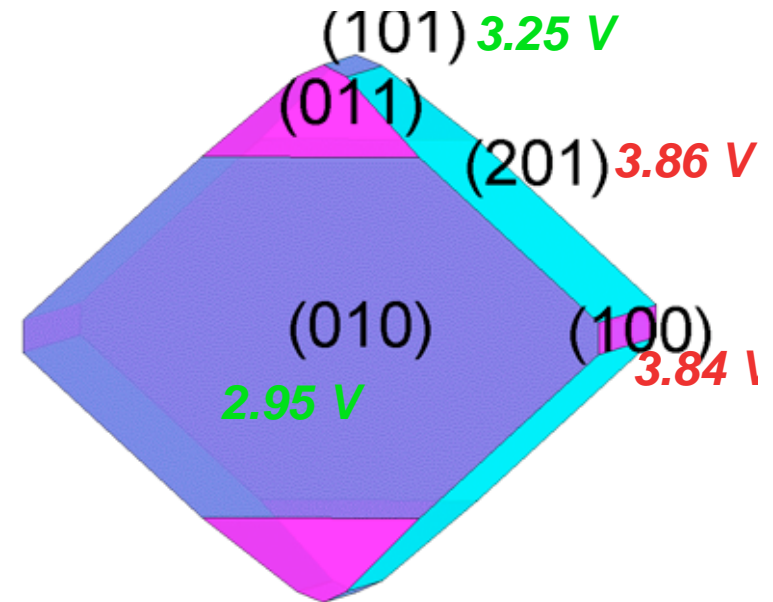
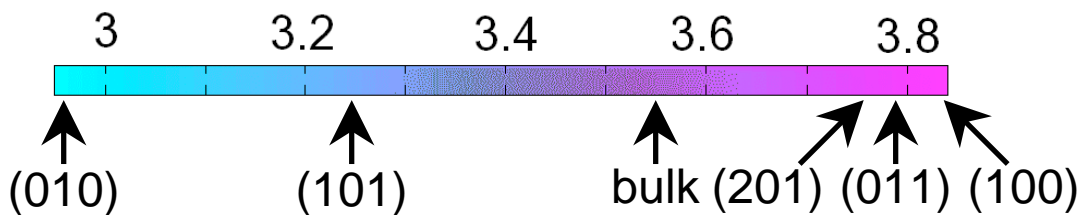
2008 DOE

## Calculated Li potential in/near surfaces



At what equilibrium potential can we extract these surface Li?

Calculated surface redox potentials:



Many consequences

# Olivine Phosphates: Role of surfaces

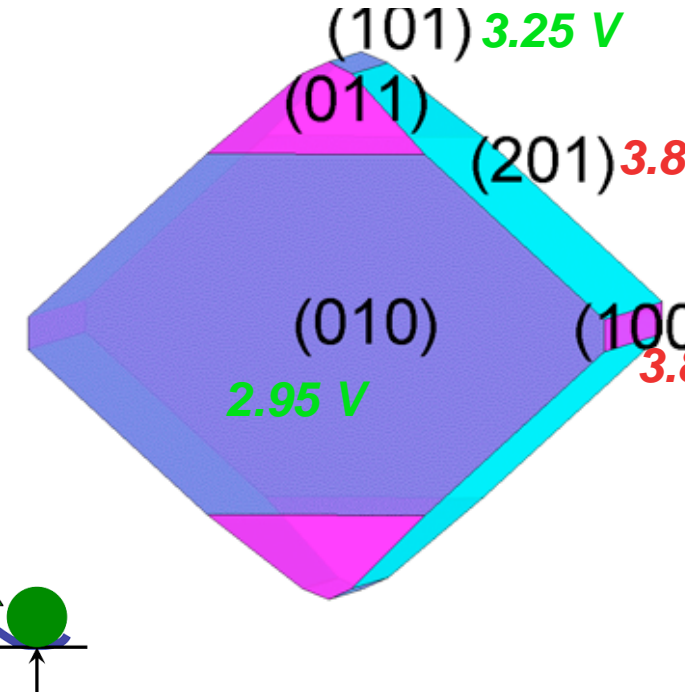
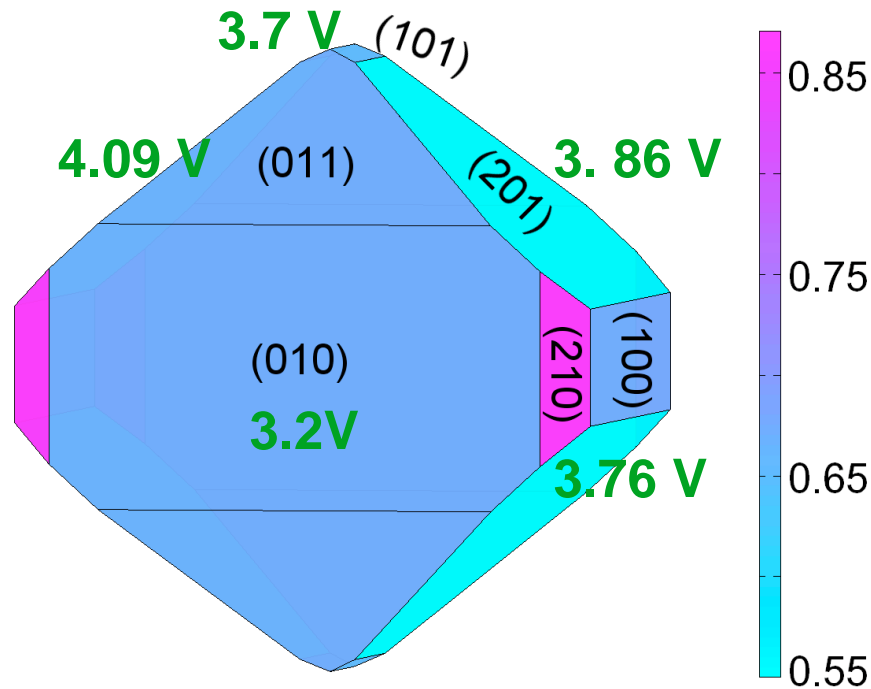
2008 DOE

## LiFePO<sub>4</sub> versus LiMnPO<sub>4</sub>

LiMnPO<sub>4</sub>

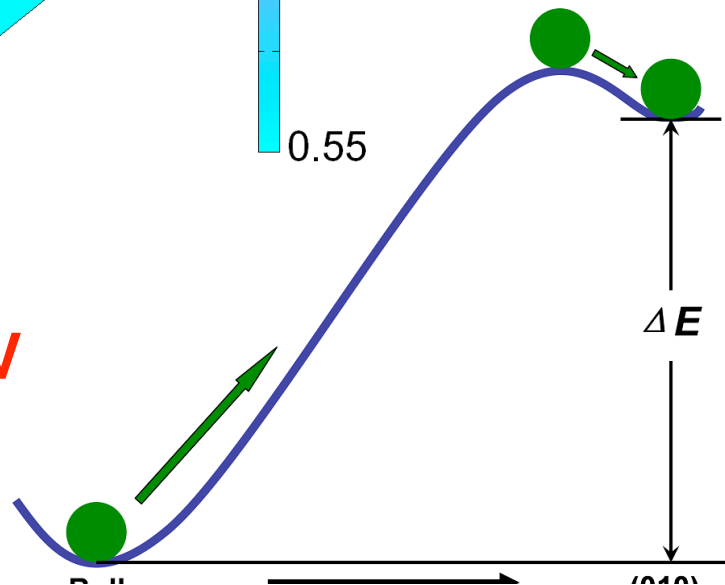
For Mn, (010) potential is more below bulk potential than for Fe

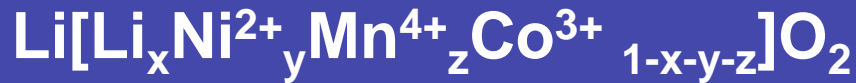
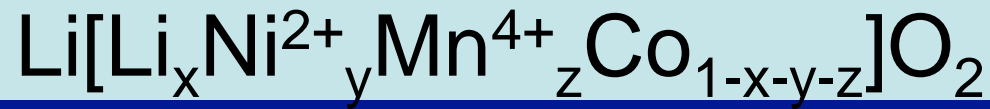
LiFePO<sub>4</sub>



