First Principles Calculations of Existing and Novel Electrode Materials

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Peer Review, Washington June 2016

Overview

Timeline

- Start Date May 1 2013
- End Date: Dec 2016

Budget

- Total budget (4 years): $964K
- FY16 funding $250

Barriers Addressed

- Low rate capabilities
- high cost
- poor stability
- low energy-density
- Poor understanding of oxygen redox

Partners/Collaborations within the VT program

- **Kristin Persson** (LBNL), **Mahalingam Subramanian** (ANL), **Dong Su** (BNL), **Feng Wang** (BNL), **Hubert Gasteiger** (Technical U of Munich), **Cosandey** (Rutgers) , **Piper** (Binghamton), **NCEM** (LBNL)

Relevance

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- Capacity improvements on stoichiometric layered materials such as LCO, NMC, NCA are becoming limited
- Li-excess materials and cation-disordered materials have shown promise for significantly higher capacity, but the physical mechanisms that control their redox behavior, mobility, capacity and stability, are poorly understood.

Objectives

- To understand the role of Li-excess in making high capacity, high energy density cathode materials
- To understand how Li-excess and cation disorder influence participation of oxygen ions in the redox activity.
- To use the concepts of cation disorder and oxygen redox to create high capacity cathodes
- Compare and contrast Na-ion and Li-ion layered intercalation cathodes and explore opportunities for Na cathodes.

Milestones

Month Year	Milestone	Status
Dec 2015	Model to predict compositions that will disorder as synthesized	Complete
March 2016	At least one Ti-based compound with high capacity	Complete
June 2016	Predictive model for the voltage curve (slope) of cation-disordered materials	On track
Sept 2016	Modeling capability for materials with substantial oxygen redox capability	On track – ahead of schedule

Approach

Use first principles computations and selected experiments to understand and design materials

Approach

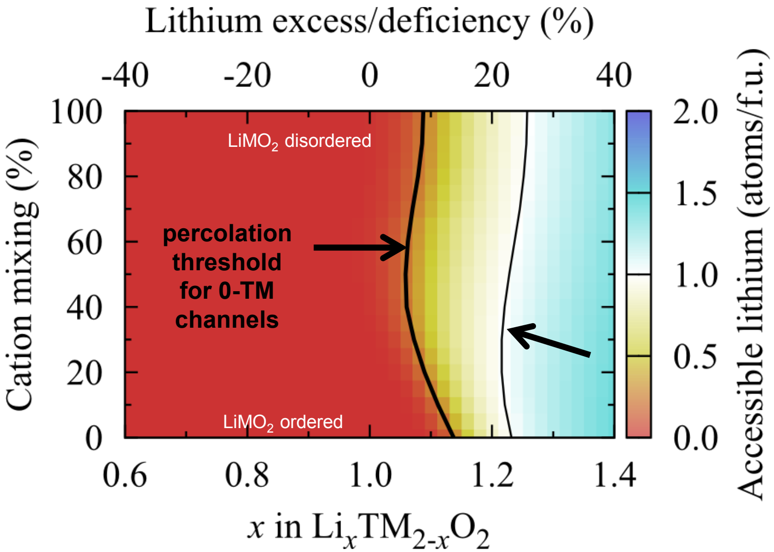
- Layered cathode materials are best bet for high energy density, but seem to be practically limited to ≈ 200mAh/g. How can we achieve theoretical capacity (280 mAh/g) ?
- Improve Li mobility at top of charge, and control cation disorder for all states of charge.
- To broaden compositional space of cathodes, need to understand effect of cation disorder
- Li-excess and cation disorder both make oxygen redox easier. Need accurate approach to predict oxygen redox and its consequences

