First Principles Calculations of Existing and Novel Electrode Materials

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ES054

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Overview

Timeline

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

Budget

- Total budget (4 years): $964K
- FY13 funding $241K, FY14 funding $241

Barriers Addressed

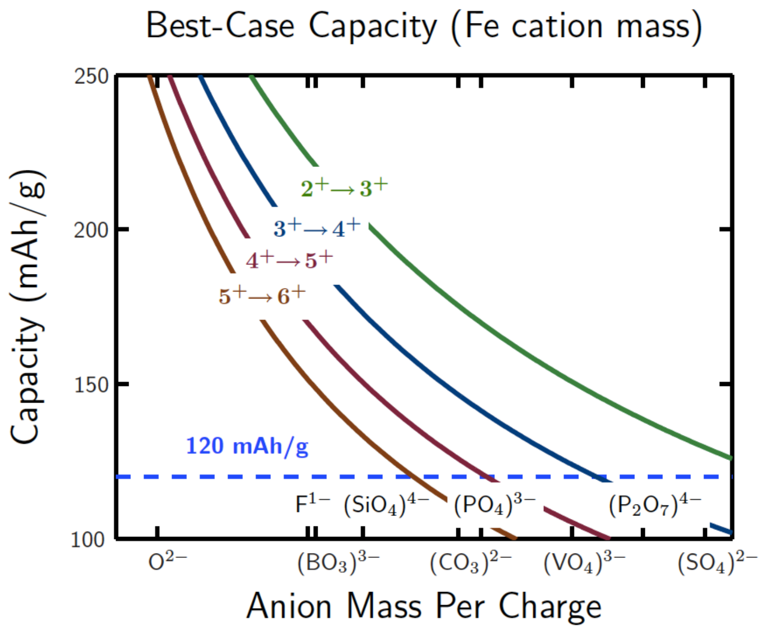
- Low rate capabilities
- high cost
- poor stability
- low energy-density

Partners/Collaborations within the VT program

- **Kristin Persson** (LBNL), **Clare Grey** (Cambridge U)

Relevance

- Best case specific capacity for cathode materials using a specific anion in the structure and a particular one-electron redox couple.
- It is clear that only oxides, fluorides and borates can deliver cathode materials with specific capacity > 200 mAh/g



Objectives:

- To understand why practical capacity of layered oxides is well below theoretical capacity
- To understand the role of Li-excess in making high capacity, high energy density cathode materials
- To design high-energy density oxide cathode materials
- Compare and contrast Na-ion and Li-ion layered intercalation cathodes and explore opportunities for Na cathodes.

Relevance:

- Li-ion batteries require oxide cathodes with higher capacity and energy density
- Li excess has been demonstrated as a path towards higher capacity materials

Milestones

Month Year	Milestone	Status
Dec 2013	Identify at least three ordered states in $NaxMO_2$ compounds that can be verified with experiments.	Complete
March 2014	Obtain computed voltage curve of $Li_{1+x}M_{1-x}O_2$ compound and understand Li-excess effect on charge transport	Complete
June 2014	Obtain voltage curves for all the O_3 $NaxMO_2$ compounds where M is at least five distinct 3d metals	Ongoing
Sept 2014	Complete ground state study in Li-Ni-Mn-O and Li-Co-Mn-O system	Ongoing

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.

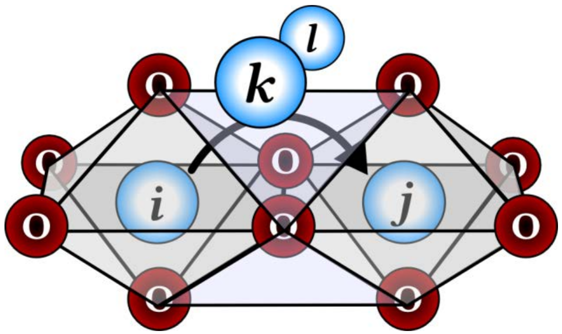
Methods

- DFT in GGA and GGA+U are used as implemented in VASP software
- High-throughput capability as implemented in Materials Project and Matgen (MIT version)
- Voltage profiles obtained from total energy calculations of partially charged states
- 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)

