



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

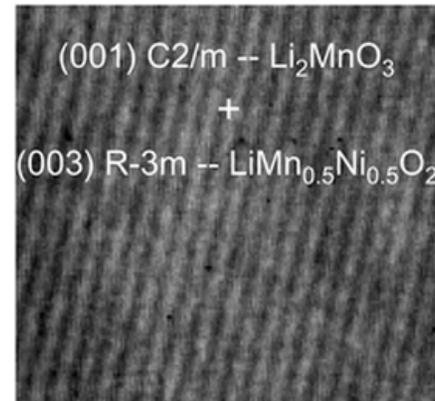
- Inadequate Li-ion battery energy density, cycle life and rate
- High cost of electrode materials

Partners/Collaborations within the VT program

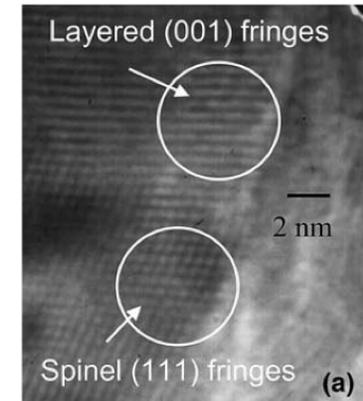
- Project lead: **Vince Battaglia** (LBNL)
- **Vince Battaglia** (LBNL), **Robert Kostecki** (LBNL), **Guoying Chen** (LBNL) and **Gerbrand Ceder** (UCB): understanding degradation mechanisms in Li-excess materials

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

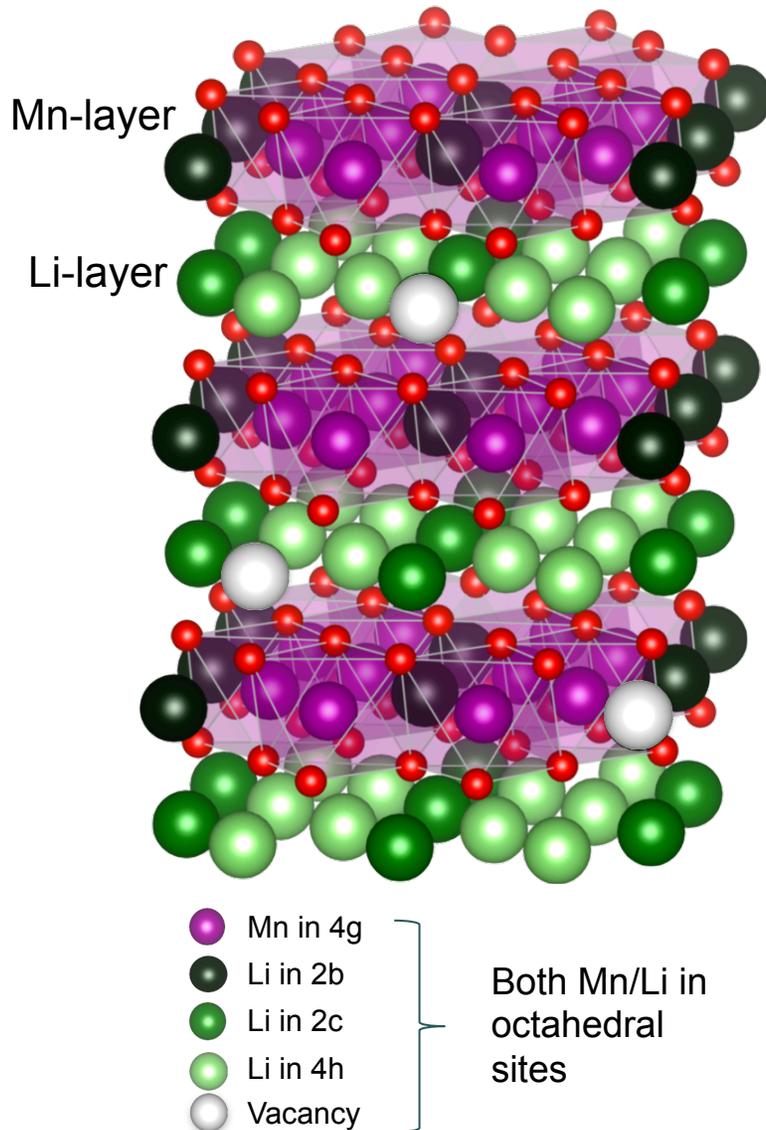
Milestones



Month Year	Milestone	Status
October 2015	Mn mobilities as a function of Li content in layered Li_xMnO_3 and related defect spinel and layered phases	Complete
	Surface facets calculated and validated for Li_2MnO_3	Complete
June 2016	Investigate surface oxygen release to prevent structural degradation	Ongoing
September 2015	Li mobilities as a function of Li content in layered Li_xMnO_3 and related defect spinel and layered phases (9/30/15)	Complete
September 2016	<u>Go/No-Go</u> : Stop this approach if facet stabilization can not be achieved.	Ongoing

Approach (1)