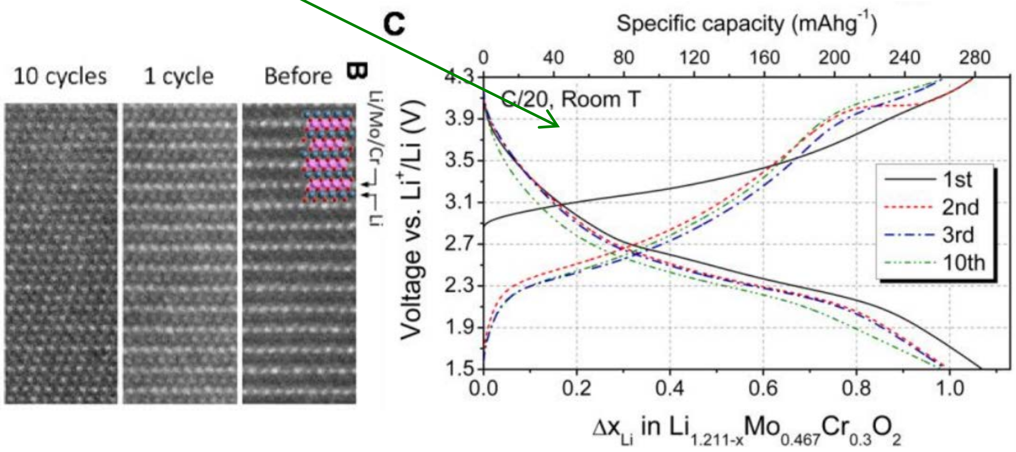
Methods

- DFT in GGA and GGA+U are used as implemented in VASP software
- Calibrated accurate HSE method on know spectral data so that competition between oxygen and transition metal redox can be computed
- Activation energies for Li/Na transport obtained from Nudged Elastic Band Calculations or Transition State assumptions
- Percolation theory (implemented with Monte Carlo) used to understand diffusion on macroscopic scale

Technical Accomplishments (1)

In previous work we have shown that cation disorder can be tolerated as long as Li-excess is above the percolation limit of ≈ 10%. As a result the composition design space can be enlarged from Co, Ni, Mn to a much broader range of metals
Even fully cation-disordered material can now cycle with large capacity





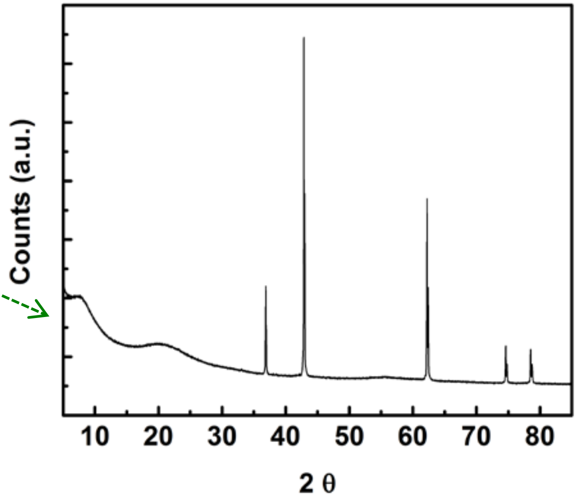
Science, 343 (6170), 519-522 (2014)

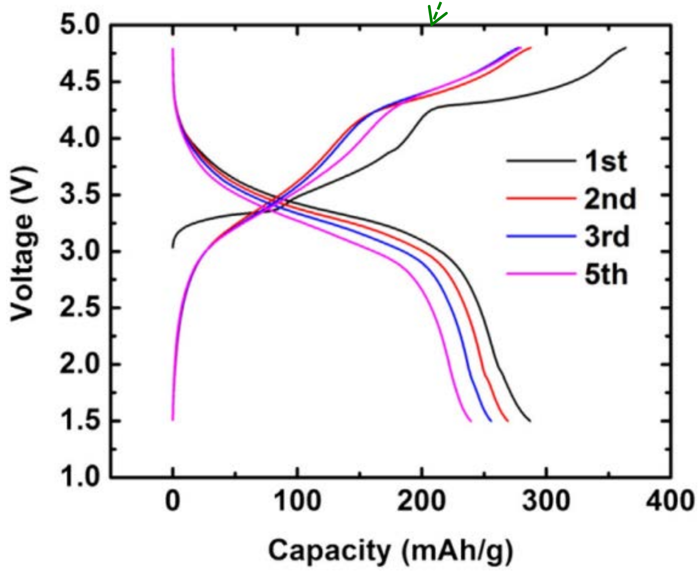
- **This year** we successfully designed, synthesized and tested several new disordered materials with large capacity and demonstrated that a significant fraction of the redox capacity cycles on the oxygen anion
- We identified the structural features that lead to oxygen redox and can now use it to design

