

Predicting and Understanding Novel Electrode Materials From First-Principles

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Timeline

- Start Date Oct 2012
- End Date: Sept 2016

Budget

- Total budget (4 years): \$1,000K
- FY13 funding \$250K, FY14 funding \$250K

Barriers Addressed

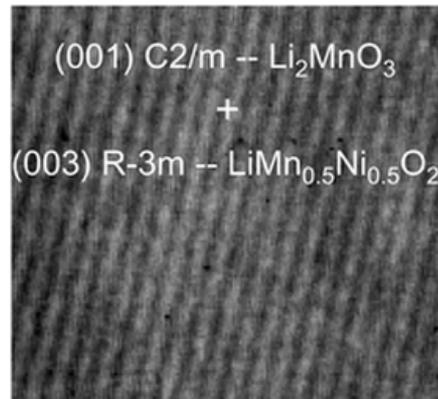
- Inadequate Li-ion battery energy density, cycle life and rate
- High cost of electrode materials

Partners/Collaborations within the VT program

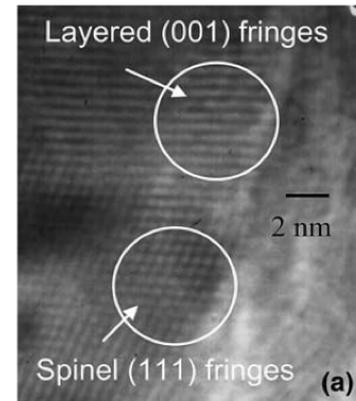
- Project lead: **Vince Battaglia** (LBNL)
- **Vince Battaglia** (LBNL), **Robert Kostecki** (LBNL), **Mike Thackeray** (ANL) and **Gerbrand Ceder** (MIT): understanding degradation mechanisms in Li-excess materials

Relevance

The Li-excess cathode materials exhibit more than 200 mAh/g initial capacity but also insufficient cycling performance, voltage fade, and long-time structural degradation



Thackeray et al., J. Mater. Chem. **17**, 3112 (2007)



Johnson et al., Electrochem. Comm. **7**, 528 (2005)

The Li_2MnO_3 component correlates with higher capacity but increased fade in the composite materials

Objectives:

- To understand the origin of the charge mechanism in the Li_2MnO_3 component
- To find the underlying atomistic mechanism for the voltage fade and structural degradation of the material

Relevance:

- To investigate whether there may be chemical mitigation strategies (doping, coating, structural changes) possible to increase the stability of the material or to recommend charging protocols

