# First Principles Calculations of Electrode Materials

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**Massachusetts Institute of Technology**

**DOE review 2010**

Project ID # **es054**

# Overview

## Budget

- Funding for FY09: $380,000
- Funding for FY10: $320,000 (10 months)

## Barriers

- Low rate capabilities
- High cost
- Low energy

## Objectives

- Determine the effect of structure on stability and **rate capability** of cathodes and anodes.
- Predict thermal stability of materials at TOC
- Understand nanoeffects on lithiation of materials
- Develop **new materials**

## Partners

- **Clare Grey (SUNY) (co-PI)**

- Collaborators (BATT):
- Dr. K. Persson, LBNL
- Dr. R. Kostecki, LBNL
- Dr. Vince Battaglia, LBNL
- Prof. S. Whittingham (SUNY)

# Relevance –Objectives–Approach

The **objectives** of our program are to determine how structure and chemistry influence the electrochemical performance of an electrode material, including rate, energy density, stability, and safety, and to use these insights to develop *new, stable, cathode materials* with high energy-density.

Our **approach** is to 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 oxidation strength at top of charge. Validate predictions by collaboration with experimental groups. Use high-throughput computing to identify promising cathode materials for BATT applications.

**Specific focus for 2010**: Thermal stability, nano-effects in olivines, rate capability of materials, new materials

# Milestones (joined with Clare-Grey project)

(a) November 1, 2009: Obtain size effect on Li mobility in olivines. THEORY COMPLETE. Identify potential new electrode materials for synthesis experiments. DONE(*) Complete Si PDF data. DATA COLLECTION COMPLETE, ANALYSIS ONGOING. Initiate *in situ* NMR studies of multicomponent electrode - DONE. Initiate Li mobility calculations in other materials such as graphite and spinel. GRAPHITE DONE, SPINEL DONE
(b) May 1 2010: Identify pathways for charge/discharge reactions in olivines and materials with first order transitions. STARTED. Perform relevant experiments to test proposed mechanisms for doped phosphates. Indentify potential new electrode materials for synthesis experiments. DONE Complete analysis of Si nanoparticles. STUDY OF Si NANOPARTICLES ONGOING.

(*) We are not reporting on the new materials this year for confidentiality reasons, but expect to report on them in the beginning of next year

# Approach

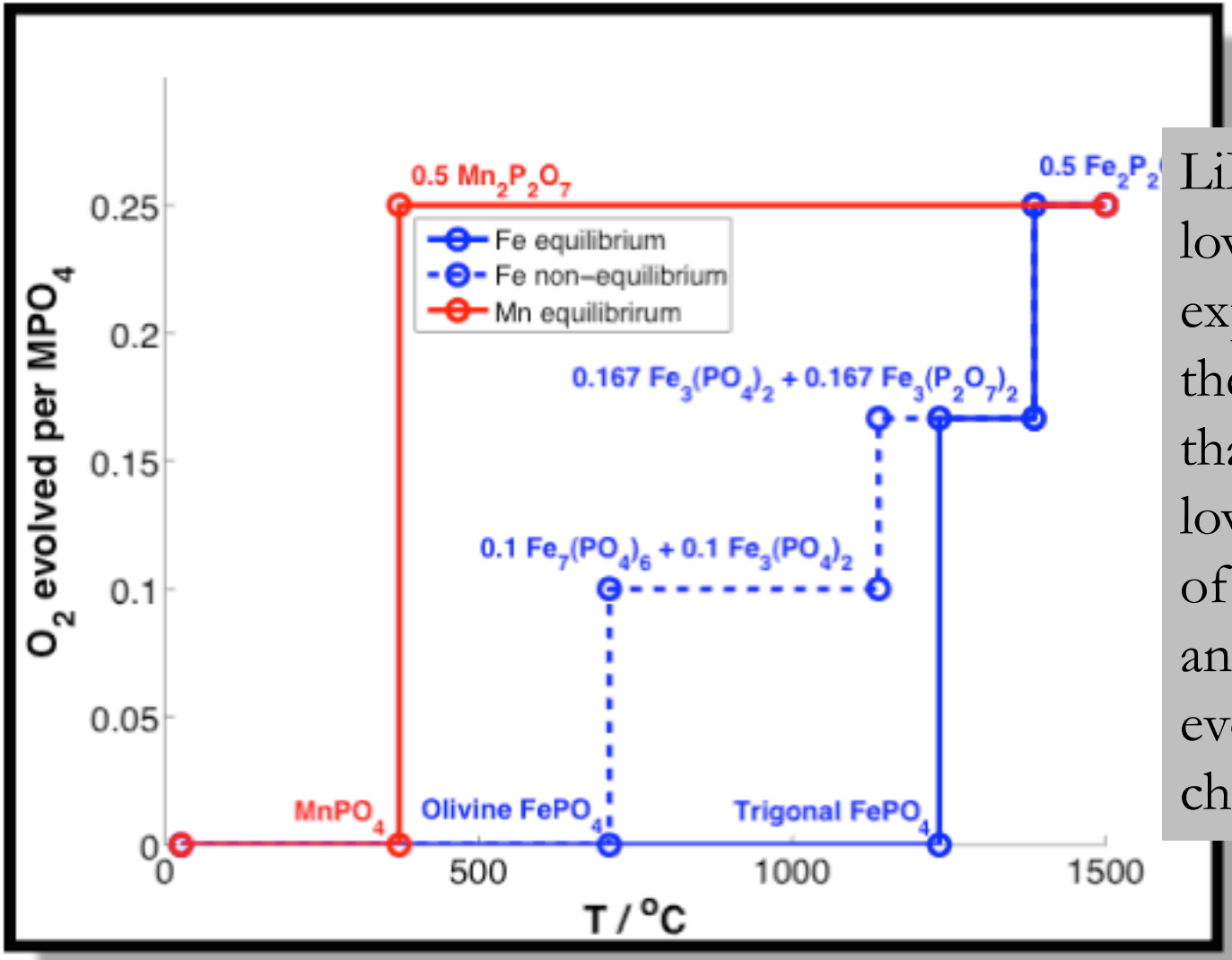
**Thermal stability:** Thermal stability is determined from the oxidation strength of the cathode at the TOC, which is calculated as the oxygen chemical potential developed as the charged cathode decomposes. Temperatures for decomposition are estimated by assessing when the environment becomes reducing enough to decompose the cathode

