Predicting and Understanding Novel Electrode Materials From First-Principles

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Overview

Timeline

- Start Date Oct 2012
- End Date: Sept 2016

Budget

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

Barriers Addressed

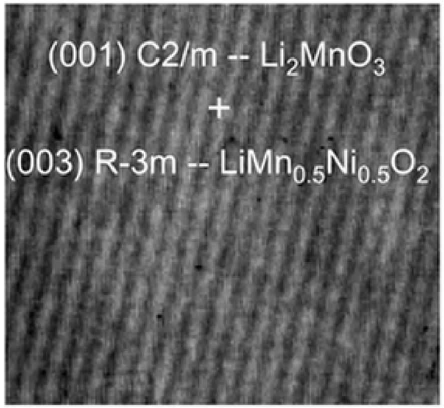
- Inadequate Li-ion battery energy density, cycle life and rate
- High cost of electrode materials

Partners/Collaborations within the VT program

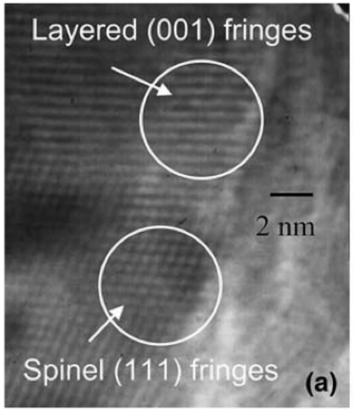
- Project lead: **Vince Battaglia** (LBNL)
- **Vince Battaglia** (LBNL), **Robert Kostecki** (LBNL), **Mike Thackeray** (ANL) and **Gerbrand Ceder** (MIT): understanding degradation mechanisms in Li-excess materials

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:

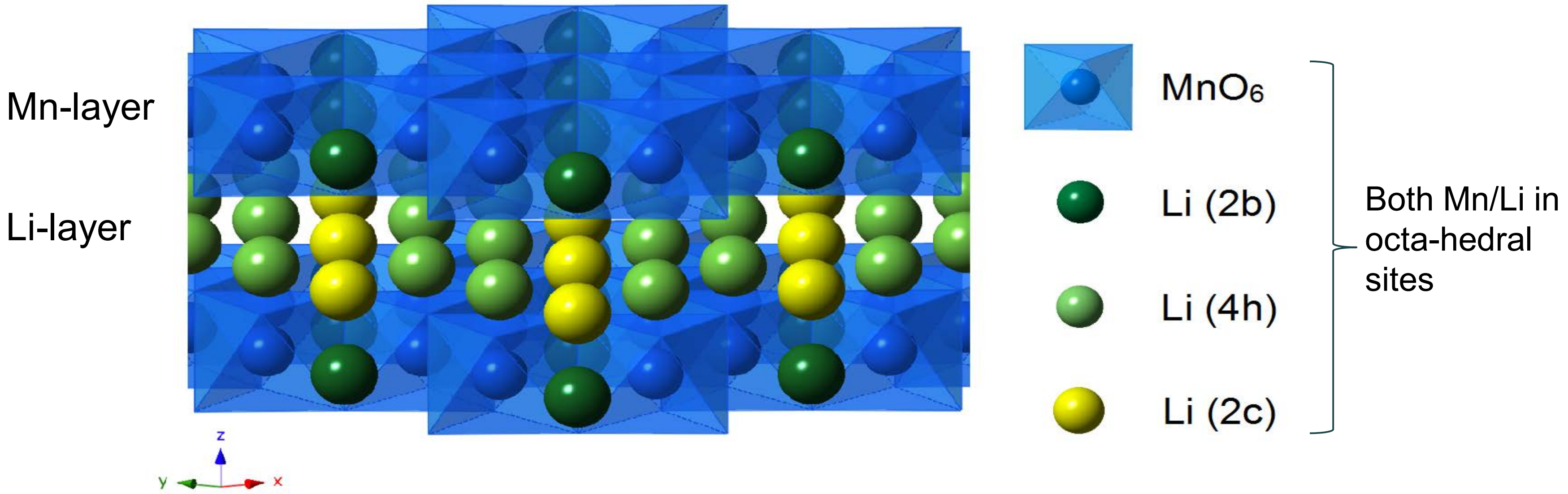
- To investigate whether there may be chemical mitigation strategies (doping, coating, structural changes) possible to increase the stability of the material or to recommend charging protocols

Milestones

Month Year	Milestone	Status
December 2013	Finalize low T phase diagram including relevant bulk Li, O and Mn and defect phases in layered Li_xMnO_2, spinel Li_xMnO_3 and spinel $Li_xMn_2O_4$	Complete
March 2014	Over-charge mechanism processes: oxygen migration paths and activation barriers obtained in lowest energy defect structures; oxygen redox potentials obtained	Complete
June 2014	Go/No-Go: On over-charge mechanism. Criteria: Oxygen release, migration or oxygen redox process; process down select based on data.	Complete
September 2014	Composite voltage profiles as function of structural change and Li content.	Complete

Approach (1)

Li_2MnO_3 crystal structure



- During cycling, the Li_xMnO_3 material and related solid solutions {Mn, Co, Ni} are known to deteriorate resulting in structural changes and voltage fade
- Using atomistic simulations, we have determined how and why Mn defects are formed in Li layer as a function of Li content
- The effect of the Mn defects on the materials' structural and electrochemical properties is compared to experiments, validating the approach
- The Li diffusivity is being investigated at high Li concentrations which gives insight into how the Li move in the material and how the defects affect rate capability.