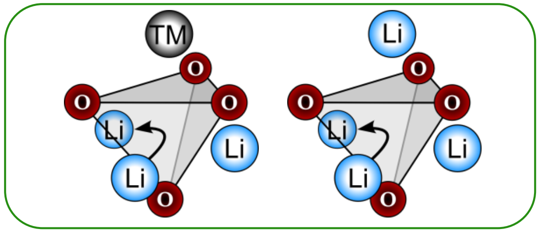
We identified by which mechanisms Li diffuses in close packed oxides and how this limits capacity

Li hopping mechanism

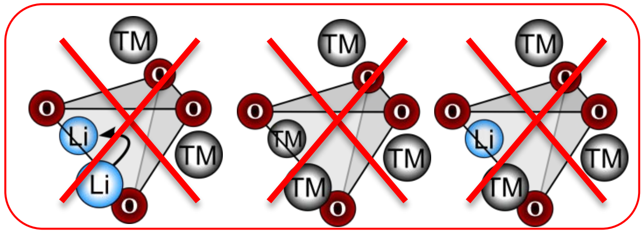


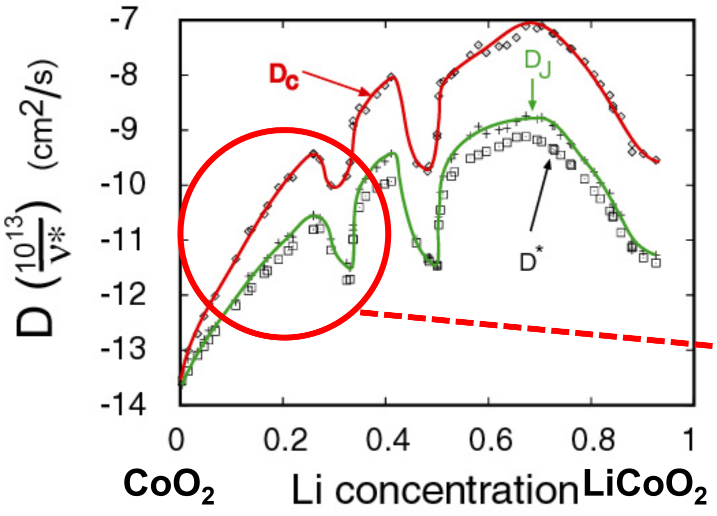
- High capacity requires good Li mobility over the full range of Li concentrations
- Li transport between oct sites occurs by hopping through tetrahedral sites
- Only tetrahedral sites with 1 transition metal or no transition metals nearby allow Li to pass through

Active channels

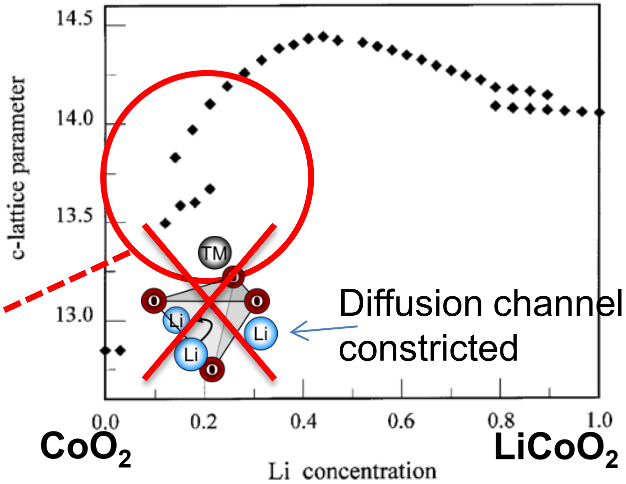


Inactive channels





In layered materials slab spacing contracts at low Li concentration, thereby reducing Li mobility, and reducing practical charge capacity