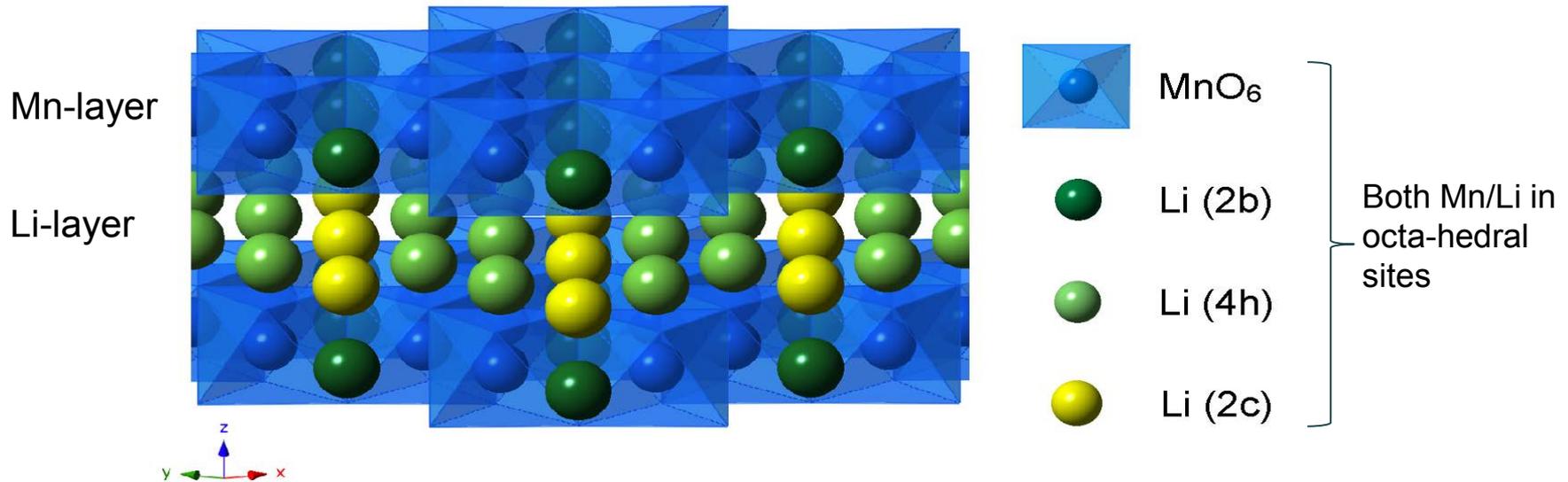
Milestones



Month Year	Milestone	Status
June 2013	Phase diagram including relevant bulk Li, O and Mn and defect phases in layered Li_2MnO_3	Complete
September 2013	Phase diagram including relevant bulk Li, O and Mn and defect phases in layered LiMnO_2	Complete
October 2013	Phase diagram including relevant bulk Li, O and Mn and defect phases in spinel LiMn_2O_4	Complete
December 2013	Composite voltage profiles as function of structural change and Li content.	Complete

Approach (1)

Li₂MnO₃ crystal structure



- Pristine Li_xMnO₃ has no Mn in Li layer
- During delithiation, the material is known to degrade, but how and why is not known
- Using atomistic simulations, we investigate for the first time how Mn defects are formed in Li layer during delithiation
- The effect of the defects on materials' structural and electrochemical properties will be compared to the voltage fade from experiments

Approach (2)



To mediate the degradation of the composite materials - exhibited in voltage and rate fade - it is necessary to understand the mechanism and driving force for the structural change:

Strategy:

- (1) Find the landscape of stable and metastable structures in the Li_xMnO_3 chemical domain – including defect formations due to ion (Mn) migration
- (2) Explore the structure stability varying ionic configuration (Li, Mn, Vacancy) in both Li and Mn layers
- (3) Track the charge compensation mechanisms during delithiation; is the charge balanced by Mn oxidation, anion oxidation or O release?
- (4) Investigate mobility of Mn and O as function of Li content to validate the proposed charging mechanism