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) 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

(5) Investigate the inherent Li diffusion mechanisms in the pristine layered material

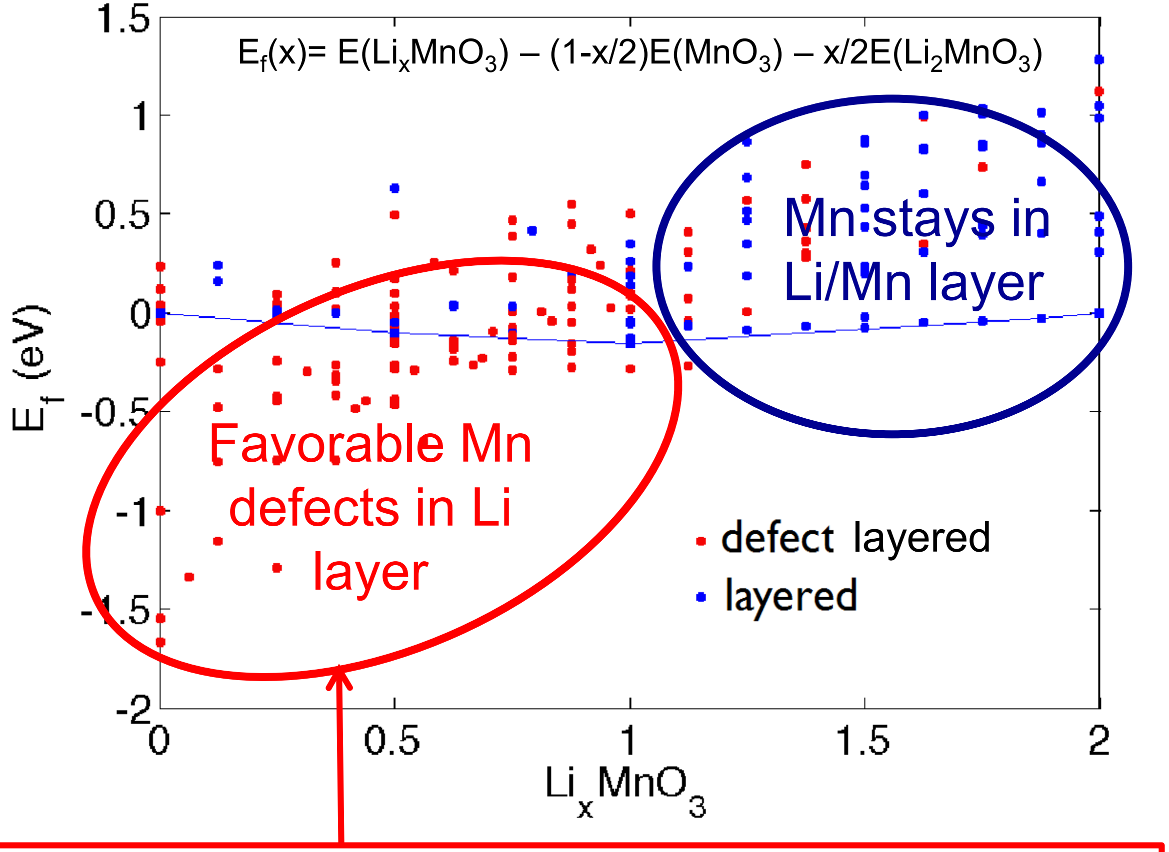
(6) Investigate the impact on Li diffusion from Mn migration into the Li layer

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

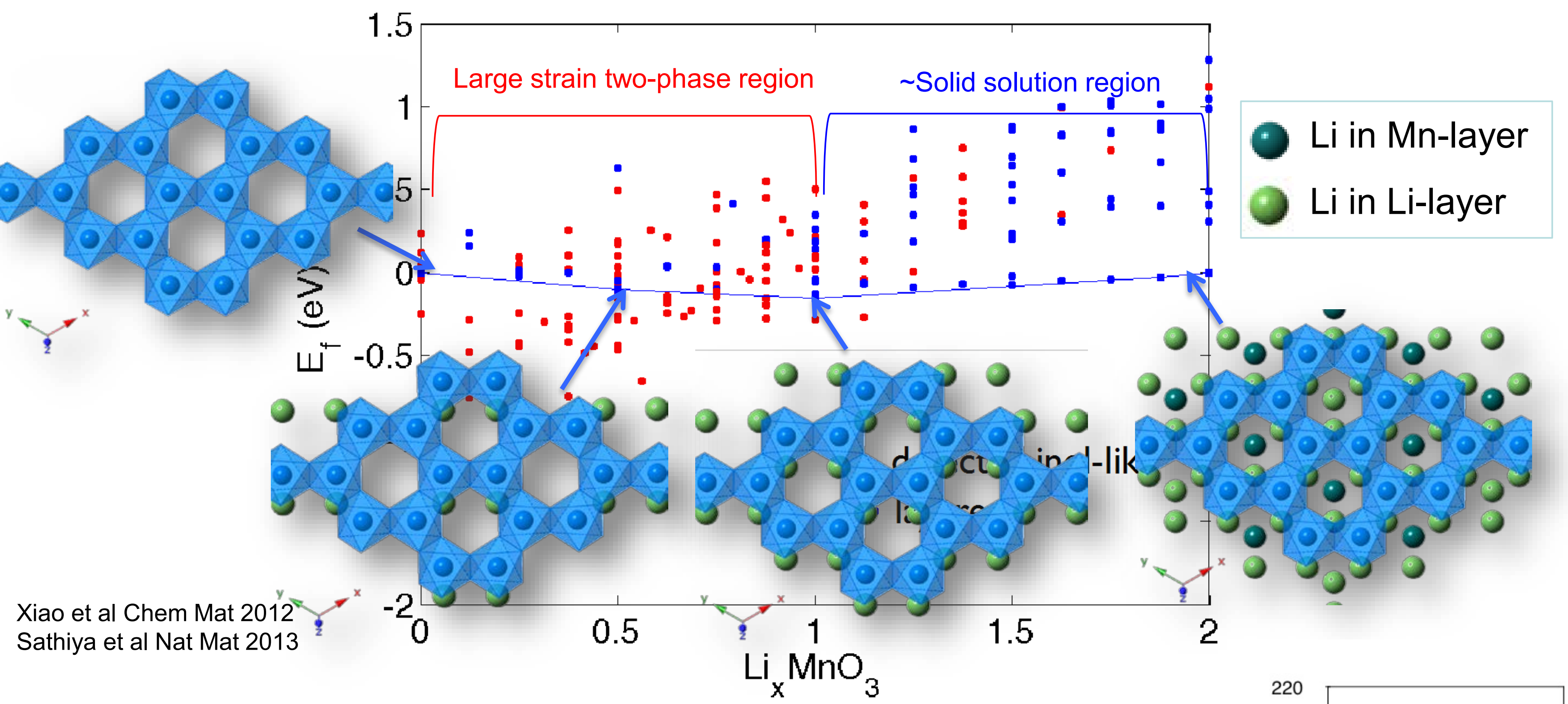
The blue dots correspond to structures retaining the pristine Li_xMnO_3 structure while the red dots represent structures where at least one Mn is displaced into the Li layer