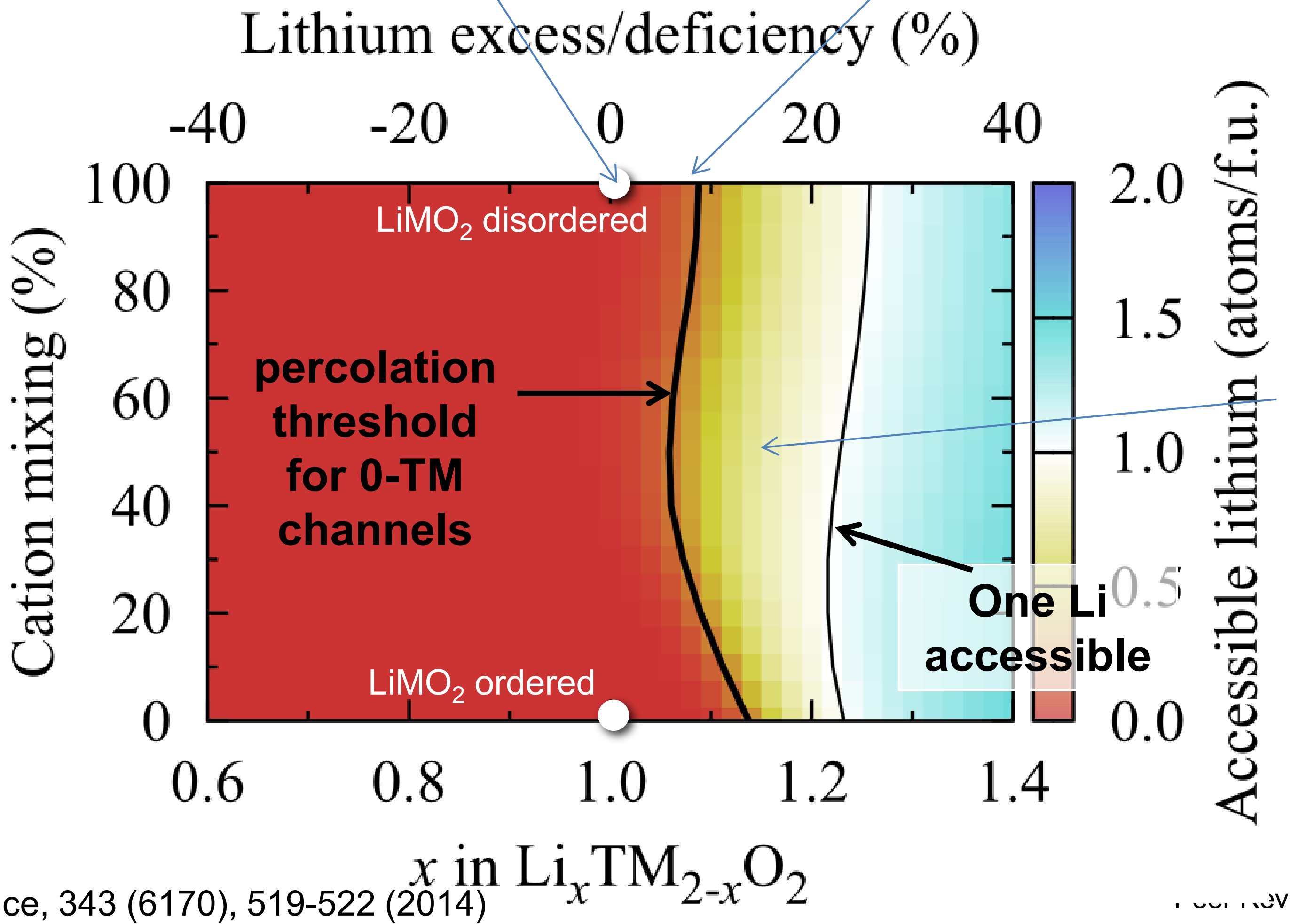
Diffusion channel constricted

Technical Accomplishments (2)

We now understand the role of Li-excess: A minimum of Li excess is needed to to make the Li diffusion tolerant to cation disorder

Disordered stoichiometric composition is not percolating for Li diffusion through 0-TM channels

Even for fully disordered rocksalt, good capacity should be achieved with more than 10% Li excess