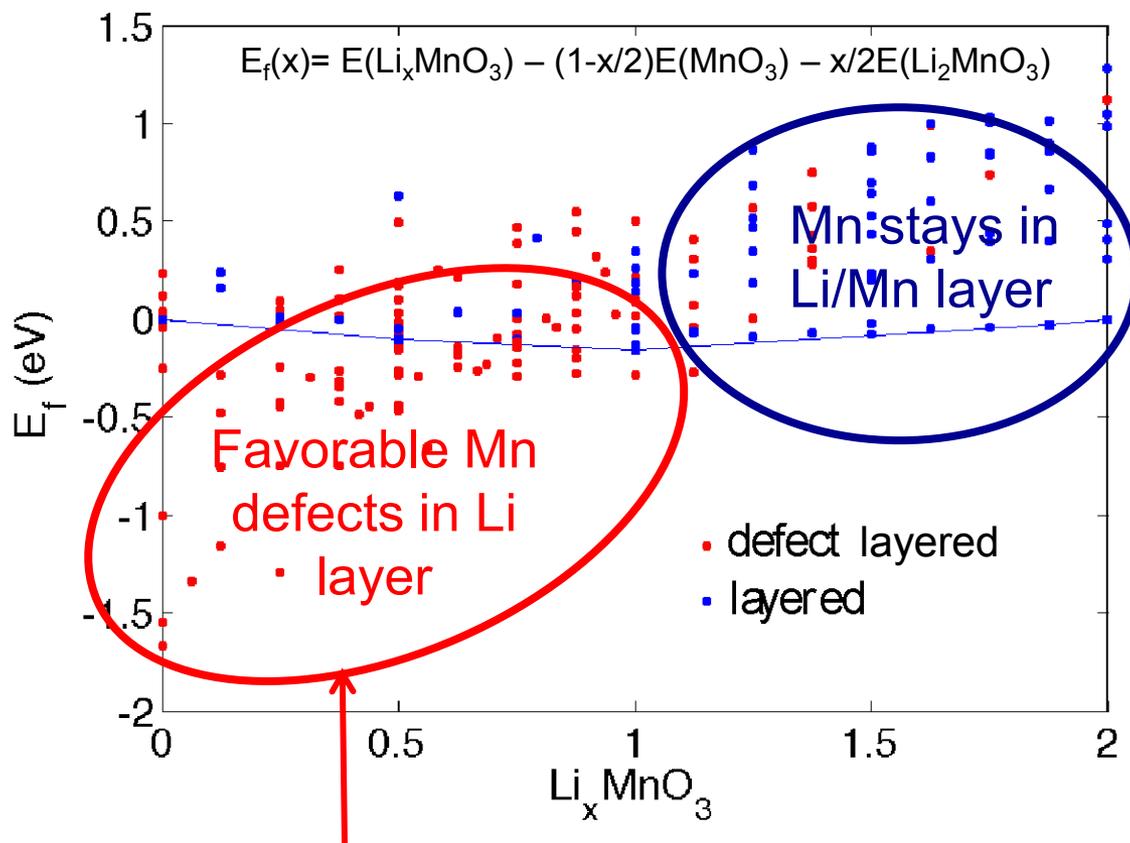
Technical Accomplishments (1)



Every point on the curve represents one of the 183 calculated structures and their energy

Stable structures have an energy at or below zero

The blue dots correspond to structures retaining the pristine Li_xMnO_3 structure while the red dots represent structures where at least one Mn is displaced into the Li layer