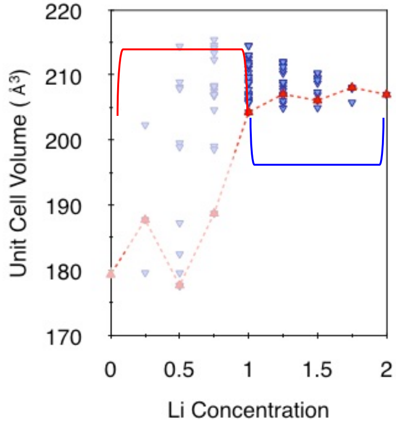
Results (1)

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

Delithiation Process in Li_xMnO_3



Xiao et al Chem Mat 2012
Sathiya et al Nat Mat 2013



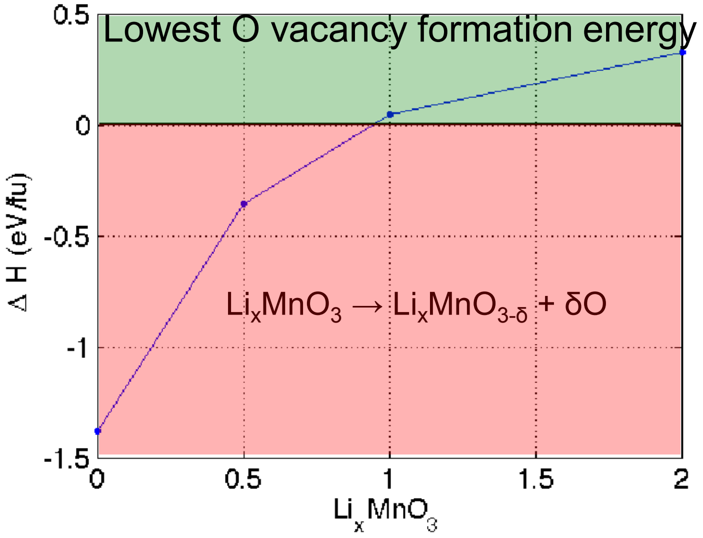
- Li is first extracted from Li/Mn layer
- Weak two-phase/solid solution behavior at high Li content x >1
- Two two-phase regions at lower Li content
- Significant volume difference/strain between two-phase regions for x < 1

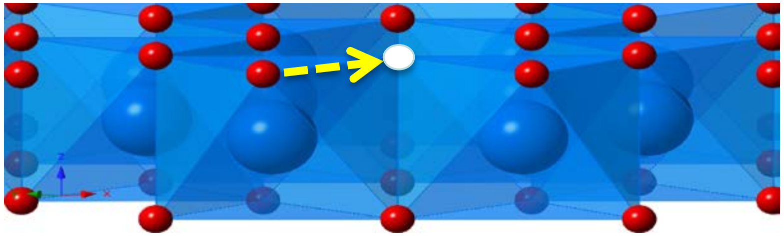
Technical Accomplishments (3)

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 occurs on some of the oxygen ions (not the Mn)** : $O^{2-} \rightarrow O^{-1}$
- 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**