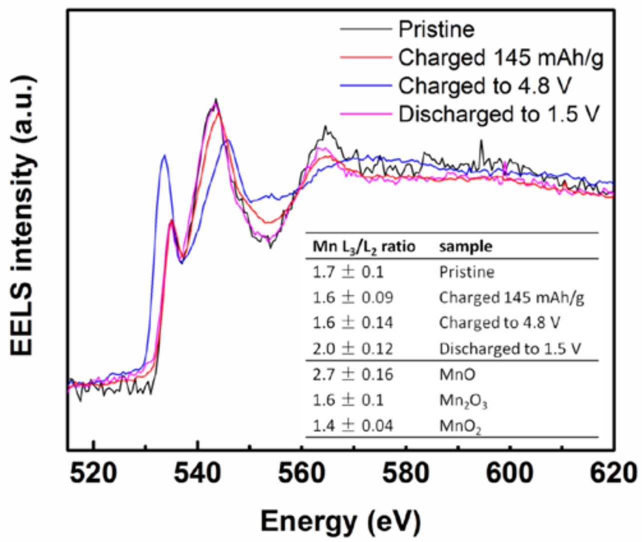
Technical Accomplishments (2): Materials

$Li_{1.25}Nb_{0.25}Mn_{0.5}O_2$ confirms two exciting new ideas:

1) Even though it is fully cation-disordered (see XRD) it has large capacity
2) Capacity is much larger than theoretical capacity from Mn^{4+}/Mn^{3+} redox couple. EELS shows that capacity is from reversible oxygen redox





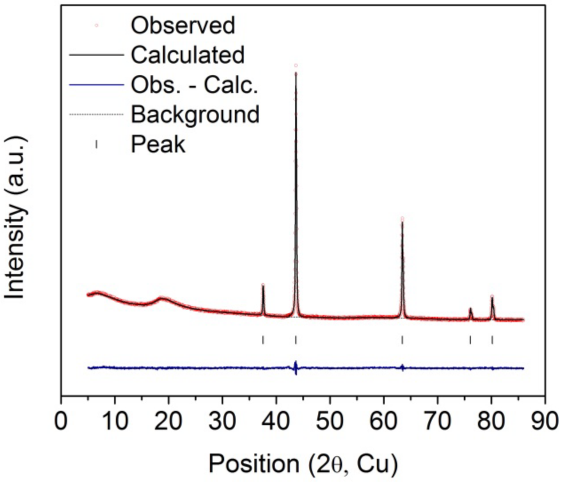


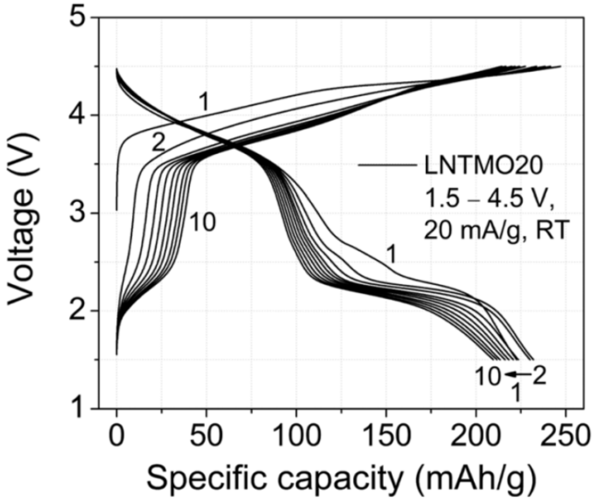
Mn L_3/L_2 ratio	sample
1.7 ± 0.1	Pristine
1.6 ± 0.09	Charged 145 mAh/g
1.6 ± 0.14	Charged to 4.8 V
2.0 ± 0.12	Discharged to 1.5 V
2.7 ± 0.16	MnO
1.6 ± 0.1	Mn_2O_3
1.4 ± 0.04	MnO_2

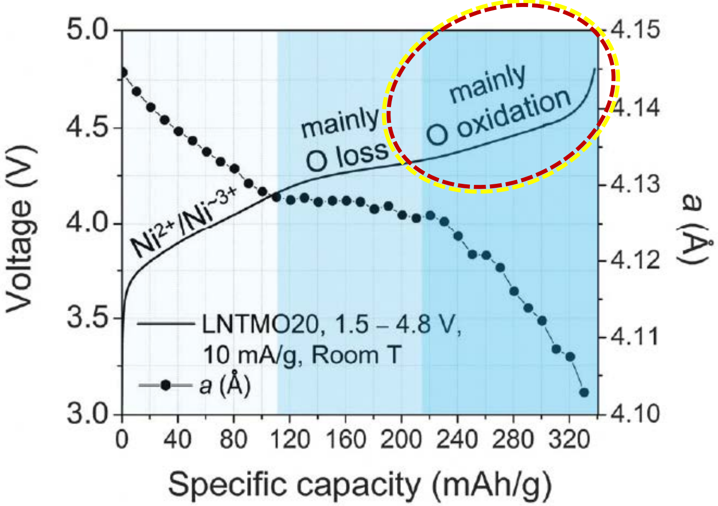
Technical Accomplishments (3): Materials