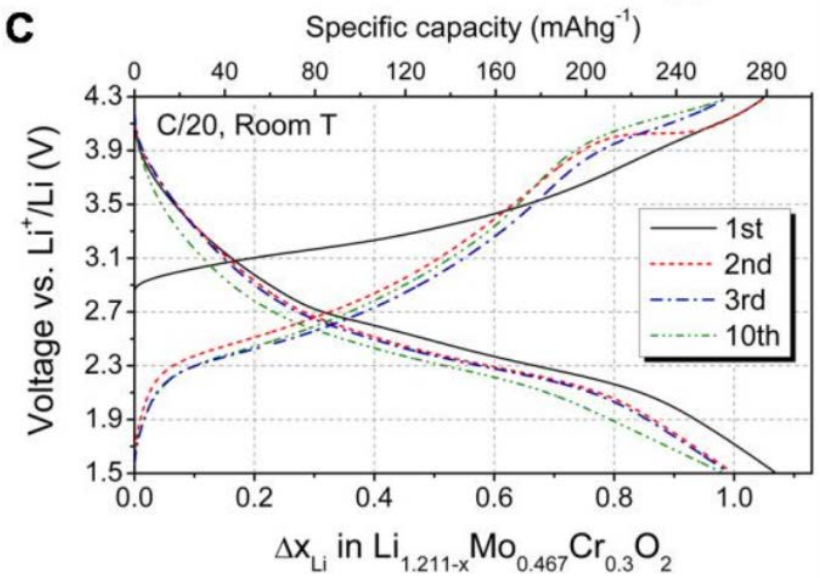


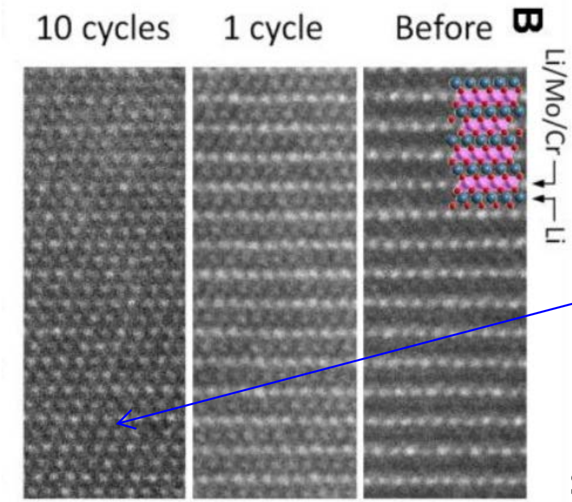
When 0-TM channels are percolating, the structure is very tolerant to cation disorder

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

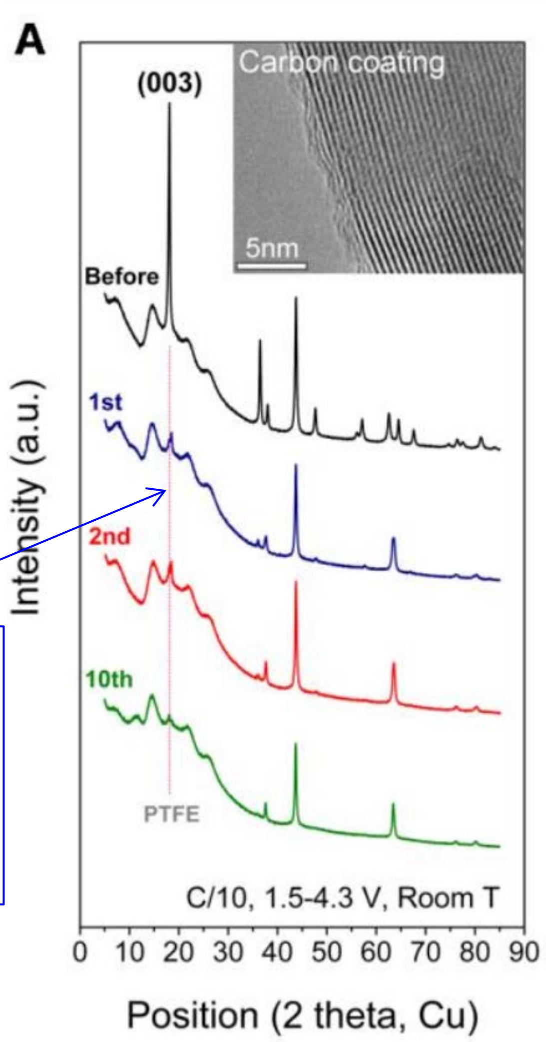
Technical Accomplishments (3)

Fully disordered material has very high capacity, when Li excess is above percolation threshold of 10%





Material disorders after a few cycles as evidenced by loss of 003 peak in diffraction, and loss of STEM contrast between layers