For Mn, surface barrier is  $\approx 0.8$  eV

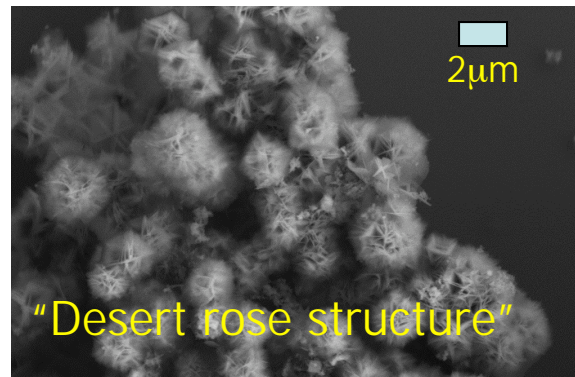
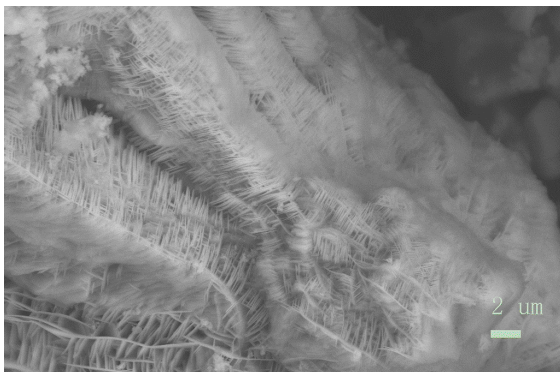
For Fe, surface barrier is  $\approx 0.5$  eV





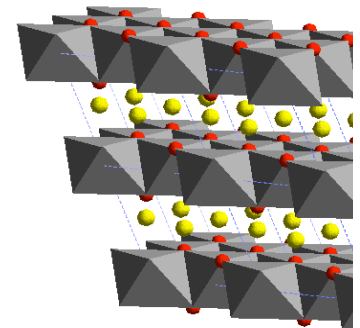
## •How to improve rate? →

2. Systematic study of particle morphology  
*Chen et al. Adv Mater., in press*

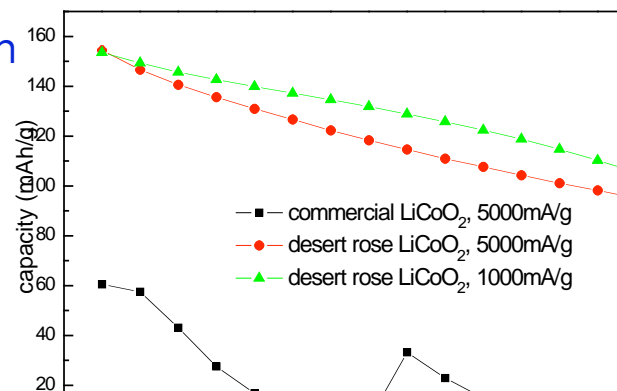
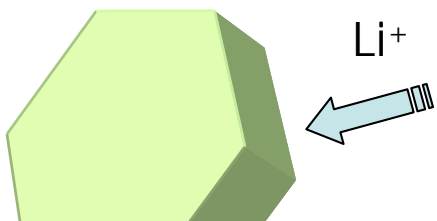


1. Presence of  $\text{M}^{2+}$  cations reduces  $\text{Li}^+$  activation energy  
 Minimize Li/Ni exchange between layers (prepare  $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$  from Na form =>  $> 175 \text{ mAhg}^{-1}$   
*Kang et al. Science '06*

Desert rose  
 7C, 36 C



- Maximize active surface +  $\text{Li}^+$  diffusion length
- Wire particles together

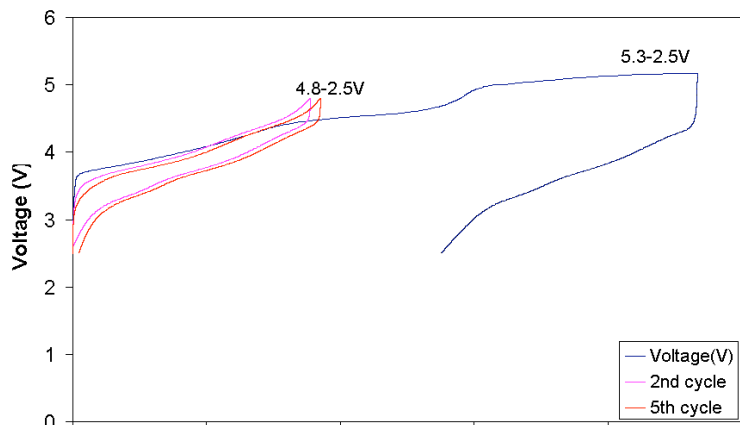
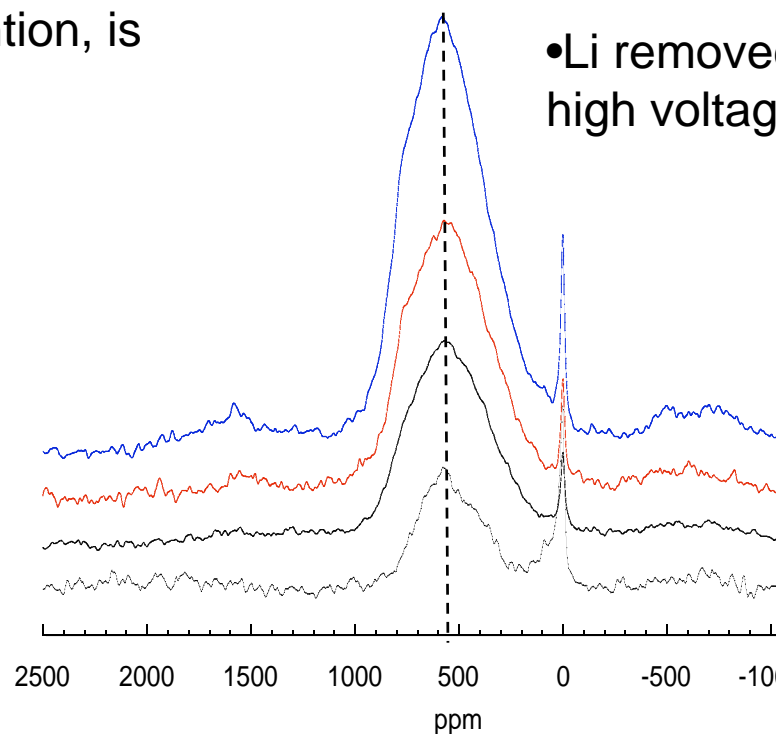
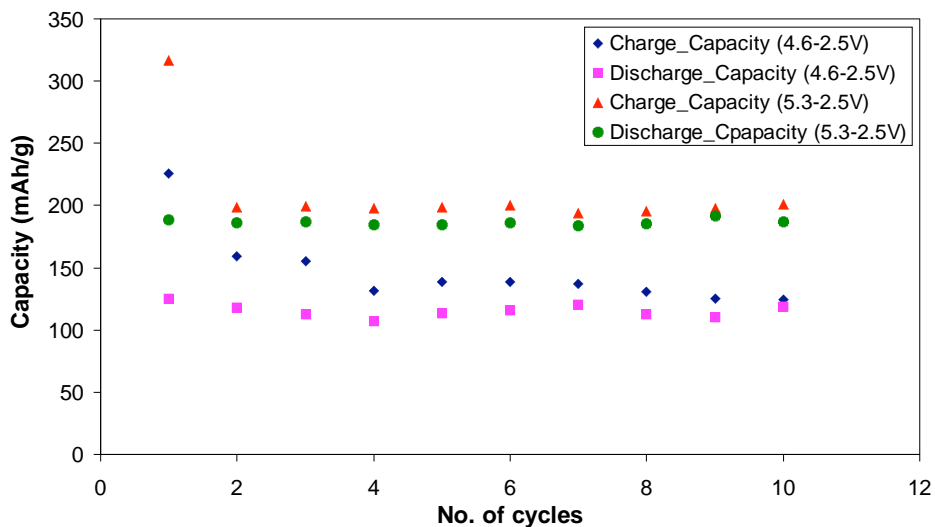