High capacity cation-disordered Li-excess Ni-Ti-Mo oxides

e.g. $Li_{1.2}Ni_{1/3}Ti_{1/3}Mo_{2/15}O_2$







Energy & Environ. Sci. 8, 3255-3265 (2015)

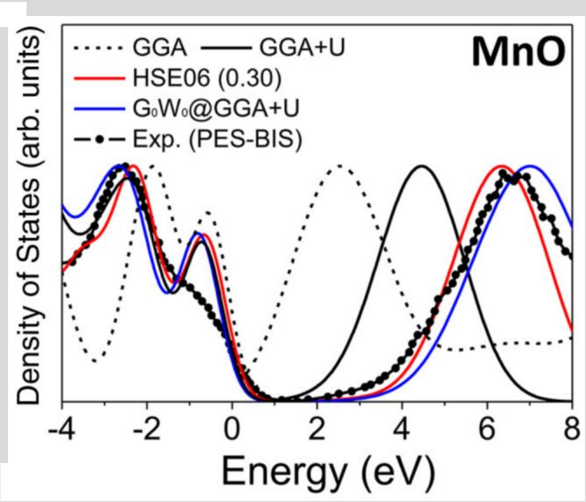
We developed high-capacity cation-disordered Li-excess Ni-Ti-Mo oxides (>220 mAh/g) whose increase in reversible capacity with Li excess is consistent with our percolation theory. We found substantial reversible oxygen redox activity in these materials, together with some irreversible oxygen loss capacity in the first cycle

Technical Accomplishments (4): Methodology

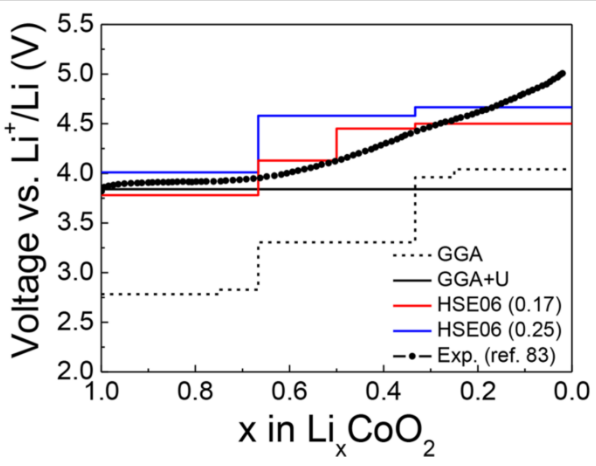
Optimized electronic structure calculations to accurately represent the competition between anion and transition metal oxidation

Anion oxidation is a double-edged sword for cathode materials: One one hand it can significantly extend the capacity of cathode materials. On the other hand it may enhance oxygen loss on the surface of the materials. No predictive method existed to accurately predict when anion oxidation is preferred over transition metal oxidation.

