First Principles Calculations (and NMR Spectroscopy of Electrode Materials)

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Massachusetts Institute of Technology

March 20, 2009

Project ID # **es_26_ceder**

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 $LiMPO_4$ 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*

*As of March 20, 2009

Approach

- Use **first principles calculations** (density functional theory) to identify redox-active 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$_4$ 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$_4$.

☐ **NANO EFFECTS:** Investigated **surfaces** of **LiFePO$_4$** and **LiMnPO$_4$**: structure, potentials, stability and developed theory on the **size-dependence** of the miscibility gap

☐ **CONVERSION REACTIONS** Studied **conversion reactions** and **nano-size 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 $LiFePO_4$ and $LiMnPO_4$
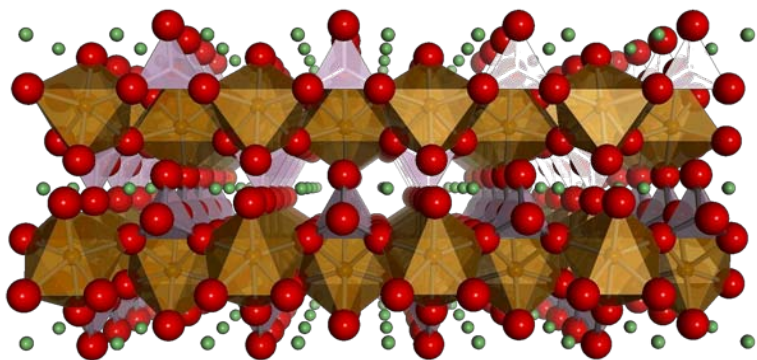
Li migration barrier calculation indicate that very high rate is possible
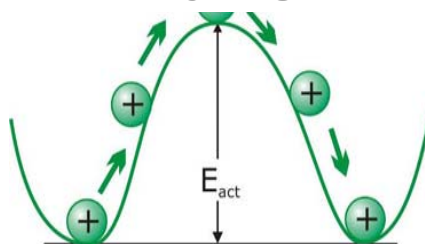
1D diffuser:
 barrier of 200-300meV
diffusion length:
50 nm in about 1 ms

Phase diagram calculations indicate how to achieve it

$LiFe_{0.9}P_{0.95}O_{4-\delta}.$
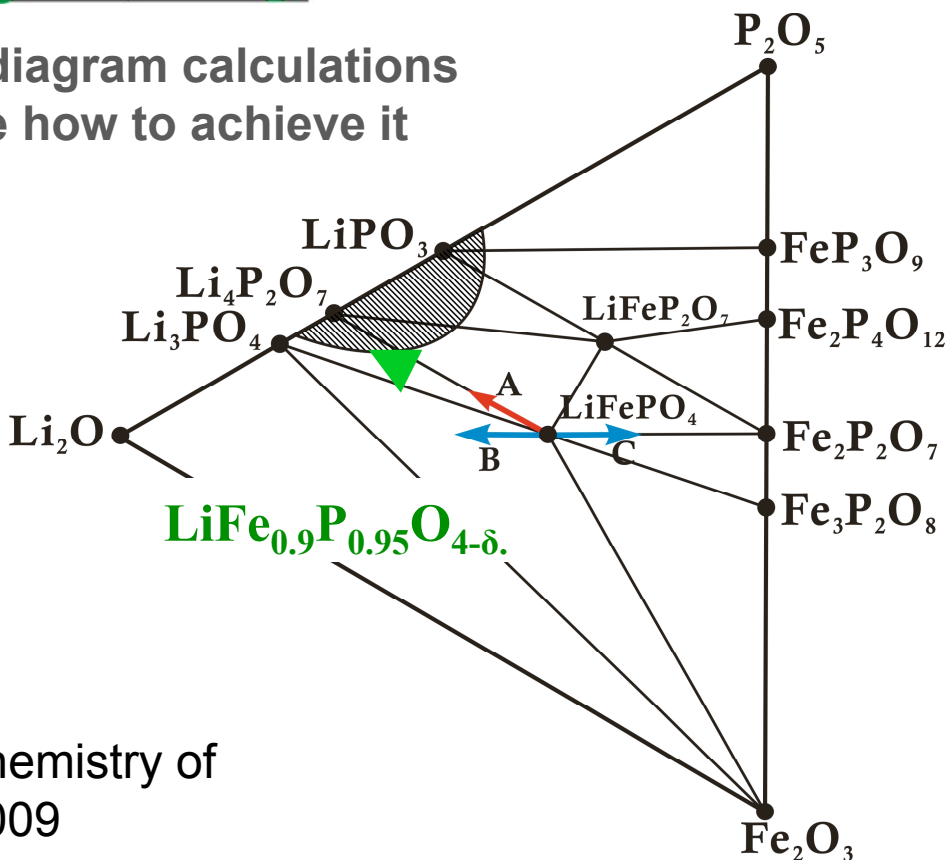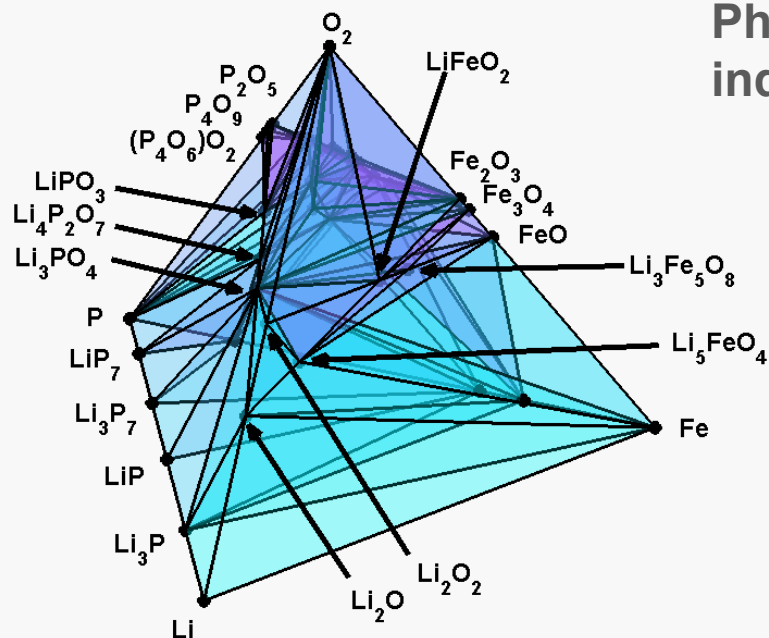
Morgan, Ceder, ESSL 2004; Ping,Ceder Chemistry of Materials 2004; Kang and Ceder, Nature 2009

Nano material with optimized surface treatment gives very high Power density
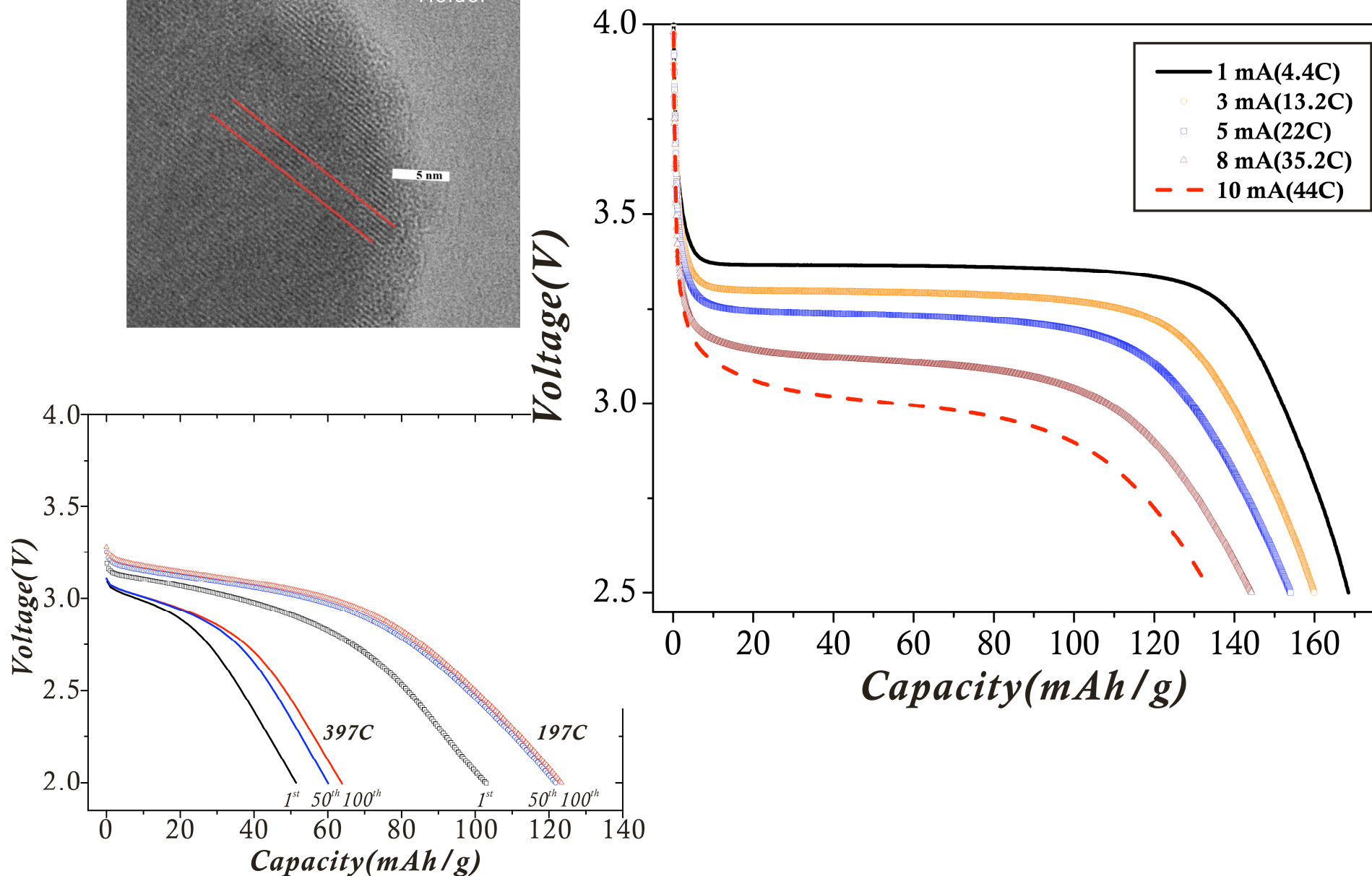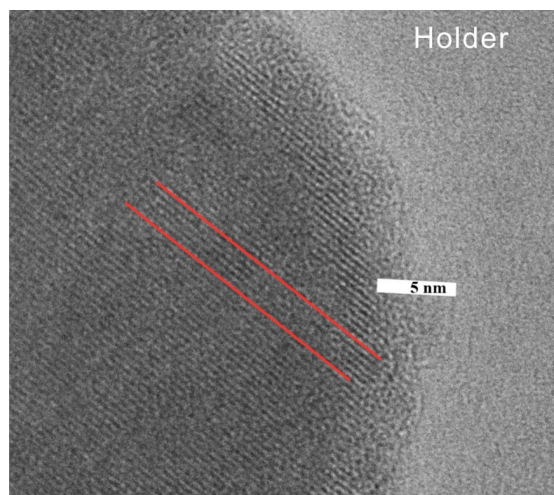
Ab initio processing ? (under development)