Extensions to layered material

# Layered Materials: High Voltage Processes in “Li-excess” Phases

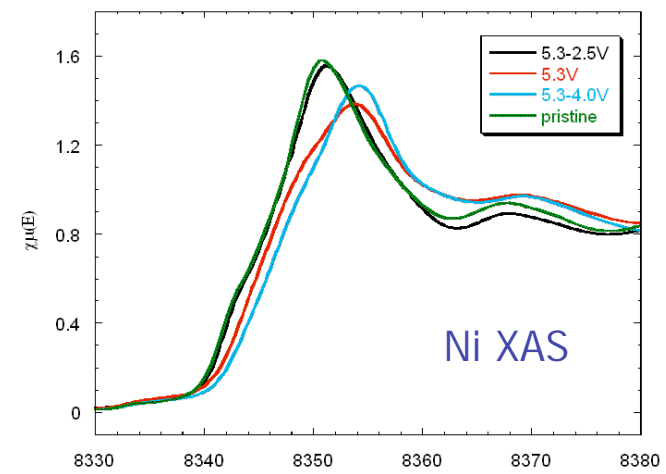
Significant capacity enhancement, and capacity retention, is observed following charging to 5V (and higher) (e.g., Thackeray et al. Electrochem. Commun., '07)

Why?



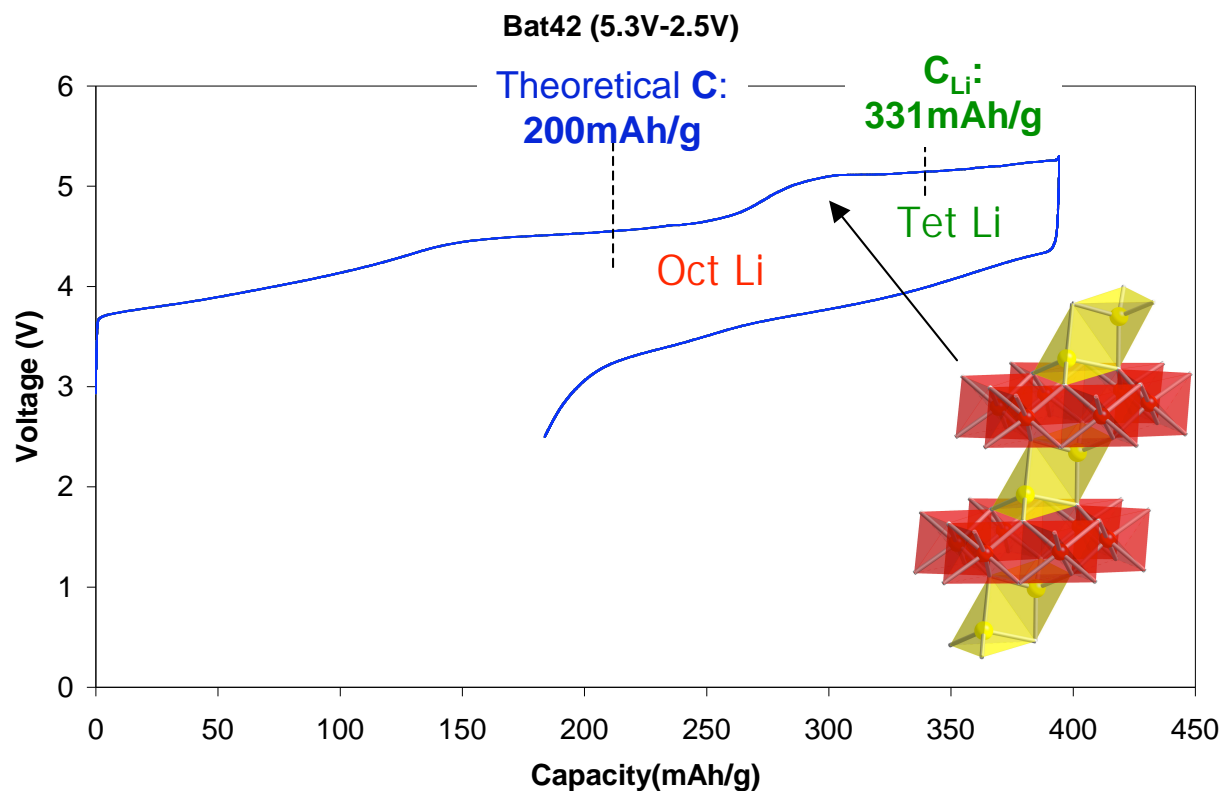
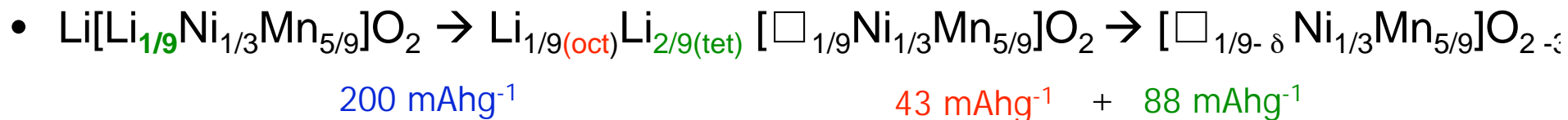
•Voltage profile changes following high V charging

•Superstructure in XRD patterns due to Li/Mn ordering lost above 5 V

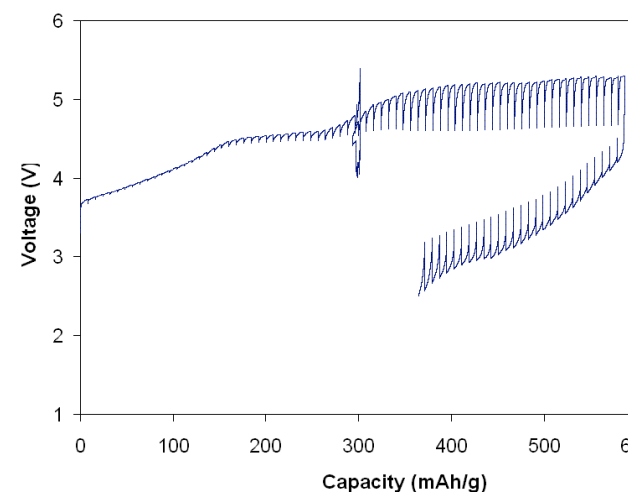


# Layered Materials: High Voltage Processes

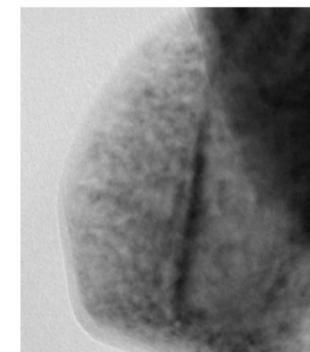
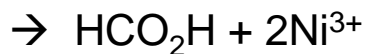
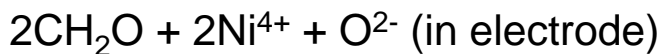
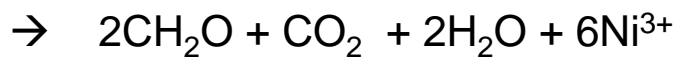
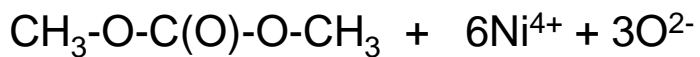
2008 DOE



• No O<sub>2</sub> seen in plastic (bag) c



• Oxygen-loss mechanism, at least in our cells, appears to involve Ni<sup>4+</sup> and the electrolyte