**Diffusion**: Diffusion is studied with kinetic Monte Carlo models, in which the hopping barriers and interactions are parameterized from first principles computations.

**Polaron migration** is studied with the Hybrid Screened Exchange method to properly localize the electron/hole. This is an improvement over the previously used GGA+U, and gives better results in $LiMnPO_4$

(*) We are not reporting on the new materials this year for confidentiality reasons, but expect to report on them in the beginning of next year

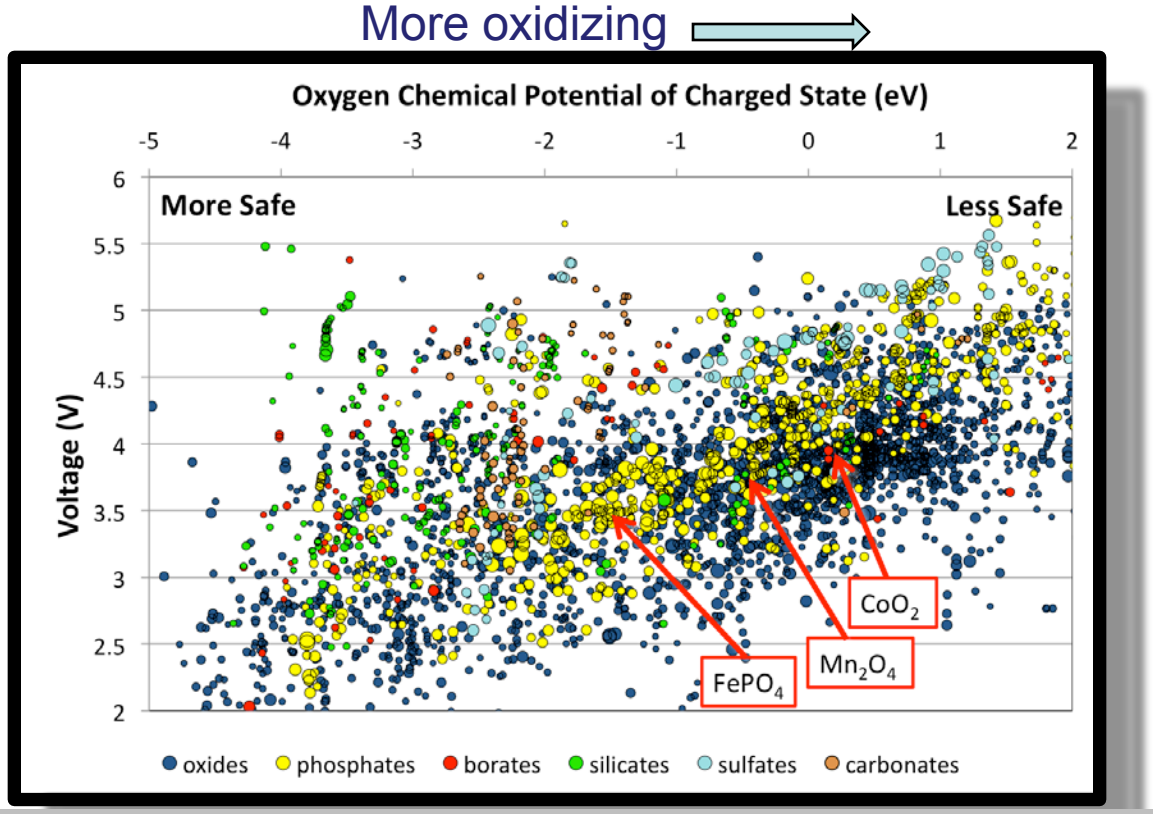
# Thermal Stability of $LiFePO_4$ and $LiMnPO_4$




$LiMnPO_4$ has a lower predicted and experimental thermal stability than $LiFePO_4$ – lower temperature of decomposition and more $O_2$ evolved per mol of charged cathode