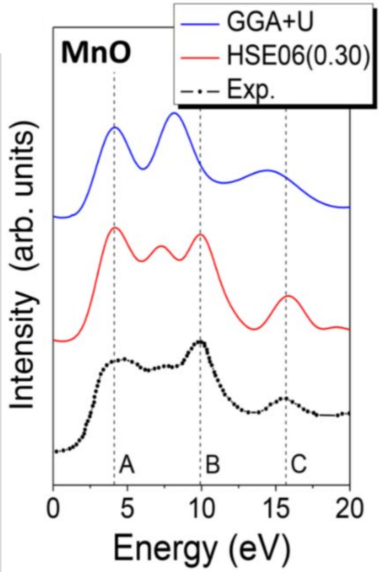
CALIBRATION



Computed DOS and Measured PES-BIS Spectra



Computed and Measured Voltage Profile



Computed and Measured O K-Edge EELS

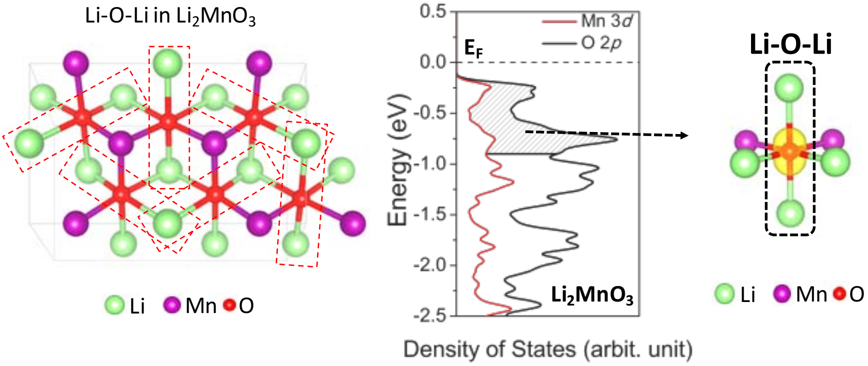
We devised a methodology to obtain optimal HSE06 mixing parameters by calibrating with experimental photoelectron spectroscopy (PES) and Bremsstrahlung isochromate spectroscopy (BIS) or highly accurate GW calculations. Such **optimized HSE06 calculations predict EELS and voltage profiles with great accuracy** and are the basis for our investigation of oxygen redox participation.

Technical Accomplishments (5): Oxygen redox

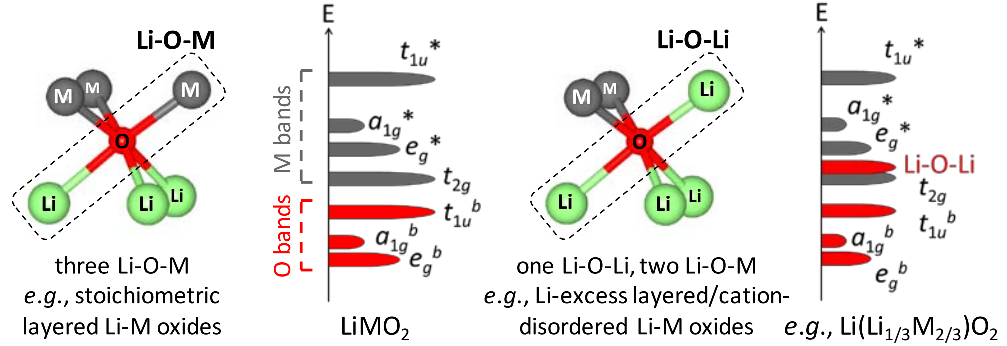
Why do many Li-excess or disordered material have oxygen redox activity ?

Extra capacity beyond the transition metal (TM) redox capacity in Li-excess cathode materials has been explained by reversible oxygen redox. Oxygen redox is often ascribed to covalency in the hybridized TM d states (*e.g.* e_g^* states), but oxygen charge transfer by covalency cannot lead to extra capacity because the number of accessible electrons stays the same regardless of oxygen contribution to the states.♪

projected density of states of O 2*p* electrons along Li-O-Li configurations



schematics of band structures of stoichiometric layered Li-M oxide and Li-excess metal oxides