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

Example: LiFePO$_4$ in solution

pH=5.5   pH= 6.0   pH= 7.5
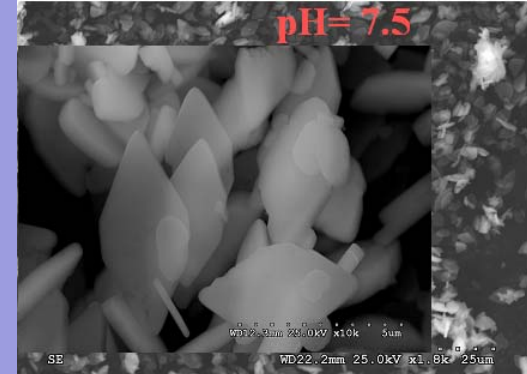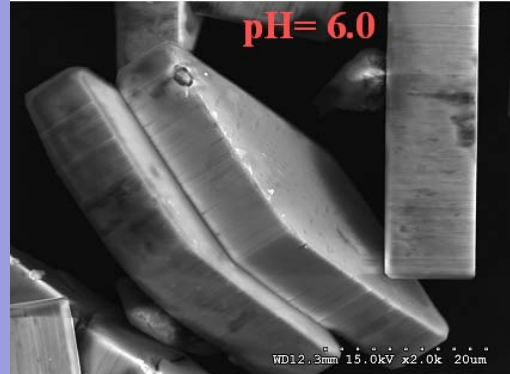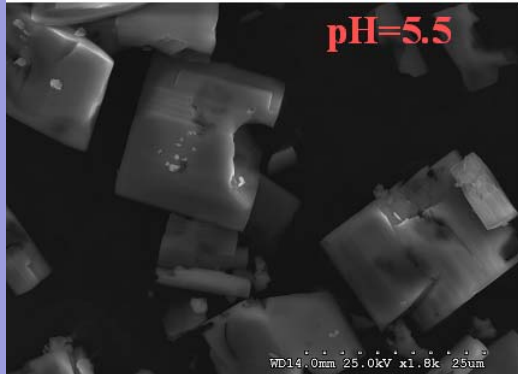
Morphology of olivine system can be depends on pH, T, precursor concentration, …

[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

H	H_2O	OH	O

[010]

[001] [100]

H_2O on [010]

Last year: stable crystal shapes in vacuum

(011) (201)

(010) (100)

0.75
0.70
0.65
0.60
0.55
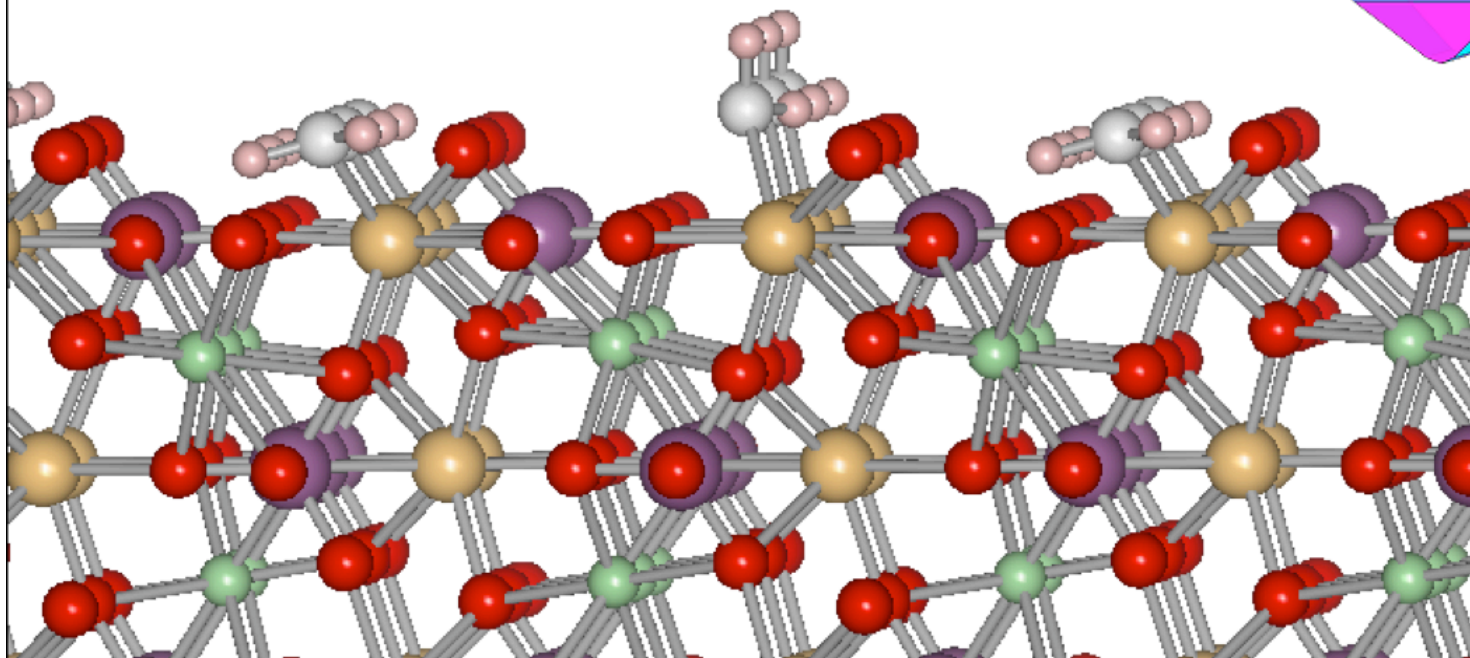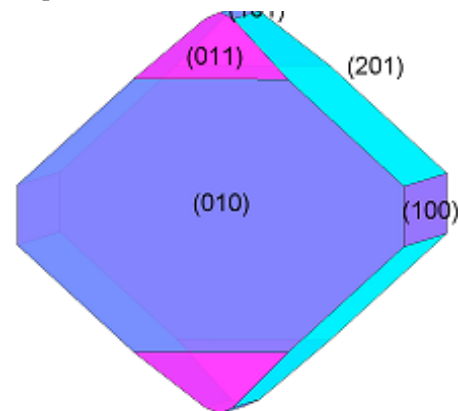
Study all relevant surfaces
with typical adsorbants + potential Li dissolution