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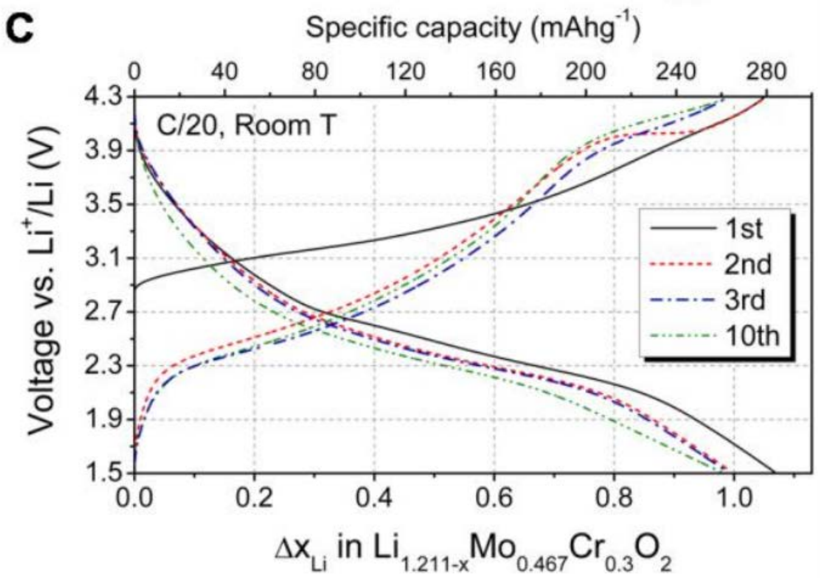
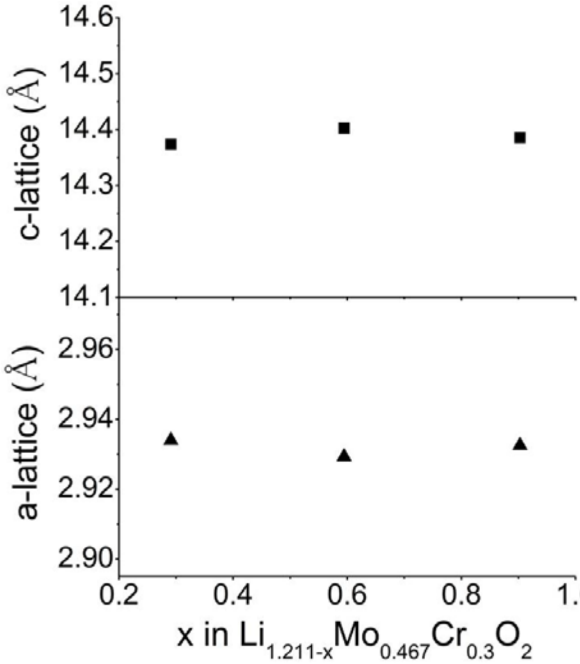
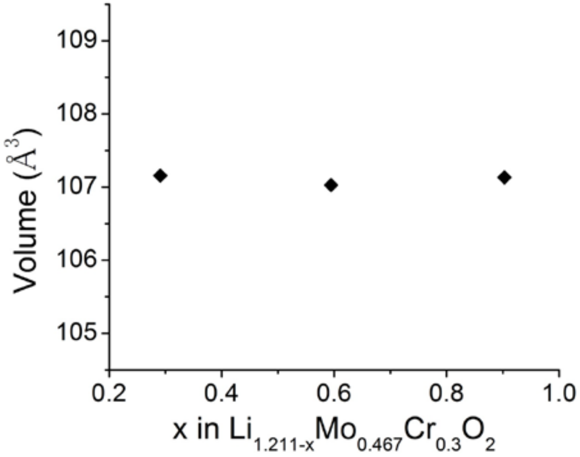
Technical Accomplishments (4)

Very high capacity, but with minimal volume change. The first zero strain cathode material !