three Li-O-M
e.g., stoichiometric
layered Li-M oxides

$LiMO_2$

one Li-O-Li, two Li-O-M
e.g., Li-excess layered/cation-disordered Li-M oxides

e.g., $Li(Li_{1/3}M_{2/3})O_2$

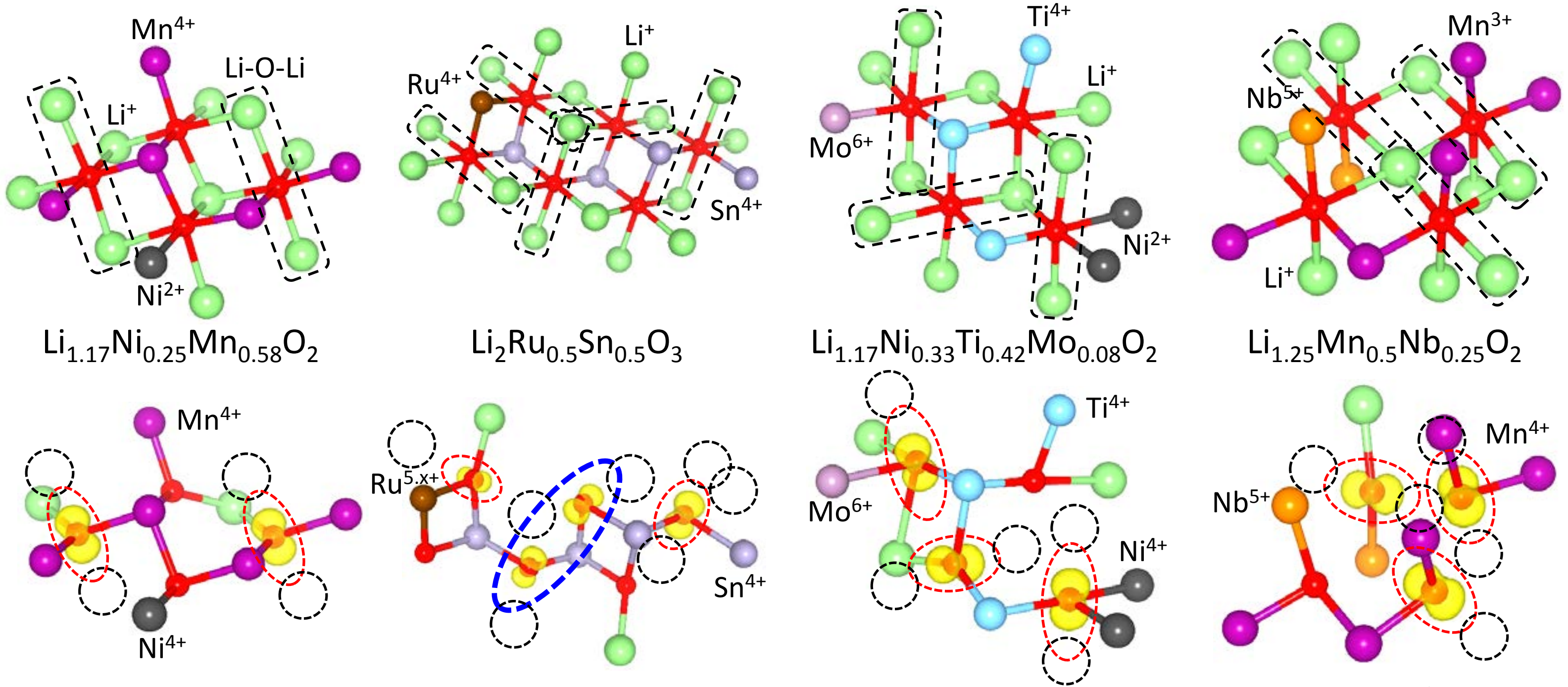
Nature Chem., *in press* (2016)

In stark contrast to current understanding, we find that the **oxygen oxidation** occurs from "unhybridized" O 2*p* states along the Li-O-Li configurations in Li-excess materials, and hence it is not at all related to TM-O covalency. These configurations only occur when Li is present in the TM layer, hence in **Li-excess** or in **cation-disordered materials**. The lack of any TM bonding with these oxygen raises their energy and makes them available for oxidation.

Conclusion: Oxygen Oxidation is fundamentally different from covalency

Technical Accomplishments (5) -continued

Examples of preferred oxygen oxidation along the Li-O-Li configuration in Li-excess materials



$Li_{1.17}Ni_{0.25}Mn_{0.58}O_2$ $Li_2Ru_{0.5}Sn_{0.5}O_3$ $Li_{1.17}Ni_{0.33}Ti_{0.42}Mo_{0.08}O_2$ $Li_{1.25}Mn_{0.5}Nb_{0.25}O_2$

$Li_{0.33}Ni_{0.25}Mn_{0.58}O_2$ $Li_{0.5}Ru_{0.5}Sn_{0.5}O_3$ $Li_{0.33}Ni_{0.33}Ti_{0.42}Mo_{0.08}O_2$ $Li_{0.25}Mn_{0.5}Nb_{0.25}O_2$