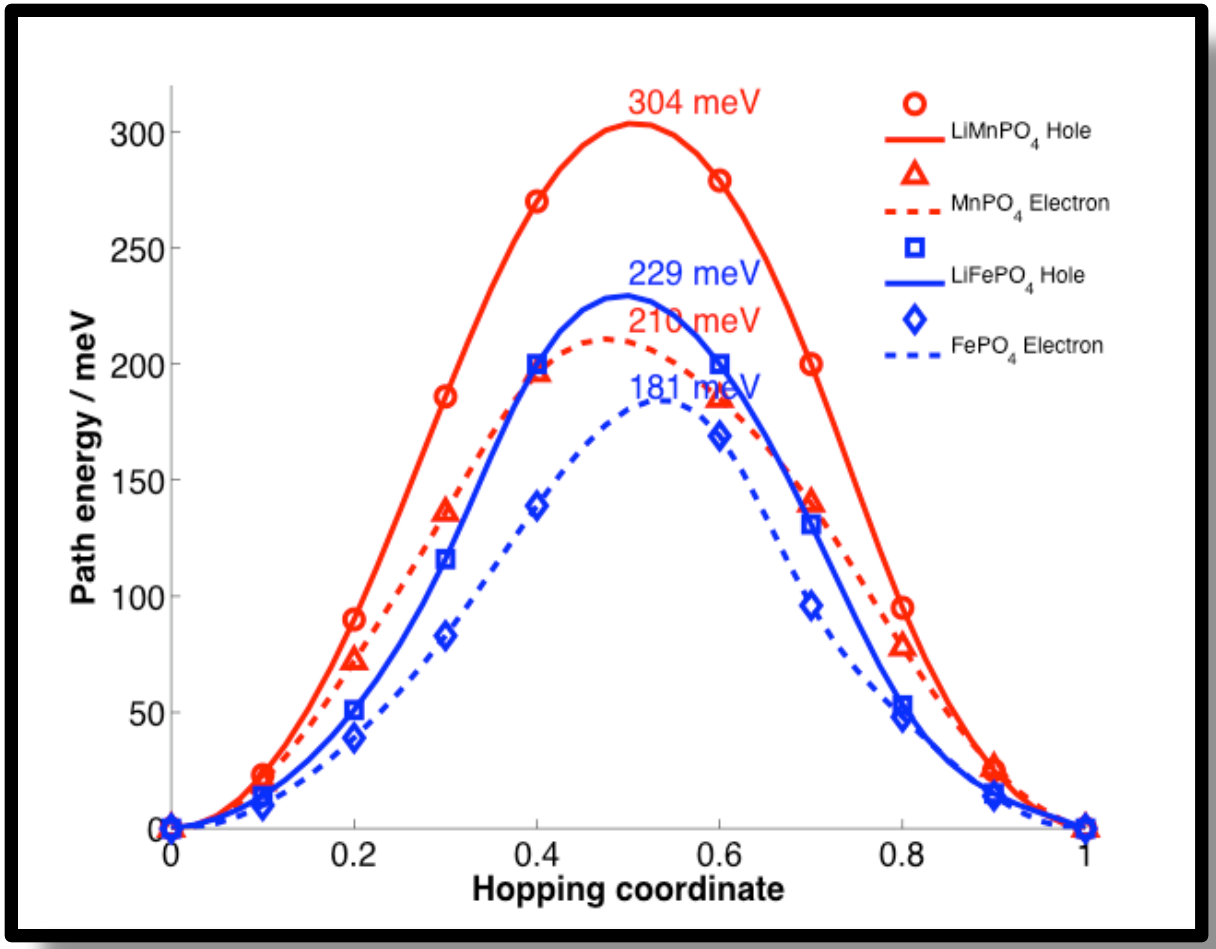
Temperatures are slightly overestimated in calculations

# Relationship between Voltage and Thermal Stability



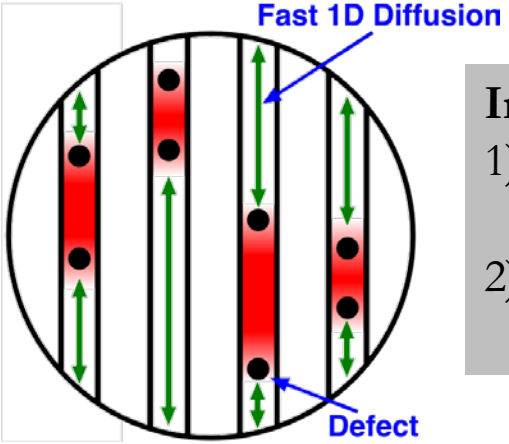

- Generally, higher voltage ➔ Higher Oxidation strength at TOC ->Worse thermal stability
- **BUT** new polyanion structures offer potential avenues to achieve a better tradeoff between voltage and thermal stability.
- Borates and silicates seem to offer the best voltage to thermal stability performance.