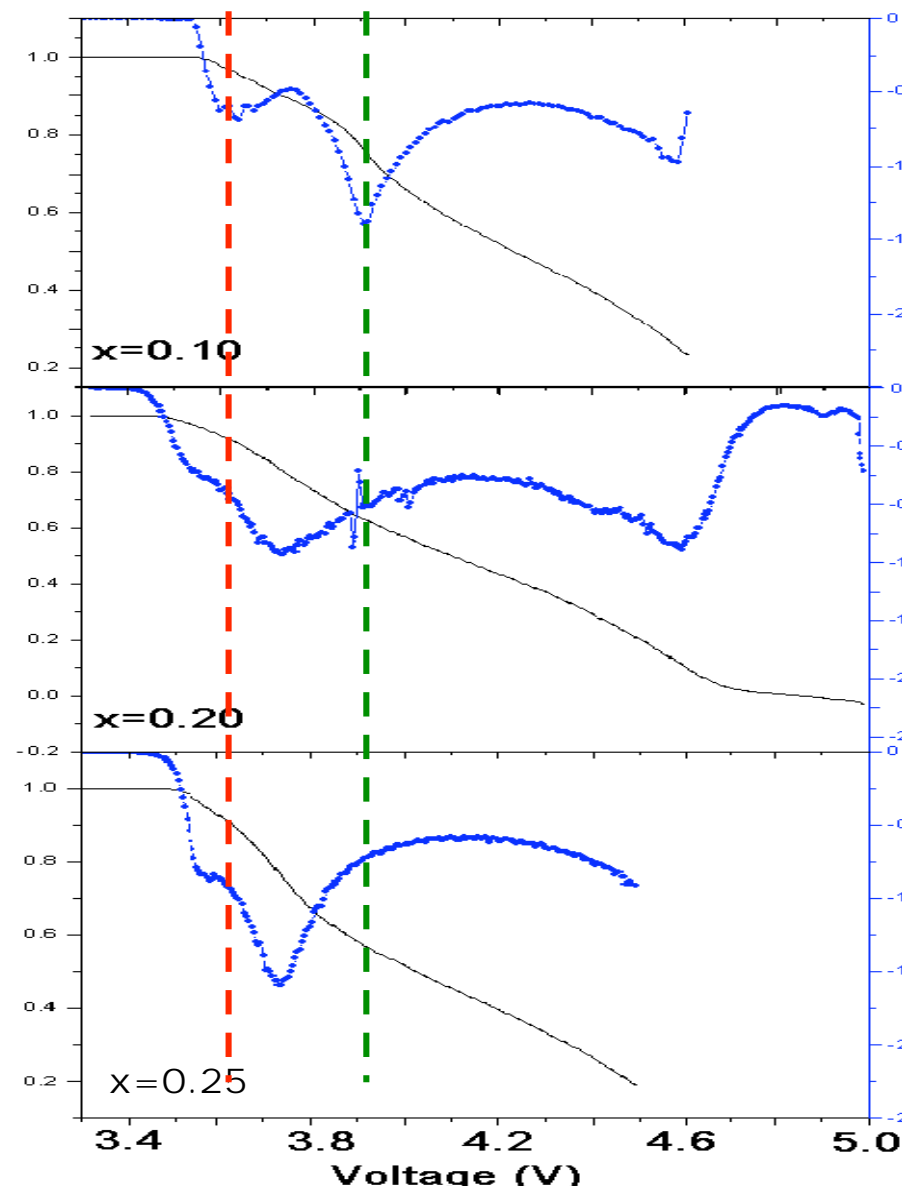
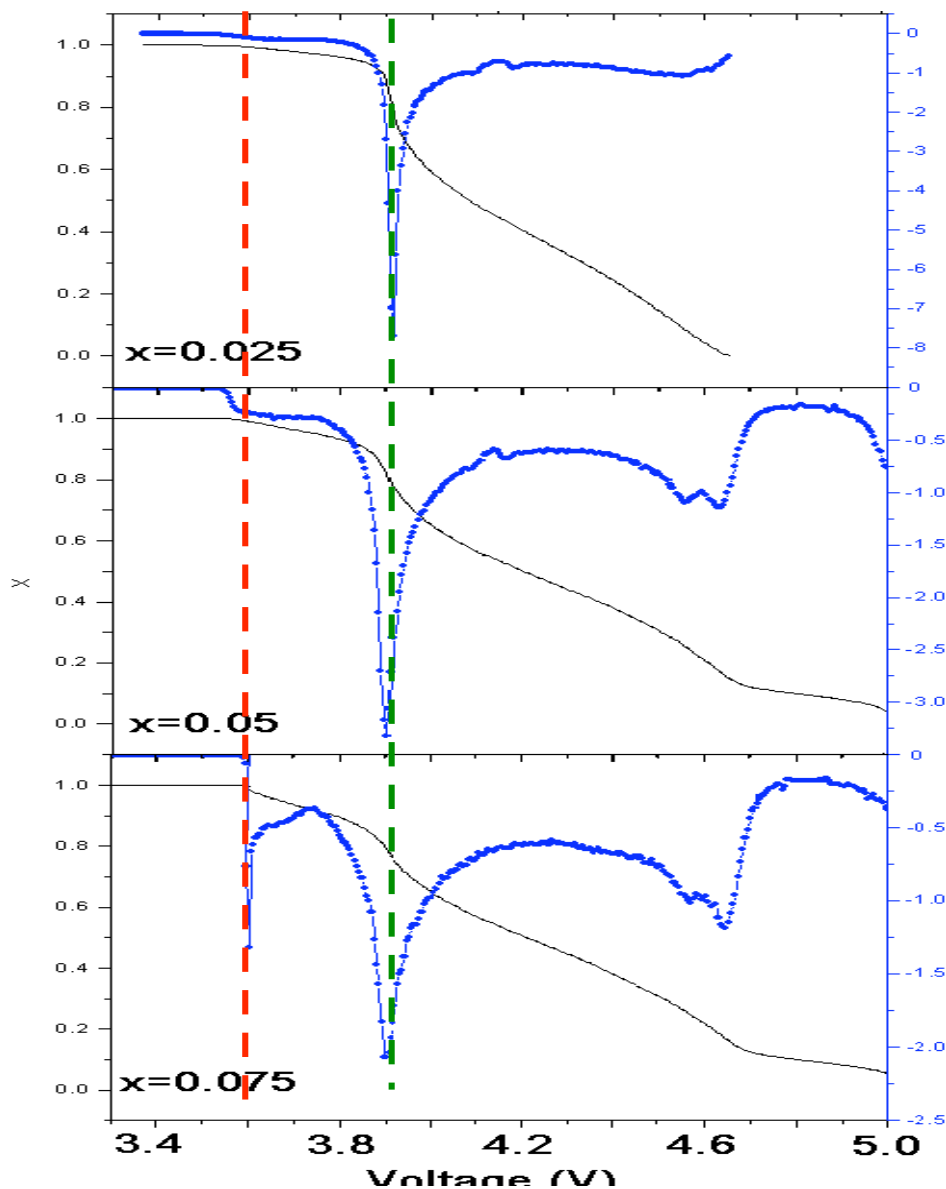


# Li[Co<sub>1-2x</sub>Ni<sub>x</sub>Mn<sub>x</sub>]O<sub>2</sub> : How does ordering affect electrochemical function?

2008 DOE

Co<sup>3+</sup> - Co<sup>4+</sup> MIT?

