ATOMISTIC MODELING OF ELECTRODE MATERIALS

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BERKELEY LAB

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: $966K
- FY08 funding $100K: FY09 funding $353K: FY10 funding $513K

Partners/Collaborations within the VT program

- Project lead: John Newman
- Marca Doeff (LBNL) on layered Li-TM-O_2 for effects of Al substitution
- Phil Ross (LBNL) on nano-$LiFePO_4$ for nano-scale effects on performance
- Robert Kostecki (LBNL) on the Li-graphite system for increased rate
- Jordi Cabana (LBNL) on Cu extrusion cathodes for increased capacity
- Gerbrand Ceder (MIT) on the Li-graphite system and materials design

OBJECTIVES

- **Predict new chemistries and crystal structures for improved electrode materials**
  - ➢ Investigate extrusion mechanism in new cathode materials
  - ➢ Study structural-chemistry relationships in successful electrode materials to find rules for inverse design
- **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 properties

MILESTONES

- **Completed work FY 2008 – 2009**
  - ➢ Postdoc hired, software and computing capabilities obtained
  - ➢ Evaluated Li diffusion in bulk graphite by first-principles calculations
- **Current work FY 2010**
  - ➢ Quantify the 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 (03/2010)
  - ➢ Characterize and evaluate different Cu-Metal-O electrode compounds that can combine high voltage copper extrusion with a stable M-O framework to facilitate stability and good cycle life (09/2010)

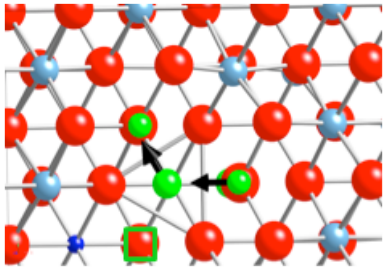
APPROACH

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

Lawrencium cluster at LBL

- Evaluate stability and potential synthesis issues of proposed compounds using calculated phase diagrams, phase competition and oxygen chemical potential ranges
- Combine and make efficient access to all relevant calculated knowledge in a searchable database, which will greatly facilitate computational materials design

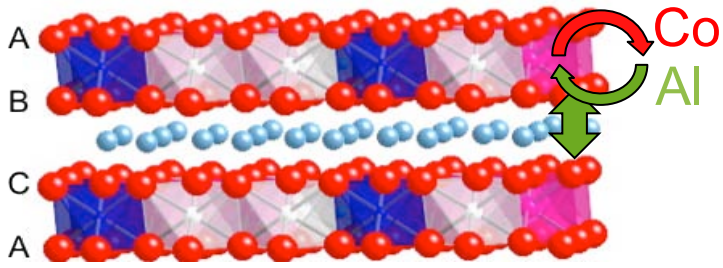
- **Calculate processes relevant to Li diffusion in electrode material bulk and surfaces**
  - Use atomistic modeling to determine Li migration barriers
  - Use statistical mechanics models to understand Li diffusion in different materials



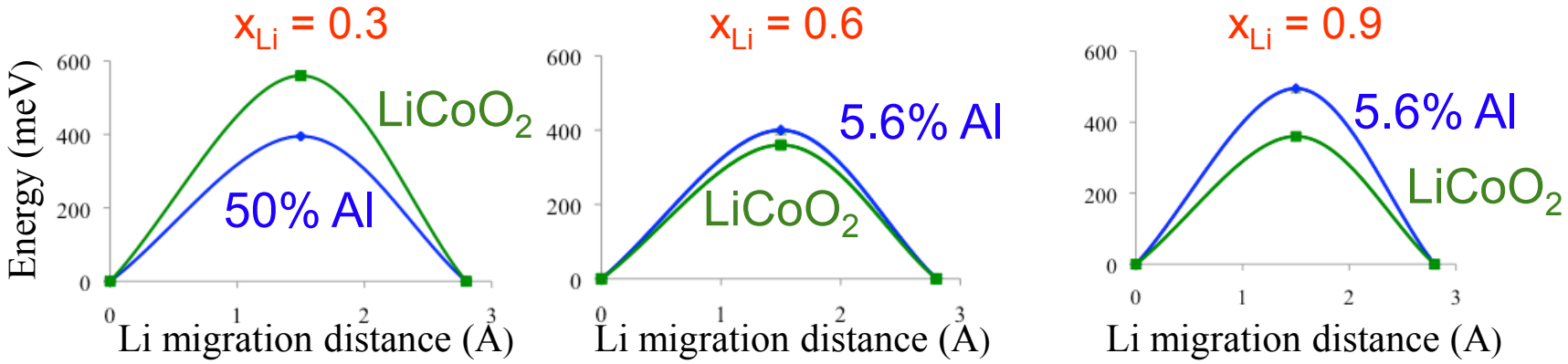
Li diffusion mechanism in layered $LiTMO_2$