Li_2MnO_3 crystal structure

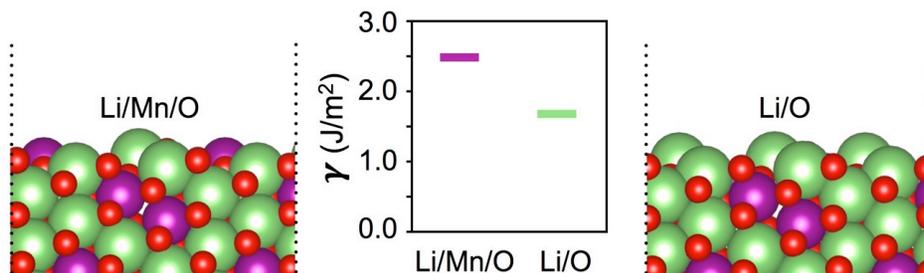
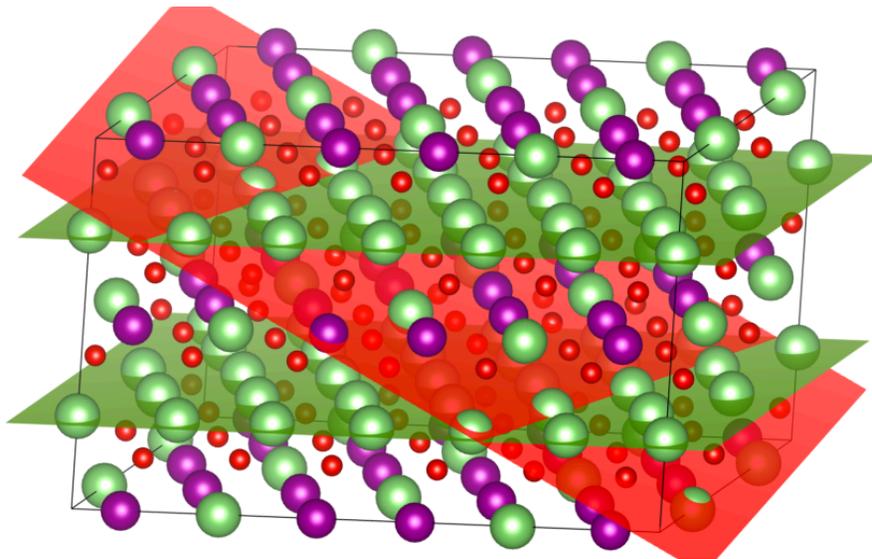


Li and Mn rich compositions yield high capacity but correlates with the chemical and structural degradation of Li excess materials. This work aims to elucidate the atomistic mechanisms behind the degradation.

- Li_2MnO_3 is taken as a model worst-case scenario of the Li excess, Mn rich materials.
- The Li migration from the two Li-containing layers is investigated by **first-principles density functional theory**.
- All Li migration paths are systematically investigated; including **inter- and intra-layer** migration.

Approach (2)

We aim to investigate whether the observed poor Li mobility in Li_2MnO_3 is due to first charge release of oxygen which in turn leads to structural and chemical surface densification and poor electron and/or ion transport.



- All possible low miller index surfaces with various cation ordering on each surface are calculated.
- The lowest-energy surface atomic arrangements are found by i) surface reconstruction swapping surface Mn for sub-surface Li and ii) allowing Li ions to re-arrange on the surface.
- Oxygen loss is investigated by selectively removing the less stable surface oxygen and calculating the resulting energy.

Approach (3)



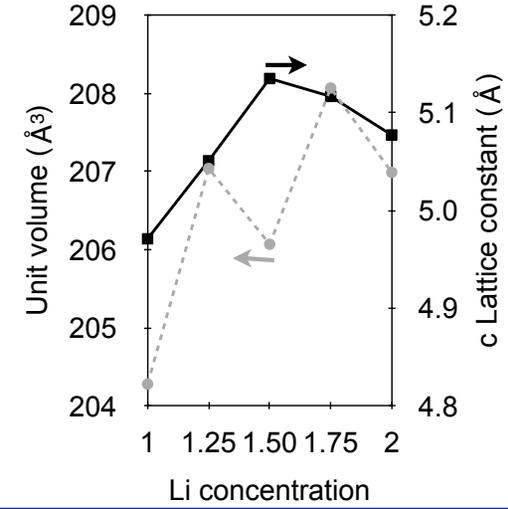
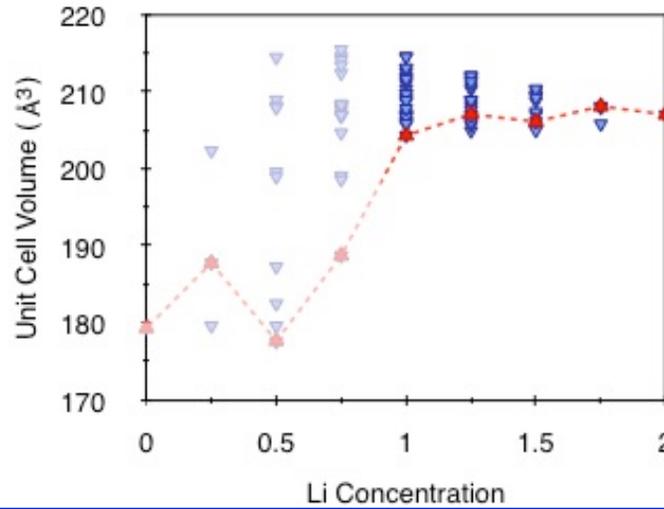
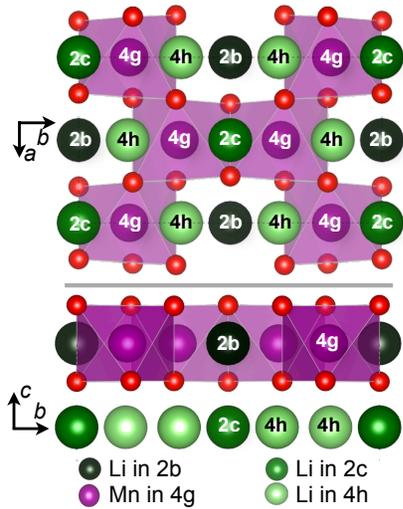
To elucidate the Li mobility in Li_xMnO_3 , $1 < x < 2$ - in the pristine material as well as a function of Mn defect formation during cycling - we employ the following steps:

- (1) Find the minimum energy path for both Li intra- and inter-layer migration.
- (2) Investigate the vacancy cluster effect on the Li migrations in both intra- and inter-layer directions.
- (3) Elucidate the local Mn defect environment and its effect on the Li migration mechanism.

