ATOMISTIC MODELING OF ELECTRODE MATERIALS

Kristin Persson

Principal Investigator, Project ID ES091

Lawrence Berkeley National Laboratory, Berkeley, California 94720

Overview

Timeline

- PI at 50% LBNL Aug 2008 - Feb 2009
- PI full-time LBNL Feb 2009 - now

Barriers Addressed

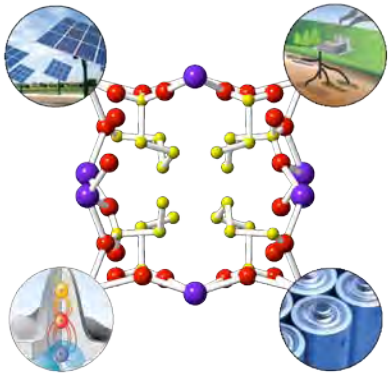
- Inadequate Li-ion battery energy density, cycle life and rate
- High cost of electrode materials

Budget

- Total budget since 2008: $1,600K
- FY09 funding $420K, FY10 funding $515K, FY10 funding $640K

Partners/Collaborations within the VT program

- Project lead: **Venkat Srinivasan** (LBNL)
- **Marca Doeff** (LBNL): Al-substituted layered Li-TM-O_2
- **Phil Ross** (LBNL) and **Gerbrand Ceder** (MIT): $LiFePO_4$ for performance-changing surface effects
- **Robert Kostecki** (LBNL): Li-graphite system for increased rate
- **Gerbrand Ceder** (MIT): Materials Genome for accelerated materials design



Objectives

Objectives	Descriptions
Predict new chemistries, crystal structures and morphologies for improved electrode materials	Study structural-chemistry relationships in successful electrode materials to find rules for inverse design
	Investigate electrode material surface structures and morphologies to optimize performance
Understand rate-limiting behavior in current electrode materials	Study factors that influence ionic and electronic conductivity in known electrode materials to target and design optimal diffusion

Selected Project Highlights in this Report and Their Relevance to Objectives

- *Rate-limiting bottle necks in the Li-graphite system*
- *Materials Genome for accelerated materials design*
- *Understanding and tuning LiFePO4 surfaces for performance enhancement*

Milestones

Completed work FY 2009 – 2010

- Evaluate changes in Li mobility and electronic conductivity in $LiNi_{1/3}Mn_{1/3}Co_{1/3-x}Al_xO_2$, as a function of Al content
- Predict $LiFePO_4$ surface absorbents and particle morphologies as function of aqueous synthesis environment for optimal Li-ion diffusion

- **Current work FY 2011**
  - Benchmark $LiCoO_2$, $LiMnO_2$ and $LiFePO_4$ bulk and surface electronic structures to move towards understanding changes in surface electronic state with different absorbents
  - Evaluate Li diffusion on graphite and graphene surface

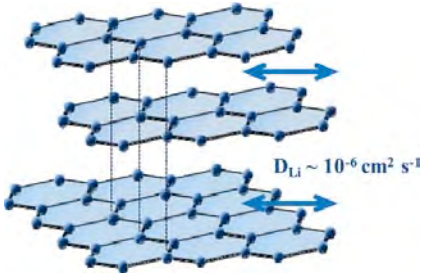
Approach

- **Use computational *ab initio* atomistic modeling methods to optimize and predict new Li-ion battery electrode materials**

Lawrencium cluster at LBL

  - ➢ Evaluate stability and potential synthesis routes of proposed compounds using calculated phase diagrams, phase competition and oxygen chemical potential ranges
  - ➢ Calculate electrode surfaces with different absorbents to simulate particle morphology development and its related performance
  - ➢ Combine and make efficient access to all relevant calculated knowledge in a searchable database, which will greatly facilitate computational materials design

- **Calculate processes relevant to Li diffusion in electrode material bulk and surfaces**
  - ➢ Use atomistic modeling to determine Li migration barriers
  - ➢ Use statistical mechanics models to understand Li diffusion in different materials