TECHNICAL ACCOMPLISHMENTS

I. Li Mobility in Layered $Li_xNi_{1/3}Mn_{1/3}Co_{1/3-y}Al_yO_2$



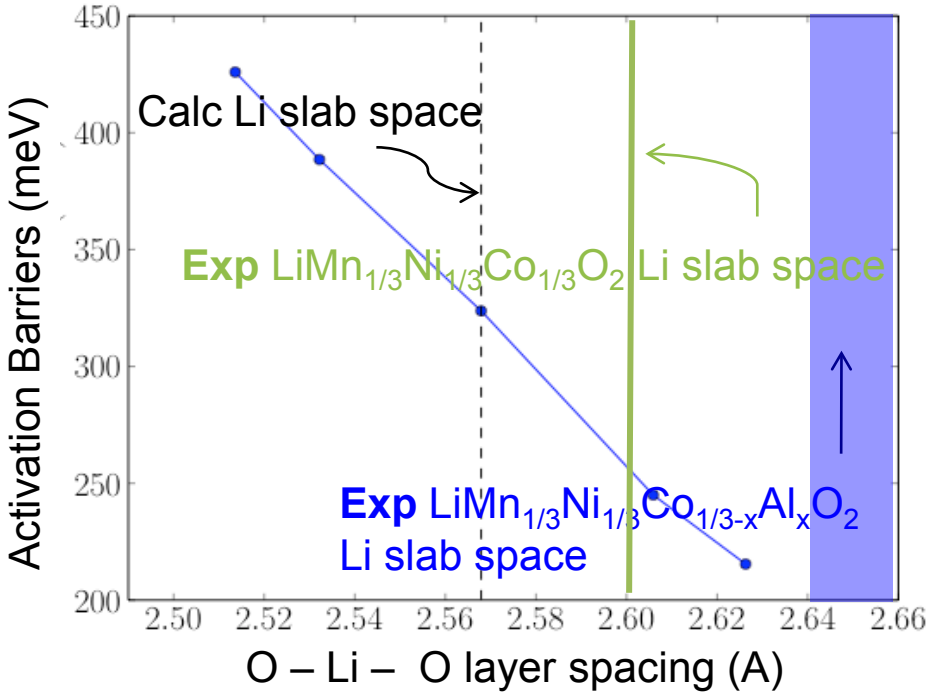
Motivation: Co is expensive and full charge to Co^{4+} is not used. Replacement with Al (5-10%) gives higher voltage, thermal stability, lower electronic conductivity and **better rate capability**[1-3]. Why?