# Polarons in $LiFePO_4$ and $LiMnPO_4$




LiMnPO4 has higher hole and electron polaron migration barriers => possibly lower electronic conductivity

# Nano-size effects on Diffusion in $LiFePO_4$: I

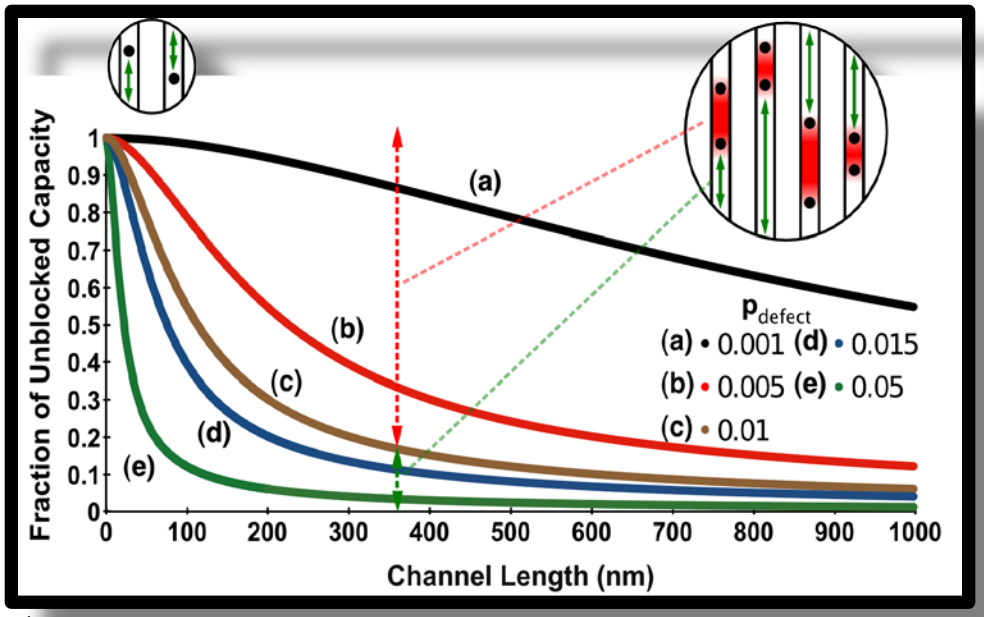



Nano Size Diffusion in $LiFePO_4$

**Immobile Point Defects Trap Capacity**

1) Immobile point defects ($Fe_{Li}$)residing in the 1D diffusion path can impede Li transport.
2) When more than 2 defects in a channel, the capacity between is trapped.