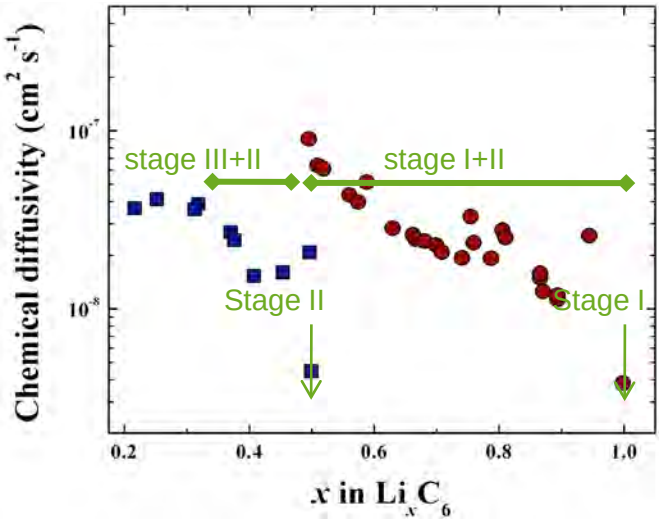


Predicted Li diffusivity in graphite

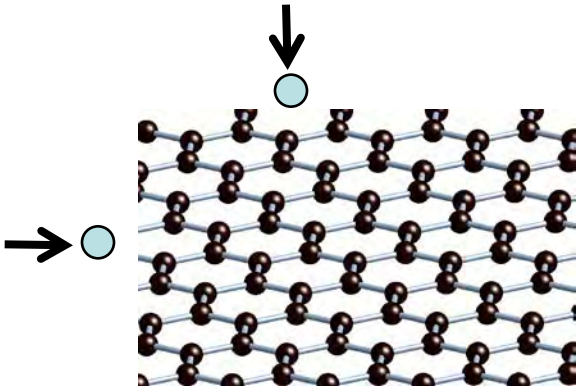
Technical Accomplishments

I. Li Diffusion Bottle-necks in Graphite

Motivation: Li diffusion measurements in graphite span 10^{-7} – 10^{-12} cm^2/s. At low temperature the rate capability of carbon anode deteriorates ➔ Li plating. Last year[1-2] we established that inherent Li diffusion in bulk graphite can be very fast: ~ **10^{-7} cm^2s^{-1}**. Moving forward, we aim to identify the rate-limiting bottle neck in graphitic materials.



Li chemical diffusivity as function of Li content in graphite from first-principles

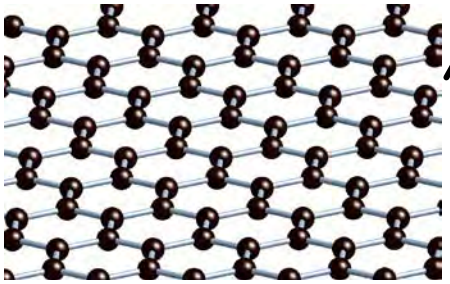


If the bulk is fast – what about the Li transport on the stable surfaces?

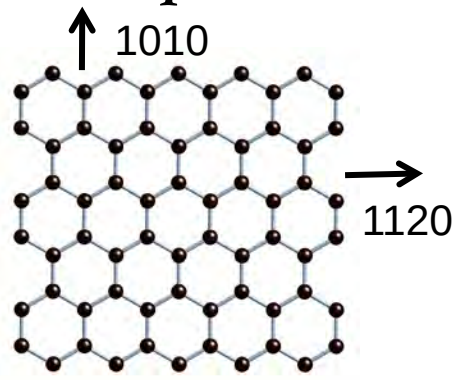
[1] K. Persson, V. A. Sethuraman, L. J. Hardwick, Y. Hinuma, Y. S. Meng, A. van der Ven, V. Srinivasan, R. Kostecki and G. Ceder, J Phys Chem Lett 1176–1180, 2010.
K. Persson, Y. Hinuma, Y. S. Meng, A. Van der Ven and G. Ceder *Thermodynamic and Kinetic Properties of the Li – Graphite System from First-Principles Calculations*, Physical Review B 82, 125416, 2010.