LiFePO$_4$

At neutral potential all the surfaces are water capped for any pH
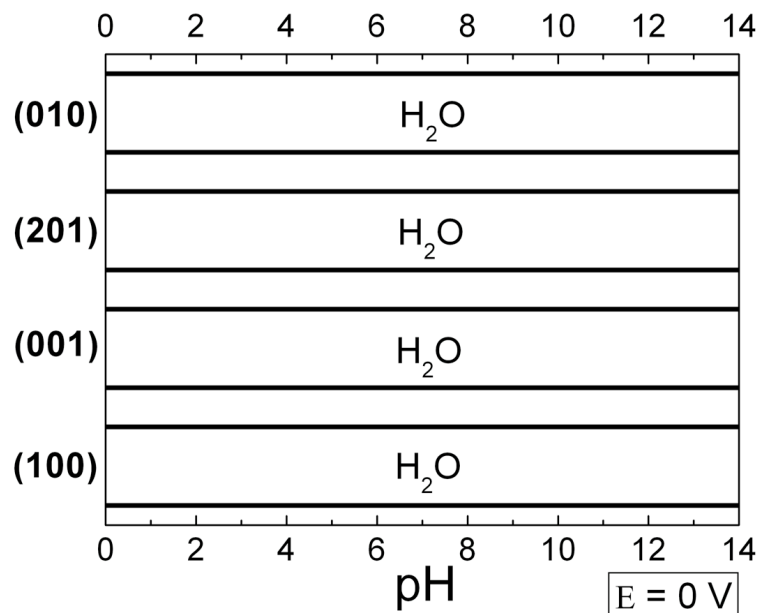
At high potential all the surfaces are water capped for any pH
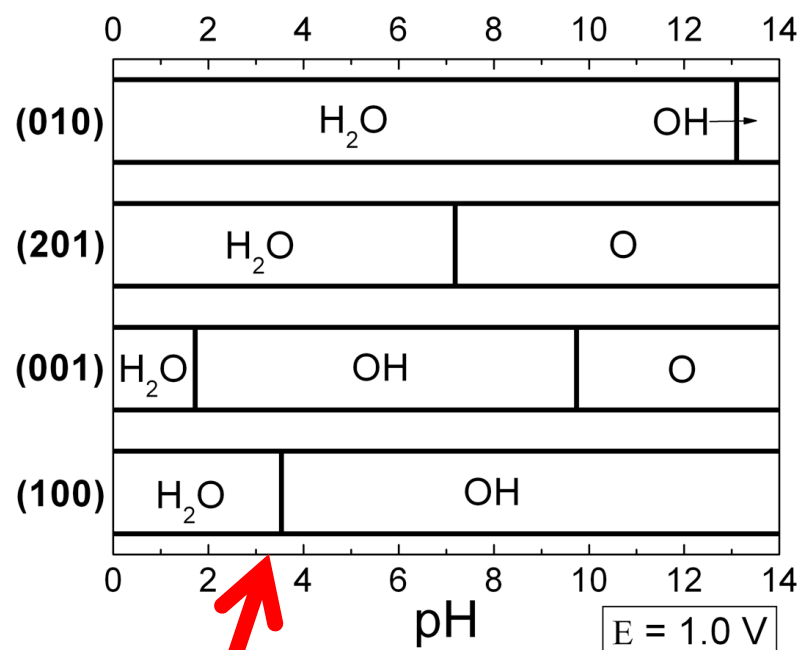
Surface adsorption/structure, and hence surface energy, can be modified by pH !   -> gives control over stable morphology of the surfaces

Stable Wulff shapes as function of environment
Shape control through pH !
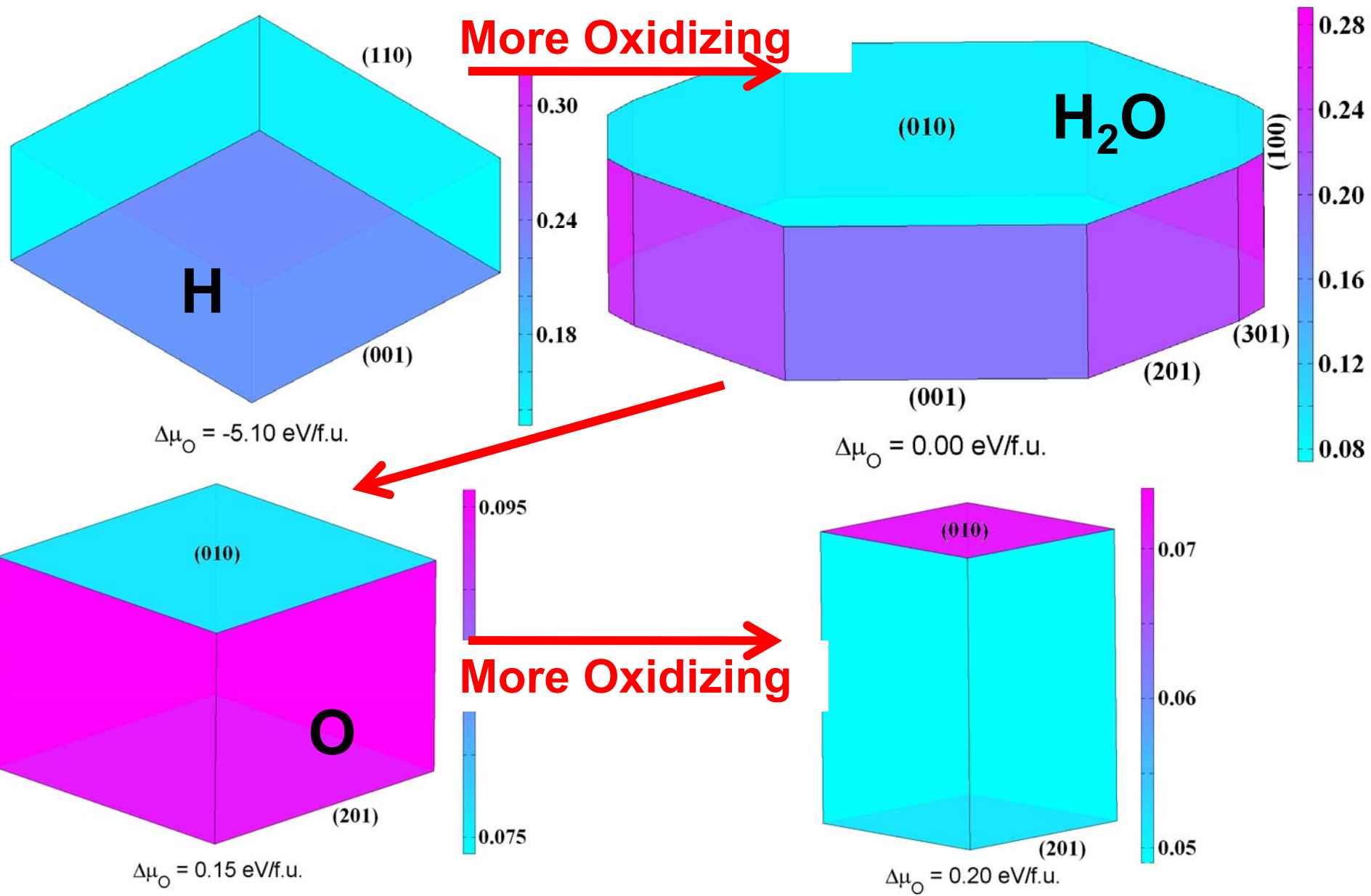
Similar ab-initio shape control in LiCoO$_2$
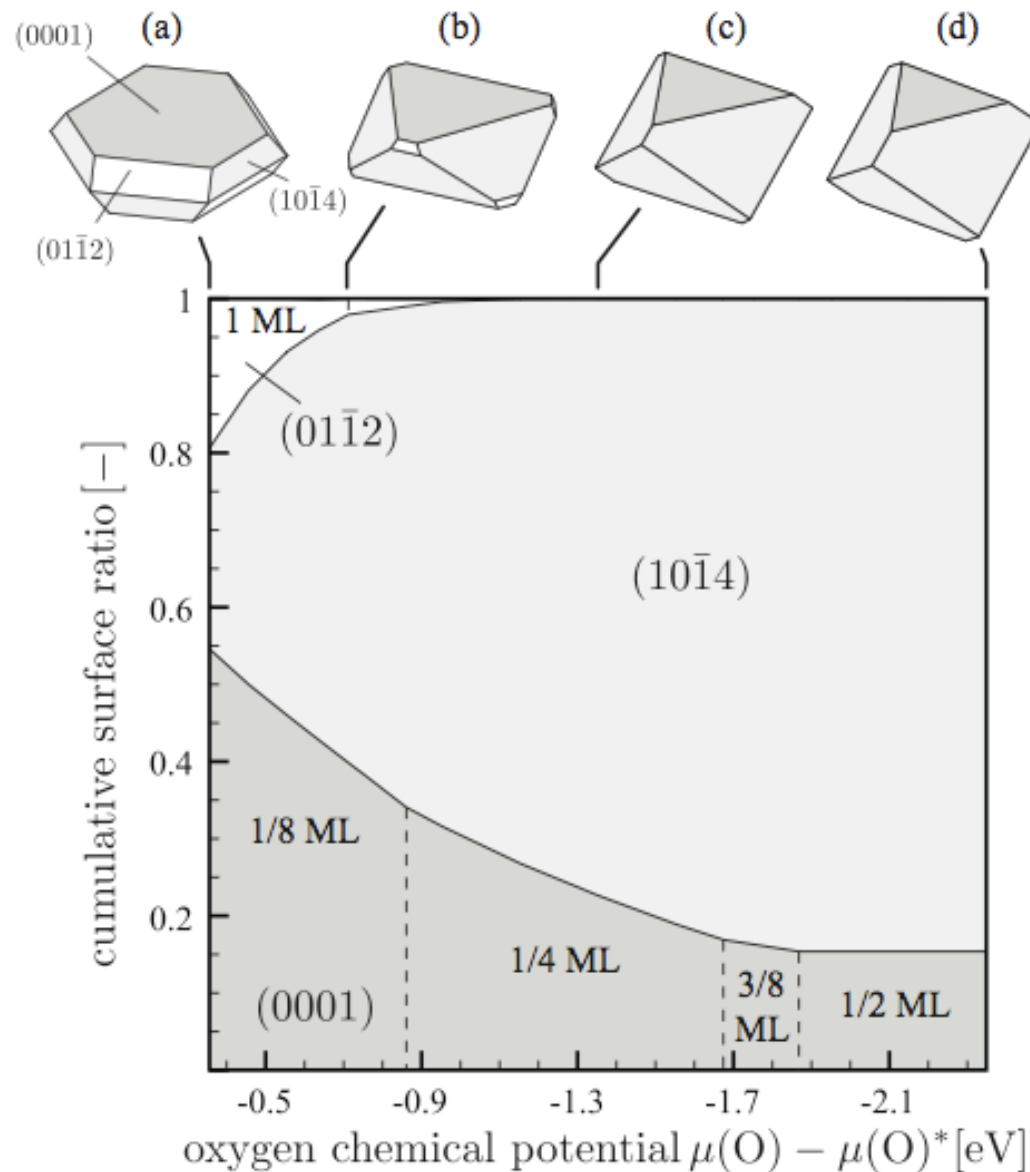
Mixed Olivine Systems: Li(Fe,Mn)PO$_4$

