# First Principles Calculations (and NMR Spectroscopy of Electrode Materials)

## G. Ceder Massachusetts Institute of Technology March 20, 2009

Project ID # es\_26\_ceder

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## Overview

### Budget

• Funding for FY08: \$270,001

# **Objectives**

- Determine the effect of structure on stability and rate capability of cathodes and anodes.
- Explore relationship between electrochemistry and particle size and shape.
- Understand and predict **reactivity** of anode and cathode electrode materials with electrolytes.
- Develop new materials

### Barriers

- Low rate capabilities
- High cost
- Poor stability

#### Partners

- Clare Grey (SUNY) (co-PI)
- Collaborators (BATT):
- Dr. K. Persson, LBNL
- Dr. R. Kostecki, LBNL
- Drs. Smith/Borodin, Utah
- Prof. J.–M. Tarascon
- Prof. D. Aurbach
- Prof. Bazant

## Milestones

- (a) November 1, 2008: Demonstrate the application of the *in situ* NMR technology to investigate nanoparticle deintercalation/intercalation methods. COMPLETE
- Complete studies of structural changes that occur at high voltages in nickel and manganese containing layered materials. COMPLETE
- (b) May 1 2009: Computational results on lithiation of nanomaterials; Produce initial results on broad search for new materials. In progress\*
- Complete NMR/electrochemical studies of coatings on lithium nickel manganese oxides materials. In progress\*
- Complete NMR and pair distribution function (PDF) studies study of silicon, during the 1st cycle; initiate structural and reactivity studies on the effect of cycling Si to different states of (dis)charge. COMPLETE
- Complete investigation of mechanisms for phase transformations in LiMPO<sub>4</sub> as a function of shape for M = Fe. Initiate studies for (M = Mn, Ni, Co and solid solutions of Fe and these elements). In progress\*

# Approach

#### \*As of March 20, 2009

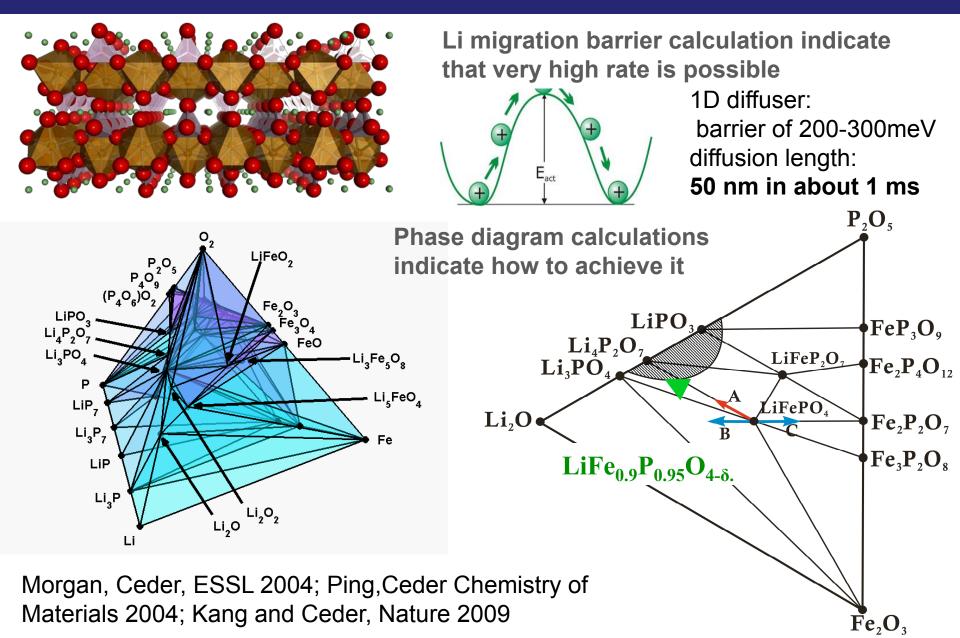
- Use first principles calculations (density functional theory) to identify redoxactive metals, relative stability of different structures, the effect of structure and particle size on cell voltages and rate capability, and to identify promising cathode materials for BATT applications.
- Anticipate possible instabilities in materials at high states of charge by using calculations. Use calculations and NMR to identify low activation energy pathways for cation migration and to investigate electronic conductivity.