**Hence, nano LFP has fundamentally different diffusion than micron LFP !**

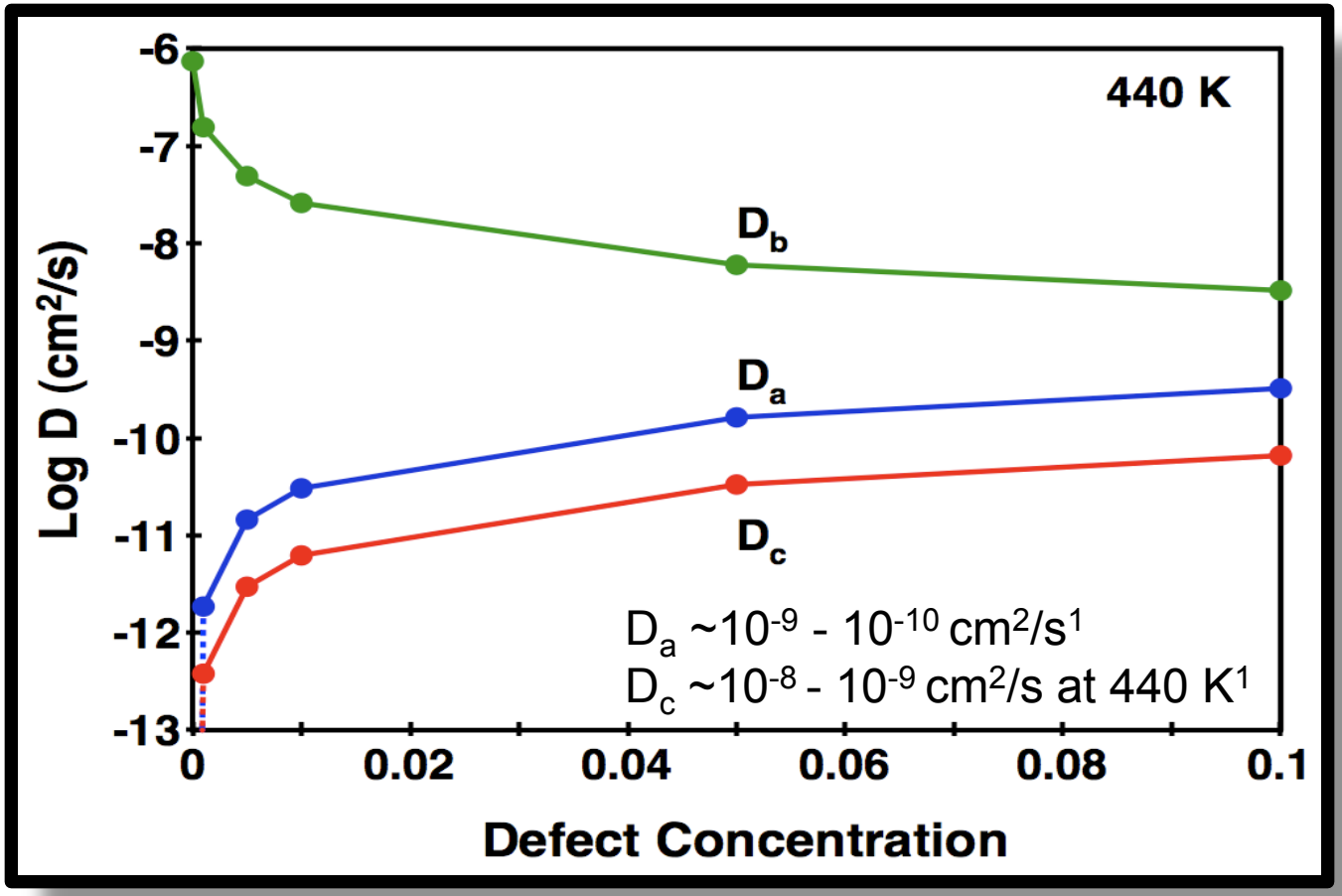



**Trapped Capacity Increases with Particle Size**

1) In small particle limit, trapped capacity tends to zero and fast 1D diffusion can be accessed. No unblocked capacity is accessible in large particles.
2) With just 1% defects, 50% of capacity is trapped at 100 nm particle sizes.

[1]R. Amin, *et al.*, *Solid State Ionics* **2008**, *179*, 1683.

# Nano-size effects on Diffusion in $LiFePO_4$: II



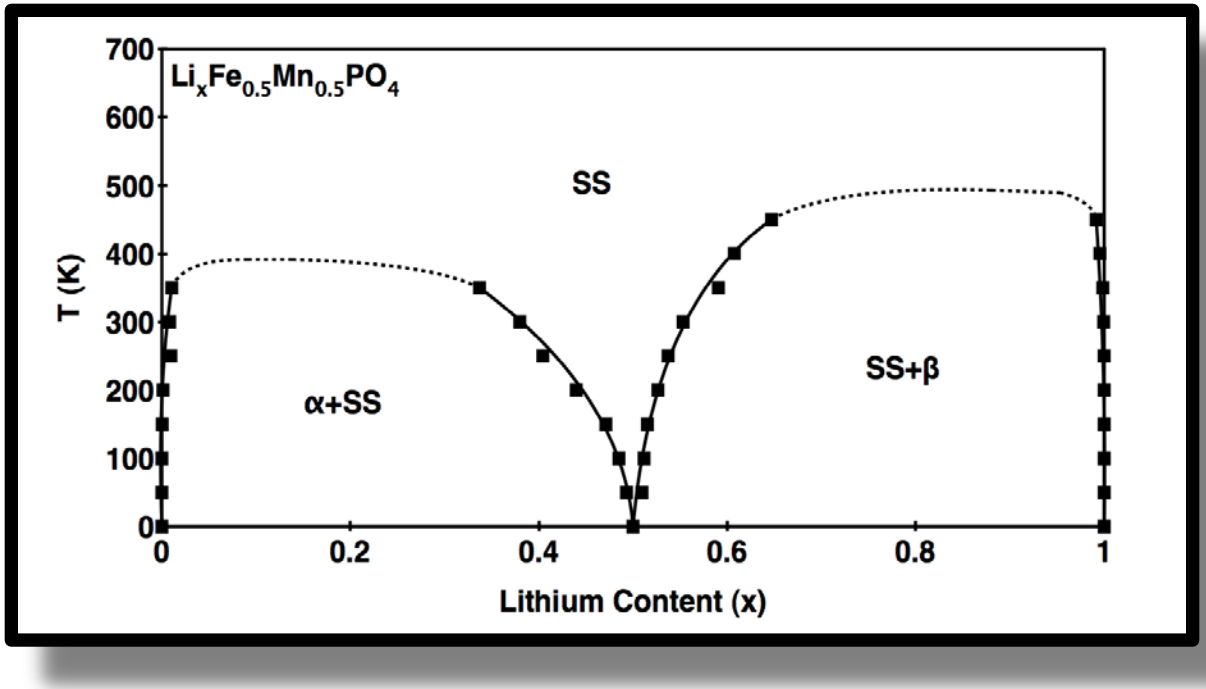

*Diffusion is one dimensional for nanomaterial or for low defect concentration, but becomes more isotropic (and slower) for micron material or for more defects*

**Size-dependent Diffusion Regimes in $LiFePO_4$**

1) With modest defect concentrations, near defect-free diffusion times can be accessed in nano particles.
2) Inherently slow diffusion of trapped capacity in defective $LiFePO_4$ results in significantly increased diffusion time with even dilute defect concentrations.

