

Electroactive Iron Oxides: Rusty Electrodes for Next Generation Lithium Ion Batteries

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Phenomena in Nanostructured
Materials and Devices

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Potential Energy Storage





Why Batteries?



Batteries are both enabling and impeding the development of new energy-related technologies.

Solar energy



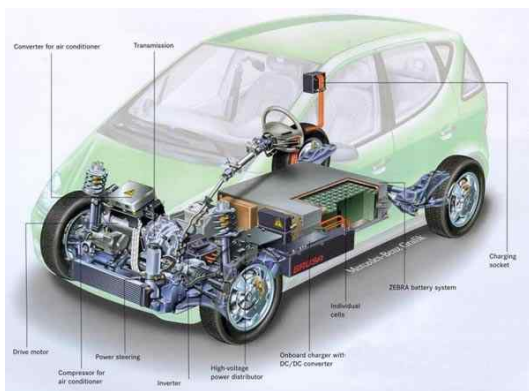
Utility infrastructure



Wind power



Vehicle electrification



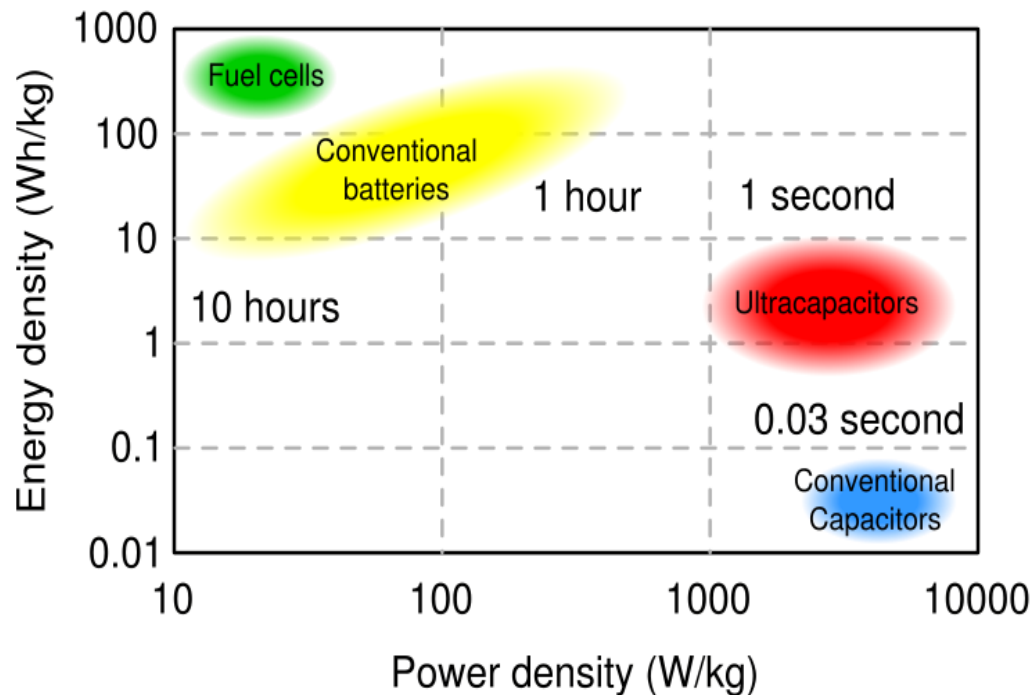
Portable electronics



Battery Materials Motivation

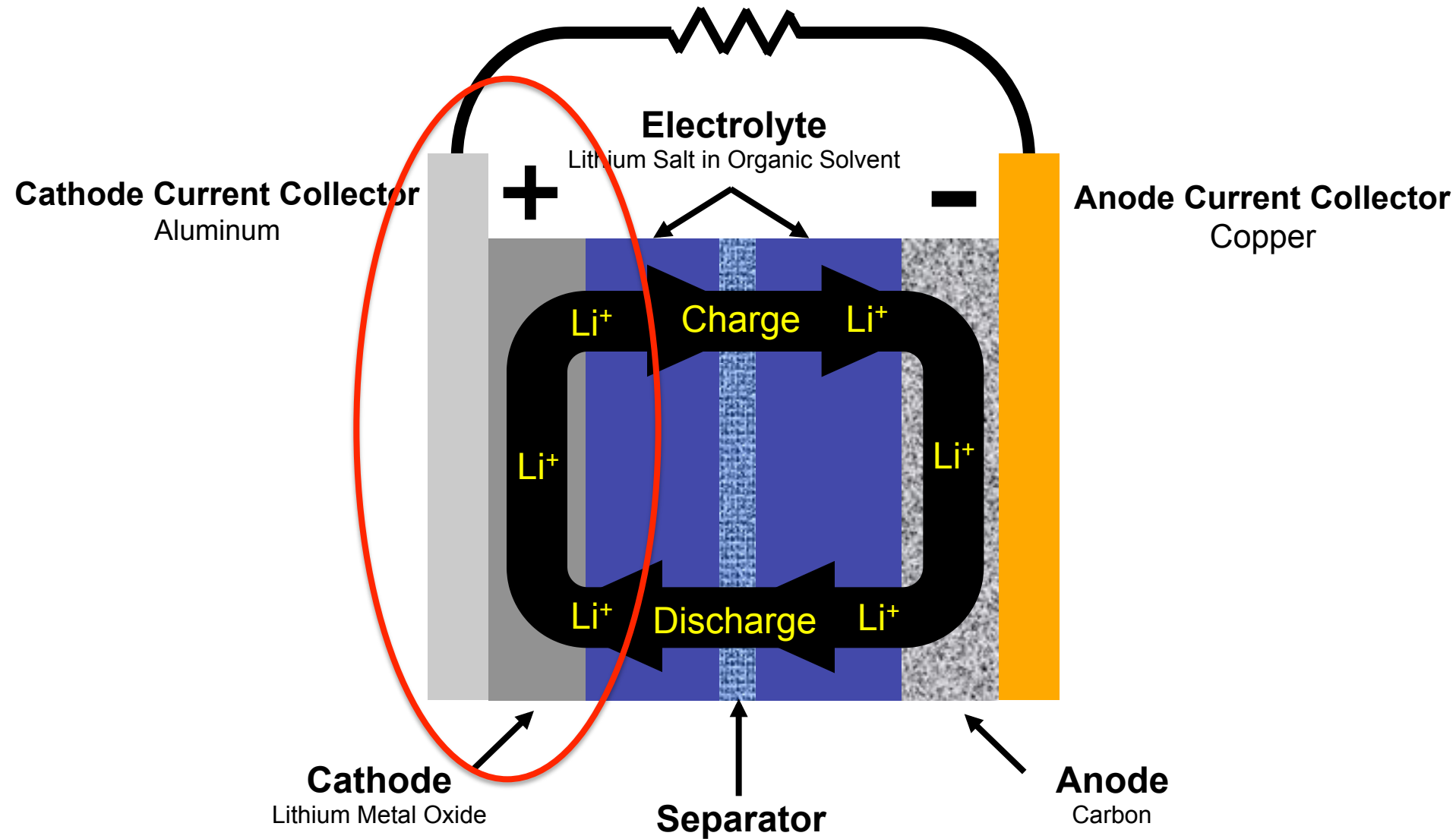


What are the focal points of modern battery research?