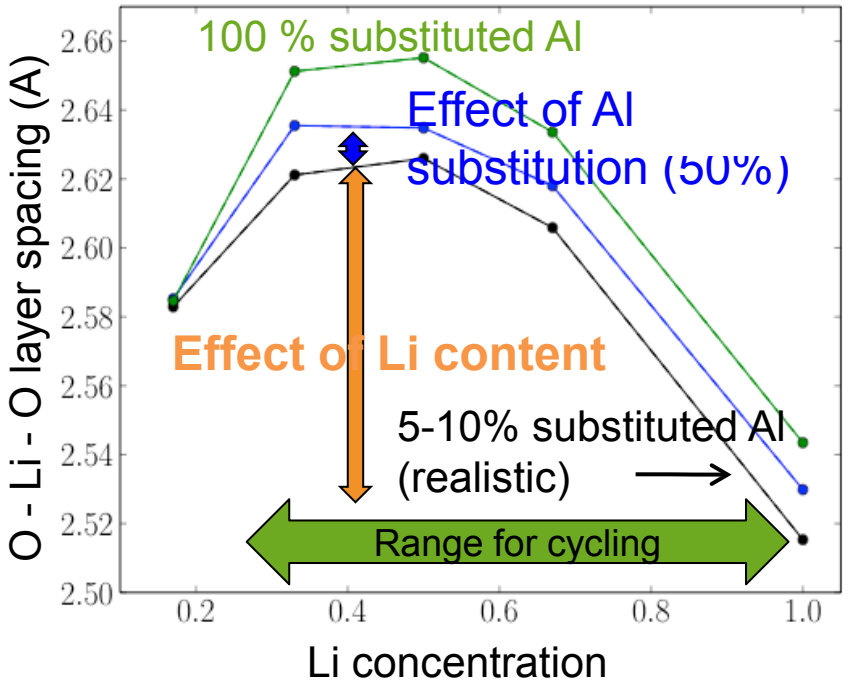


➢ **Al lowers local Li migration barriers at low Li concentration, but not at high Li concentration, i.e. discharge**

[1]*Wilcox JD, Rodriguez EE, Doeff MM, JECS 156 (12), A1011-A1018, 2009.*
[2] *Wilcox, Patoux and Doeff JECS 156, 2009,* [3] *Kang and Ceder, Phys Rev B 74, 2006.*