Technical Accomplishments

I. Li Diffusion Bottle-necks in Graphite

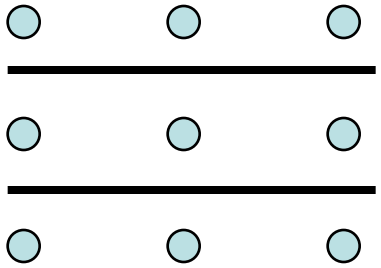


Most stable surface

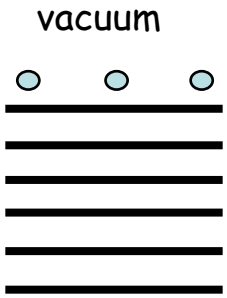


Most stable edge planes

- The 0001 surface is by far the most thermodynamically stable surface



0.1 V



-0.6 V

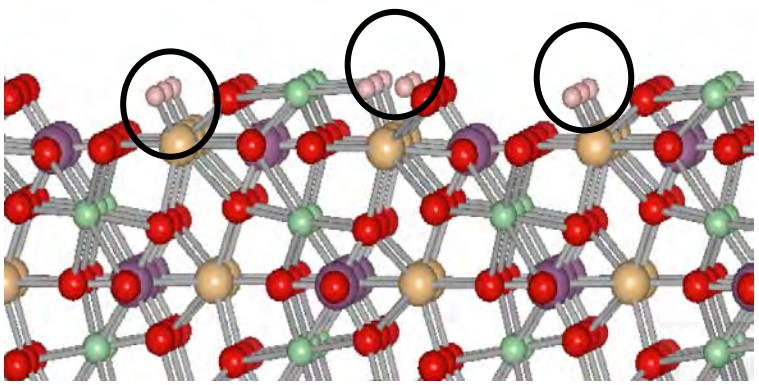
- We find that Li does not absorb on the predominant 0001 surface
- To optimize rate performance in graphitic anodes, our findings suggest to increase the fraction of edge-planes which are exposed to the electrolyte. Very high discharge rates has recently been observed for one single MCMB particle[1]

[1] *Dokko, Nakata, Suzuki, and Kanamura J Phys Chem C, 114, 8646, 2010.*

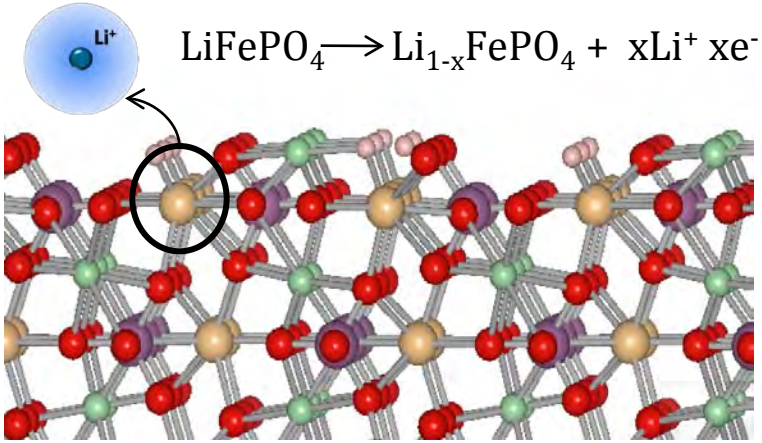
Technical Accomplishments

II. Predicting and tuning LiFePO4 particle morphology

Motivation: Due to its one-dimensional Li diffusion, $LiFePO_4$ performance is very dependent on particle size and shape. It is of interest to tune the particle morphology for Li intercalation, especially promoting the active *ac* facet.[1] In this study we combine first-principles calculations of $LiFePO_4$ surfaces with experimental aqueous states to predict particle shape as a function of the environment, mimicking hydrothermal synthesis conditions.



Relevant $LiFePO_4$ surface facets were calculated with absorbents H, OH, H_2O and O



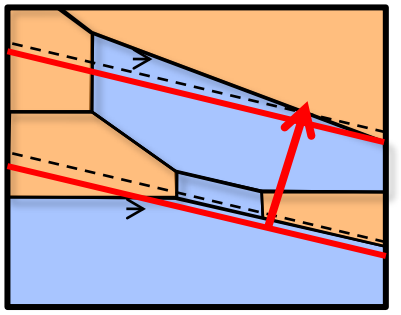
Li dissolution is predicted from certain surface facets as function of environment

[1]Chen, Song and Richardson, ESSL 9, A295 (2006).