- 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

Mn2+/Mn3+ voltage increases with more Mn

Fe2+/Fe3+ voltage increases with more Mn

20% Mn · 30% Mn · 50% Mn · 70% Mn · 90% Mn

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Mn2+/Mn3+ voltage increases with more Mn

Fe2+/Fe3+ voltage increases with more Mn

90% Mn

70% Mn

50% Mn

30% Mn

20% Mn

(a)

(d)
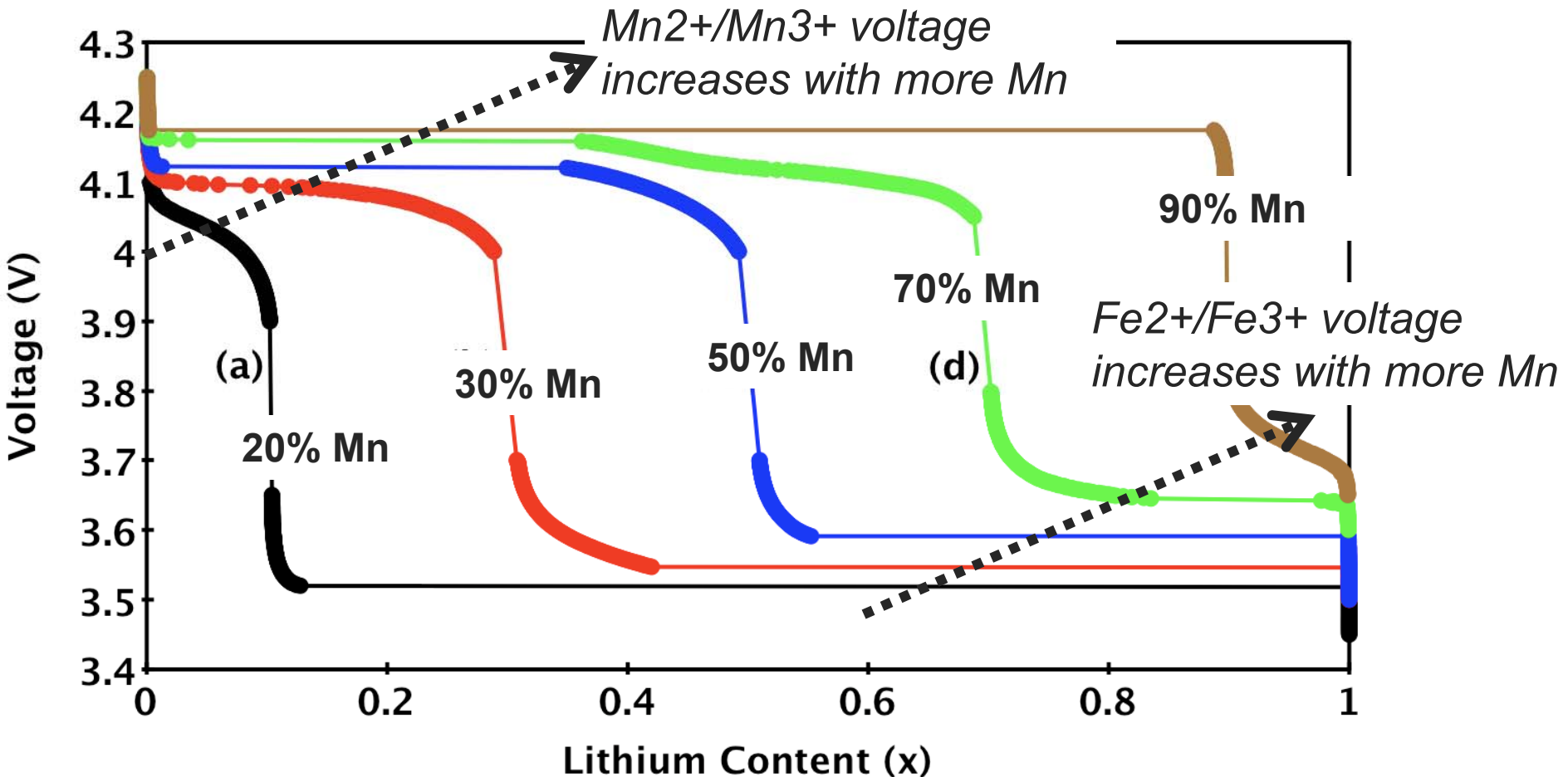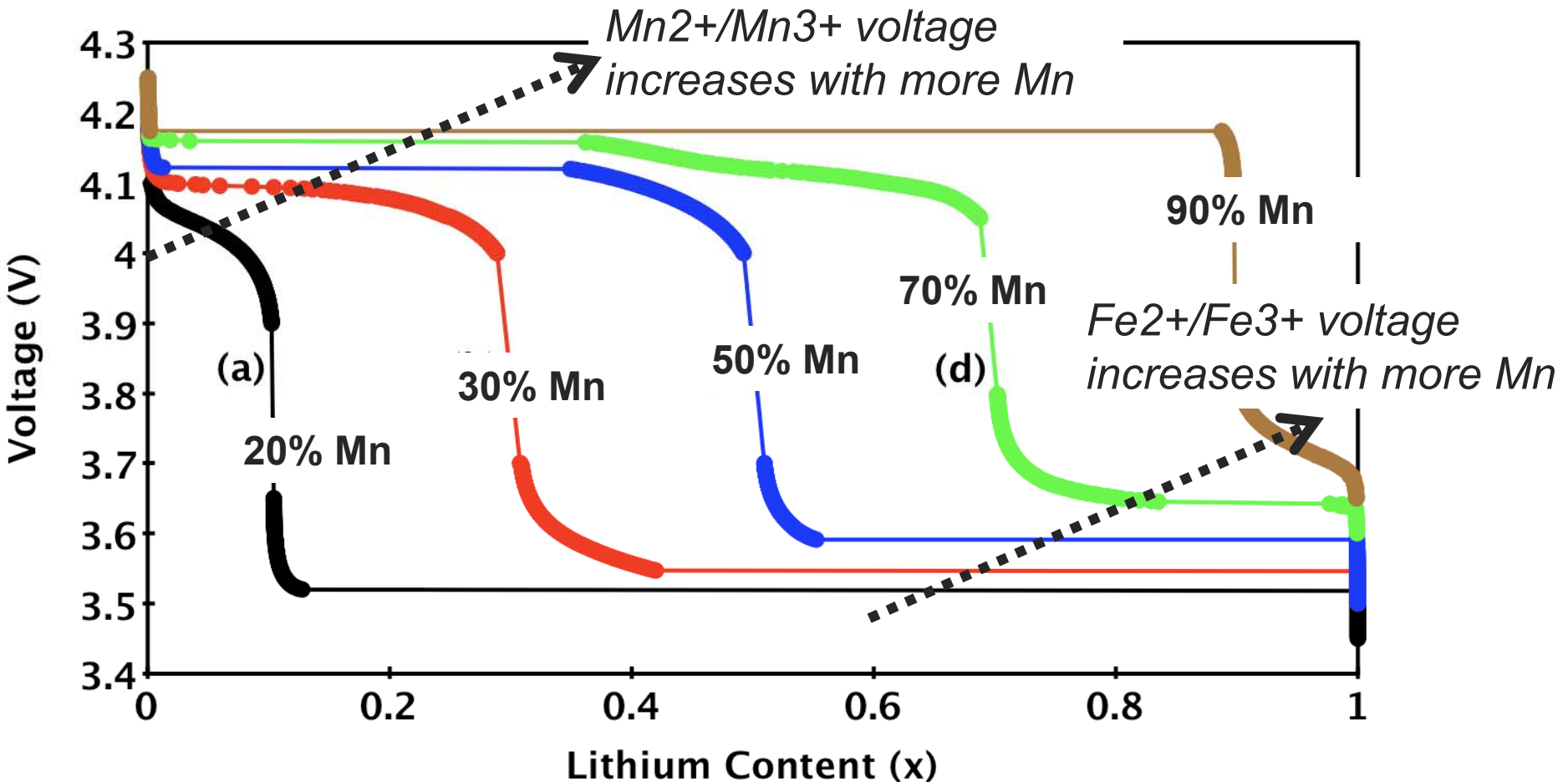
Mixed Olivine Systems: $Li_{0.4}(Fe_{0.2}Mn_{0.8})PO_4$