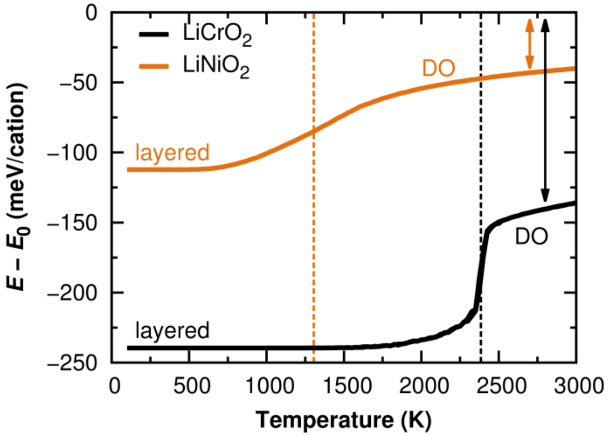
Nature Chem., *in press* (2016)

Oxygen oxidation occurs from these O 2*p* electrons along the Li-O-Li configurations in all Li-excess layered and cation-disordered cathode materials. We find that neighboring oxidized Li-O-Li states can slightly rotate to form peroxo-like O-O bonding under certain conditions.

Technical Accomplishments (6)

Computational identification of novel cation-disordered cathode materials

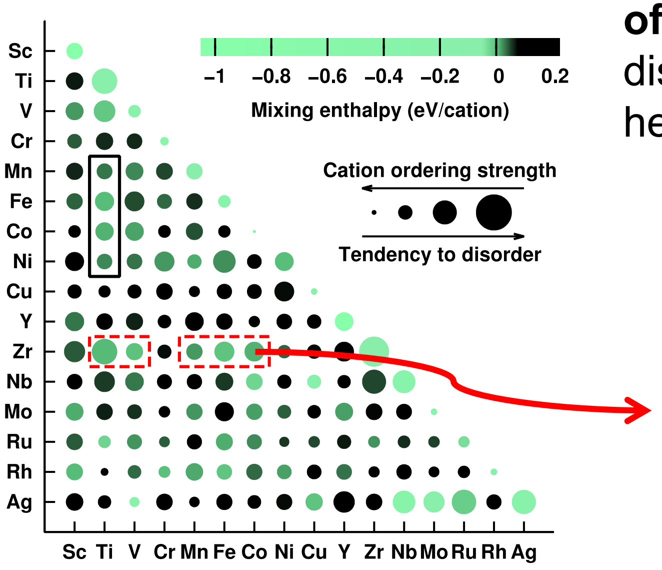
Without the restriction to well-layered structures, the chemical space of potentially cation-disordered cathode materials becomes vast and exploration by synthesis is cumbersome.

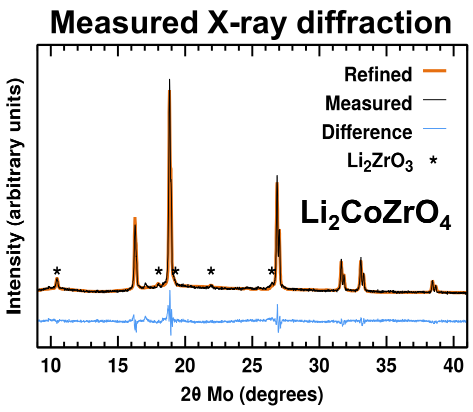


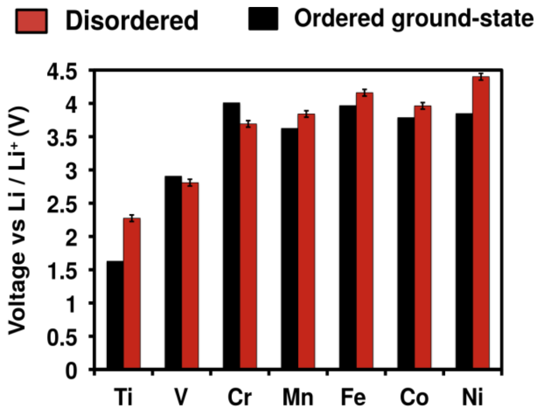
We showed that the **cation-ordering strength** in Li-TM oxides can be estimated based on Monte-Carlo simulations (figure top left) and by using a rapid methodology based on special quasi-random structures.

Using this approach, **we pre-screened Li-TM oxides for their stability and tendency to disorder** (bottom left), and we synthesized the previously unknown cation-disordered Li_2CoZrO_4 as a proof of concept.

A similar approach allowed us to **compare the average voltage of ordered and disordered cathodes**, finding that cation disorder can both raise and decrease the average voltage and hence energy density (bottom right).