I. Li Mobility in Layered $Li_xNi_{1/3}Mn_{1/3}Co_{1/3-y}Al_yO_2$

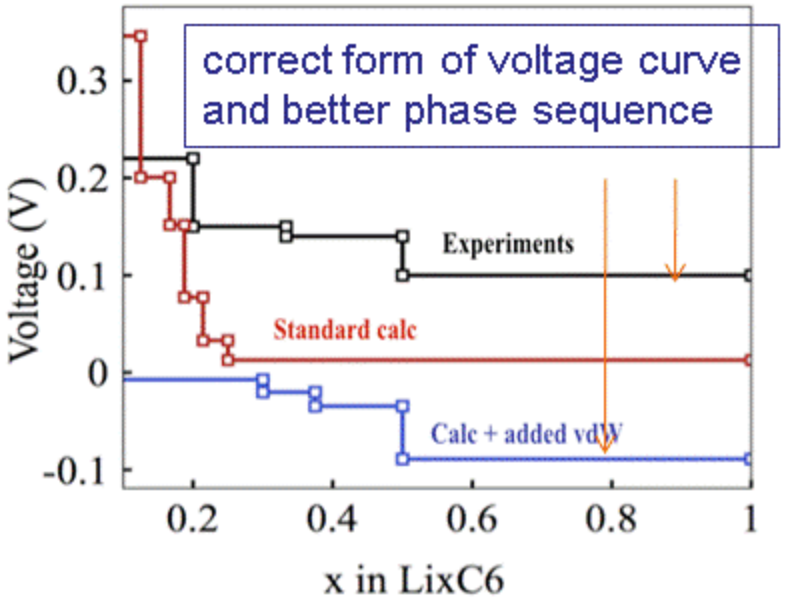


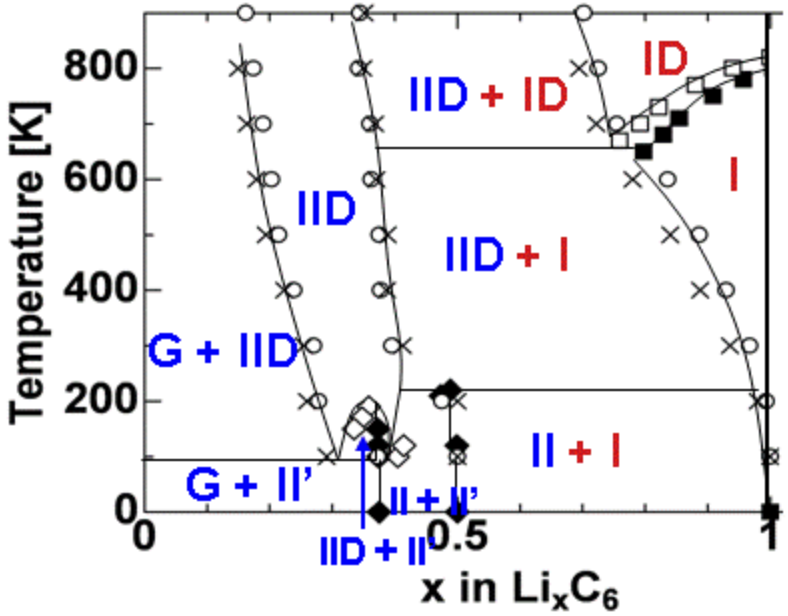


- Li migration barriers decrease with increased Li slab space
- Al favors increased Li slab space, but predicted effect is lower than seen in experiments (can Al decrease Ni defects in Li layer?)
- Al substitution may increase Li mobility at charge but overall effect of Li concentration is predicted to be more important than Al content

II. Li Diffusion Bottle-necks in Graphite

Motivation: Li diffusion measurements in graphite span $10^{-7} - 10^{-12}$ cm^2/s. At low temperature rate capability of carbon anode deteriorates ➔ Li plating? What is the intrinsic Li diffusivity in graphite and can we expect to increase the rate capability of graphitic anodes?



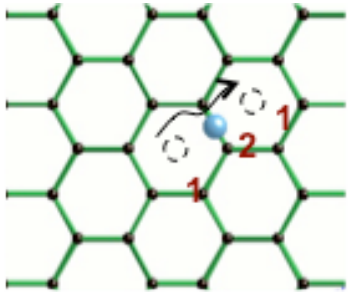


➢ **Adding van der Waals forces in graphite yields better agreement with experimental voltage curve**

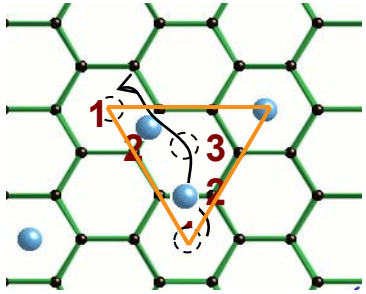
➢ **Phase diagram including only stage II and I agrees well with experiments in relevant Li concentration region (x > 0.4)**

DiVincenzo and Koch PRB 30(12), 7092, 1984,
J. Dahn, Phys Rev B 74, 2006.

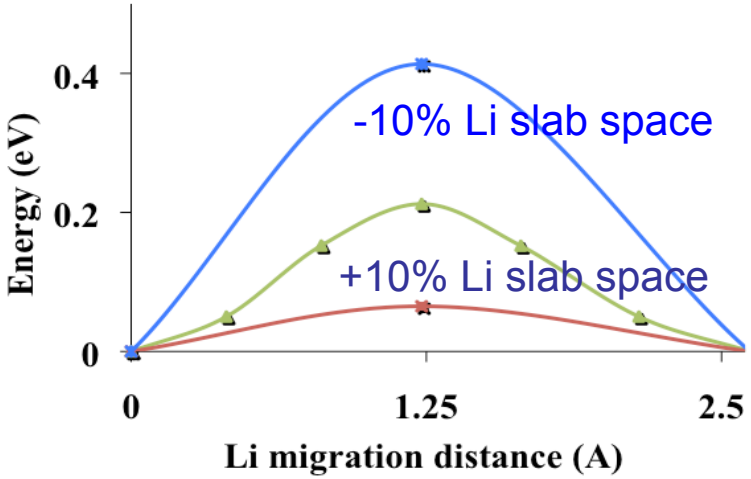
II. Li Diffusion Bottle-necks in Graphite