tunnels

Partially ordered chain fragments

Li

vac

M2+

M3+
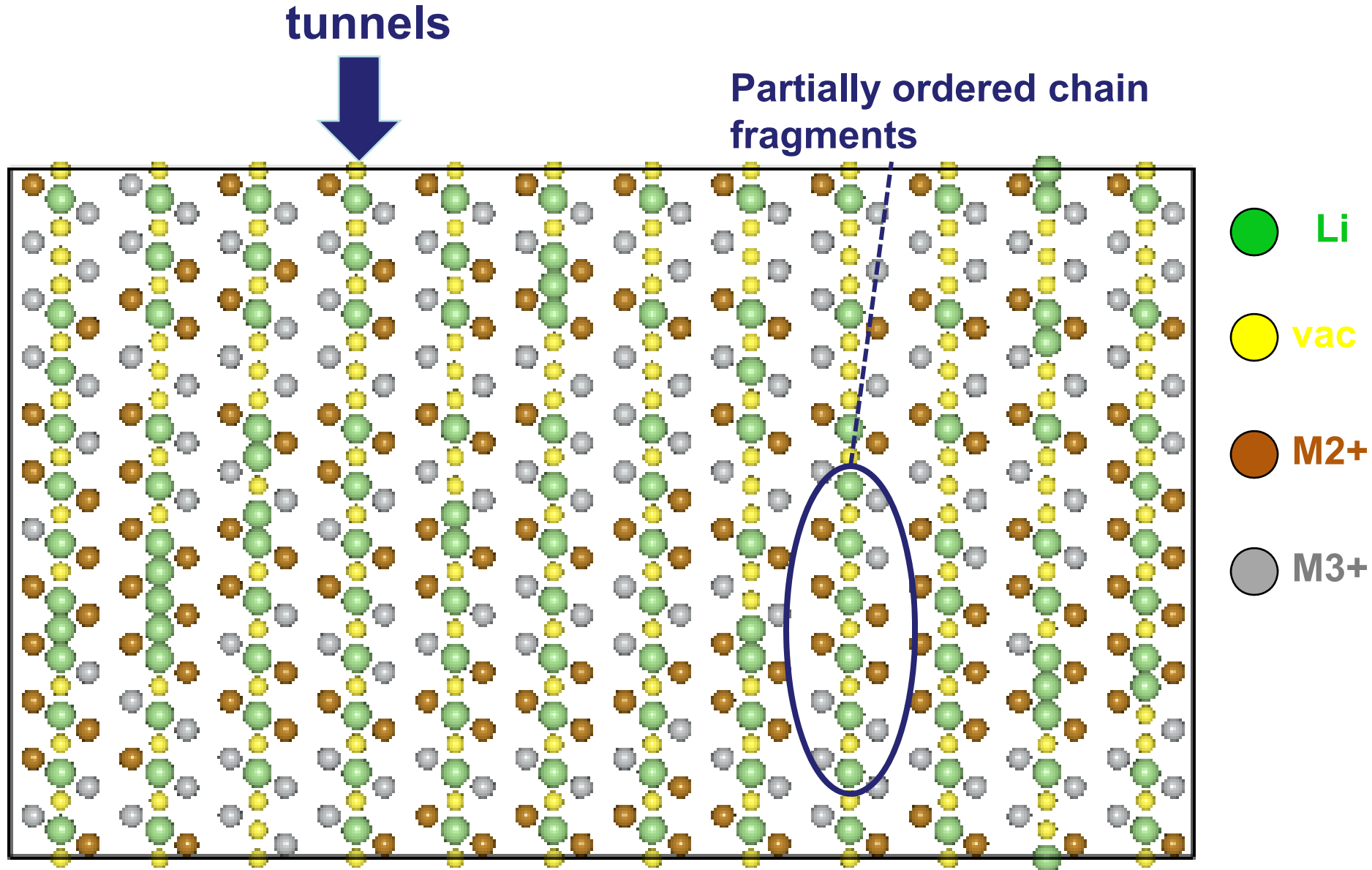
Nanoeffects

- Effects on solubility ($LiFePO_4$)

- 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 $LiFePO_4$ due to increased contribution from surface or more intrinsic?
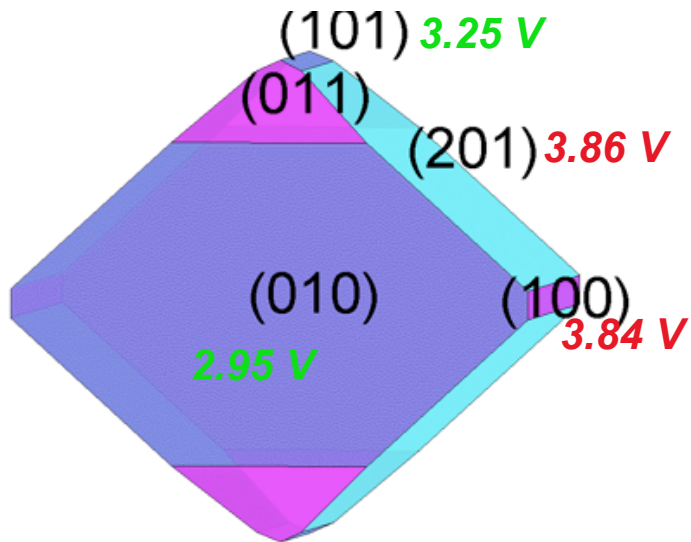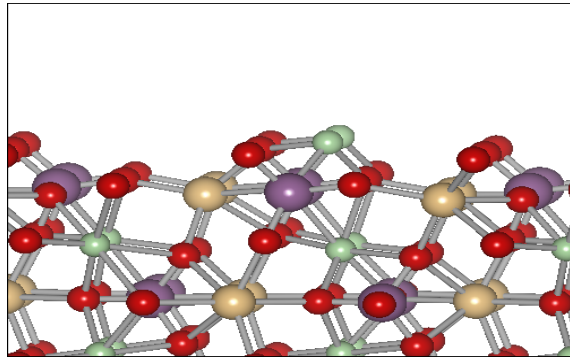
Calculated surface redox potentials:

(010)   (101)   bulk (201) (011) (100)