### **Technical Focus and Accomplishments**

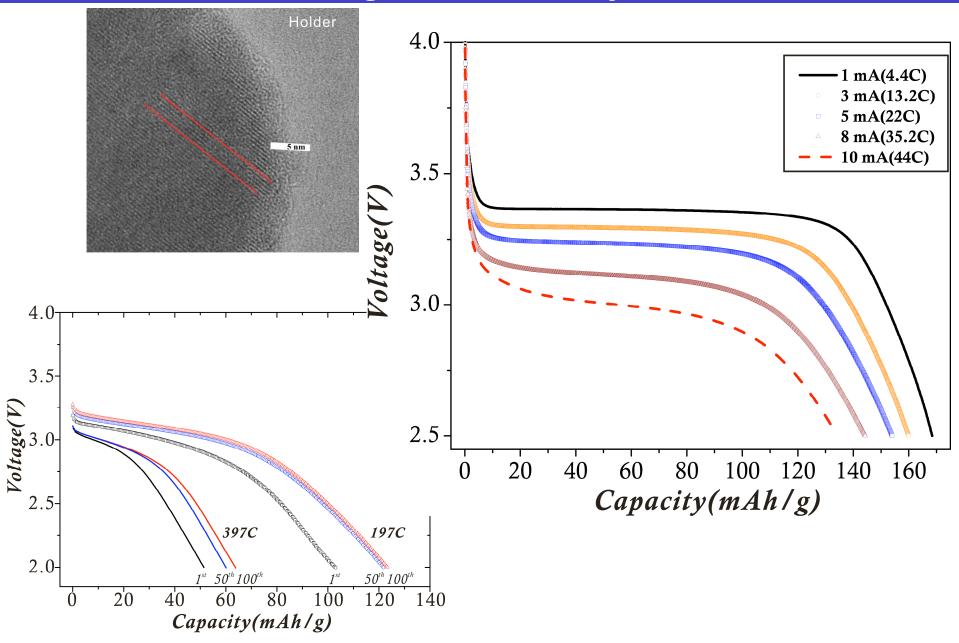
■ **RATE:** Computed **quaternary phase diagrams** of Li-M-P-O systems with = Fe, Mn, Ni and used to develop **LiFePO**<sub>4</sub> with extreme rate capability.

- □ AB-INITIO METHODS FOR MORPHOLOGY CONTROL: Developed first principles approach to predict particle morphology as function of environment (in solution and in oxygen) (with K. Persson, BATT, LBNL)
- □PHASE TRANSFORMATIONS IN OLIVINES: Developed formalism to study mixed metal olivines and applied to Li(Fe,Mn)PO<sub>4</sub>.
- ❑NANO EFFECTS: Investigated surfaces of LiFePO₄ and LiMnPO₄: structure, potentials, stability and developed theory on the sizedependence of the miscibility gap
- CONVERSION REACTIONS Studied conversion reactions and nanosize effects in Fe-fluorides, Bi-F, Cu-F and Ag-F. Developed a hypothesis/model to explain hysteresis in Fe-F.
- **NEW MATERIALS:** Developed **high-throughput computational** screening ability to find **new electrode materials**.

# Thermodynamics, morphology, and size dependence of properties of LiFePO<sub>4</sub> and LiMnPO<sub>4</sub>



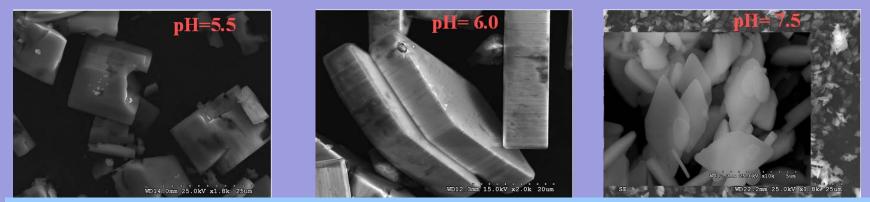
#### Nano material with optimized surface treatment gives very high Power density



#### Ab initio processing ? (under development)

Can we use first principles computations to guide processing to make a particular structure or morphology?