# Phase Diagrams and Voltage Curves Mixed Olivine Systems: I

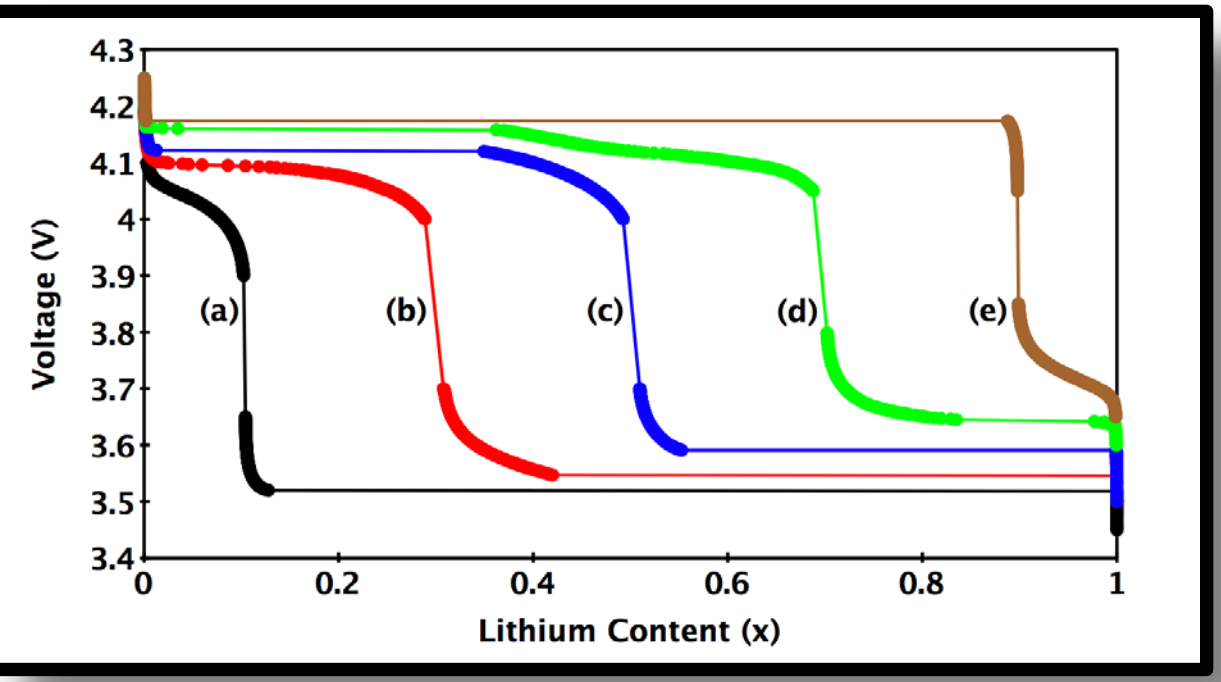
**Phase Diagram of $Li_x(Fe_{0.5}Mn_{0.5})PO_4$**




Disordered transition metal cation substitution dilutes phase separating interactions and stabilizes low-temperature solid-solution (SS) phase, in good agreement with expt..

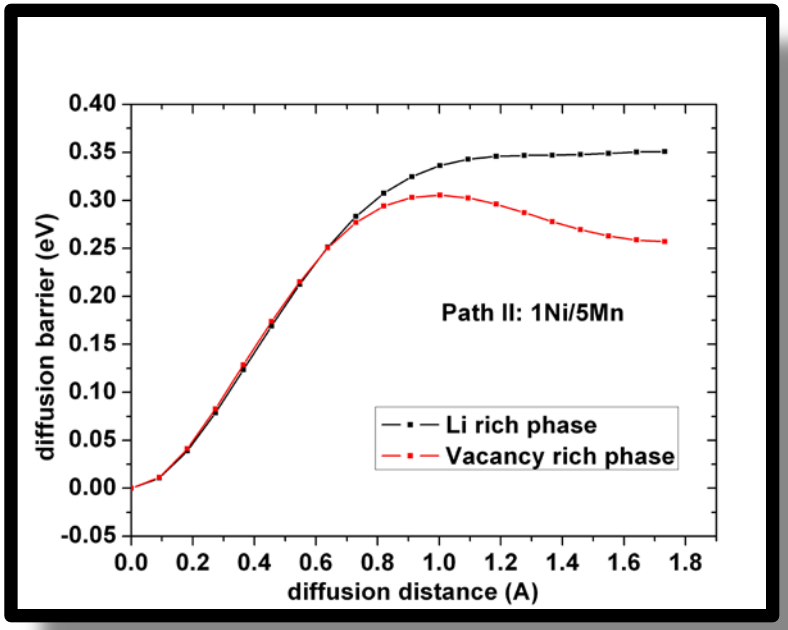
# Phase Diagrams and Voltage Curves Mixed Olivine Systems: II

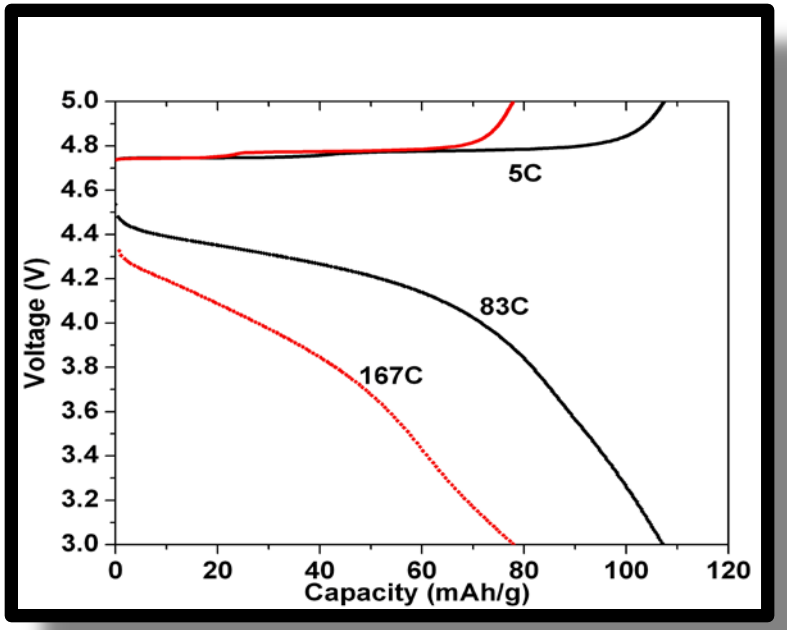
**Equilibrium voltage curves of $Li_x(Fe_{1-y}Mn_y)PO_4$ at 300 K for (a) y = 0.1, (b) y = 0.3, (c) y = 0.5, (d) y = 0.7, and (e) y = 0.9**