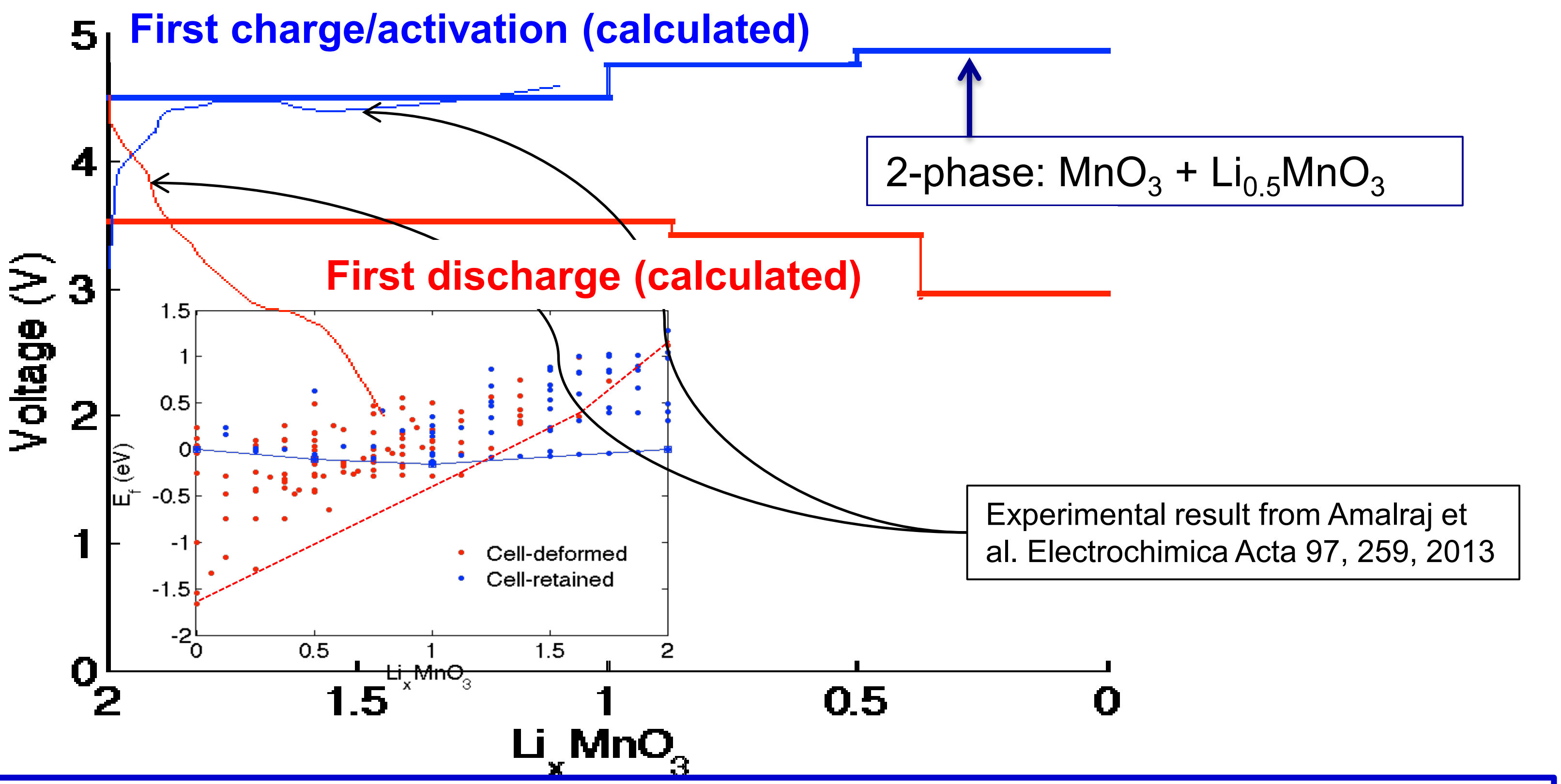


Example O migration path shown

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)



2-phase: MnO_3 + $Li_{0.5}MnO_3$

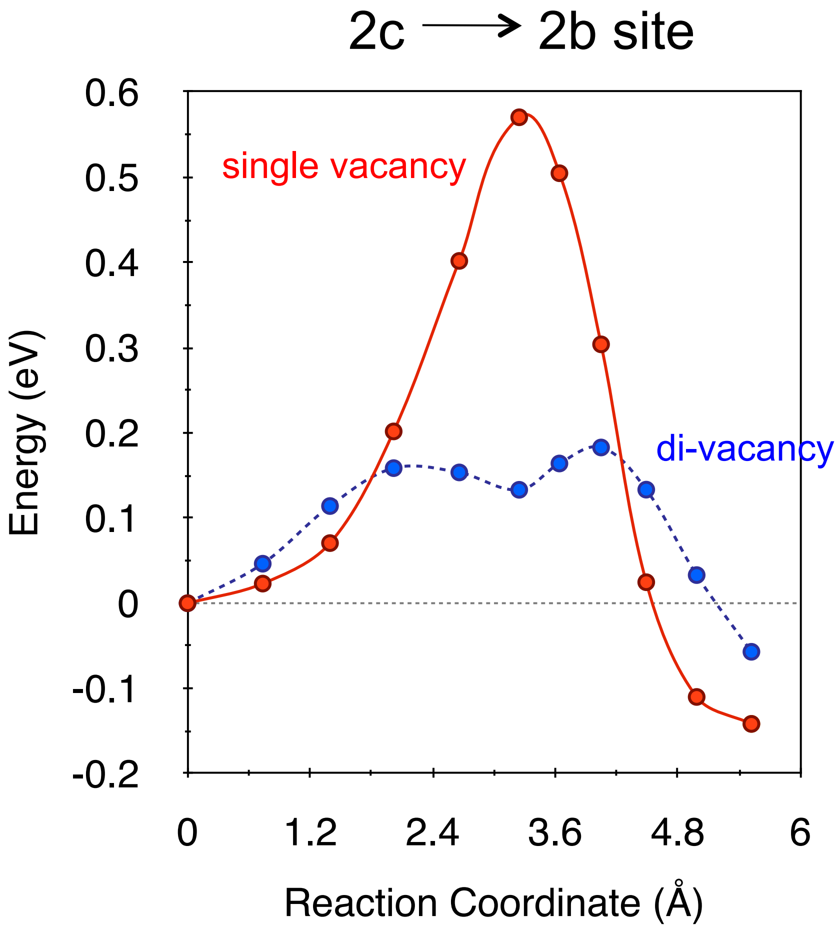
Experimental result from Amalraj et al. Electrochimica Acta 97, 259, 2013

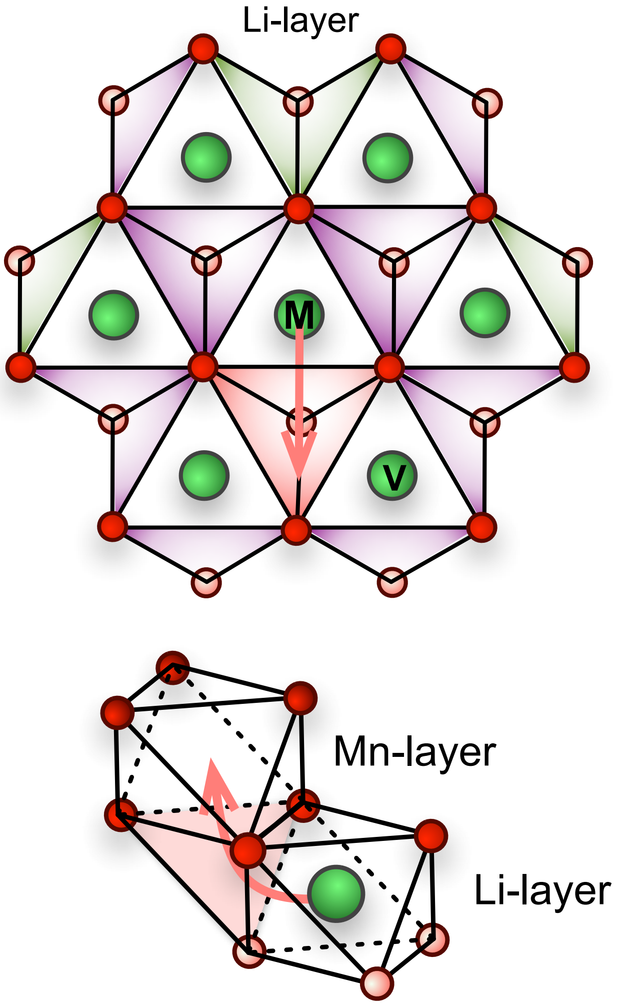
Results (4):