#### **Example:** LiFePO<sub>4</sub> in solution

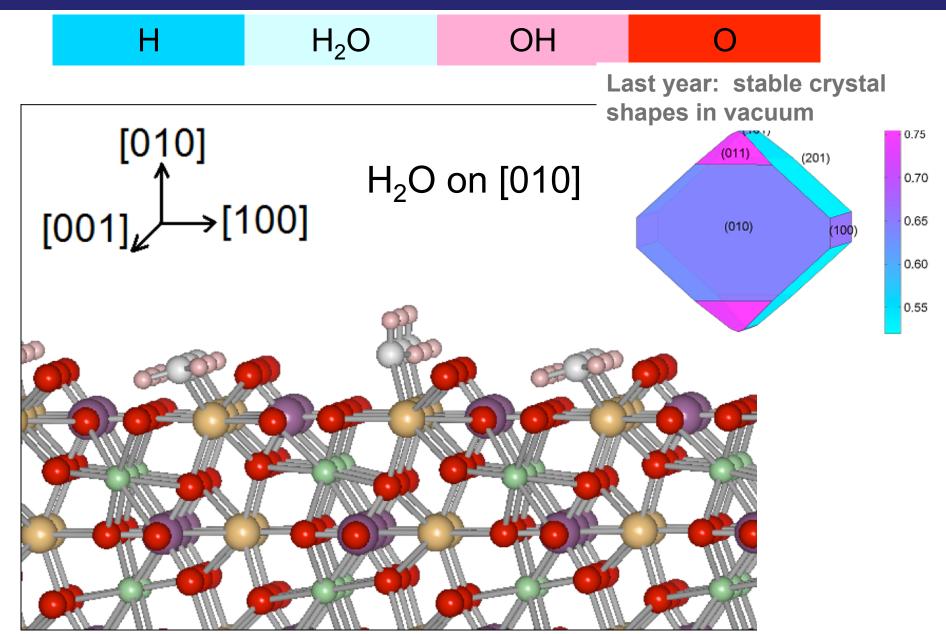


Morphology of olivine system can be depends on pH, T, precursor concentration, ...

[1] T. Richardson, et. al. private communication

Investigate surface energetics in solution. Need to develop open-system first principles methods to allow for adsorption of species from solution.

#### Study all relevant surfaces in solution with typical adsorbants + potential Li dissolution

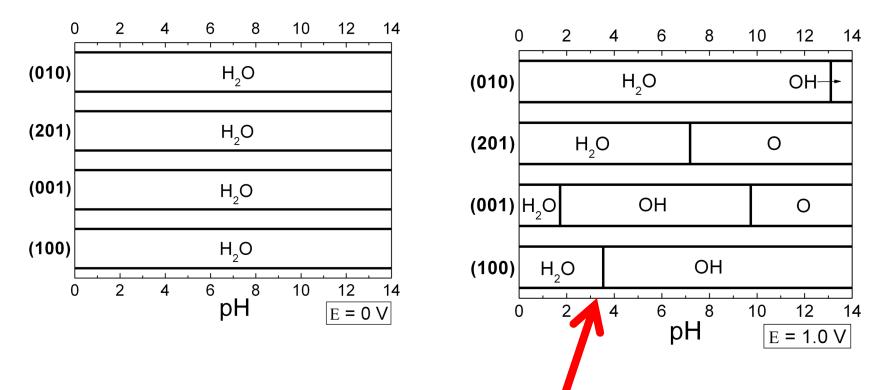


#### Study all relevant surfaces with typical adsorbants + potential Li dissolution

#### LiFePO<sub>4</sub>

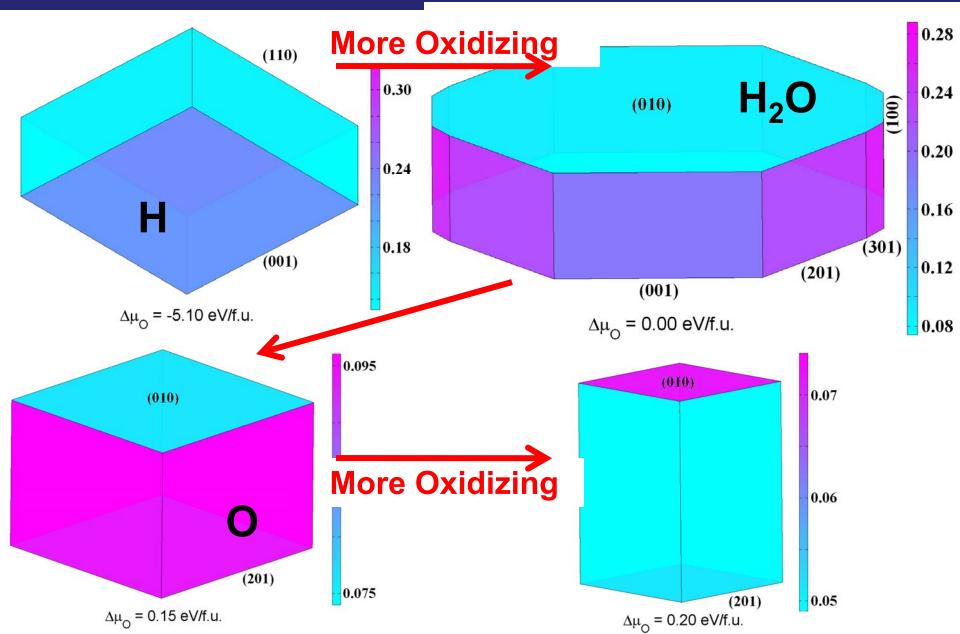
At neutral potential all the surfaces are water capped for any pH