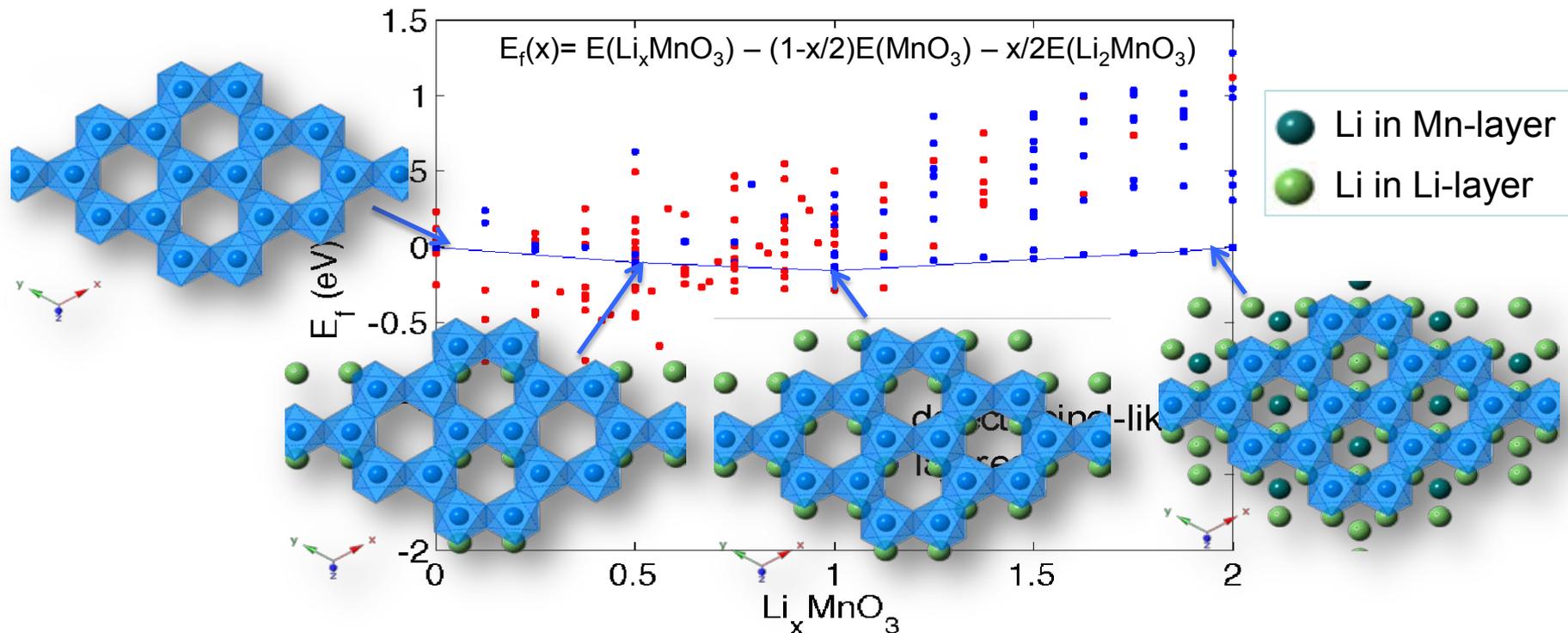


Results (1)

- For charge $x < 1$, the layered Li_xMnO_3 material is extremely unstable towards Mn defect formation in Li layer

Technical Accomplishments (2)

Simulation of 'activation process' during first charge, assuming small to no structural change:



Results (2)

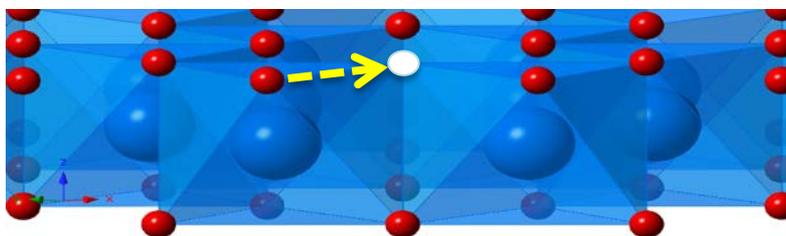
- Simulating the first charge, we assume that the material retains the original structure (blue dots) we find:
- Li is first extracted from Li/Mn layer
- Between $x = 1$ and 0, we identify two-phase charging behavior

Technical Accomplishments (3)

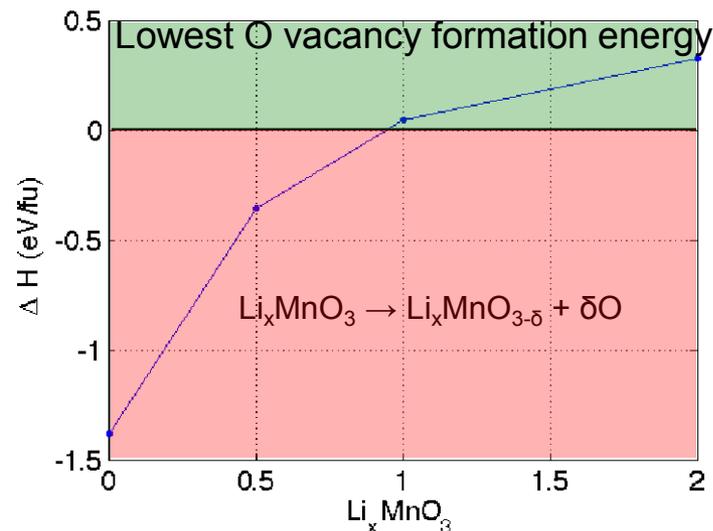
Tracking the magnetic moment during delithiation, and calculating the oxygen vacancy formation enthalpy as well as the oxygen migration barriers it is established that:

Results (3):

- The redox process during activation (first charge) occurs mainly on the oxygen
- While the material is also found to be thermodynamically unstable against O release for $x < 1$, the kinetic barriers for O release from the bulk are found to be too high for *bulk* oxygen release to happen during the activation process
- Hence, O release from bulk is inhibited but *surface oxygen release* is deemed possible



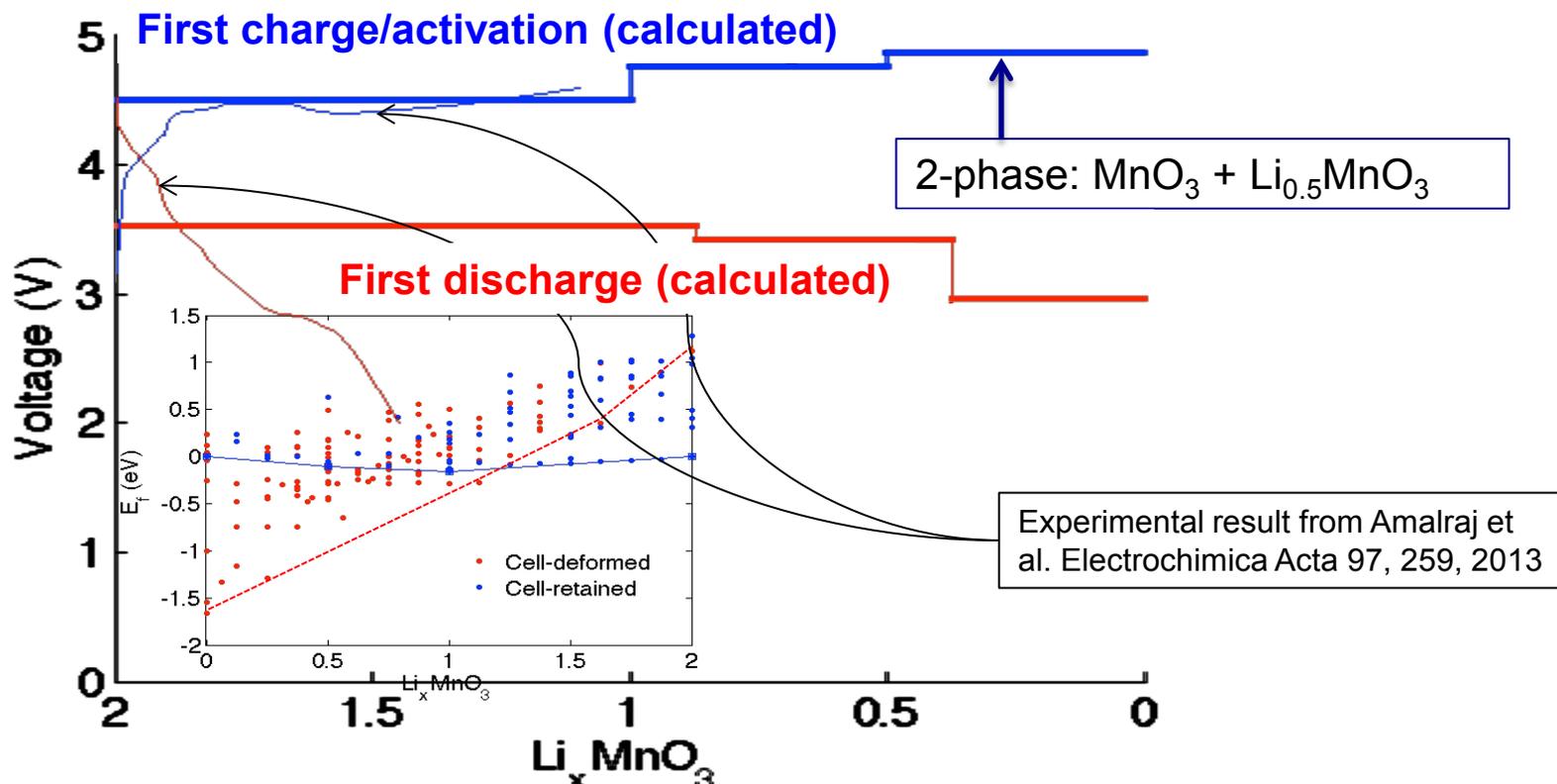
Example O migration path shown



x in Li_xMnO_3	O migration barrier
0	3.9 eV
0.5	2.0 eV
1	0.9 eV
2	2.1 eV

Lowest O migration barrier found was 0.9 eV

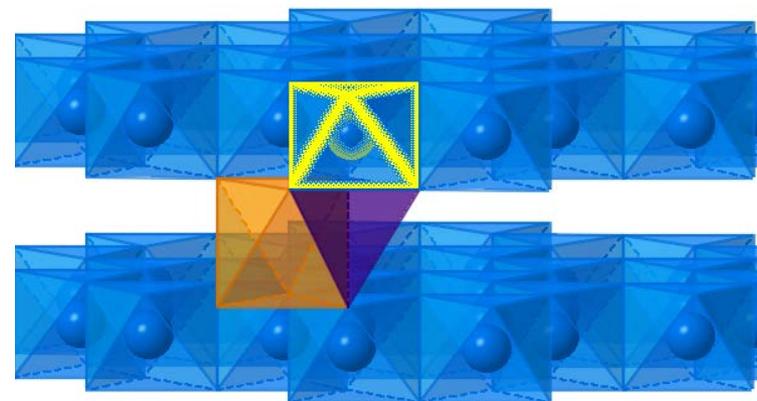
Technical Accomplishments (4)



Results (4):

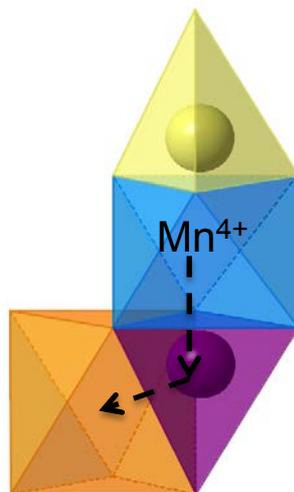
- Very good agreement between the calculated and experimental first charge and the activation process (blue curves). Charging/Activation process correctly identified.
- Subsequent discharge profile (red curves), where the pristine material is assumed to have transformed to a structure with significant Mn defects formed in Li layer, agrees qualitatively with experimental second discharge (Amalraj et al 2013) indicating that the voltage fade is likely to correspond (at least in part) by a structural and chemical change of the material corresponding to Mn migration

In order for Mn defects to form, there needs to be a migration path with low Mn migration barrier. Hence, we investigate Mn^{4+} migration from Mn layer to nearest octahedral site in Li layer:



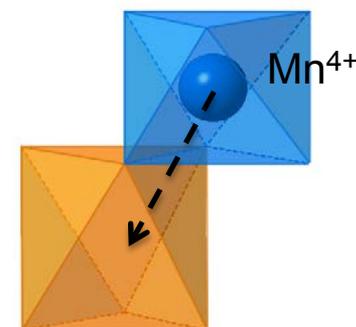
I. Known from Literature: Dumbbell Path

Octahedral site (Blue)
→
Tetrahedral site (Purple)
→
Octahedral site (Orange)



II. New Path suggested by this work: Edge Path

Octahedral (Blue)
→
Octahedral (Orange)