- 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

Technical Accomplishments (5)

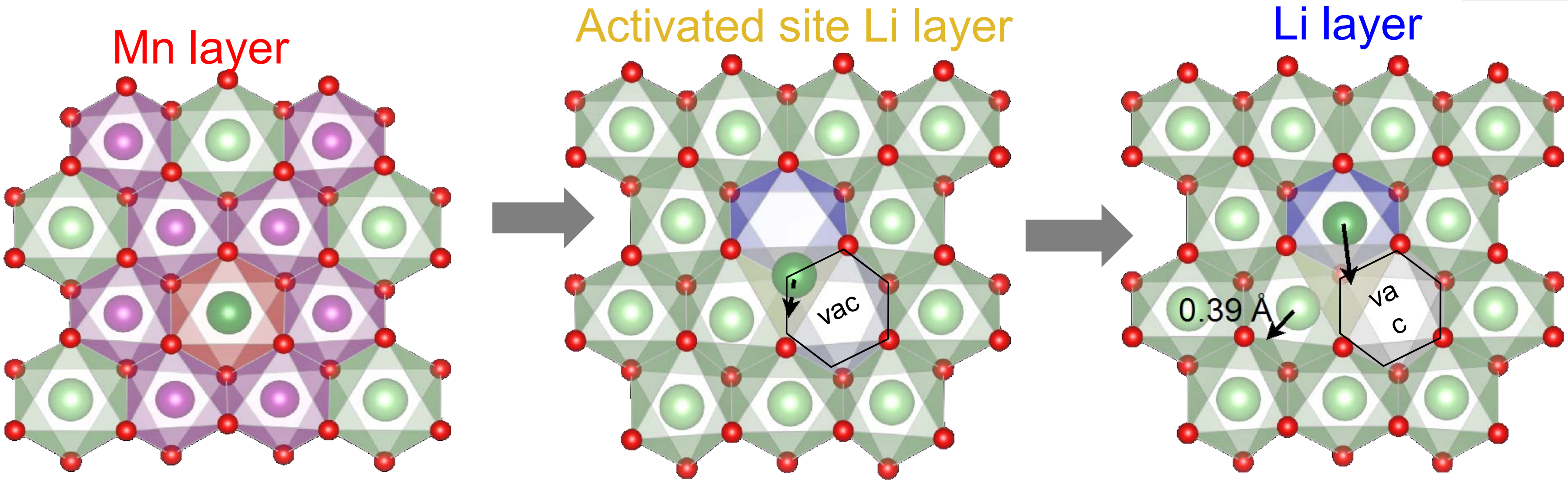
Inter-layer Li migration at high Li content

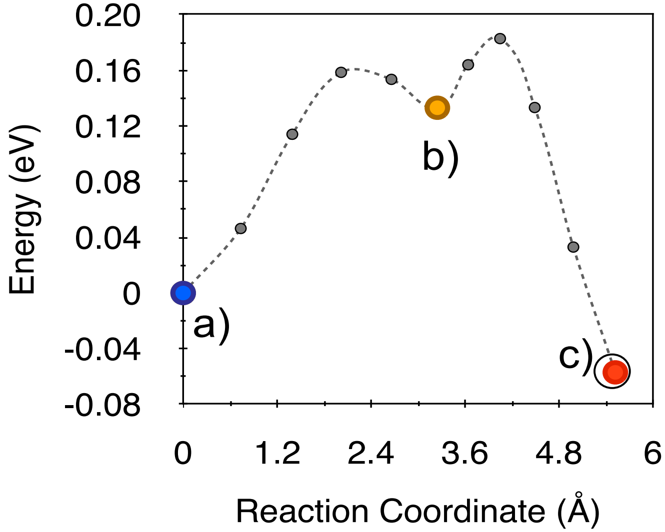


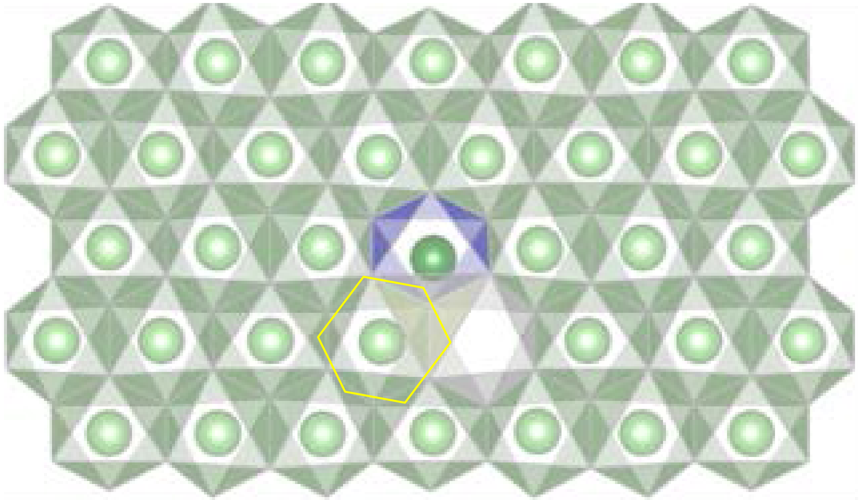


- Multiple Li-vacancy configurations were examined, and a very low migration energy between the Mn layer and the Li layer was obtained for Li layer di-vacancy configuration

Technical Accomplishments (6)