At high potential all the surfaces are water capped for any pH

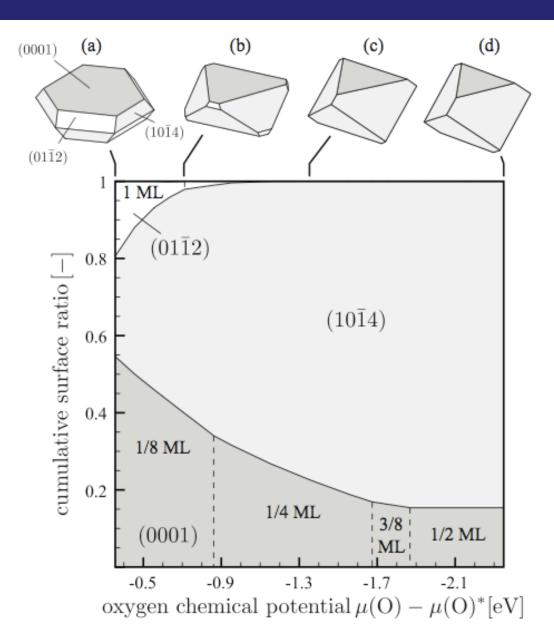


Surface adsorption/structure, and hence surface energy, can be modified by pH ! -> gives control over stable morphology of the surfaces