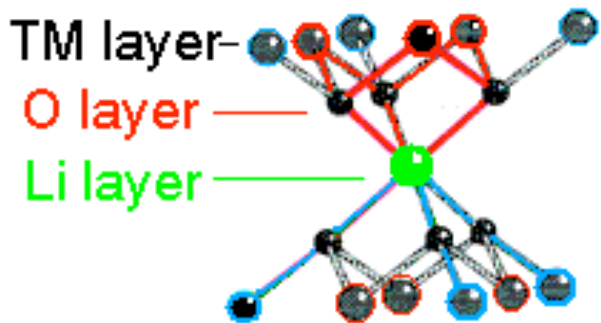
What is the optimum value (



# NMR spectra are consistent with Ni/Mn clustering, even for low Ni/Mn contents

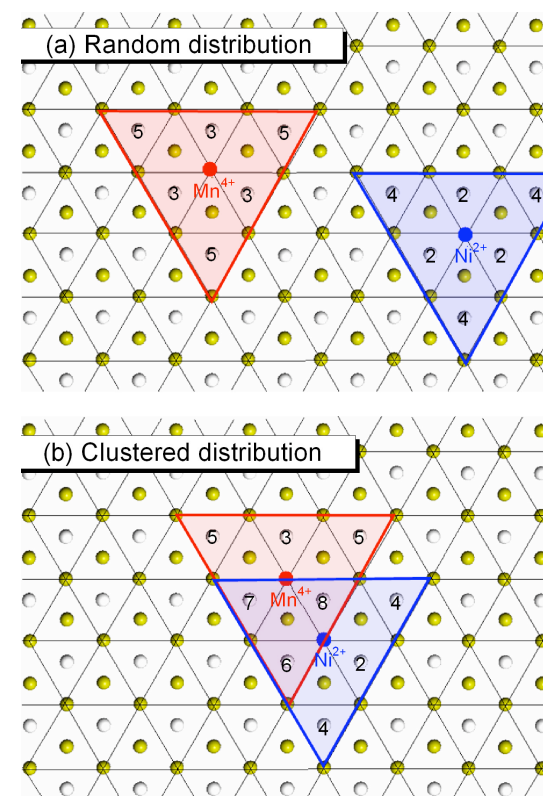
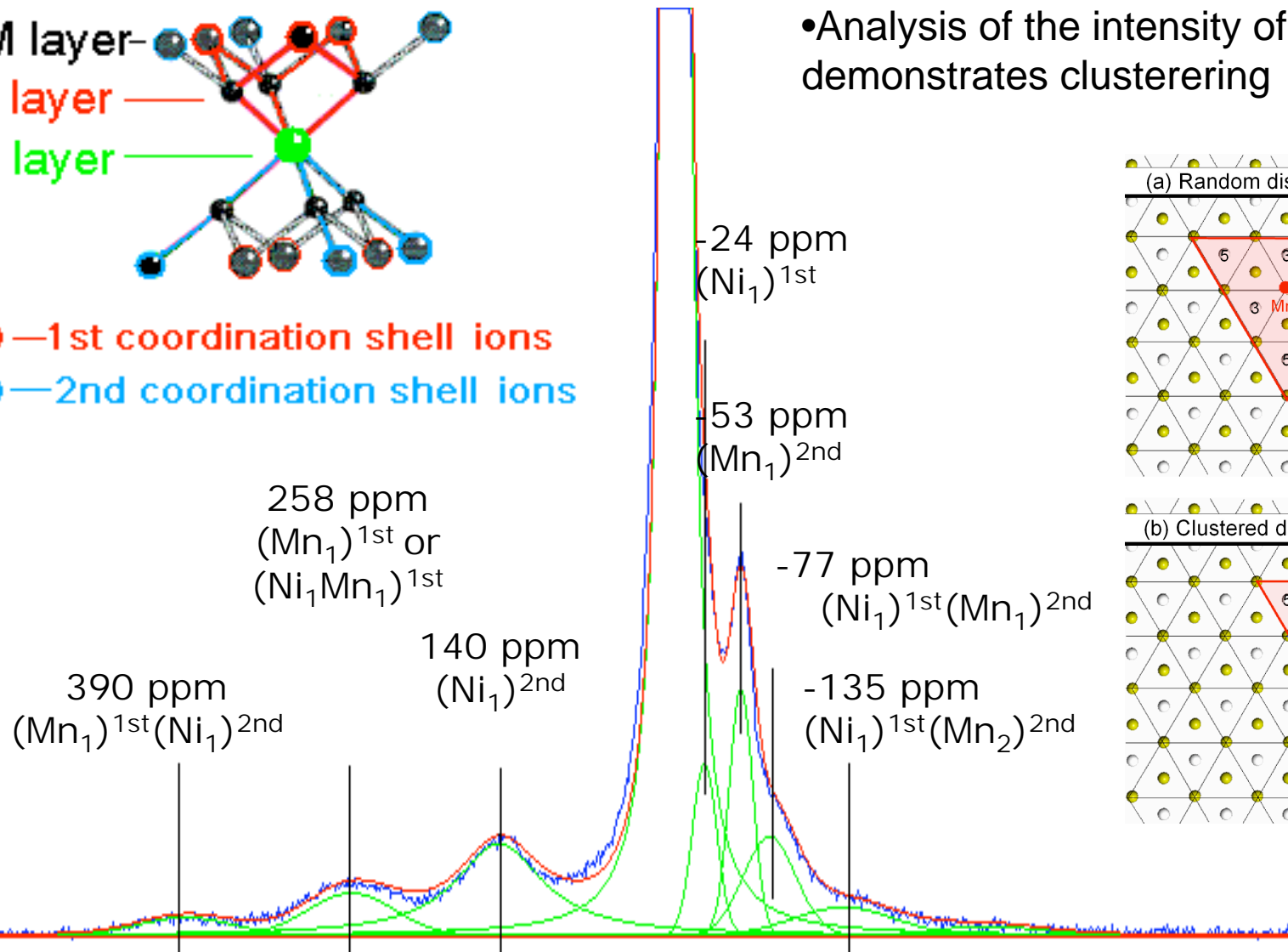
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${}^6\text{Li}$  MAS NMR spectrum of  ${}^6\text{Li}[\text{Ni}_{0.02}\text{Mn}_{0.02}\text{Co}_{0.96}]\text{O}_2$



○ — 1st coordination shell ions  
 ○ — 2nd coordination shell ions

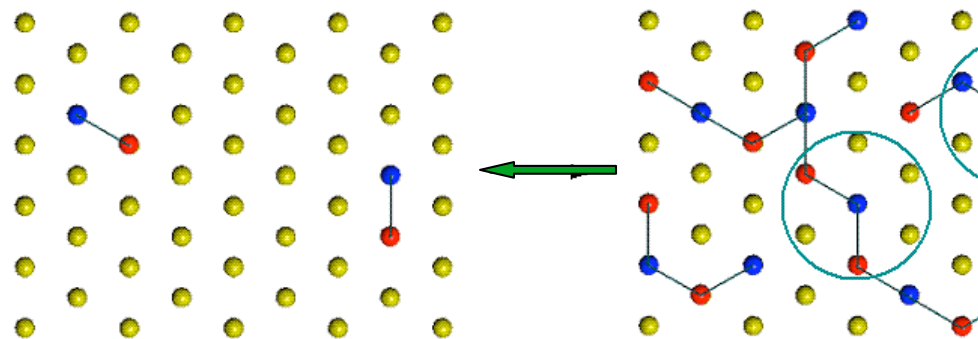
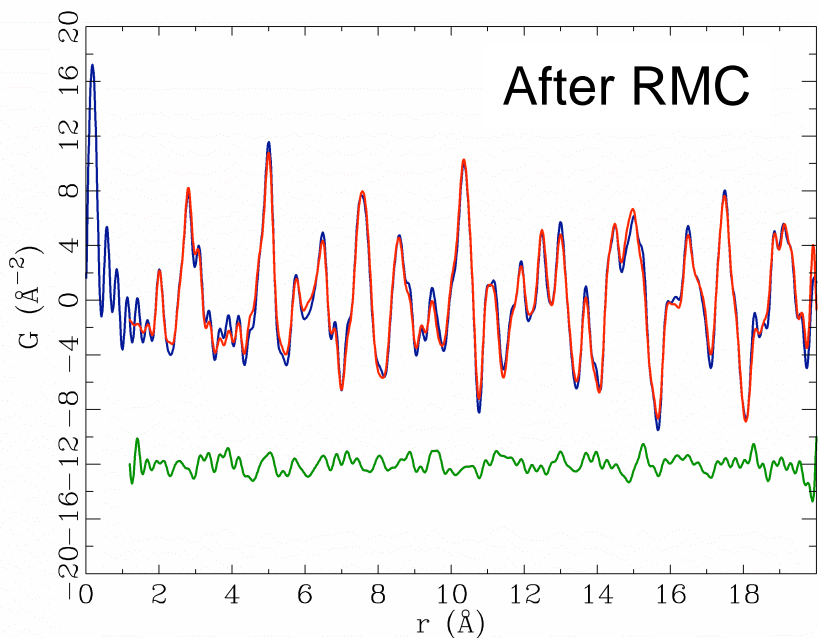
- Shifts are consistent with the presence of I and  $\text{Mn}^{4+}$
- Analysis of the intensity of the resonances demonstrates clustering



Zeng et al.  
 Chem. Mater.