(101) *3.25 V*
(011)
(201) *3.86 V*
(010)
(100) *3.84 V*
2.95 V

$$FeF_3 + 3\,Li \rightarrow Fe + 3\,LiF$$
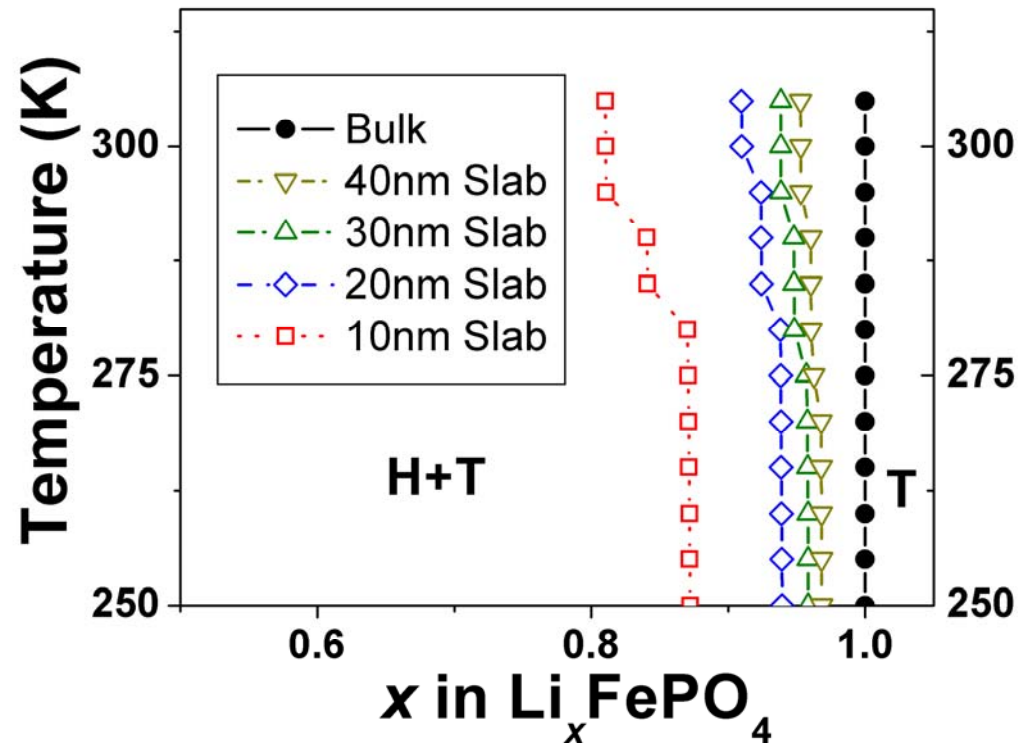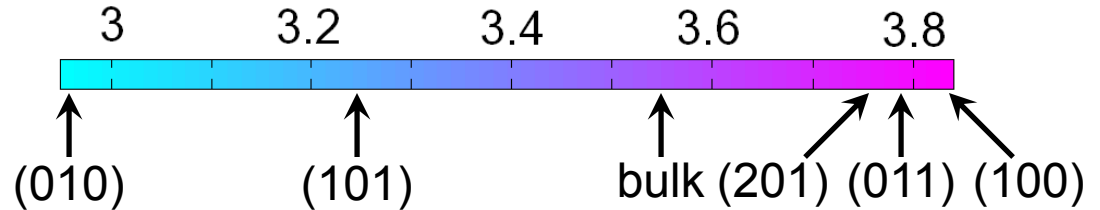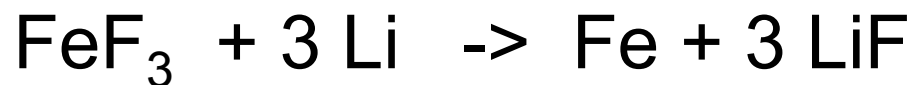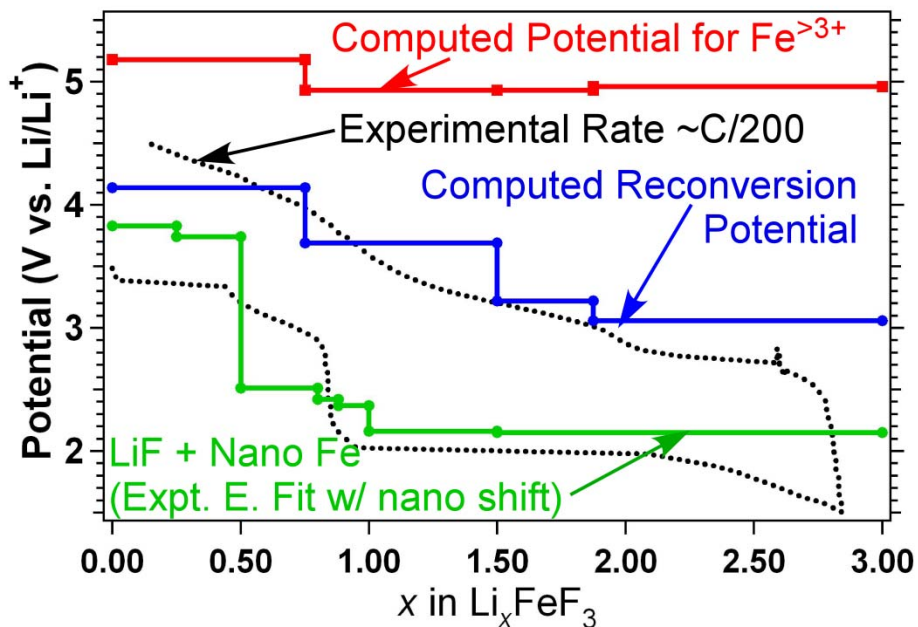
Why is there so much hysteresis ?

Calculated phase diagram
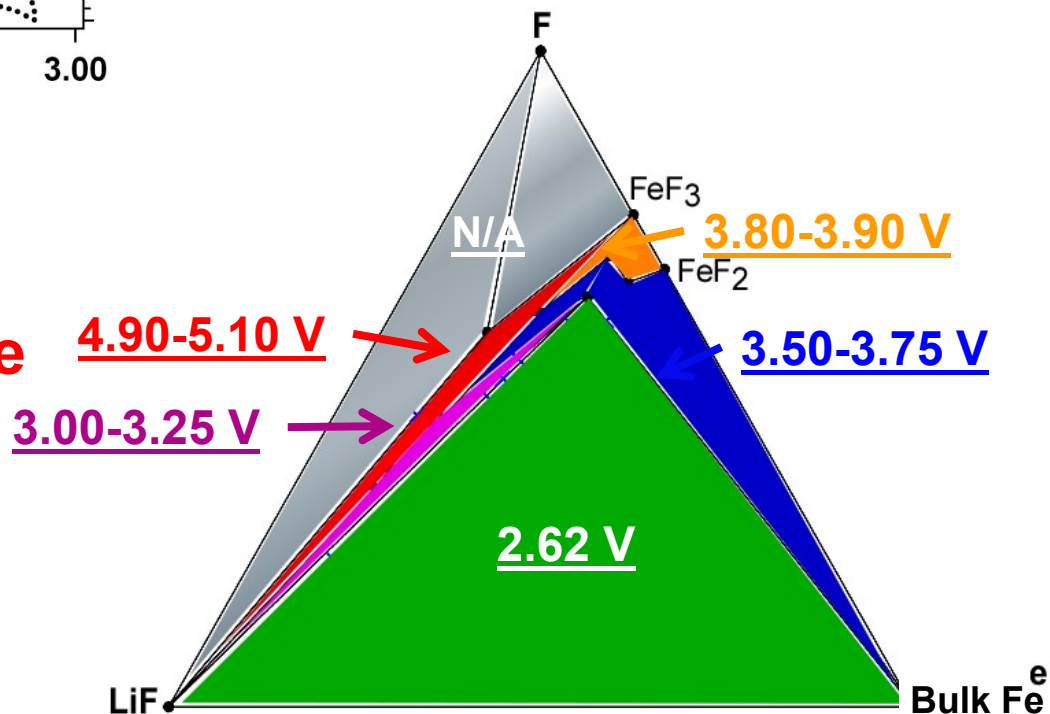
4.90-5.10 V

3.80-3.90 V

3.50-3.75 V

3.00-3.25 V

N/A

2.62 V

FeF₃

FeF₂

F

LiF

Bulk Fe

Li$^+$ migrates into fluoride as Fe migrates out

F

Defect Rutile FeF$_3$

$_4$F$_3$

Li$_{3/2}$Fe$_{1/2}$F$_3$

Li$_{15/8}$Fe$_{3/8}$F$_3$

FeF$_2$

Upon charge, maximum oxidation of Fe in the host

Upon discharge, maximum reduction of Fe in the host (Fe2+)

LiF

Precipitate Nanoscale Fe and LiF

Nano Fe (Expt. E. Fit w/ nano shift)