#### Stable Wulff shapes as function of environment Shape control through pH !

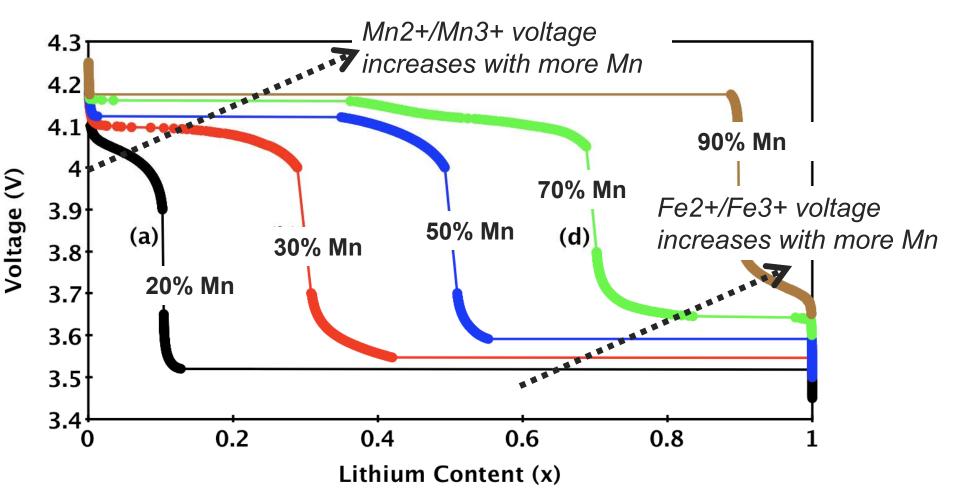


#### Similar ab-initio shape control in LiCoO<sub>2</sub>



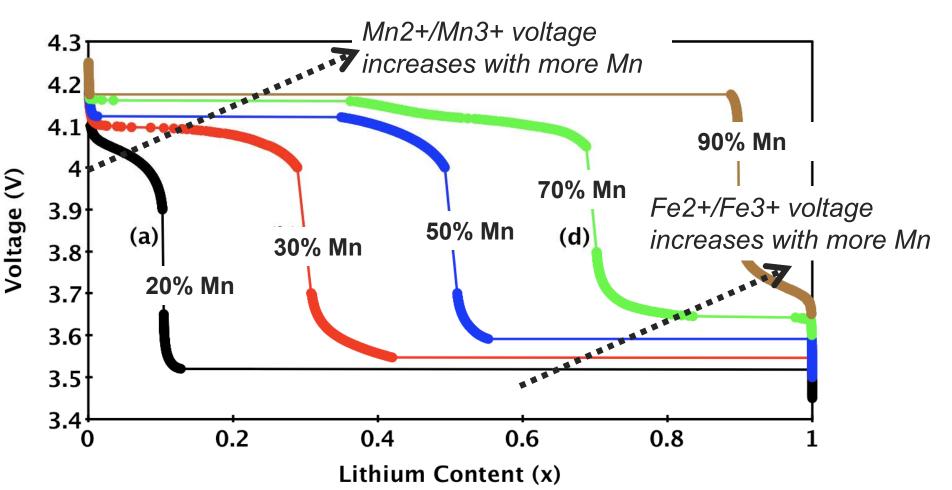
#### Mixed Olivine Systems: Li(Fe,Mn)PO<sub>4</sub>

Developed a simulation model to study mixed olivines with ab initio
Developed theory for change in potential of plateau voltages
Currently addressing diffusion, polarization and phase transformation kinetics in mixed olivines

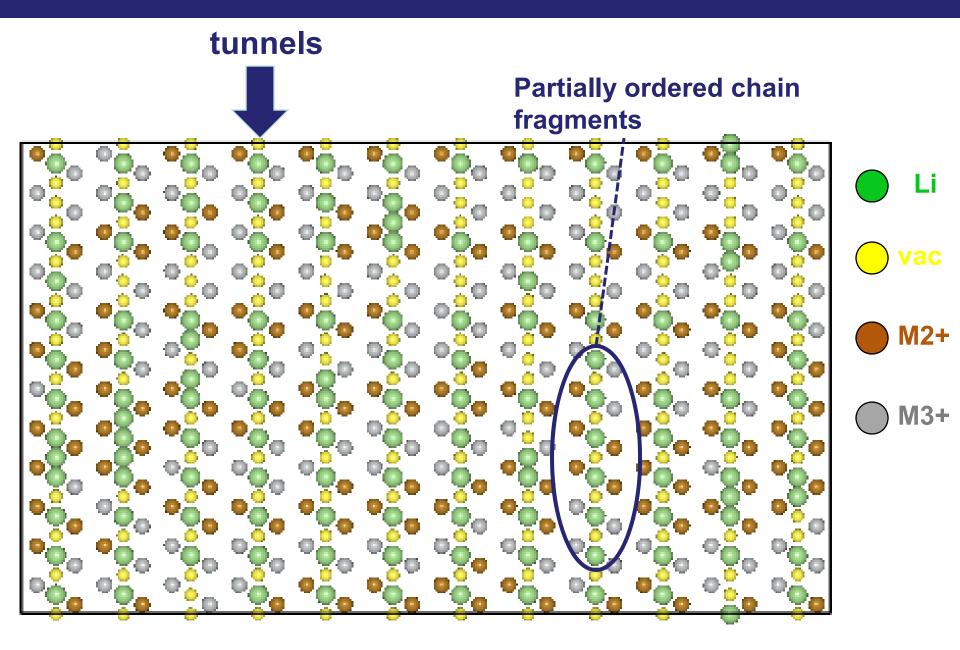


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### Mixed Olivine Systems: Li<sub>0.4</sub>(Fe<sub>0.2</sub>Mn<sub>0.8</sub>)PO<sub>4</sub>