# Pair distribution function (PDF) analysis of higher Ni/Mn content materials

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Co disrupts the Ni-Mn ordering; but weak correlations persist

$$g_C(r) = \frac{1}{r} \sum_i \sum_j \left[ \frac{b_i b_j}{\langle b \rangle^2} \delta(r - r_{ij}) \right] - 4\pi r \rho_0$$

Coherent scattering

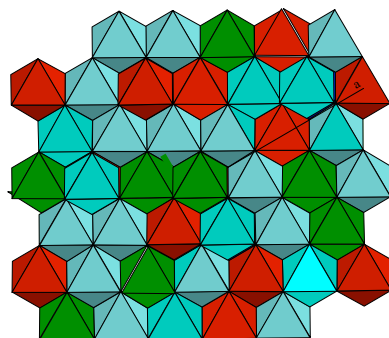
lengths (fm):

Ni: 10.30

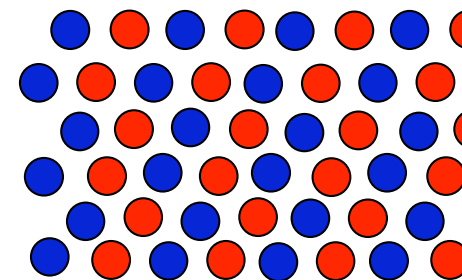
Li: -2.22

Mn: -3.75

Co: 2.49



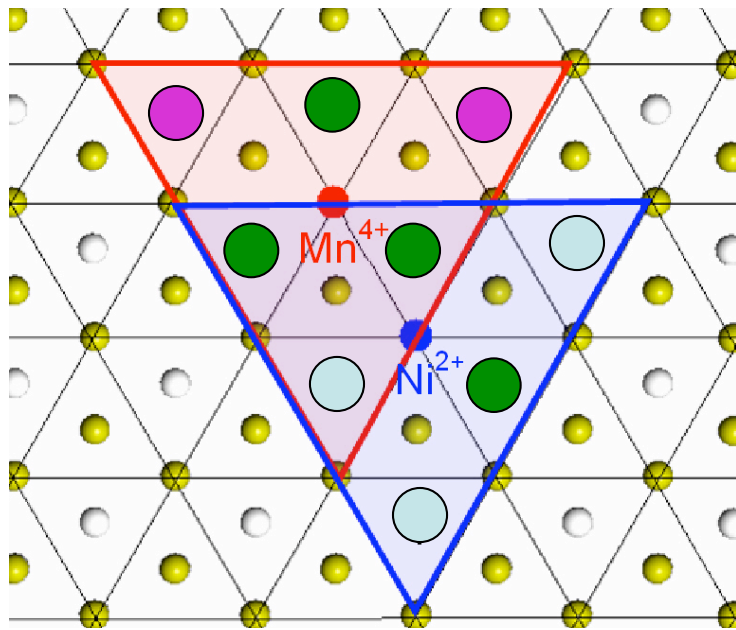
$\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2^*$   
derived from  
 $\text{Na}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2$



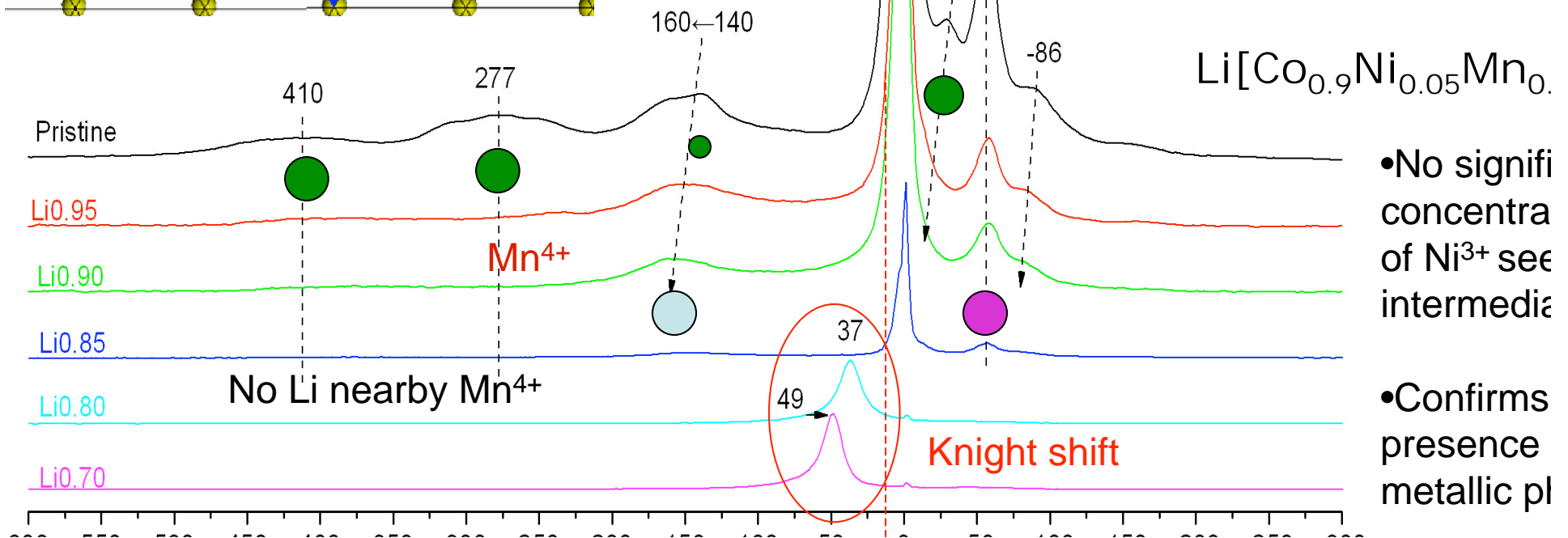
\*Science '06;  
I Mater Chem '07

# Li NMR spectra can be used to identify the electrochemical processes

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- Loss of Metal-to-Insulator Transition as Ni/Mn content increases, correlates with loss of Co rich clusters

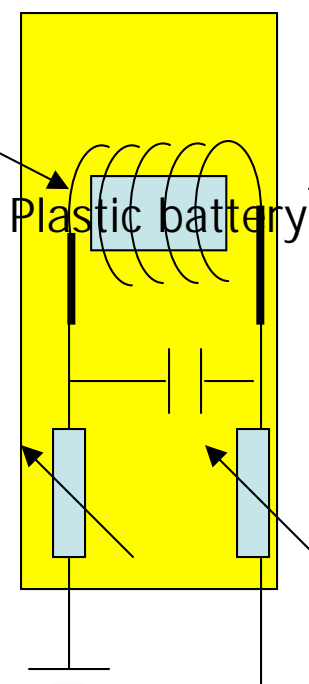
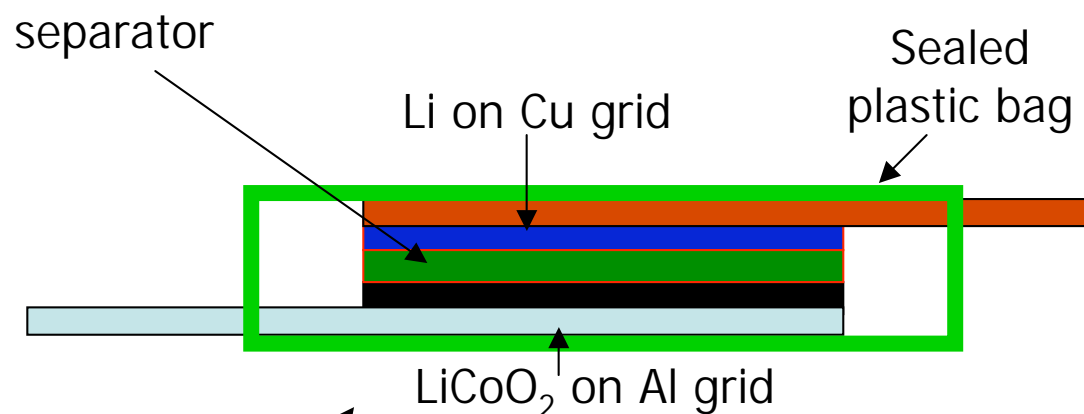


- No significant concentration of  $\text{Ni}^{3+}$  seen in intermediate states

- Confirms presence of metallic phase

# Advanced Diagnostic Methods: *In situ* NMR

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Chevallier, F.; Letellier, M.; Morcrette, M. Tarascon, J. M.; et al.; *Electrochem. Solid State Lett.* '03, 6, A225.