712 Wh/kg
3350 Wh/l
Density = 4.7





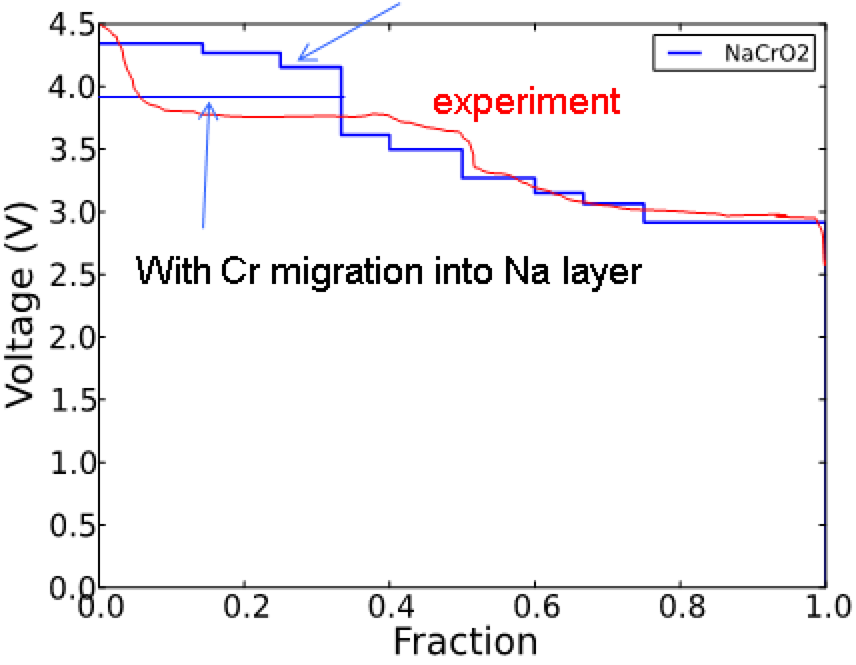
Volume change over 280 mAh/g cycling is ≈ 0.1 %

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

Technical Accomplishments (5)

Modeling capability for layered Na-ion cathodes. Already developed highest specific energy Na-ion cathode

Benchmarked ab-initio modeling of Na-intercalation voltage curves with experiment, under various assumptions:

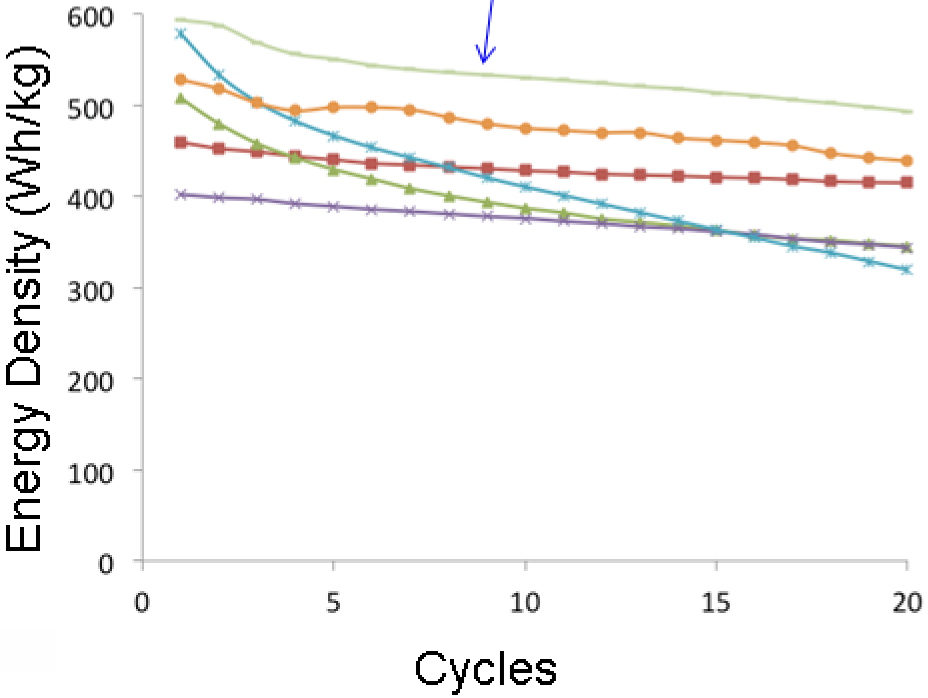


Topotatic Na removal

experiment

With Cr migration into Na layer

Achieved highest specific energy of any Na-cathode material (composition not disclosed)



Summary

We have established and demonstrated the design guidelines to achieve high capacity layered cathodes with capacities > 200 mAh/g