- Two voltage plateaus at ~ 4.1 V and ~ 3.5 V corresponding to $Mn^{2+/3+}$ and $Fe^{2+/3+}$, respectively, with solid-solution phase in between showing good agreement with experiments.
- $Fe^{2+/3+}$ phase transition voltage increases with Mn content due to increased energy arising from unfavorable $Li^+ – Fe^{3+}$ interactions in the SS phase. Reverse trend is seen on the $Mn^{2+/3+}$ couple with increasing Fe.

# High rate micron-sized $LiNi_{0.5}Mn_{1.5}O_4$

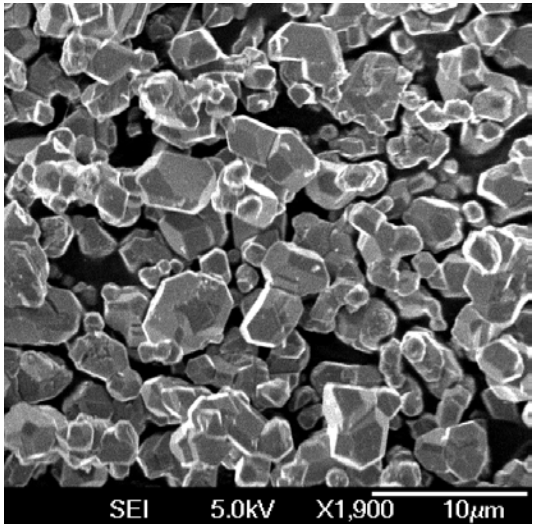



Li diffusivity ~ **1.41-8.25x10$^{-9}$ cm$^2$/s** (**~3μm in 10s)** from calculations.

Confirmed by expt. showing very high rate capability with 78mAh/g at 167C (21 seconds for full discharge).

**Primary particles are several microns !**



# Collaborations

## Within BATT

- Kostecki: Carbon rate capability
- Persson (LBNL): Li in carbon
- Battaglia (LBNL): High rate LFP scale-up
- Shrinivasan: Modeling of LFP: integration over length scales
- Whittingham: Mixed olivine systems
- Grey: Synchrotron and NMR characterization of novel electrode materials

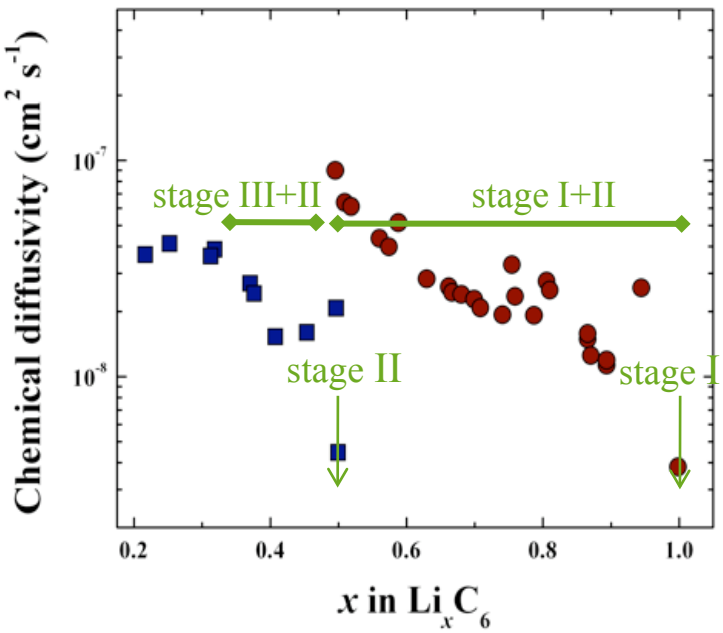
## Outside BATT

- Bazant (MIT): First order phase transformation rate modeling
- Aurbach (Bar-Ilan): Surface characterization; novel materials

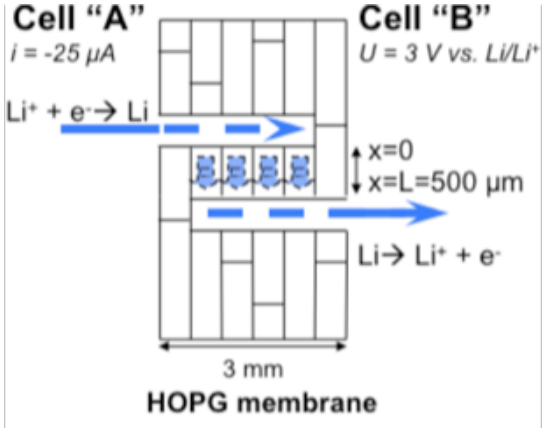
# Collaborations: Example (1)