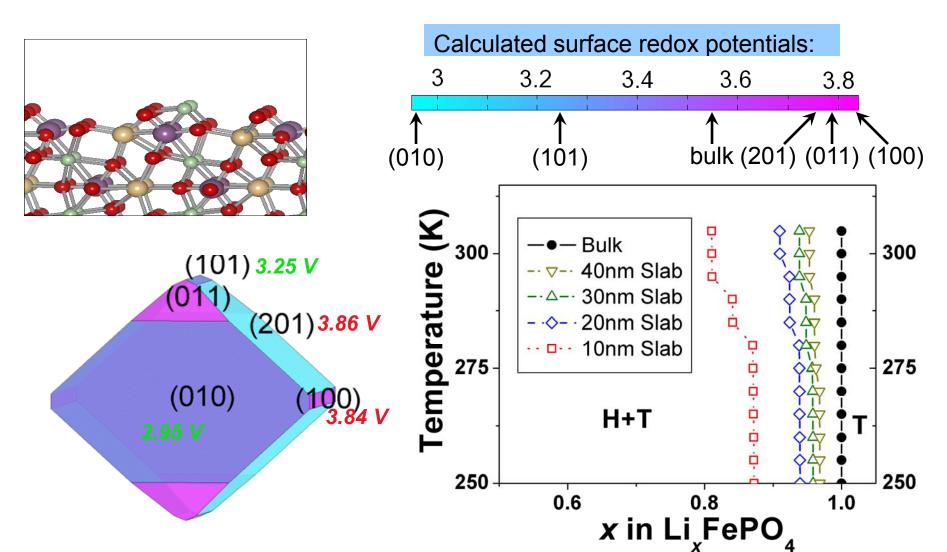


#### Nanoeffects

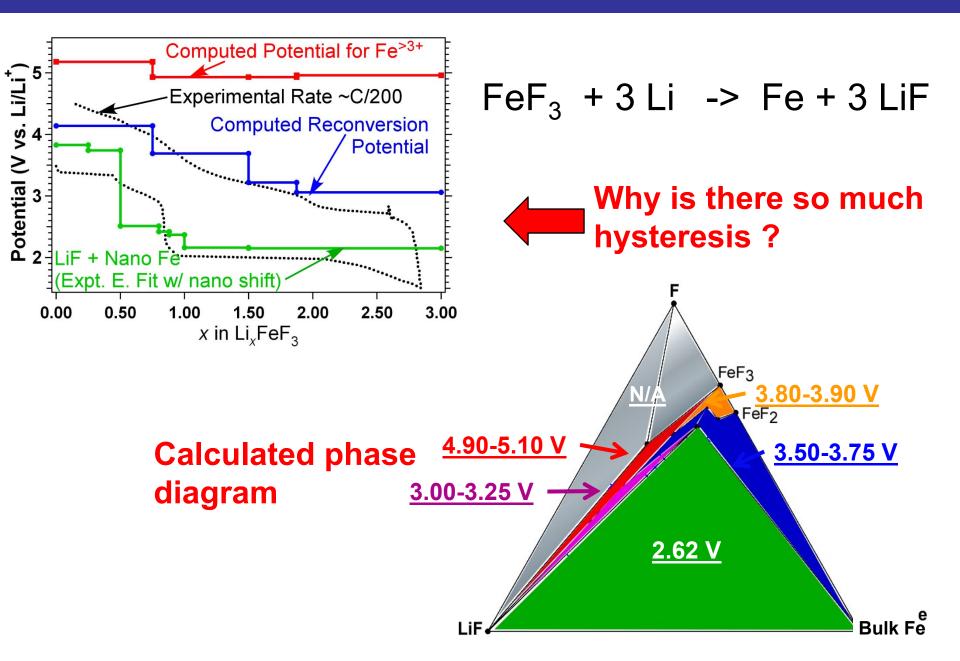
- •Effects on solubility (LiFePO<sub>4</sub>)
- •Effects on Potential (Fe-fluoride conversion systems)
- •Effects on storage mechanism (in progress)