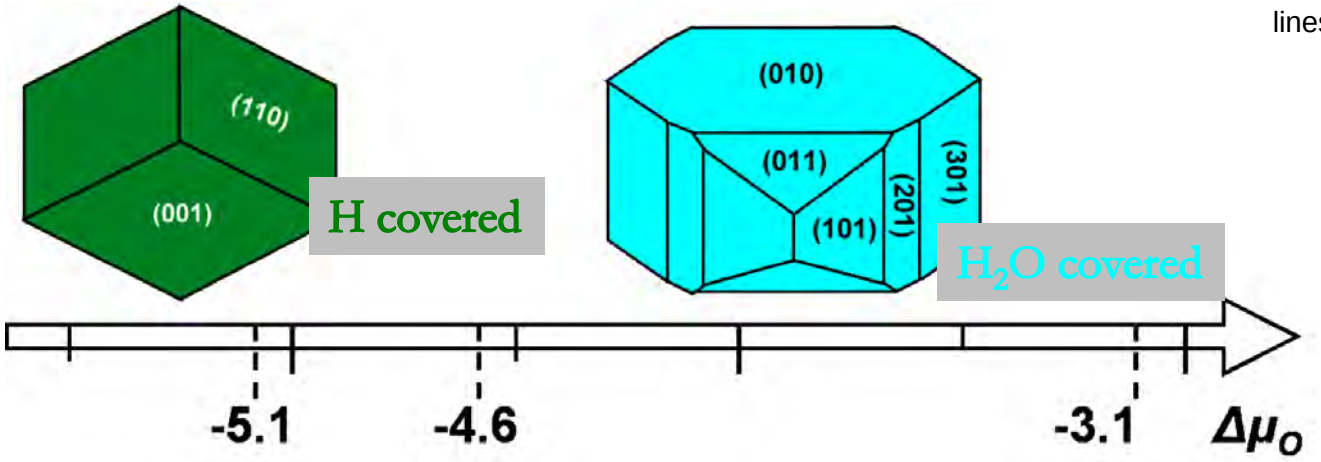
Technical Accomplishments

II. Predicting and tuning $LiFePO_4$ particle morphology

Equilibrium particle shapes can be predicted as function of solution pH, oxygen chemical potential and Li^+ concentration. For each oxygen chemical potential, the Wulff shape is constructed, given the thermodynamically stable surface absorbents.



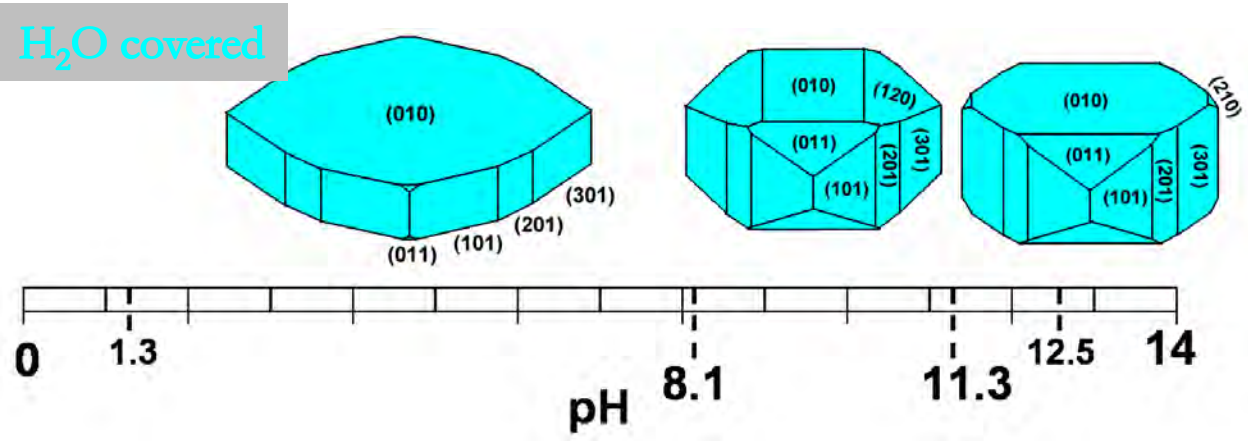
Schematic Pourbaix diagram indicating the lines of constant oxygen chemical potential

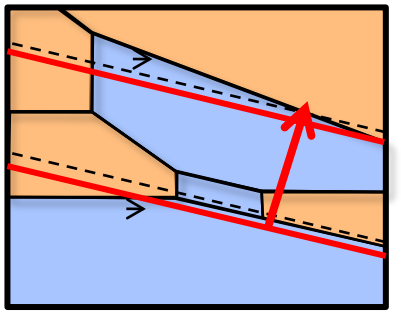


➢**For low oxygen chemical potential (reducing conditions), the $LiFePO_4$ particle is rhomboid and covered with hydrogen. As the oxygen chemical potential increases, the shape changes into more plate-like as water absorbs on the surface.**