To uncover the most stable surface facets and their most stable atom arrangements we employ surface reconstructions :

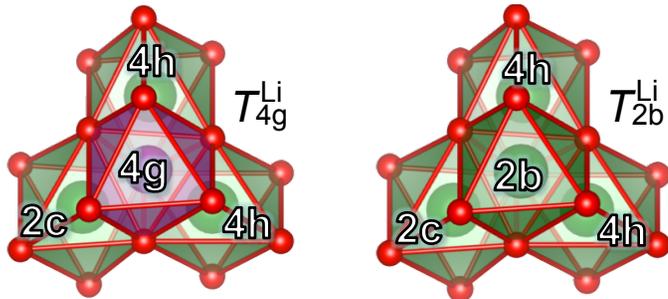
- (1) Systematically categorize all low miller index surfaces.
- (2) Find controlling rules of surface stabilization.
- (3) Calculate the minimal surface energies for each stable surface.
- (4) Verify the Wulff shape (equilibrium particle shape) by means of atomistic computations.
- (5) Investigate the driving force, for each surface facet, towards oxygen release; leading to first cycle structural and chemical deterioration

Technical Accomplishments (1)

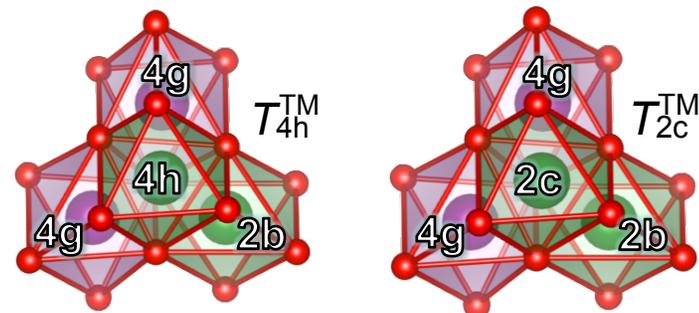


- Many Li arrangements with similar energy and insignificant volume changes for $1 < x < 2$ indicate solid solution behavior at room temperature in this concentration range.
- Slab space and volumes are not correlated with Li concentration between $1 < x < 2$
- Li migration tetrahedral sites are distinguished by their local cation topology.

Saddle point tetrahedral sites in Li layer



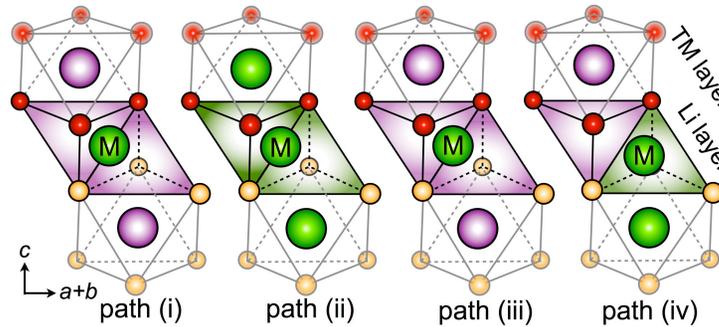
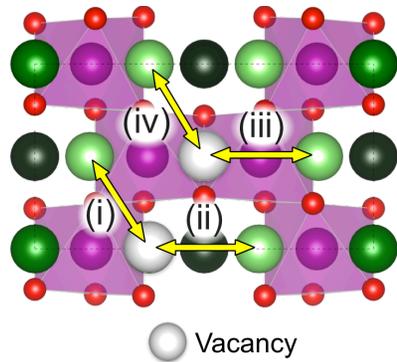
Saddle point tetrahedral sites in TM layer



Technical Accomplishments (2)

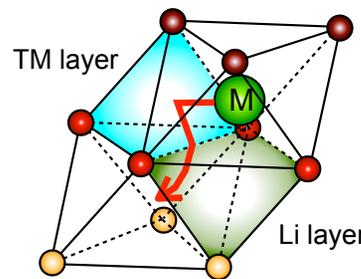
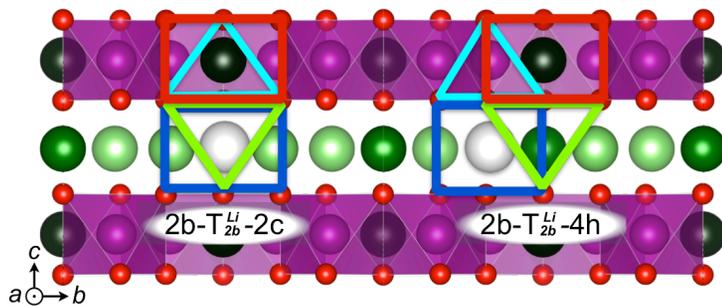


Intra-layer migration



- Four distinguishable paths exist for **intra-layer** single vacancy Li migration.
- Path IV and III are energetically more favorable due to lower neighboring cation repulsion.