$$FeF_3 + 3\,Li \rightarrow Fe + 3\,LiF$$
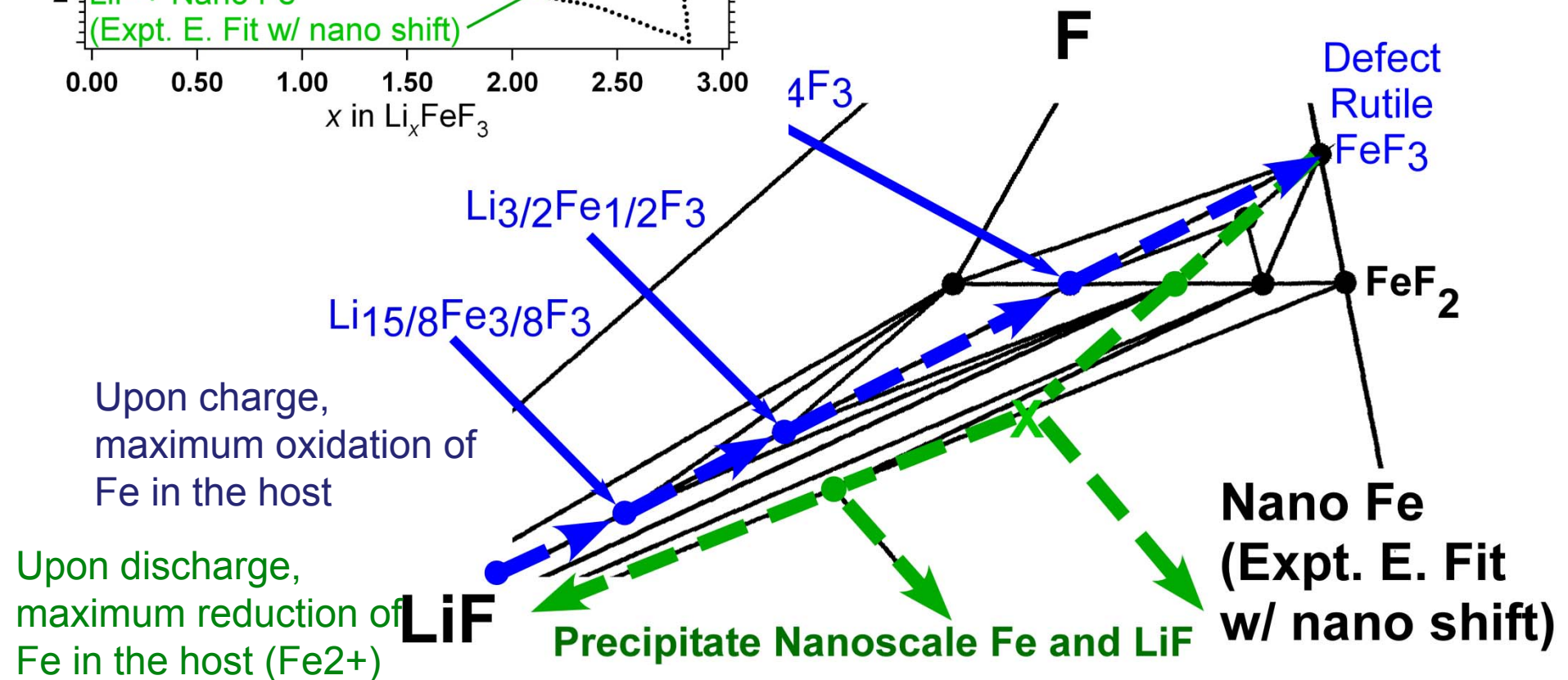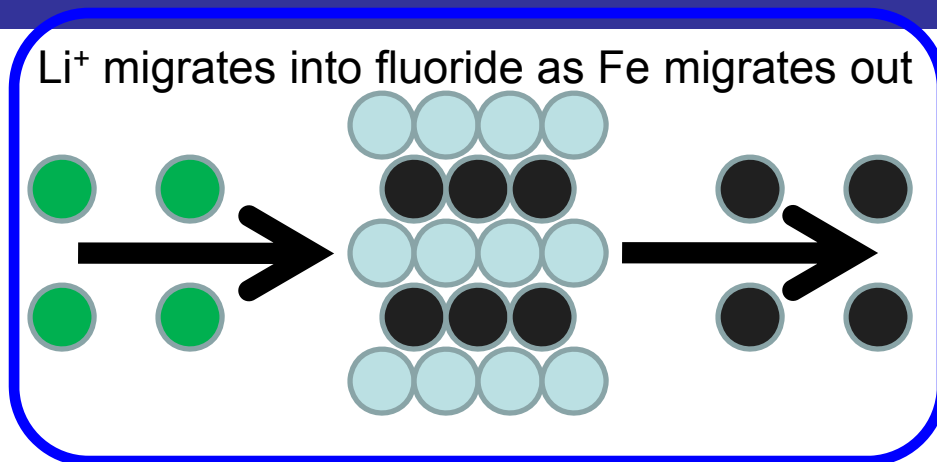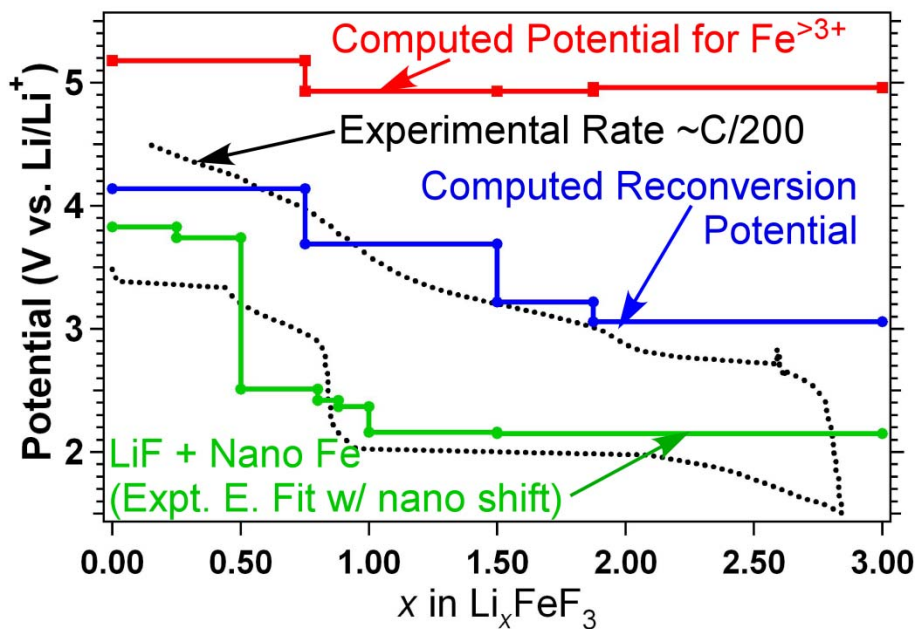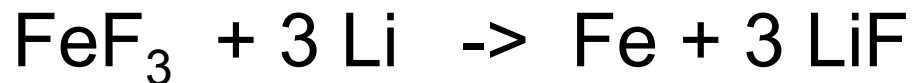
What happens when Fe precipitates as nano ?

Experimental Rate ~C/200

LiF + Nano Fe
(Expt. E. Fit
w/ nano shift)

Ik

Nano

Computed Discharge Potential

Potential (V vs. Li/Li$^+$)

x in Li$_x$FeF$_3$
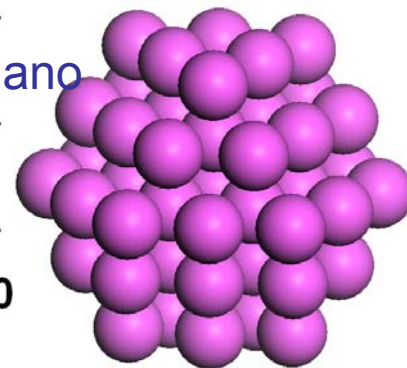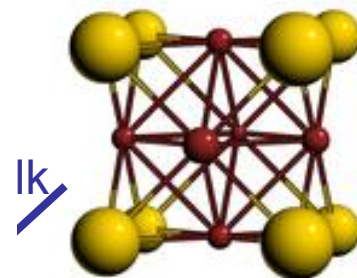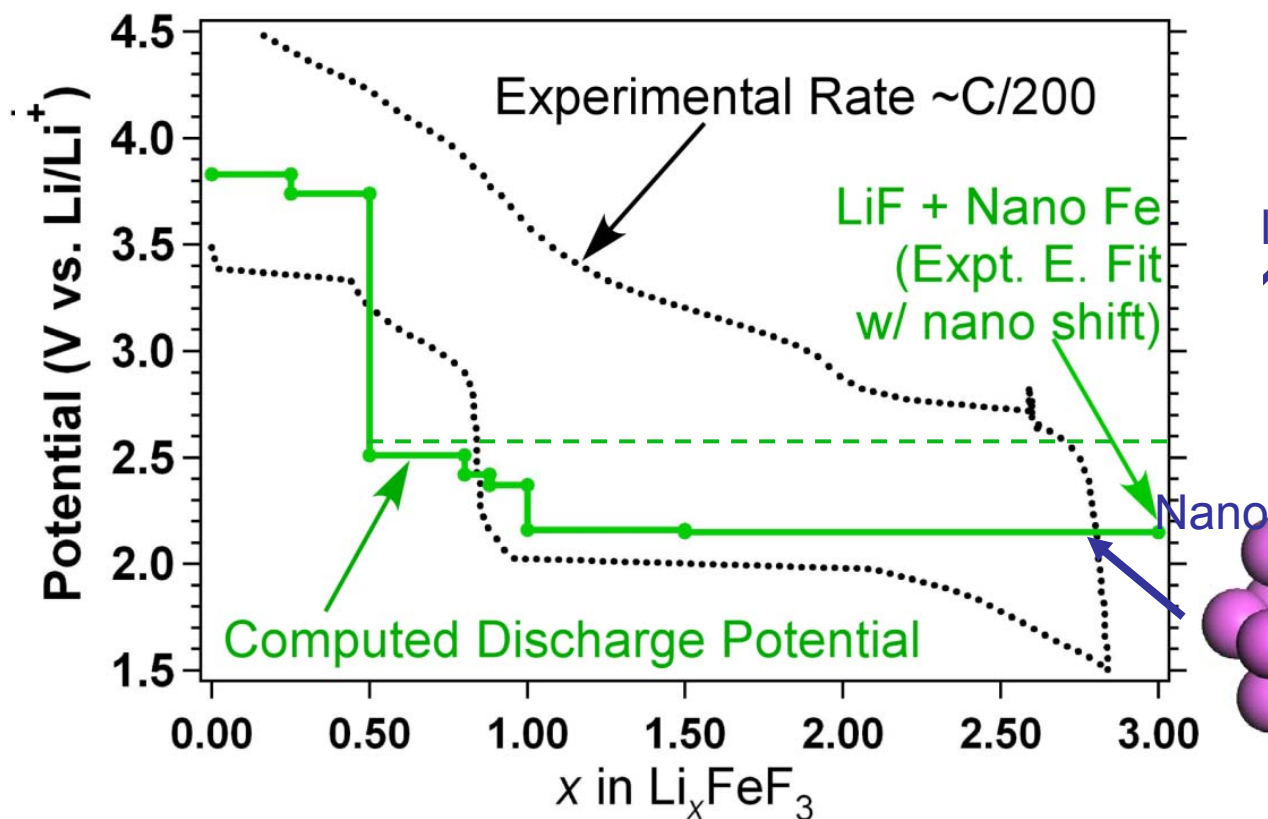
Novel Materials Discovery