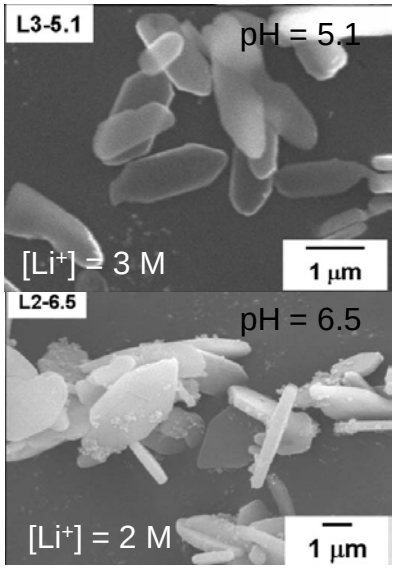
Technical Accomplishments

II. Predicting and tuning $LiFePO_4$ particle morphology





Schematic Pourbaix diagram indicating the lines of constant oxygen chemical potential

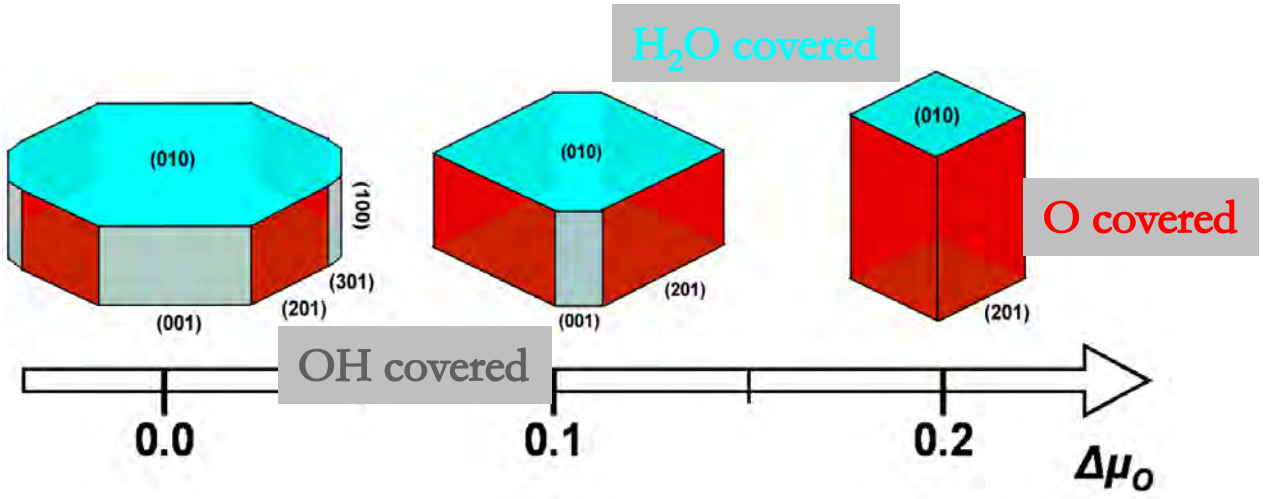


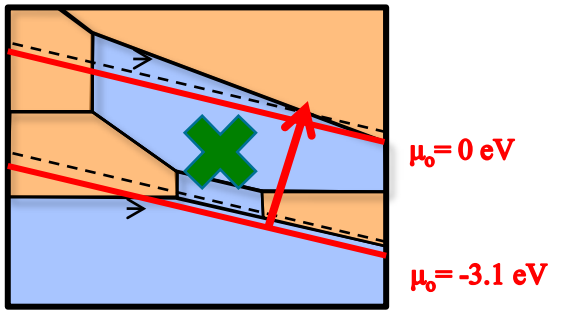
➢ For $0 < \mu_O < -3.1$ the particle morphology change is due to Li ions dissolving from the surfaces which affects the surface energies and therefore the shape. This result is supported by experiments[1] where increasing Li in solution enables synthesis of plate particles at lower pH.

[1] K. Dokko, S. Koizumi, H. Nakano, and K. Kanamura, J. Mater. Chem. **17**, 4803 (2007).