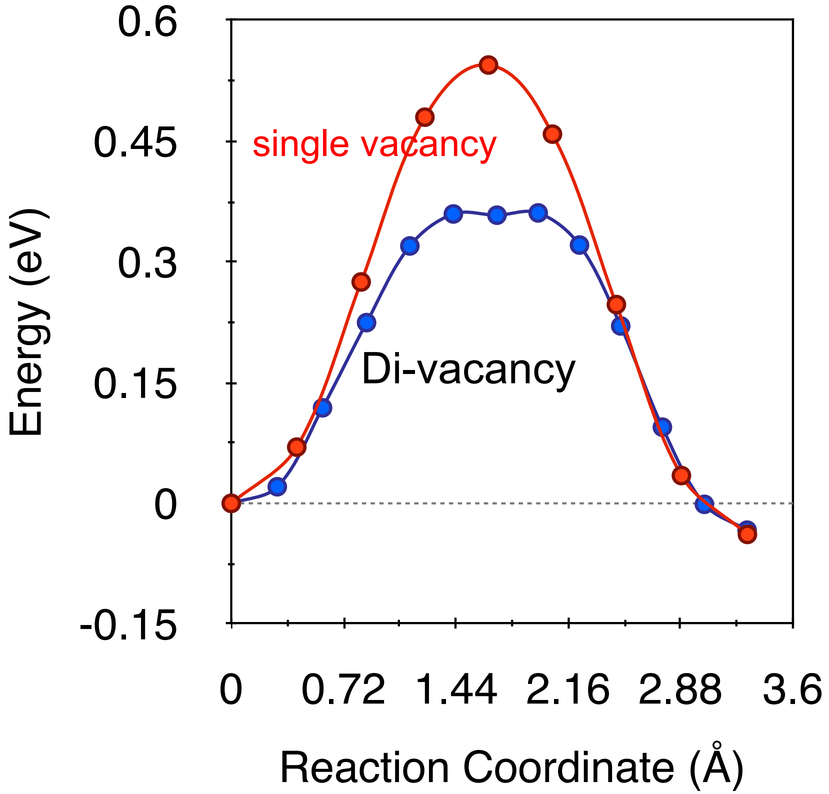


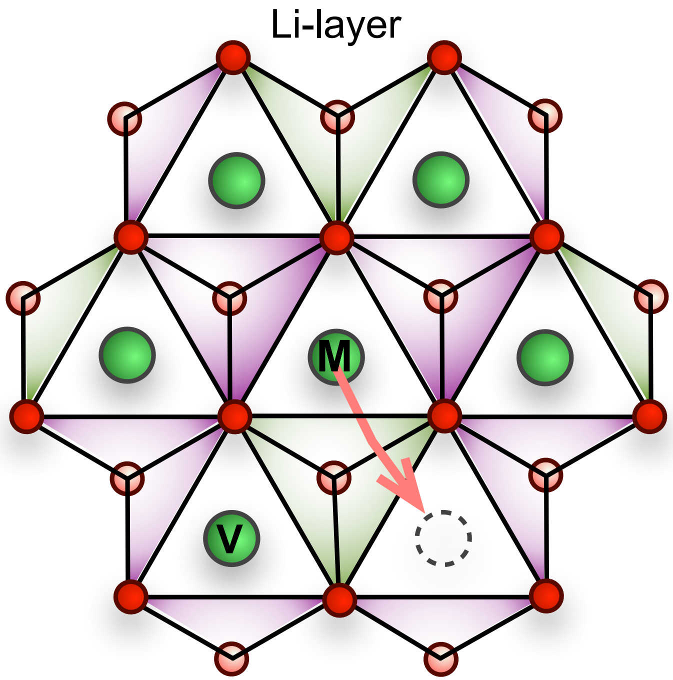
- Main repulsion/force along migration path originates from neighboring Li ion (see movie)
- Neighboring Li ions move up to 0.4 A to avoid repulsion

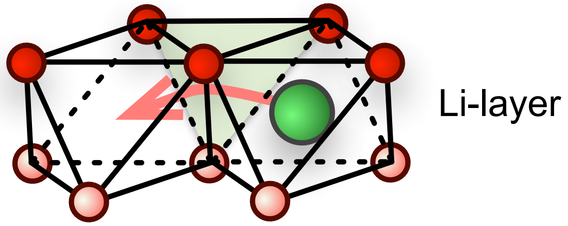
Technical Accomplishments (7)