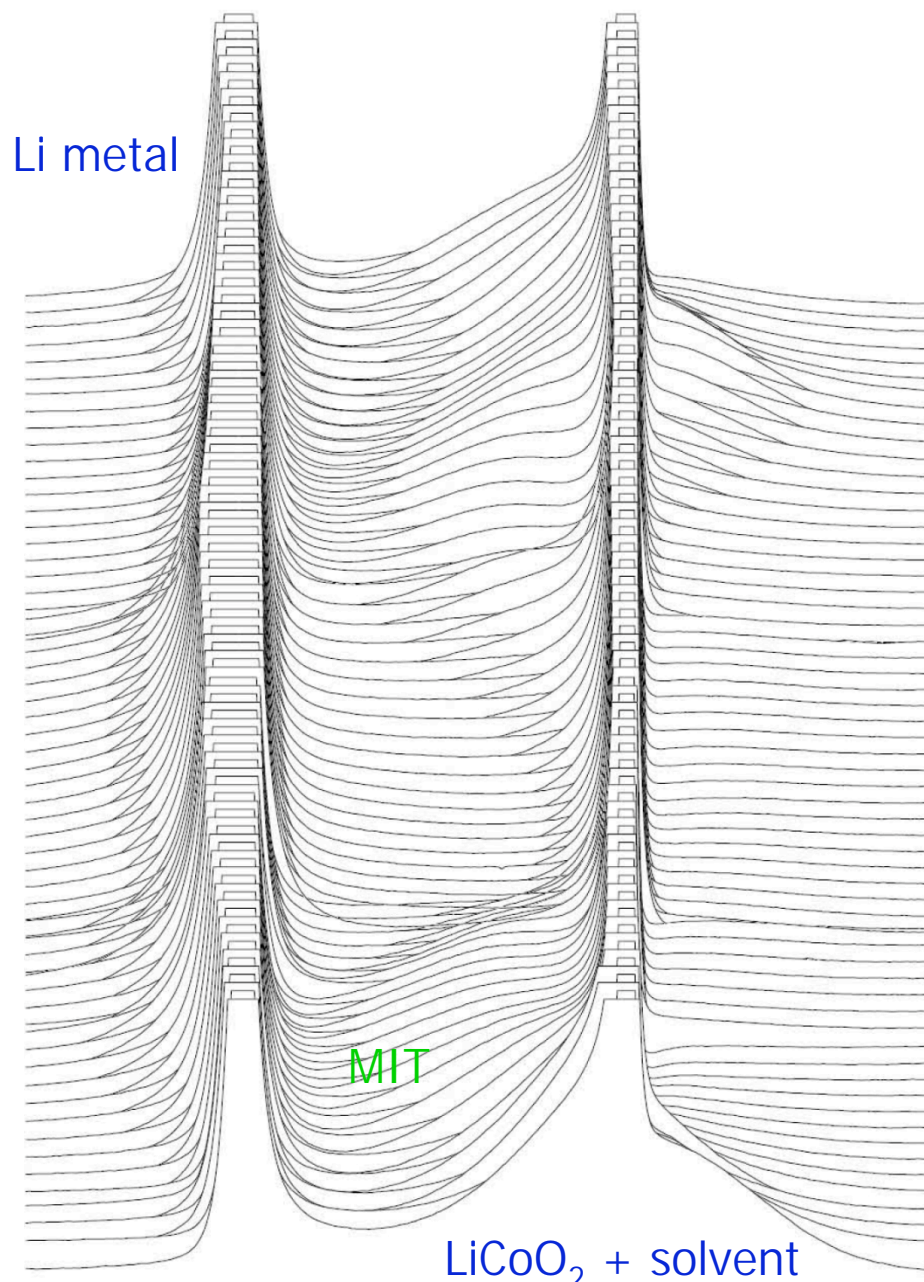
Challenges:  
Develop high resolution approach  
Separate different NMR signals  
Synchronize NMR spectroscopy and e-chem. to monitor fast dynamics