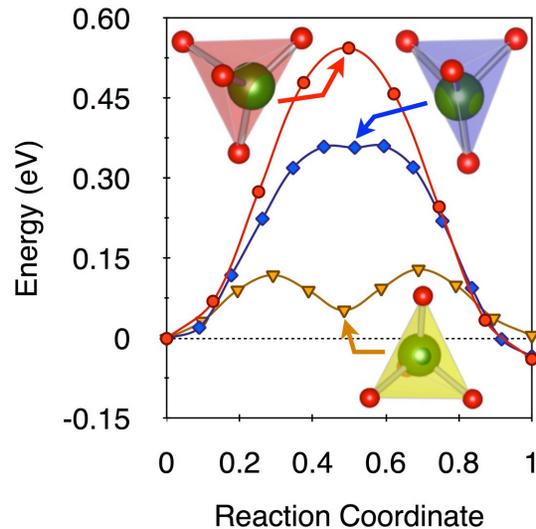
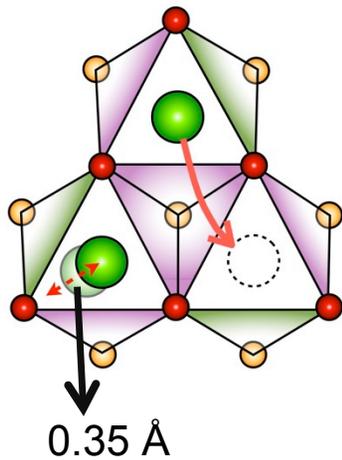
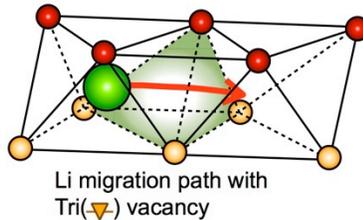
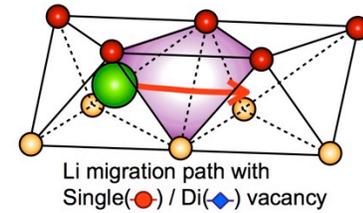
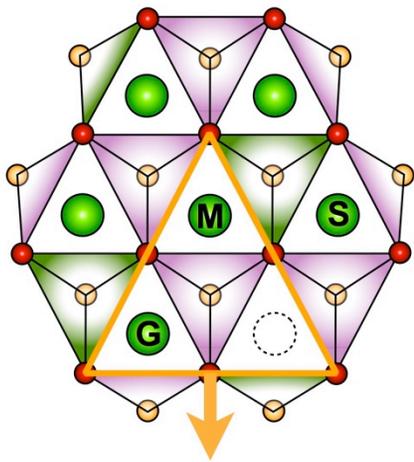
Inter-layer migration



- Two distinguishable paths exist in **inter-layer** single vacancy Li migration.
- Inter-layer Li migration occurs through the tetrahedral site in Li the layer.

Technical Accomplishments (3)

Intra-layer migration



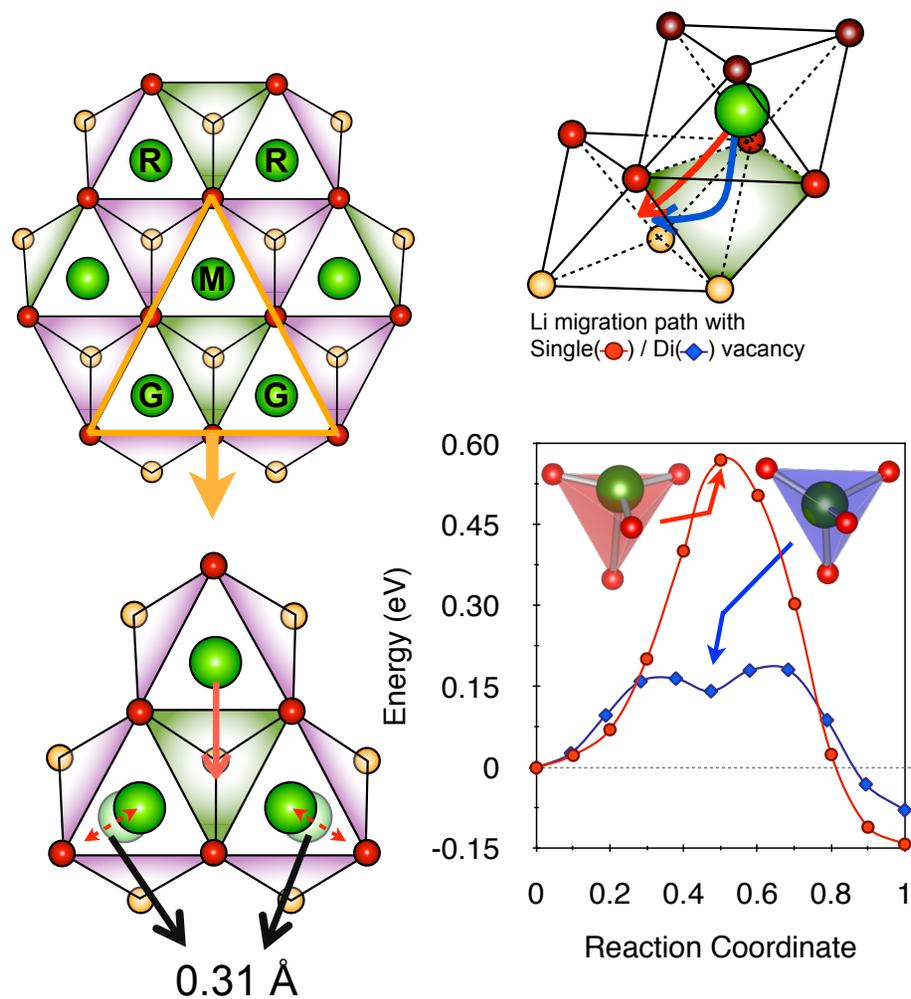
- The neighboring gate Li ion moves 0.35Å to accommodate mobile Li migration.
- Vacancy clusters significantly reduce the Li migration energy barrier.
- The saddle point tetrahedral site is stabilized by neighboring di- and tri-vacancies.
- **Intra-layer Li migration has similar behavior and activation barriers as LiCoO₂ – e.g. facile Li diffusion.**