# Surface properties contribute to observations in small particles

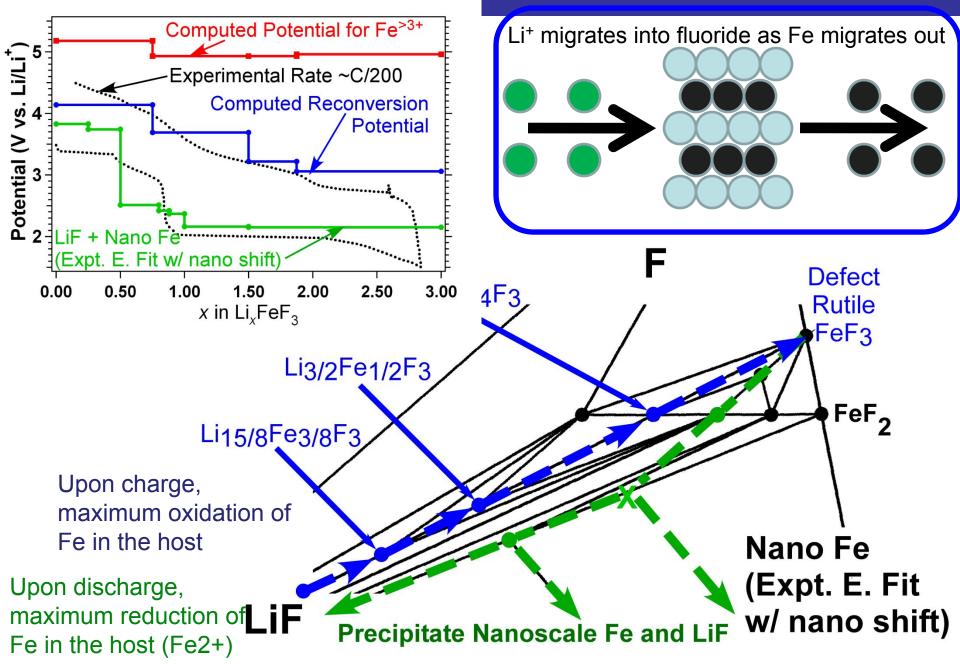
**Issue**: Is the increase in solubility observed in nano LiFePO<sub>4</sub> due to increased contribution from surface or more intrinsic ?



#### **Conversion Reactions: Understand hysteresis**



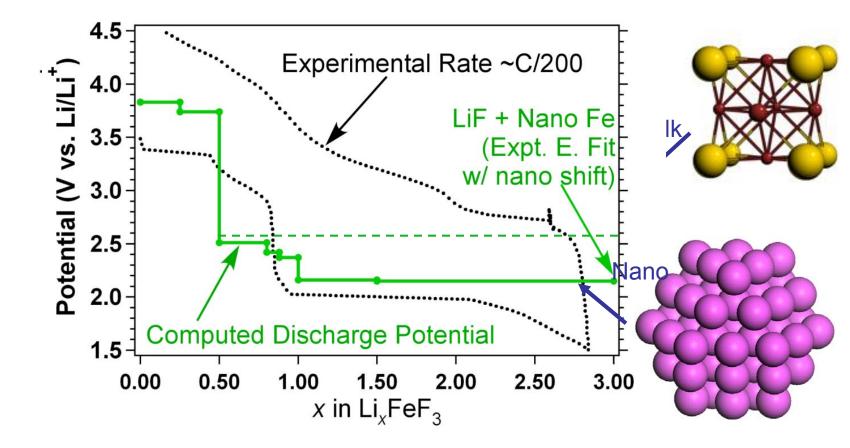
#### **Conversion Reactions: Understand hysteresis**



#### **Conversion Reactions: Nanoeffects on potential**

$$FeF_3 + 3Li -> Fe + 3LiF$$

What happens when Fe precipitates as nano?



### **Novel Materials Discovery**

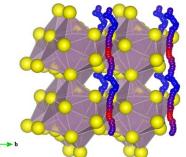
- *High-throughput computing*
- Integration of ab initio methods with database of known compounds and design strategies to make new ones
- Automation

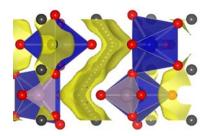
#### High-Throughput Searching for New Materials: Calculate thousands of known and new compounds

First principles methods have been developed for many relevant electrode properties: voltage, Li mobility, phase stability, thermal stability ...
Now developed ability to predict/calculate these properties on thousands of compounds by automation of computation

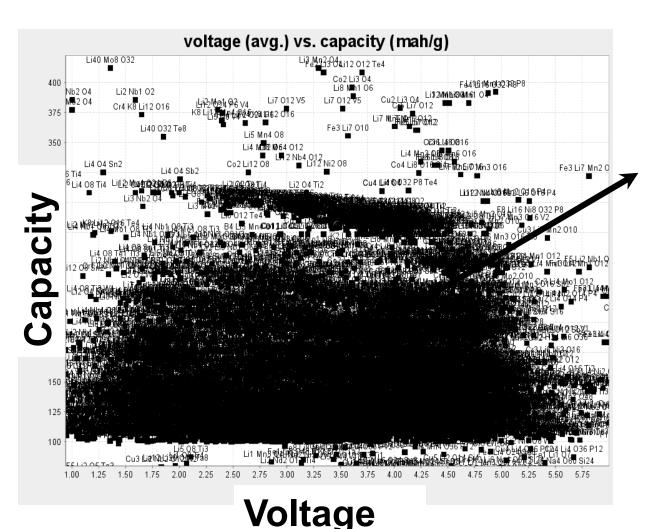
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#### Voltage and theoretical capacity of over 4000 compounds calculated