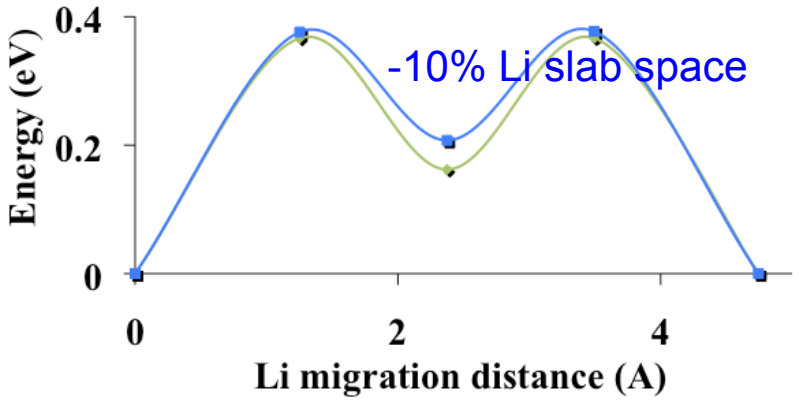


Li migration mode at low Li concentration



Li migration mode at high Li concentration

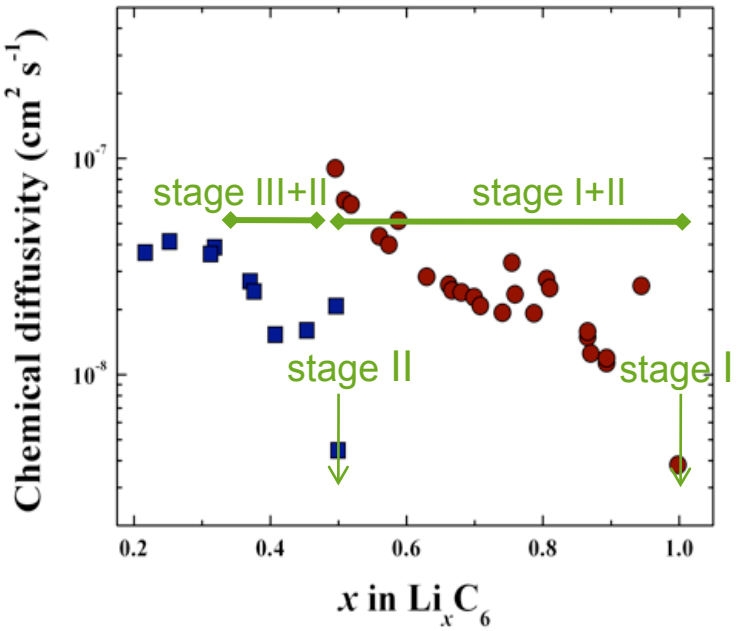




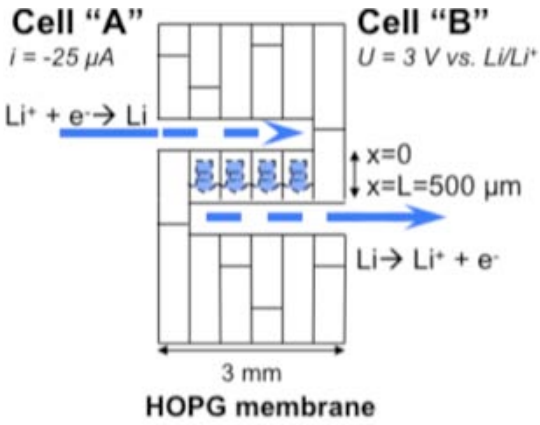
- **At dilute in-plane Li concentrations, the Li migration barrier is set by inter-plane distance**
- **At high in-plane Li concentrations, the Li migration barrier is determined by Li – Li repulsive interactions**

II. Li Diffusion Bottle-necks in Graphite

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}

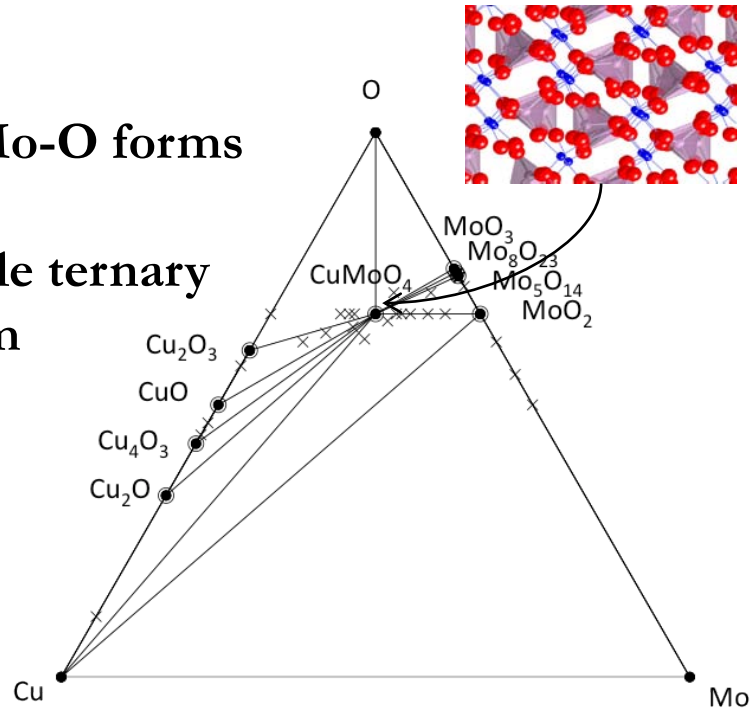
- We have established that inherent Li diffusion in bulk graphite is very fast! Assuming a design which efficiently utilizes the fast in-plane lithium diffusivity of 10^{-7} cm^{2}s^{-1}, graphitized natural graphite (MCMB) with typical crystalline domain sizes around 45 nm could be intercalated/deintercalated in less than 0.2 ms