- In close packed oxide materials only two microscopic Li migration channels can be active: These are the ones where the activated state is either coordinated by one-transition metal (1-TM) or by zero transition metals (0-TM). At least one of these has to be percolating through the structure to have macroscopic diffusion (and hence reversible capacity)
- In well ordered layered materials, 1-TM channel is active and percolating, but becomes sluggish at the end of charge due to the c-lattice parameter contraction, thereby limiting the practical capacity of layered materials
- Cation disorder reduces mobility through the 1-TM channel
- By adding Li-excess, 0-TM channels are introduced making the structure more tolerant to cation disorder. Above 10% Li-excess 0-TM channels are percolating, and even fully disordered rocksalt structures can sustain macroscopic Li diffusion, as demonstrated by the $Li_{1.211}Mo_{0.467}Cr_{0.3}O_2$ compound which fully disorders after one cycle, but delivers 280 mAh/g with zero volume change.
- In Na-intercalation oxides we have achieved the highest energy density of any cathode so far.

Future Work

Further developing Li-excess ordered and disordered materials

- Develop compositions with higher voltage than $Li_{1.211}Mo_{0.467}Cr_{0.3}O_2$
- Understand how to make Li-excess compositions with controlled amount of disorder
- Make further connections with the Li-excess Argonne style materials, which also show some disorder after overcharge
- For Layered Na-cathode materials: use modeling to understand limits at top of charge and end of discharge. Resolving these would lead to cathode specific energies ≈ 750 – 800 Wh/kg

Collaborations

Collaboration with **K. Persson** (LBNL) on Li-excess materials, and with **C. P. Grey** on oxide cathodes

Part of Li-excess focus group in BATT

Discussions with **Thackeray** (ANL), **A. Burrell** (ANL) on Li-excess materials.

Response to Reviewers Comments

This project started in 2012 and was not reviewed last year

Publications and Presentations

Publications:

1. J. Lee, A. Urban, X. Li, D. Su, G. Hautier, G. Ceder, *Unlocking the Potential of Cation-Disordered Oxides for Rechargeable Lithium Batteries,* Science, 343 (6170), 519-522 (2014).
2. A. Urban, J. Lee, G. Ceder, Advanced Energy Materials, *The Configurational Space of Rocksalt-type Oxides for High-capacity Lithium Battery Electrodes,* in press (2014).
3. H. Chen, Q. Hao, O. Zivkovic, G. Hautier, L-S Du, Y. Tang, Y-Y Hu, X. Ma, C.P. Grey, G. Ceder, *Sidorenkite (Na3MnPO4CO3): A New Intercalation Cathode Material for Na-Ion Batteries,* Chem. Mater., 25 (14), 2777-2786 (2013).
4. A. Jain, S.P. Ong, G. Hautier, W. Chen, W.D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, K.A. Persson, *Commentary: The Materials Project: A Materials Genome Approach to Accelerating Materials Innovation*, APL Materials 1, 011002, 1-11 (2013).
5. G. Hautier, A. Jain, T. Mueller, C. Moore, S.P. Ong, G. Ceder, *Designing Multielectron Lithium-Ion Phosphate Cathodes by Mixing Transition Metals*, Chemistry of Materials, 25 (10), 2064-2074 (2013).
6. S.P. Ong, Y. Mo, W. D. Richards, L. Miara, H.S. Lee, G. Ceder, *Phase Stability, Electrochemical Stability and Ionic Conductivity of the Li10 +/- 1MP2X12 (M = Ge, Si, Sn, Al or P, and X = O, S or Se) Family of Superionic Conductors*, Energy & Environmental Science (6), 1, 148-156 (2013).

Presentations: (all **Invited**; only invited presentations are tracked in my group)

1. Electrode Materials for Na-ion batteries, Beyond Li-ion meeting, Boulder, June 4-6 2013
2. Electrode Materials for Na-ion batteries, ICMAT meeting, Singapore, July 3 2013
3. Diffusion of Li, Na and multi-valent ions in Battery Cathode Materials, MRS Spring April 22, San Francisco
4. Li-ion transport revisited: The route towards very high-capacity Li-cathode materials, IBA, Brisbane, Jan 2014
5. Accelerated and Large-Scale Materials Discovery through Computation, Argonne National Laboratory, April 3 2014

Critical Assumptions and Issues

- First principles computations may not always be accurate. In addition, they may result in false positives if certain failure mechanisms of electrode materials are not understood, and hence are not included in the design and screening
- We may not be able to synthesize the materials that are computationally designed/modified