Technical Accomplishments (4)



Inter-layer migration

- Two neighboring gate Li ions move 0.31\AA to enable mobile Li migration.
- Di-vacancies significantly reduce the Li migration energy barrier and stabilizes the saddle point tetrahedral site.
- Tri-vacancies enables spontaneous Li ion migration from the TM layer to the Li layer.
- **Extremely favorable inter-layer Li-ion migration activated by di-vacancies.**

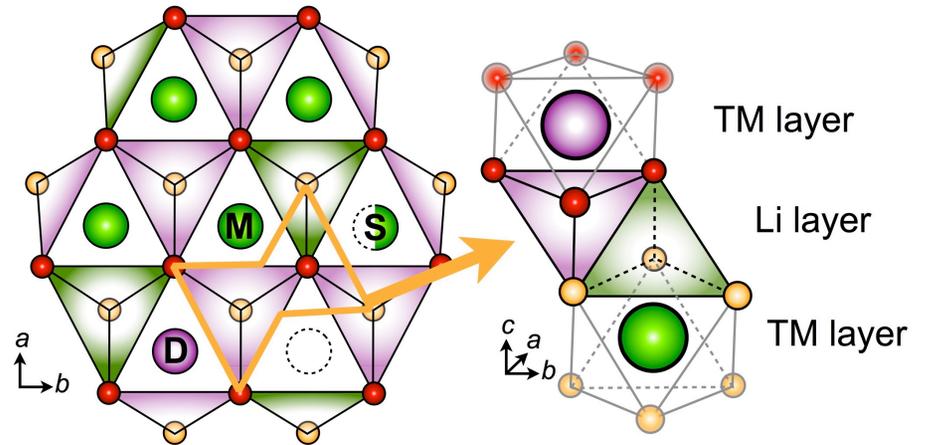


Technical Accomplishments (5)

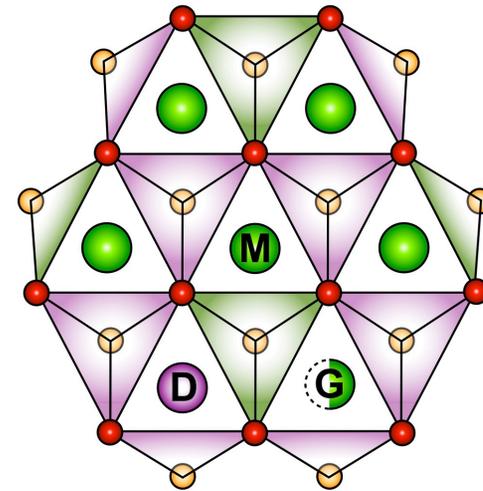


- Mn migration and subsequent structural rearrangement is predicted in bulk which is highly probable to impact Li migration.
- Mn defects are formed by Mn migration from TM layer to Li layer.
- For intra-layer Li migration, a single neighboring Mn defect does not significantly affect Li mobility as alternative paths exist.
- **For inter-layer Li migration, Mn defects significantly prevent Li migration for both single- and di-vacancies. This deterioration in Li inter-layer mobility will lock out the Li capacity in the Mn layer, as Mn defect forms in the Li layer during cycling.**

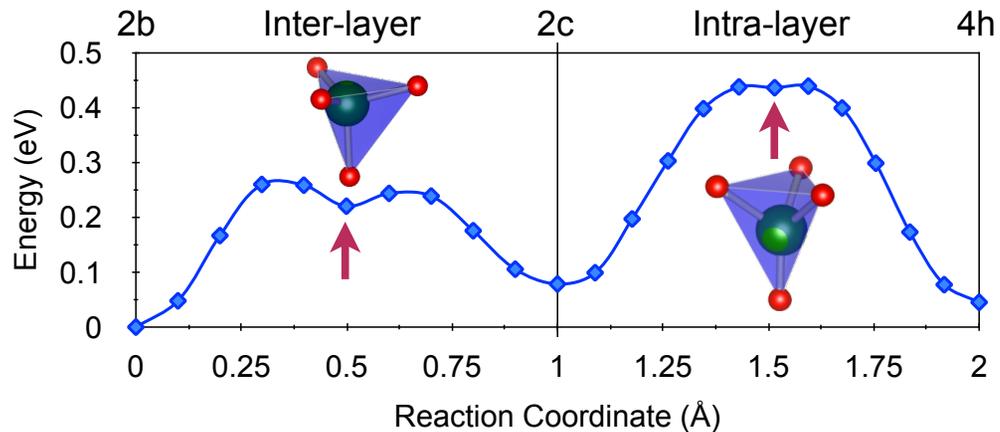
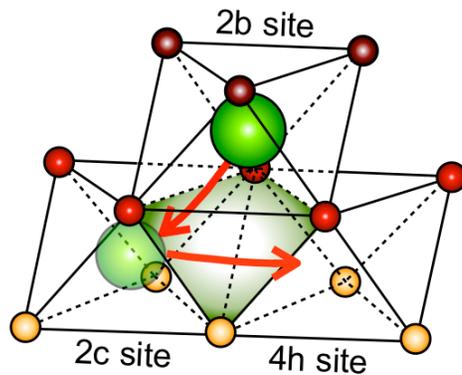
Intra-layer migration with Mn defect