[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.

III. Novel Cu Extrusion Materials

Motivation: Li/Cu extrusion mechanism cathodes can yield higher capacities than traditional insertion materials[1]

- **First system calculated is Cu-Mo-O, as Mo-O forms stable framework**
- **We predict that $CuMoO_4$ is the only stable ternary composition in the Cu-Mo-O phase diagram**



- **The predicted extrusion voltage $CuMoO_4 + 2Li \rightarrow Li_2MoO_4 + Cu$ yields 3.2 V in good agreement with experimental results: 3 - 3.5 V[2]**

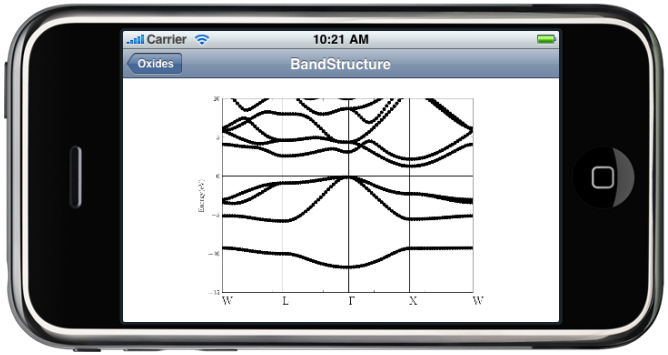
- **Stable Li_2MoO4 and $CuMoO_4$ are found to be structurally *unrelated* which is detrimental for successful extrusion mechanism**

[1]*M. Morcrette et al, Nature Materials 2, 755, 2003.*[2] *Internal communcation with Dr J Cabana.*

IV. Database Development for Accelerated Materials Design

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

- **Quantum mechanical methods are used to calculate selected properties for all relevant materials in the Inorganic Crystal Structure Database (ICSD)**
- **We are organizing the data using a modern web framework for easy access and searching**



Materials Design Web application by M. Kocher (postdoc in K. Persson's group) won 1st prize in LBL Mobile Competition 2009.

FUTURE WORK

Explore impact of nano-sizing electrode materials, by investigating surface effects on electronic conductivity as well as ionic conductivity

- Study Li thermodynamics and transport on graphite surfaces. Which surfaces can transport Li efficiently?
- Study Al substitution effects on layered Li-TM-O_2 surfaces. Does Al/Co solid solution on surface facilitate Li transport?
- Explore surface morphologies and their impact on electronic conductivity of $LiFePO_4$
- Continue exploring new Cu-TM-O systems for extrusion mechanism
- Continue development of materials design database

SUMMARY

- **Using first-principles calculations and statistical mechanics, inherent properties of Li electrode materials are elucidated:**
  - Al-substituted layered $Li_xNi_{1/3}Mn_{1/3}Co_{1/3-y}Al_yO_2$ exhibits Li mobility improvement at charge, but overall effect less than in-plane Li concentration.
  - Li diffusion in graphite is very fast which, with proper design, may enable faster rate and stability against Li plating
- **Novel Cu extrusion mechanism compounds are being investigated for higher capacity cathode materials**
- **Future work will focus on Li-ion electrode surface effects, relevant for nano-effects on electrode materials**