Intra-layer Li migration at high Li content

2c → 4c site

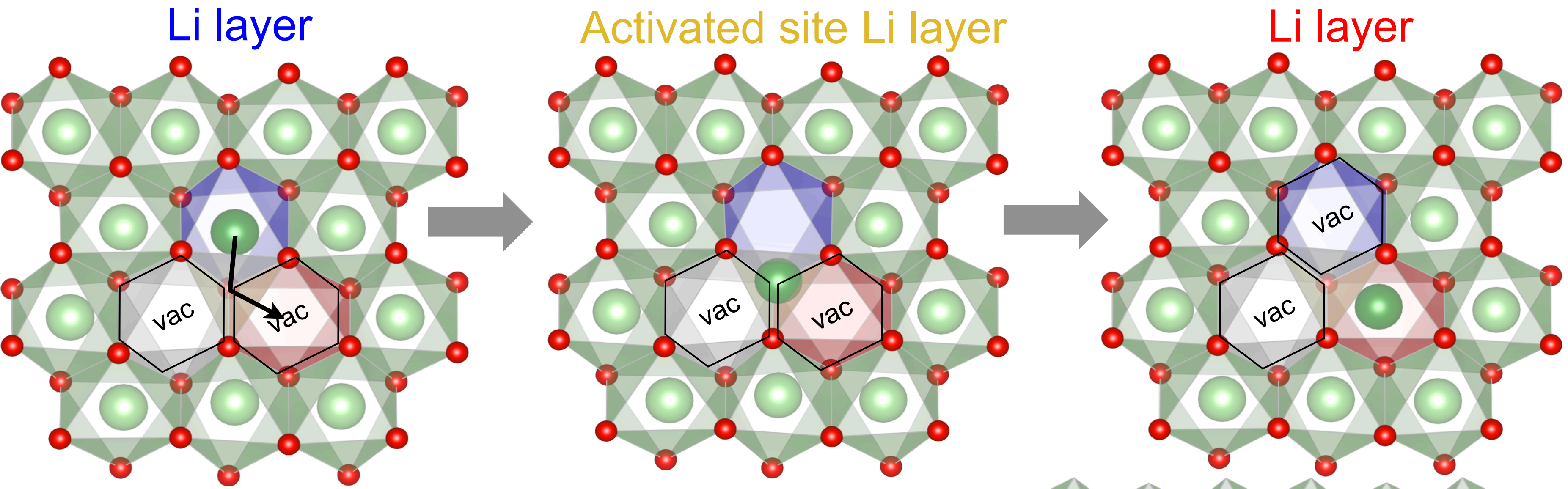


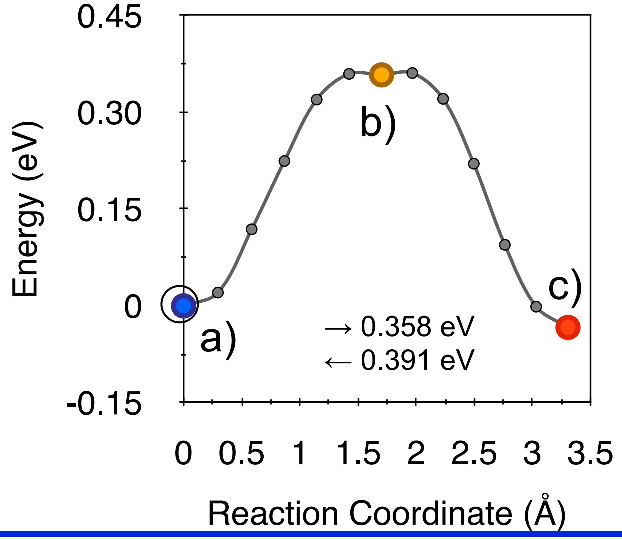


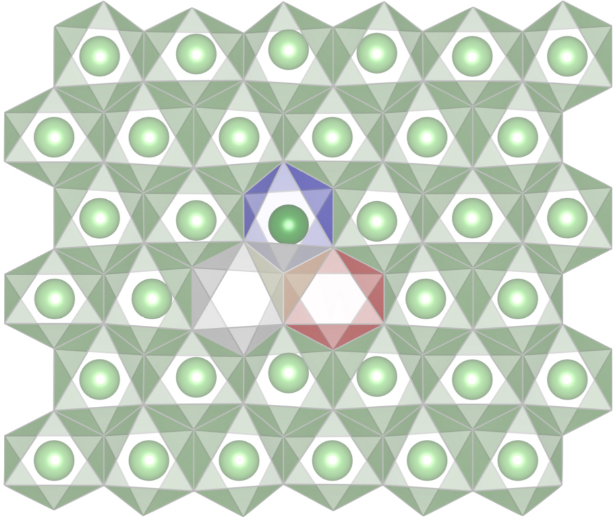


- Multiple Li-vacancy configurations were examined, and a facile migration energy for in-layer Li migration was obtained for the di-vacancy configuration

Technical Accomplishments (8)



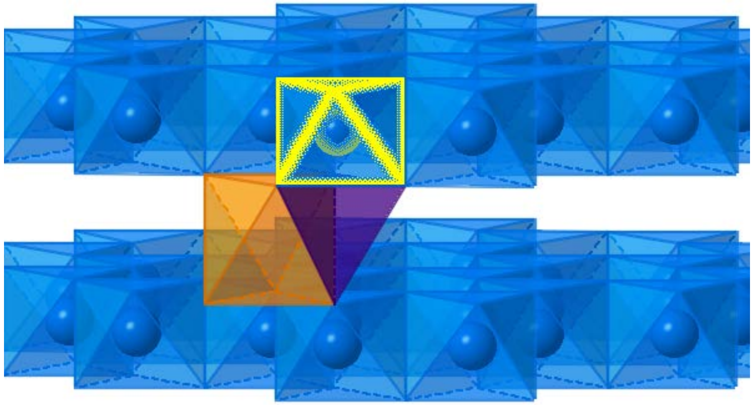




- Main repulsion/force originates from neighboring Li ion but less effect than inter-plane motion
- Neighboring Li ions move up to 0.4 A to avoid repulsion

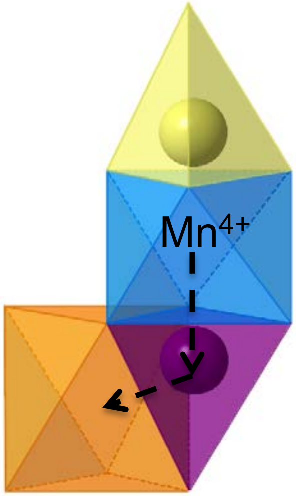
Technical Accomplishments (9)

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

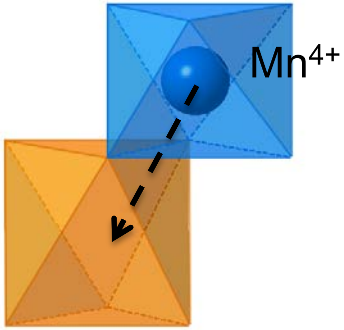
Octahedral site (Blue)
→
Tetrahedral site (Purple)
→
Octahedral site (Orange)



Reed and Ceder Chem. Rev 2004

II. New Path suggested by this work: Edge Path

Octahedral (Blue)
→
Octahedral (Orange)