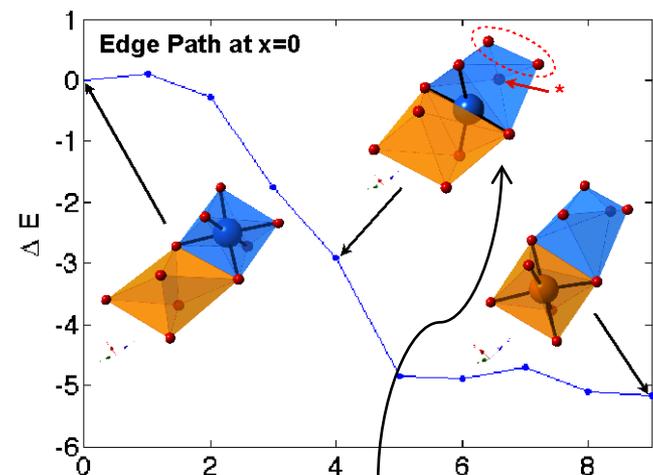


Technical Accomplishments (6)

* E_b unit: in eV

Li content	Dumbbell Path (O→T)	Edge Path
x=0	1.0	0.1
x=0.5	0.7	2.0
x=1	1.9	3.6

Sluggish Mn migration at RT



Instantaneous Mn migration enabled by distortion of O environment

Results (6)

- For overall charging $x > 1$, Mn is kinetically inhibited from migration
- At $x = 0.5$, the dumbbell path exhibits a migration barrier yielding sluggish migration of Mn from TM layer to Li layer
- At high charge (even locally), the edge path yields *instant Mn migration to the Li layer*

The structural and chemical stability of Li_xMnO_3 ($0 \leq x \leq 2$) have been studied using first principles modeling and we have established that

- The Li is first extracted from the Mn layer from Li_2MnO_3
- The charge on activation is mainly balanced by oxygen oxidation – not Mn oxidation nor bulk oxygen release
- At $x < 1$, Mn defects in Li layer are thermodynamically very favorable
- Mn migration into the Li layer is feasible for locally highly charged particles ($0 < x < 0.5$) through the dumbbell path as well as the newly discovered edge path
- Mn migration will result in defect layered material with local spinel nuclei – however, full transformation to spinel phase is not expected
- Oxygen release from material is thermodynamically favorable for $x < 1$, but it is impeded by low O kinetics; thus oxygen gas release likely limited to surface domain
- Voltage profile for Li_2MnO_3 activation fits experimental curve excellently, indicating that mechanism for activation is correctly identified
- Subsequent voltage profile for defect layered fits discharge voltage profile from experiments, showing that a structural and chemical evolution of the material corresponding to Mn defect formation in Li layer qualitatively matches experimental results

We will continue to study the layered Li excess materials by

- Incorporating and studying the effect of Ni and Co
- Examining the effect of stress/strain to simulate composite nano-domains
- Studying reactions at the surface, particularly focusing on predicting the evolution of stable or unstable crystal facets of the layered and spinel phases as a function of O₂ release from surface and oxygen chemical potential

Collaborations



Close contact with characterization work performed by the groups of: **Vince Battaglia** (LBNL) and **Robert Kostecki** (LBNL), particularly w.r.t. experimentally confirming the predicted Mn migration behavior is ongoing

Fruitful discussions with:

Mike Thackeray (ANL), **Gerbrand Ceder** (MIT) (within BATT) and **Claude Delmas** (Bordeaux, France) (outside BATT) on understanding degradation mechanisms in Li-excess materials are gratefully acknowledged

Collaboration with **Envia** on degradation mitigation strategies of the Li excess material is ongoing (separately funded by ABR program)