- *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

High-throughput computing environment

voltage (avg.) vs. capacity (mah/g)

Capacity

Voltage

Developed ability to automatically find diffusion paths for Li in structures.
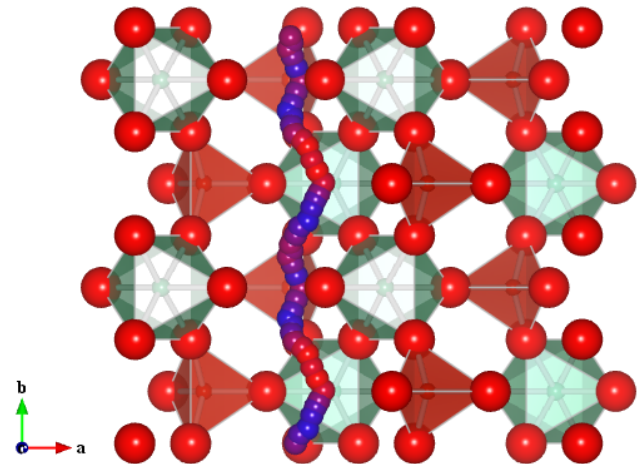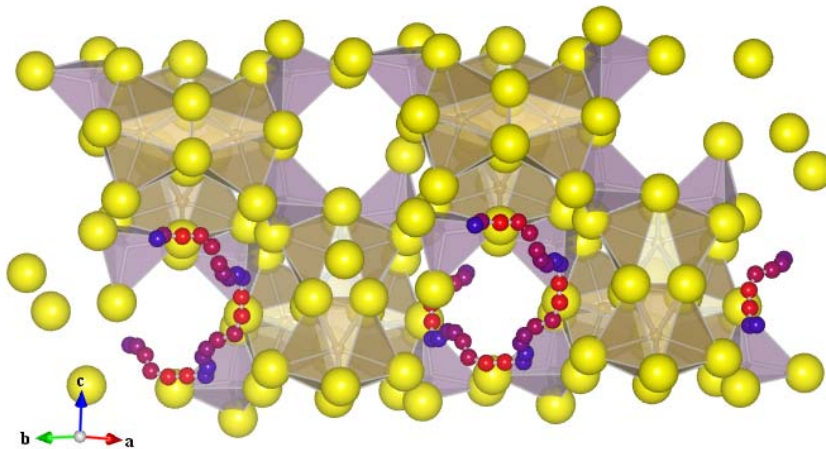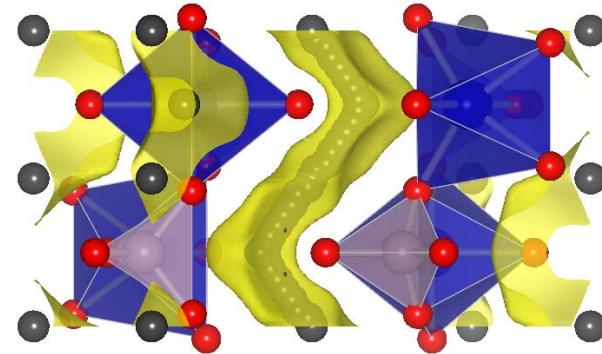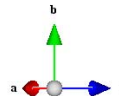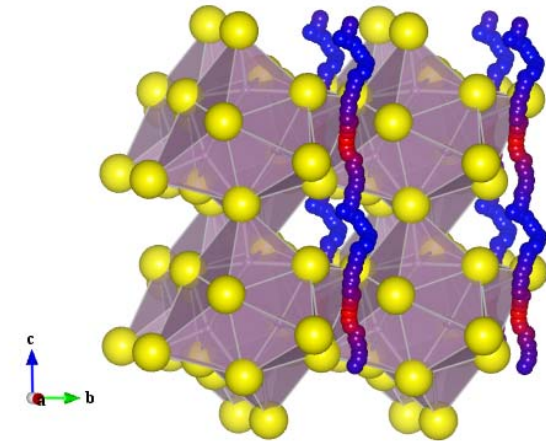
Evaluated thousands of known structures...

Calculated thousands of ternary Li-M-O phase diagrams: ternary + quaternary

Useful for stability and safety evaluations
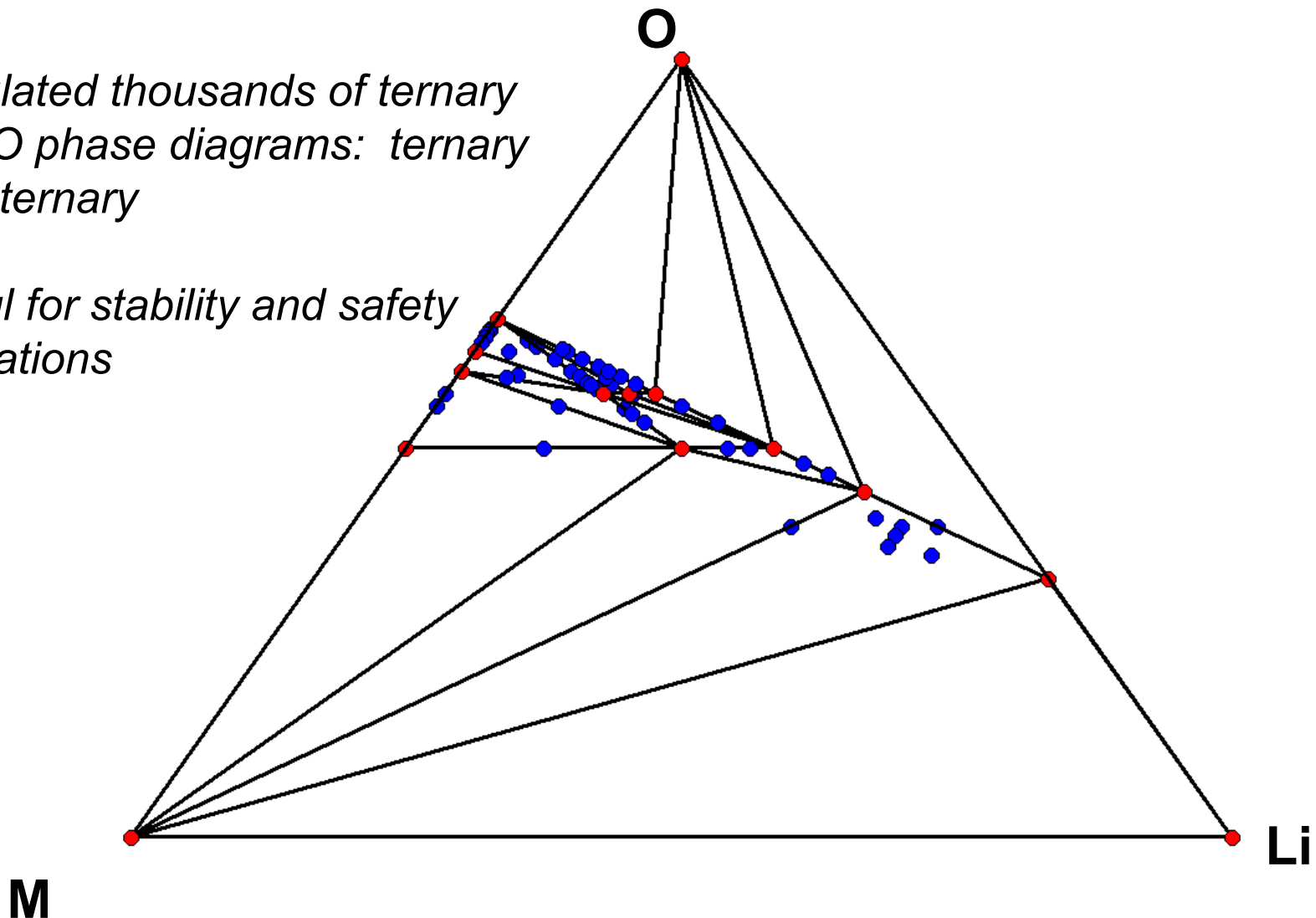
Future work (Goals)

- Further increase emphasis on **novel materials** by high-throughput 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: $LiFePO_4$, $LiMnPO_4$ 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.