With **Kostecki** and **Persson** : Measuring and calculating anisotropy of Li diffusion in graphitic carbon

Kinetic Monte Carlo Results[1]




Devanathan-Stachurski-type experiment by Kostecki et al. [1]

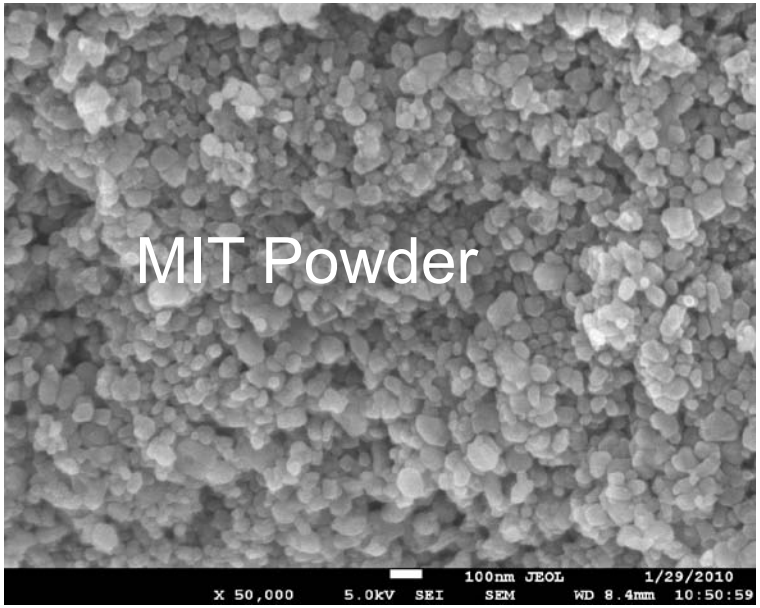


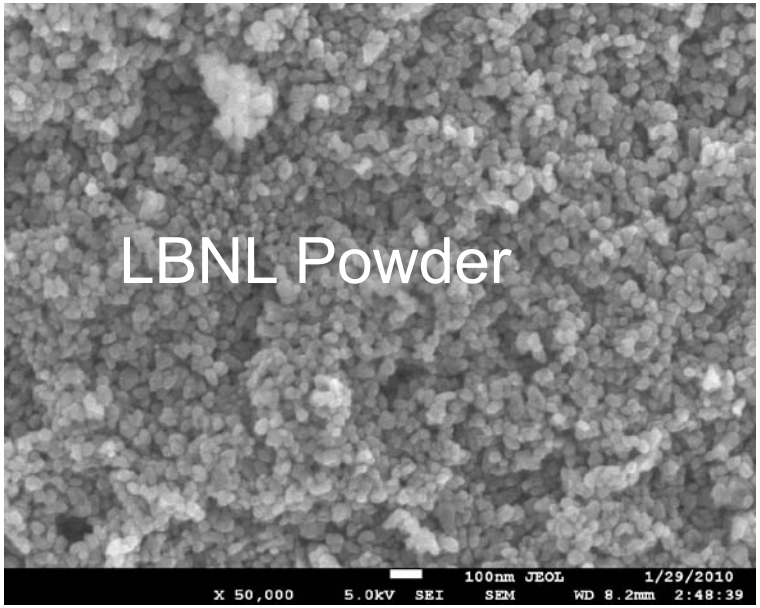

**$D_{li} \approx 4.4 \times 10^{-6}$ cm$^2$ s$^{-1}$**

[1] K. Persson, V. A. Sethuraman, L. J. Hardwick, Y. Hinuma, Y. S. Meng, A. van der Ven, V. Srinivasan, R. Kostecki and G. Ceder, J Phys Chem Lett 1176–1180, 2010.

# Collaborations: Example (2)

With **Battaglia**: Duplicate and scale-up synthesis process for very high rate LFP. Exchanged scientist between LBNL and MIT



# Future Work

- Further develop model for rate capability of electrode materials with first order phase transformations and work with characterization groups to validate model
- More broadly investigate effect of nanosizing on stability and electrochemical properties of electrode materials (currently only investigated on olivines).
- Optimize and disclose several new cathode materials we are working on
- Continue search for new higher energy density electrode materials

# Summary Slides

- **Thermal stability**: We have developed the capability to predict thermal stability at TOC and used it to show that $Li_xMnPO_4$ is less stable than $Li_xFePO_4$
- We have performed a high-throughput study evaluating the **correlation between electrode voltage and oxidation strength** at TOC, and find that while there is a substantial correlation, opportunity exists to find materials with relatively high voltage which are not oxidizing towards the electrolyte
- We have shown an unexpected **nanoeffect** for the Li diffusion in LiFePO4, which explains why it is difficult to make large-particle size LFP with high rate.
- We have shown that in the **high voltage $LiNi_{0.5}Mn_{1.5}O_4$ spinel** high rate is possible, even with large primary particle size, in agreement with theoretical predictions