Technical Accomplishments

II. Predicting and tuning $LiFePO_4$ particle morphology





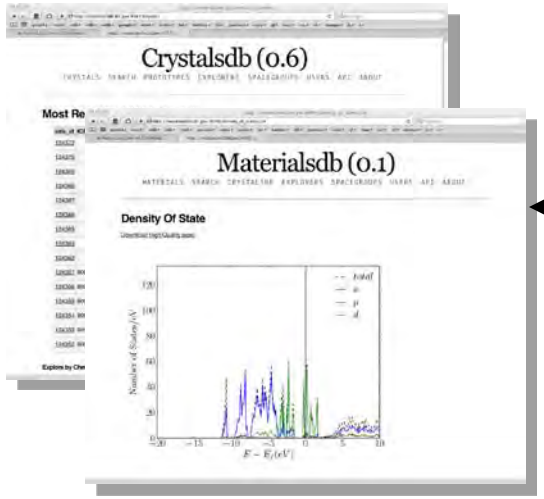
Schematic Pourbaix diagram indicating the lines of constant oxygen chemical potential and the calculated aqueous synthesis conditions for optimal $LiFePO_4$ shape.

- For higher oxygen chemical potentials ($0 < \mu_O < 0.2$ eV) different absorbing species affect the shape.
- Optimal shape, i.e. plate-like particle with high 010 surface area, is obtained for H_2O covered particle, close to neutral pH and around 0 V vs the hydrogen electrode (as seen on previous slide).

Technical Accomplishments

III. Public Materials Database for Accelerated Materials Design

Motivation: The lack of comprehensive knowledge about materials, organized for easy analysis and rational design, inhibits materials discovery.



Web

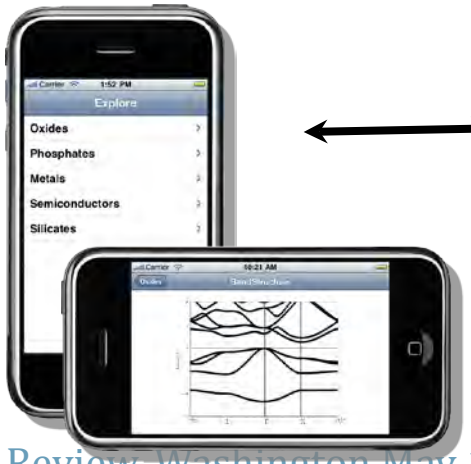
Scalable Infrastructure

(MongoDB)

$\hat{H}|\Psi\rangle$

Automation Engine

NERSC LBNL



API

Computing ~200 compounds/day

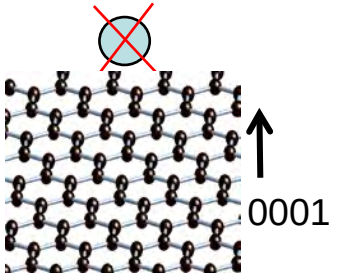
Future Work

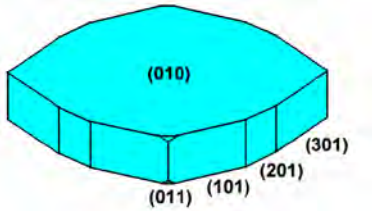
Explore surface effects on the performance of electrode materials, by investigating chemical substitution, surface absorbents, defects under different conditions

- Study Li thermodynamics and transport on carbon surfaces. Which surfaces are active and can transport Li efficiently?
- Explore surface absorbents, defects and their impact on electronic conductivity and Li diffusion in $LiFePO_4$ olivine electrode material
- Explore surface structures and morphologies of the $LiMnO_2$ spinel electrode material for improved electrolyte stability
- Continue development of a public materials database for accelerated materials design

Summary

- **Using first-principles calculations and statistical mechanics, inherent properties of Li electrode materials are elucidated and targeted design is suggested:**
  - ➢The dominant graphite surface [0001] is inactive for Li absorption which suggests that targeted design of carbon anodes with specific plane alignment towards the electrolyte should be explored for improved rate capability
  - ➢ $LiFePO_4$ particle morphology is predicted to optimize the active 010 surface facet under aqueous conditions relevant for hydrothermal synthesis
  - ➢ The public materials database for accelerated design at LBNL is underway and the collaboration now involves many divisions at LBNL as well as MIT





- **Future work will focus on Li-ion electrode surface effects, relevant for enhancing the stability and rate performance of electrode materials**