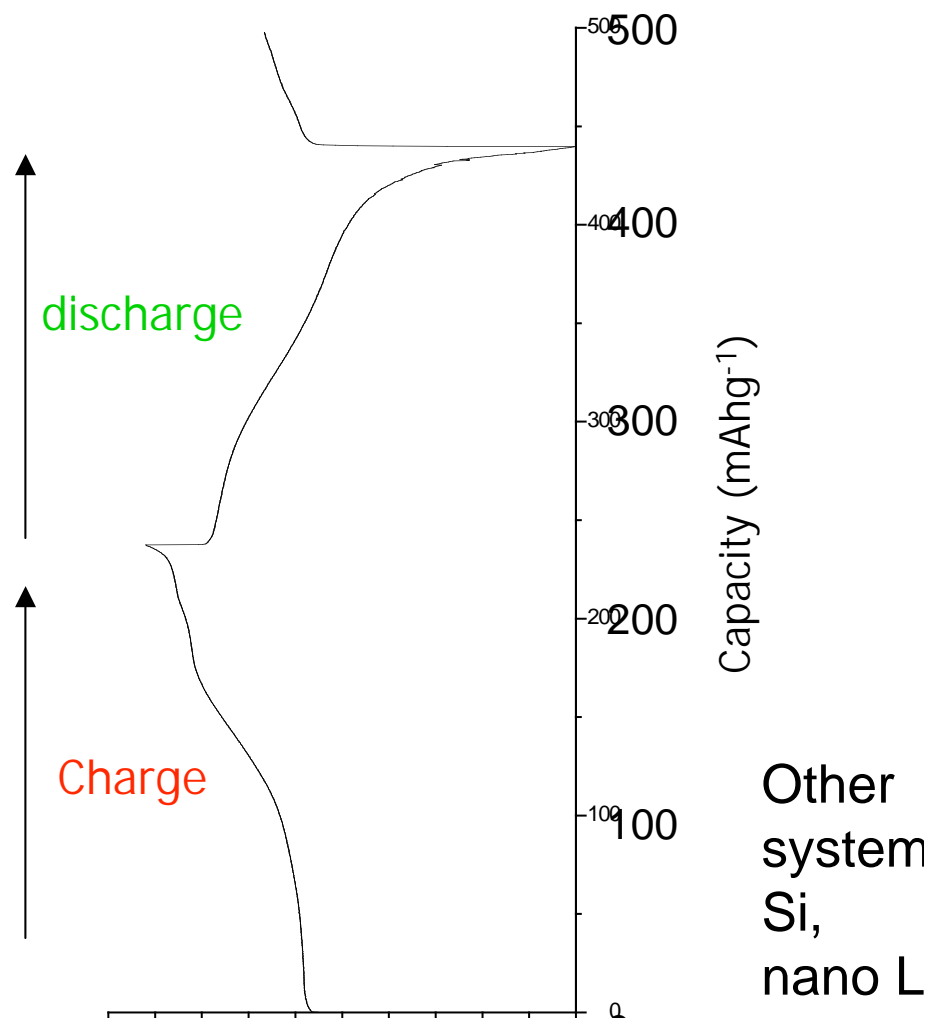
Battery Cycler

# Advanced Diagnostic Methods: *In situ* NMR: Demonstration of Methodology

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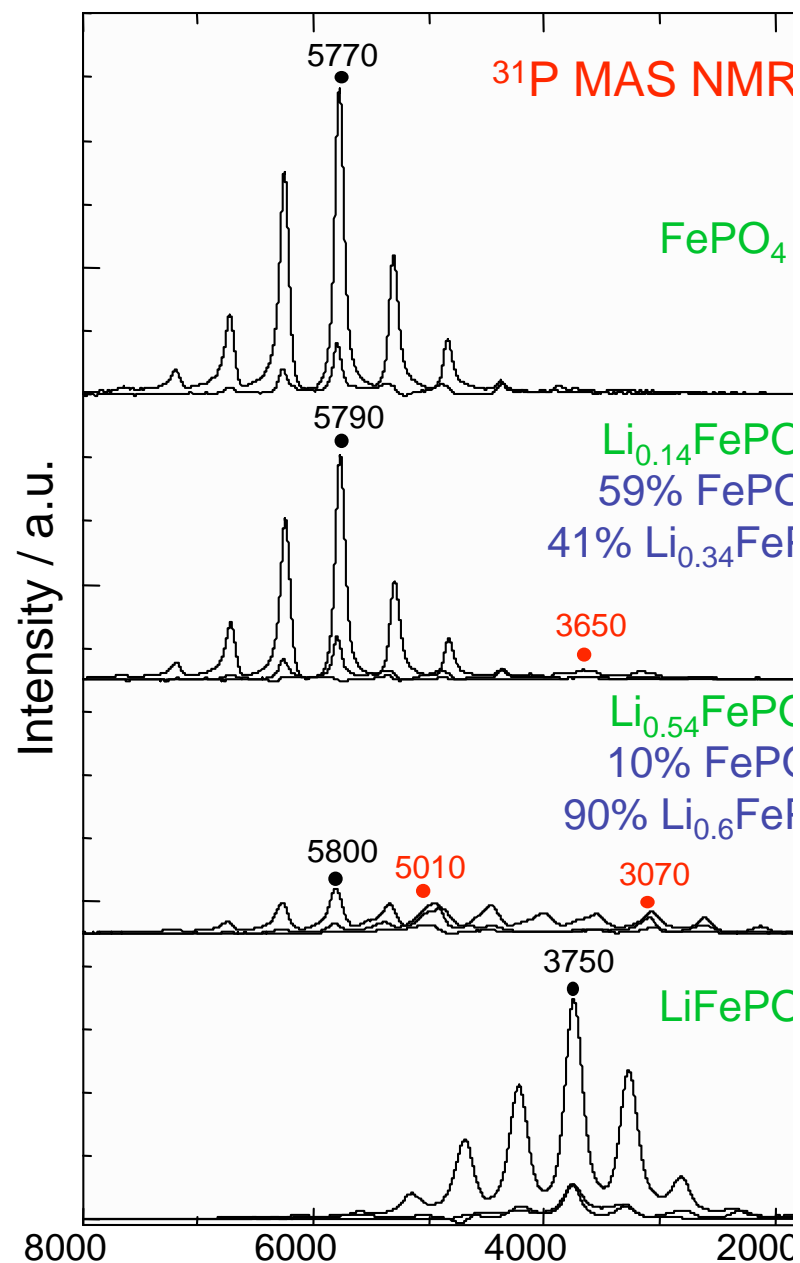


Commercial LiCoO<sub>2</sub>  
C/40, 2.5V-4.8V, alternating 0.2 and 0.02  
recycle delays



- Dr. Wonsub Yoon, Brookhaven National Laboratory
  - *In situ* diffraction and XAS studies of layered cathodes
- Prof. Stanley Whittingham, Binghamton University
  - Magnetic studies of layered cathodes
- Prof. Yang Shao-Horn, MIT
  - TEM studies of layered cathodes
- Dr. Michael Thackeray, Argonne National Laboratory
  - Li NMR studies of layered-spinel intergrowths
- Drs. Thomas Richardson and Guoying Chen, Lawrence Berkeley Laboratory
  - $^{6,7}\text{Li}$  and  $^{31}\text{P}$  studies of metastable phases in  $\text{Li}_x\text{FePO}_4$  phase diagram

(3 papers in 2007 and 2 in preparation)



# Plans for coming year

- ❑ Continue work on understanding phase transformations in olivines and origin of high/low rate behavior
- ❑ Investigate the effect of different electrolytes, and coatings on the high voltage processes, focusing on rate performance
- ❑ Broadly investigate effect of “nano” on electrochemical properties - metals, oxides, phosphates, ... Is there opportunity for “new” materials here? Use morphology/coatings to control rate?
- ❑ Broad computational high-throughput search for cathode materials.
- ❑ Exploit the use of *in situ* NMR methods to investigate anode + cathode materials, to investigate *metastability, electrolyte decomposition, and dynamics*. Determine mechanisms for intercalation (reaction) under high rates

# Publications/Patents

- 1) L. Wang, T. Maxisch, G. Ceder, *A First-Principles Approach to Study the Thermal Stability of Oxide Cathode Materials*, Chemistry of Materials, **19** (3), pp. 543-552 (2007).
- 2) Y. Hinuma, Y.S. Meng, K. Kang and G. Ceder, *Phase Transitions in the  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  System with Temperature*, Chemistry of Materials, **19**(7), pp. 1790-1800 (2007).
- 3) J. Bréger, K. Kang, J. Cabana, G. Ceder and C. P. Grey, *NMR, PDF and RMC Study of the Positive Electrode Material  $\text{Li}(\text{NiMn})_{0.5}\text{O}_2$  Synthesized by Ion-Exchange Method*, Mater. Chem., **17**, 3167-3174 (2007).
- 4) K. Tibbetts, C.R. Miranda, Y.S. Meng, G. Ceder, *An Ab Initio Study of Lithium Diffusion in Titanium Disulfide Nanotubes*, Chemistry of Materials, **19** (22), pp. 5302-5308 (2007).
- 5) X. Ma, K. Kang, G. Ceder, Y.S. Meng, *Synthesis and Electrochemical Properties of Layered  $\text{LiNi}_{2/3}\text{Sb}_{1/3}\text{O}_2$* , J. Power Sources **173** (1), pp. 550-555 (2007).
- 6) L. Wang, F. Zhou, Y. S. Meng, G. Ceder, *First-Principles Study of Surface Properties of  $\text{LiFePO}_4$ : Surface Energy, Structure, Wulff Shape, and Surface Redox Potential*, Phys. Review B, **76**, 165435 (2007).
- 7) D. Burch, G. Singh, G. Ceder, M. Bazant, *Phase-Transformation Wave Dynamics in  $\text{LiFePO}_4$* , Mat. Res. Soc. Proc., Boston, Fall '07, in print.
- 8) S.P. Ong, L. Wang, B. Kang, G. Ceder, *The Li-Fe-P-O<sub>2</sub> Phase Diagram from First-Principles Calculations*, Chemistry of Materials, in print.
- 9) G.K. Singh, G. Ceder, M.Z. Bazant, *A general theory of intercalation dynamics predicts phase-transformation waves in  $\text{LiFePO}_4$* , submitted

# Publications/Patents (continued)

- 10) H.H. Li, N. Yabuuchi, Y.S. Meng, S. Kumar, J. Breger, C.P. Grey, Y. Shao-Horn, *"Changes in the Cation Ordering of Layered O<sub>3</sub> Li<sub>x</sub>Ni<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> During Electrochemical Cycling to High Voltages: An Electron Diffraction Study"* Chem. Mater., 19, 2551- 2560 (2007).
- 11) N. A. Chernova, M. Ma, J. Xiao, M. S. Whittingham, J. Breger, and C P. Grey, *"Layered Li<sub>x</sub>Ni<sub>y</sub>Mn<sub>y</sub>Co<sub>1-2y</sub>O<sub>2</sub> Cathodes for Lithium Ion Batteries: Understanding Local Structure via Magnetic Properties"*, Chem. Mater., 19, 4682-4693, (2007).
- 12) D. Zeng, J. Cabana, J. Breger, W.-S. Yoon, and C. P. Grey, *"Cation ordering in Li[Ni<sub>x</sub>Mn<sub>x</sub>Co<sub>(1-2x)</sub>]O<sub>2</sub>-Layered Cathode Materials: A Nuclear Magnetic Resonance (NM) Pair Distribution Function, X-ray Absorption Spectroscopy, and Electrochemical Study"* Chem. Mater., in press (2007).
- 13) H. Chen and C. P. Grey, *"Molten Salt Synthesis and High Rate Performance of the "Desert-Rose" form of LiCoO<sub>2</sub>"*, Adv. Mater., in press (2008).

## Patents

**Filed January 2007** G. Ceder and B. Kang, High rate coatings