Inter-layer migration with Mn defect



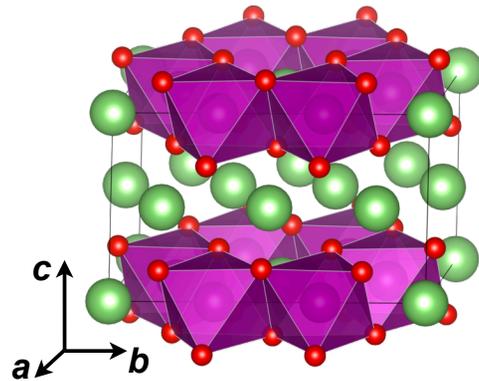
Technical Accomplishments (6)



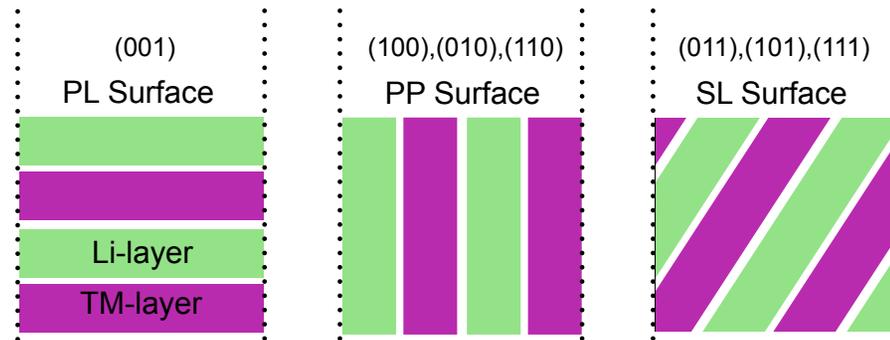
Defects	E_a^K (eV)	
	Intra-layer	Inter-layer
V_{single}	0.56	0.64
V_{Di}	0.38	0.18
V_{Tri}	0.05	-
Mn Def. V_{single}	0.56	0.80
Mn Def. V_{Di}	-0.29	0.70

- The entire Li migration process was obtained for the di-vacancy configuration; Li migrates from the 2b site in the TM-layer to the 2c site in the Li-layer, and then moves to the 4h site.
- **The activation barriers as a function of vacancy clusters/defects show facile Li diffusion behavior until Mn defects are formed – then inter-layer Li mobility deteriorates.**

Technical Accomplishments (7)



a [Å]	b [Å]	c [Å]	β [°]
5.0048	8.6525	5.0862	109.47



- Li_2MnO_3 has 7 distinguishable low Miller index surfaces.
- Any arbitrary facet of Li_2MnO_3 , excluding the (001) parallel surface inevitably includes both Mn and Li (see PP and SL surfaces).

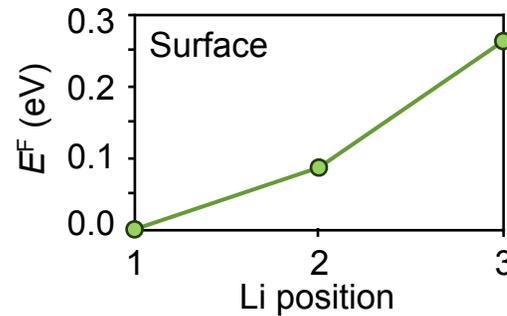
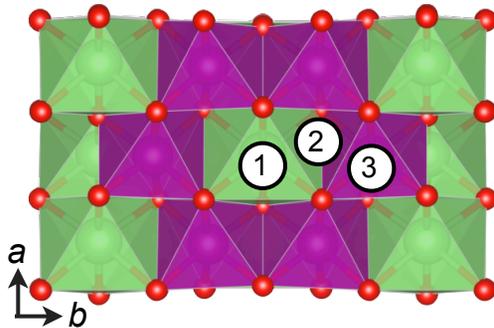
Group	Facet	Tasker	Termination	γ (J/m ²)
			n	
PL	001	III	Li	0.977
	110	III	Li	1.165
PP	010	II	Li	1.395
	100	III	Li	1.460
SL	011	III	Li/O	1.653
	101	I	Li/O	1.491
	111	II	Li/O	1.732

- There are 3 types of surfaces with low miller index (see Figures). Lowest energy surfaces are the reconstructed Li-terminated (001) and Li terminated (110).

Technical Accomplishments (8)

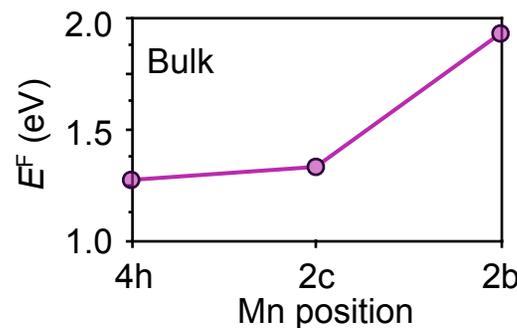
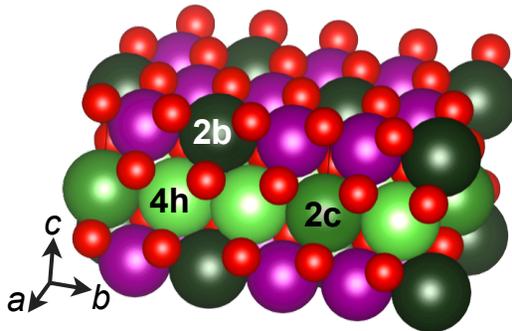


Li-ion on surface



Surface Li-ions are more stable on the top of subsurface Li-occupied octahedral sites as compared to Mn-occupied octahedral sites (cation repulsion).