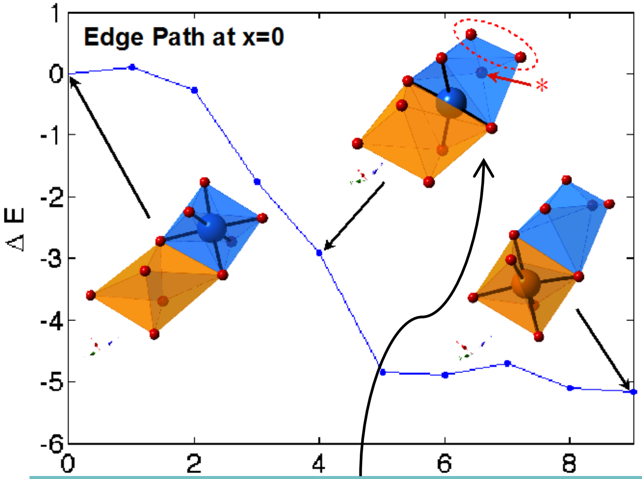


Technical Accomplishments (10)

*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



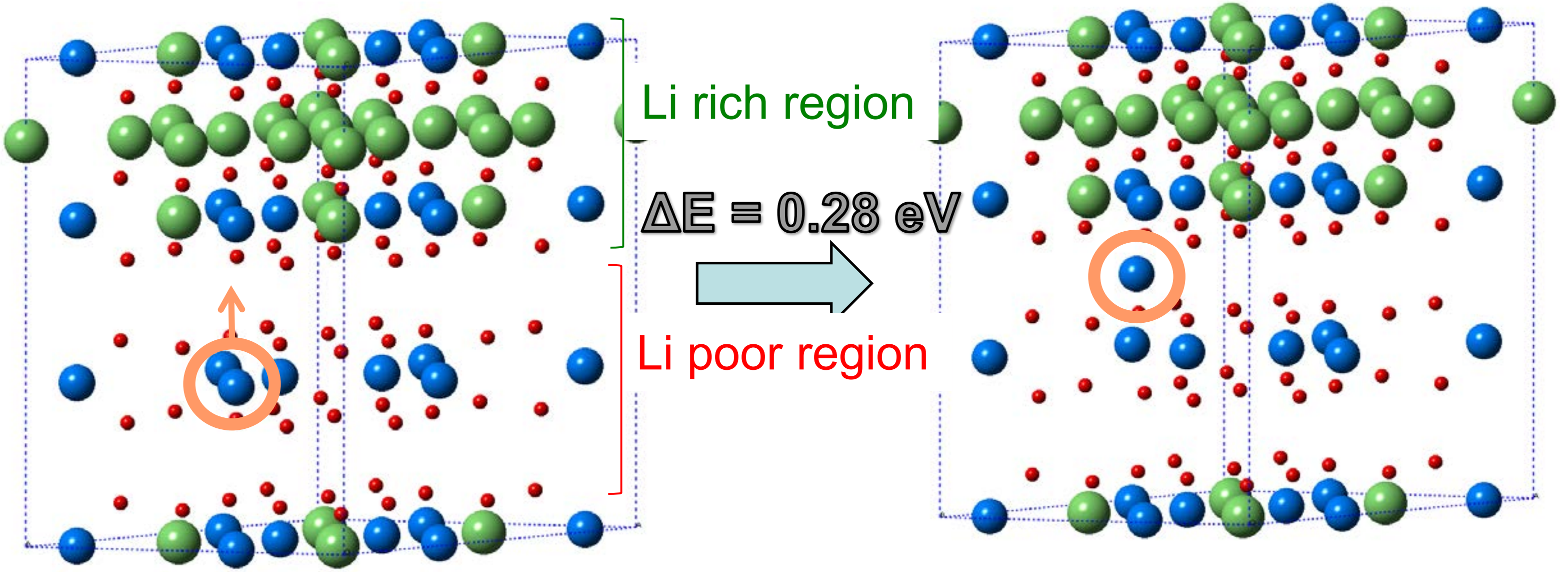
Instantaneous Mn migration enabled by distortion of O environment

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
-

Technical Accomplishments (11)

Result (11): Low barrier for locally delithiated material supports Mn migration even for locally delithiated regions



- As the delithiation process is likely inhomogeneous on the macroscopic level, some particles will be more highly charged than others **yielding local regions with x < 1, even if overall SOC is > 1**
- Hence, a material with inhomogeneous Li distribution, e.g. a locally delithiated region within a matrix of higher Li content (overall Li content x = 1), was simulated
- **Mn^{4+} migration barrier through Edge Path : ΔE = 0.28 eV which supports rapid Mn migration – even for locally (uneven) delithiated regions**

Summary

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
- 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
- Li diffusion is found to be facile – both between Li layer and Mn layer as well as in-plane Li layer - for high Li content. Hence sluggish rate capability for this material (after activation) is attributed to surface passivation or particle level transport
- For $x < 1$, 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
- 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

Future Work

We will finalize the study the layered Li excess materials by

- Finalizing the Li diffusion investigation as a function of state-of-charge as well as Mn migration into the Li layer
- Studying reactions at the surface, particularly focusing on predicting the evolution of stable or unstable crystal facets as a function of O_2 release from surface and oxygen chemical potential
- Collaboration with Envia (within the ABR program) which has focused on substitution and doping strategies – using the insights into the degradation mechanism and the change in Mn migration barriers as a function of chemical constituents as metrics

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)

Response to Reviewers Comments

Feedback was largely positive from the 2013 review with an overall rating of 3.3 and sample wordings such as : “*interesting*”, “*excellent use of modeling*”, “*absolutely critical*” and “*good insights*”.

One reviewer suggested to investigate SEI formation as one cause of the Li2MnO3 degradation. Our future surface studies will address that to some degree, although a complete modeling of the SEI is beyond the scope of this effort.

Another reviewer believed it very important that the work should be widely disseminated.

Dopants were suggested to be included in future studies. This strategy was indeed part of the PIs involvement with ABR program and collaboration with Envia.

Technical Background

Publications and Presentations

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*, **Adv Energy Materials 4 (15) (**2014)

Presentations:

1. First-Principles Calculations Study on the Electrochemical Activity and Structural Stability of the Li_2MnO_3, **ECS Cancun 2014, Contributed**

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.