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#### TRANSFORMATIONS INVERSE TRANSFORMATIONS

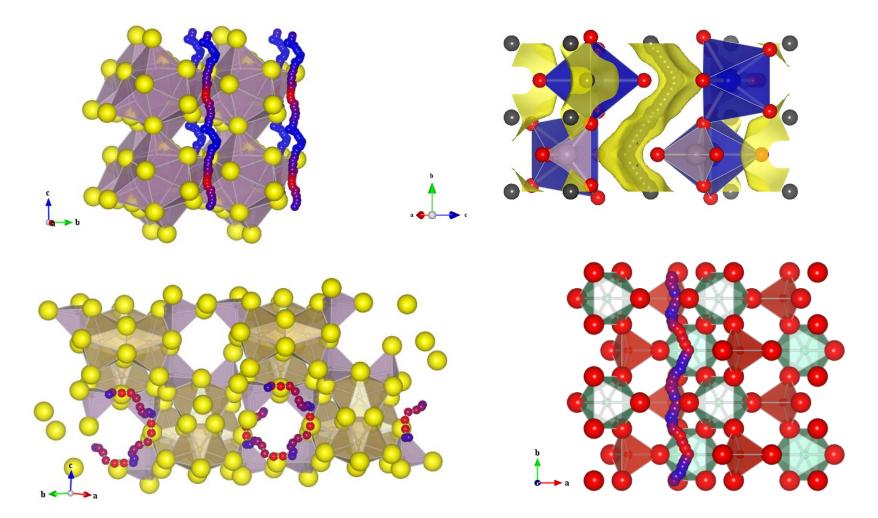
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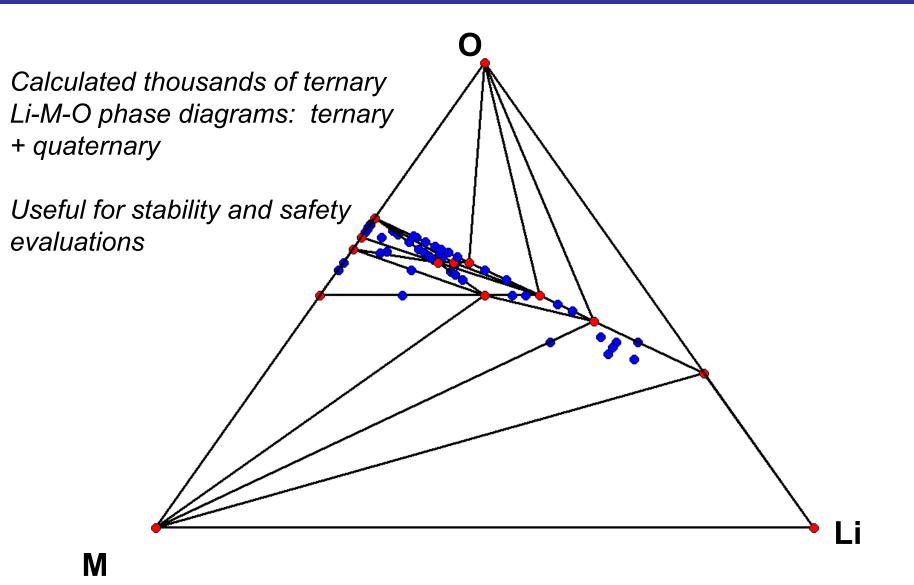
# **Li mobility:** evaluated ALL structures in ICSD database (about 30,000) and organized by prototype

Developed ability to automatically find diffusion paths for Li in structures.



Evaluated thousands of known structures...

# Thermodynamic Stability: Construct ground state diagrams of multi-component materials



- Further increase emphasis on novel materials by highthroughput computing: currently already implemented voltage, capacity, thermdynamic stability. Aim for kinetic stability, advanced Li mobility in next year.
- At least one experimental verification of a new material.
- Olivines: Get to a complete understanding of the lithiation mechanism of olivine materials: LiFePO<sub>4</sub>, LiMnPO<sub>4</sub> and mixed olivines. Understand nucleation, interface velocity, and possible surface limitations by Monte Carlo simulation and continuum theory.
- Effect of nano on performance (non-trivial): surface Li storage on metals and oxides. Change in phase transformation behavior with size.