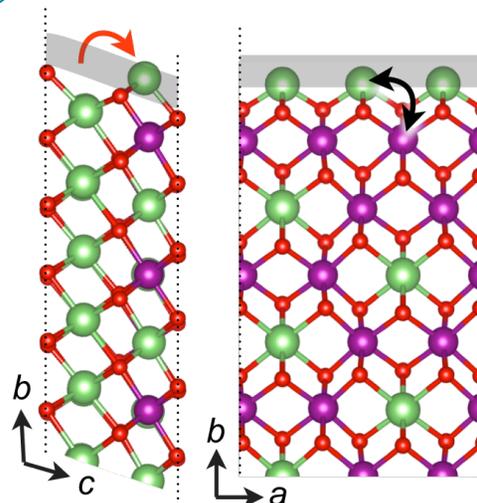
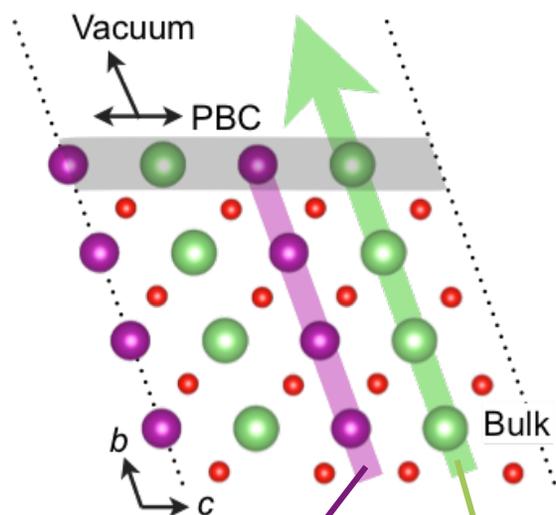
Mn-ion in bulk



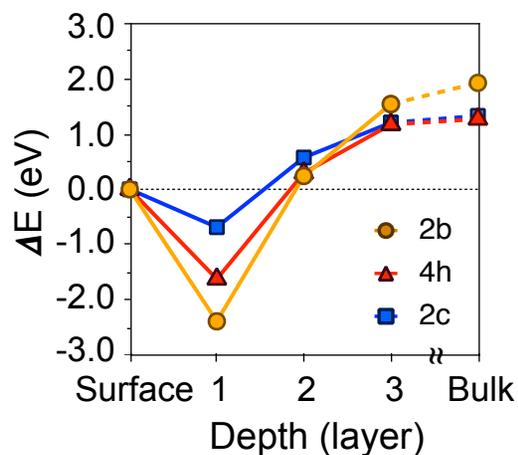
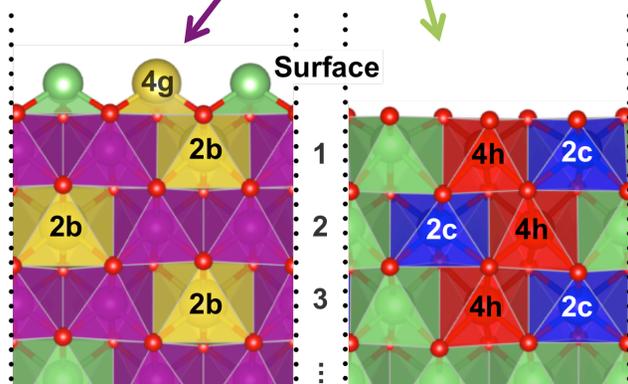
Unterminated surface Mn is favorably repositioned in subsurface layer, by swapping subsurface Li with surface Mn. **This process likely happens spontaneously during synthesis.**

Technical Accomplishments (9)

The PP/SL surfaces have Li percolation paths (green paled arrow) to the surface in accordance with a laminating structure.



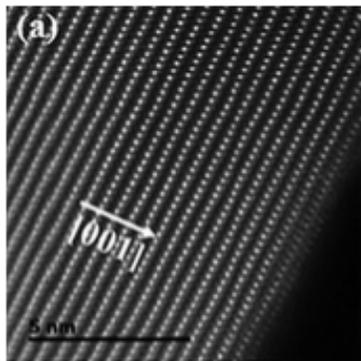
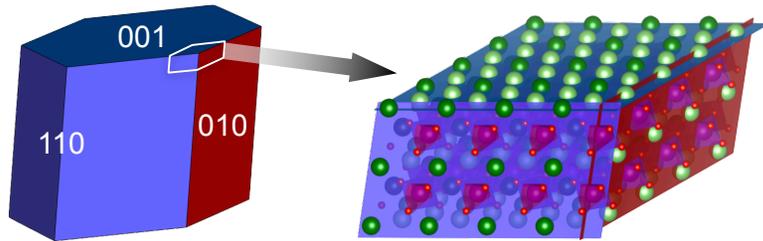
The surface under-coordinated Mn-ions are reconstructed by i) exchange with subsurface Li-ions (black arrow) or ii) surface of Li layer (red arrow).



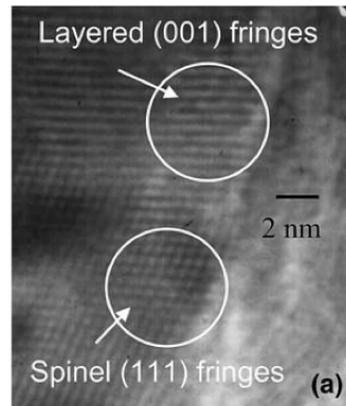
The surface reconstruction energies consistently favor one-layer depth subsurface positions for the surface Mn ions.