Remaining Challenges and Barriers

- While reversible bulk oxygen redox is now confirmed, and its structural/chemical origin understood from theory, it is important to better understand whether or not it enhances surface reactivity with the electrolyte. Combined modeling/TEM studies will be performed to look at the surface of cycled cathode materials with oxygen redox
- Many cation-disordered materials have significant voltage slope. We need to understand and investigate how to control and minimize this slope. Investigate for example whether partial disorder can create the benefits of cation disorder without the slope
- Rate capability of disordered materials needs to be improved further

Proposed Future Work

- Further confirm under which conditions reversible bulk oxygen redox activity takes place (e.g. which voltage, chemistry, structural features): Collaboration ongoing with Mali Subramanian at APS to correlate oxygen K-edge with theory results. Collaboration with National Center for Electron Microscopy (NCEM - LBNL) for advanced EELS on anion-active materials
- Modeling of voltage slope of disordered cathodes as function of degree of disorder. Correlation with state of order as measured by TEM (NCEM collaboration)
- Modeling of surface transformations that occur in cathode materials to better understand oxygen loss at cathode surface

Summary

We have achieved an understanding of the role of Li-excess and cation disorder on the performance of cathode materials, and have used this to come up with novel chemistries.

- Our percolation theory shows that once the Li excess content is > ≈ 10% rocksalt-like compounds such as layered materials become tolerant to cation disorder, even to the point where fully cation-disordered materials have large reversible capacity. This tolerance to disorder enables novel compositions as "well-layeredness" is not a requirement anymore.
- We have demonstrated the new percolation concepts on two new materials with capacity > 200 mAh/g (Nb-Mn and Ti-Ni-Mo based).
- We have demonstrated that reversible oxygen oxidation contributes substantially to the capacity of Li-excess and cation-disordered materials
- Carefully calibrated and novel first principles modeling has identified unbonded oxygen states, arising from linear Li-O-Li configurations in the cathode materials as the source of reversible oxygen redox.

Collaborations

Collaborations with Kristin Persson (LBNL) on Li-excess materials, **Mahalingam Subramanian** (ANL) on oxygen oxidation and structural characterization, **Dong Su** (BNL) and **Feng Wang** (BNL) on EELS and TEM, **Cosandey** (Rutgers) on TEM, **Piper** (Binghamton) on oxygen spetroscopy, **Hubert Gasteiger** (Technical U of Munich) on oxygen release, and with NCEM (LBNL) on HRTEM.

Response to Reviewers Comments

In general the comments from the 2015 AMR review were very positive with an average weighted score of 3.69.
R3: The reviewer called this a very interesting blend of theoretical work with experimental and practical work where new compounds are used to test the theoretical suggestions, and noted that it is very focused on the critical barriers.
R2: Noting that Li-excess, layered composite, transition metal oxide electrode materials are some of the most challenging material structures to study with first-principles calculations, the reviewer said the PI's approach was excellent, while also claiming not to be the best judge of this type of work.
R1 Seeking out new, high-energy-density positive electrode materials is a huge technical challenge, the reviewer said, adding that the PI is tackling this problem from mechanisms learned from predictive modeling.

Comment: The reviewer said the percolation concept the author found and later tested in practice is new and termed it a real accomplishment. Likewise, the reviewer found it very interesting to learn that a Li(Li,Mn,Nb)O2, with a high degree of oxygen participation in the redox process, is a stable cathode material that does not fall apart as the electrode is cycled. The reviewer looked forward to hearing the mechanism behind this behavior explained in the future.
Answer: This year we have reported the mechanism of oxygen oxidation

Response to Reviewers Comments - continued

Comment: While agreeing that the PI has done a significant amount of work and shown considerable progress, the reviewer was unclear on the PI's conclusion that over-lithiation should improve diffusion in these materials when the opposite is generally true.

Answer: We believe that this stems from some confusion. Our statement is that <u>when cation disorder occurs</u> over-lithiation (Li-excess) increase the rate of Li transport as compared to cation-disordered materials with no excess lithium. As such it makes materials more tolerant to cation disorder. But for well-ordered layered materials this strategy is not relevant as diffusivity is already good for the no-Li-excess case.

Comment: The area of oxygen participation in the redox process seemed to this reviewer to be very intriguing and in the reviewer's opinion, its relation to the oxygen loss is very important. If the authors managed to propose a mechanism for the loss of oxygen, that result, by itself, could be very useful, the reviewer predicted.

Answer: this year we have presented a precise mechanism for oxygen oxidation which is the first step towards oxygen loss