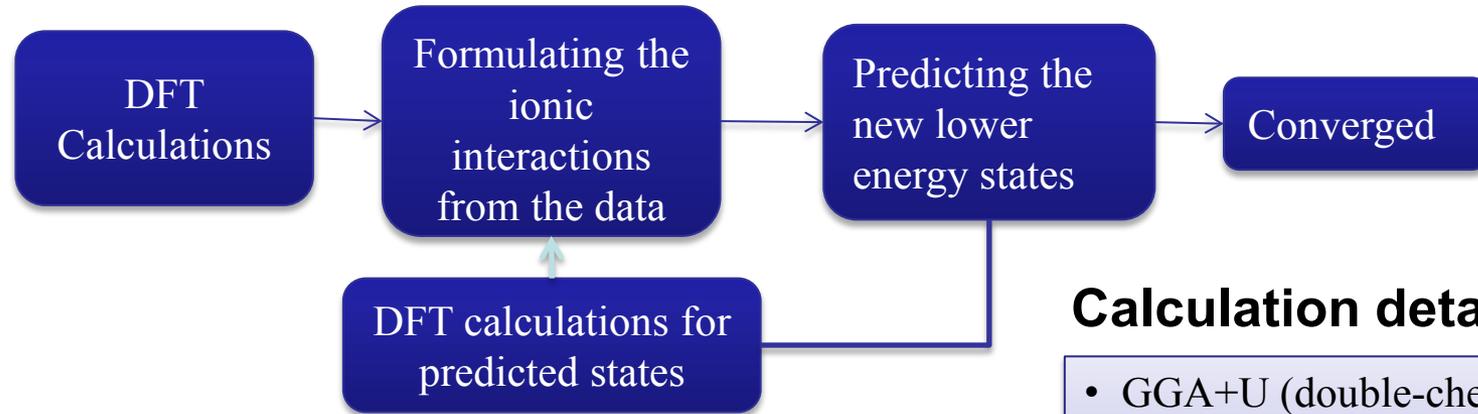
This project started in 2012 and was not reviewed last year

Technical Background

Approach (details)



Cluster expansion: Efficient method to find stable structures and chemical systems



Calculation details

- GGA+U (double-checked with GGA, HSE)
- 520 eV cutoff energy
- Spin-polarized calculation

- Supercell size: 24 formula units (144 atoms)
- Total 183 structure sets, comprising both layered, defect layered and intermediate structures between the layered and spinel structures were examined
- Error of prediction : ~ 10 meV/f.u.

Publications:

1. Eunseok Lee and Kristin A. Persson, *Structural and Chemical Evolution of the Layered Li-excess Li_xMnO_3 as a function of Li content from First-Principles Calculations*, Submitted to **Adv Energy Materials** (2014)
2. Eunseok Lee and Kristin A. Persson, *First-principles study of the nano-scaling effect on the electrochemical behavior in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$* , **Nanotechnology** 24 424007 (2013)
3. Eunseok Lee and Kristin Persson, “*Solid-Solution Li Intercalation as a Function of Cation Order/Disorder in the High-Voltage $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Spinel*”, **Chemistry of Materials** 25, 2885-2889 (2013)
4. Altaf Karim, Sonia Fosse and Kristin A. Persson, *Surface structure and equilibrium particle shape of the LiMn_2O_4 spinel from first-principles calculations*, **Phys Rev. B** 87 (7), 075322 (2013)

Presentations:

1. Structural and Chemical Transformations in Li_xMnO_3 from First-principles Modeling, **The International Battery Association, Australia 2014, Invited**
2. First-Principles Calculations Study on the Electrochemical Activity and Structural Stability of the Li_2MnO_3 , **ECS San Francisco 2013, Contributed**
3. The $\text{Li}_x(\text{Ni}_{0.5}\text{Mn}_{1.5})\text{O}_2$ Spinel from First-Principles and the Materials Project, **ICMAT Singapore 2013, Invited**

Critical Assumptions and Issues



- First-principles computational research is inherently devoid of assumptions or fitting parameters. Hence, predictions are truly obtained from the quantum mechanical state of the material.
- Any bias comes from the way the problems are phrased and what is actually calculated. Thus, the most important aspect of computational research is to phrase the research problem in such a way that it captures the relevant processes.
- In this context, an extremely important aspect of any computational work is to benchmark against experiments and collaborate with experimentalists. In this sense, the PI has found the BATT group at LBL to have an open and collaborative atmosphere which benefits her project.