Technical Accomplishments (10)

Wulff shape of Li_2MnO_3

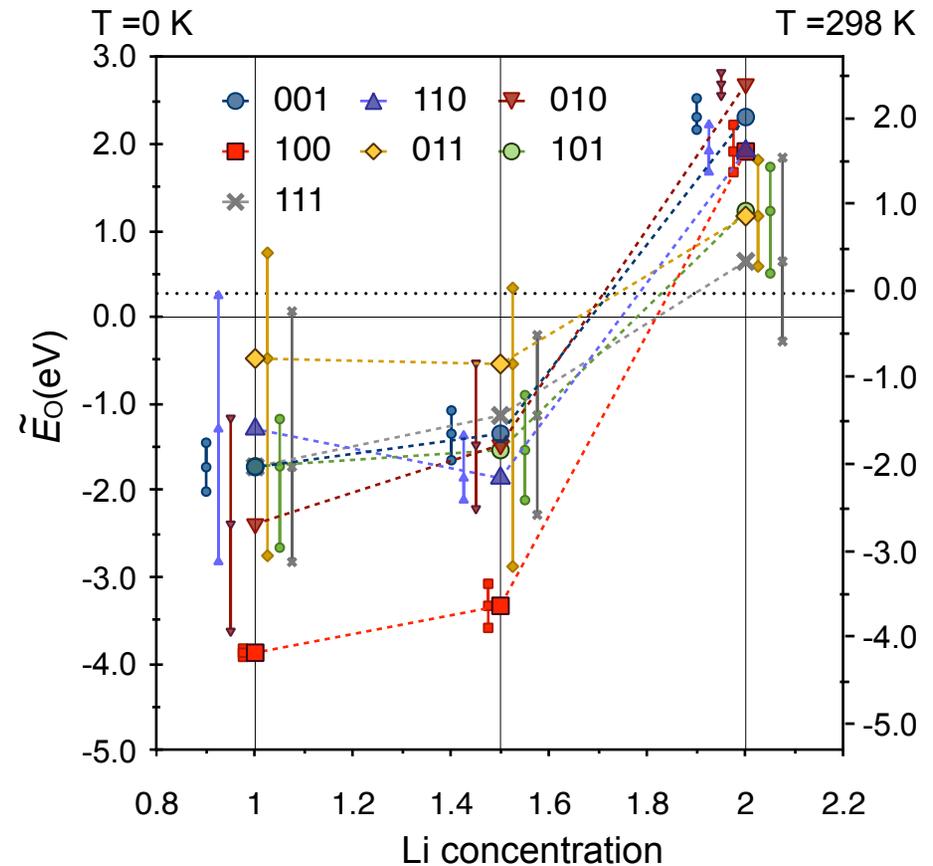


Kim et al., Chem. Sus. Chem, 8 (2015) 3255



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

Oxygen release energies on each surfaces



- Calculated Wulff shape shows that energetically dominant surfaces are (001), (110), and (010). Experiments show evidence of both (110) as well as (001) layered surface facets.
- **All surface facets are predicted to lose oxygen past $x = 1.5$. However the (011) surface is more stable.**

Summary



- We find that the pristine material exhibits excellent Li mobility enabling facile Li extraction from both the transition metal layer and Li-layer. However, we also find that the inherent Li mobility is very likely destroyed by first-charge oxygen release, surface modifications and bulk Mn defects that form during cycling.

Using the model system Li_xMnO_3 ($1 \leq x \leq 2$) and first principles modeling; we have established that

- Li migration in the pristine (no surface nor bulk structural nor chemical transformation) Li_xMnO_3 is enabled by vacancy clusters and shows facile Li diffusion similar to LiCoO_2 .
- Di-vacancy enhances the Li mobility between the layers, and tri-vacancies causes spontaneous Li migration from the TM layer to the Li layer. This means that Li can be rapidly extracted as long as the material stays chemically and structurally intact.
- Single Mn defects in the Li layer does not affect intra-layer Li migration but significantly prevent Li migration between layers.
- The Li_2MnO_3 potentially have 7 distinguishable surfaces which can be organized into three groups with respect to the orientation of the Li percolation layers.
- Surface Li favor locations on the top of Li-occupied octahedral sites.
- Surface Mn reconstruct to the subsurface bulk sites.
- Calculated Wulff shape are consistent with experimental observations.
- Unfortunately, all surface facets are predicted to lose oxygen as Li is removed past $x = 1.5$, but the (011) facet is more stable than e.g. the (001) facet.

Future Work



We will finalize the study of the layered Li excess materials by

- Finalizing the investigation of surface oxygen release and coordinating with PI Guoying Chen on the synthesis and testing of more stable Li_2MnO_3 morphologies, promoting the (011) facet.

Collaborations



Fruitful discussions with:

Guoying Chen (LBNL), **Gerbrand Ceder** (UCB) (within BATT) and **Claude Delmas** (Bordeaux, France) (outside BATT) on understanding degradation mechanisms in Li-excess materials are gratefully acknowledged.

Response to 2015 Reviewers Comments



Presentation Title	Principal Investigator and Organization	Page Number	Approach	Technical Accomplishments	Collaborations	Future Research	Weighted Average
Predicting and Understanding Novel Electrode Materials From First Principles	Persson, Kristin (LBNL)	2-53	3.67	3.67	3.67	3.50	3.65

Representative (select) 2015 Review comments:

The project is shedding light on the stability and potential improvements that can be introduced into high capacity cathode powders. That, the reviewer continued, is very related to petroleum displacement, as it will enable higher capacity batteries.

...it will be interesting to know additional details of the redox process involving oxygen. The new edge path proposed for Mn⁴⁺ migration is a nice accomplishment that can be used for the design of high-capacity materials.

[Response: we thank the reviewers for the positive reviews. Most of the suggestions related to elucidating the process of oxygen release, which has indeed been a focus of 2016.](#)

The project team have produced extensive results on the cycling of the Li₂MnO₃ active material, the reviewer noted.

Excellent collaborations and synergies with other DOE laboratories and industry were noted by this reviewer.