- High energy density
- High power density
- Low cost
- Safe (related to cost)
- Lightweight
- Small volume
- Environmentally friendly

Battery Basics: A Lithium Ion Cell

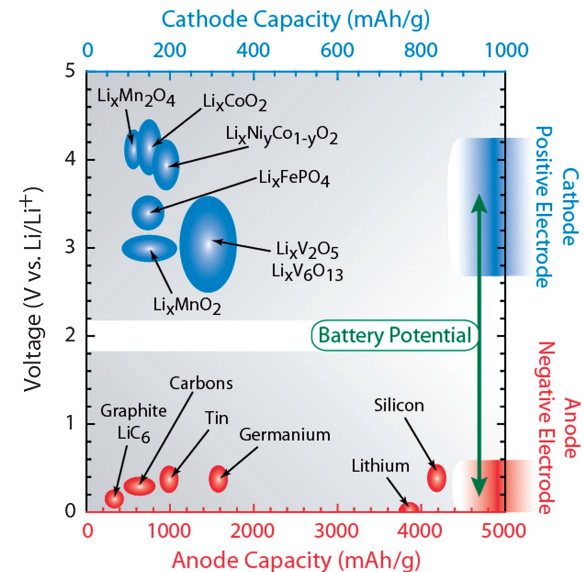


Candidate Cathodes



Typical cathodes are based on metal oxides with
“dismal” capacities

Cathode Material	Average Voltage	Gravimetric Capacity
LiCoO_2	3.7 V	140 mAh/g
LiMn_2O_4	4.0 V	100 mAh/g
LiNiO_2	3.5 V	180 mAh/g
LiFePO_4	3.3 V	170 mAh/g
$\text{Li}_2\text{FePO}_4\text{F}$	3.6 V	115 mAh/g
$\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$	3.6 V	160 mAh/g



Is there a higher capacity alternative?

Consider Iron Oxides



Iron oxides are attractive high capacity materials

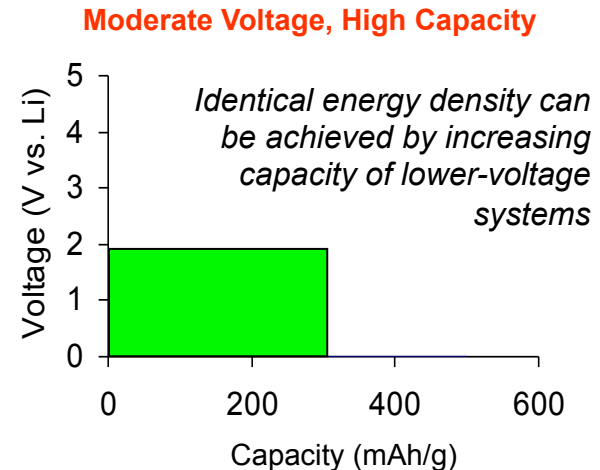
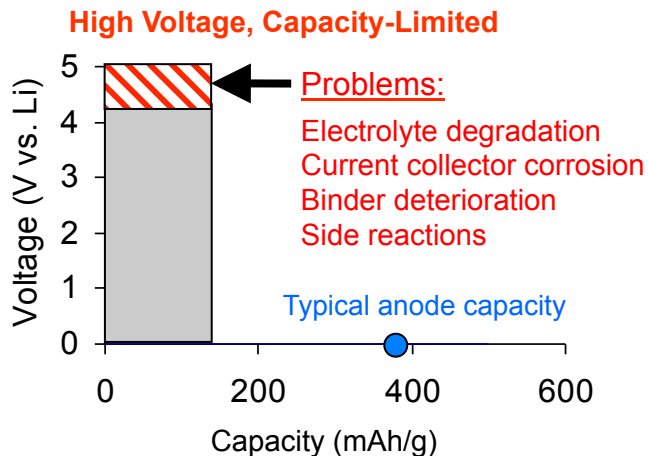
- High energy density
- High power density
- Low cost
- Safe (related to cost)
- Lightweight

volume
mentally friendly

Phase	(mAh/g)	Phase	(mAh/g)	Phase	(mAh/g)	Phase	(mAh/g)
Li_5FeO_4	1118	Li_3FeO_3	774	Li_2FeO_2	610	$\text{Li}_2\text{O} + \text{Fe}$	1007
Li_3FeO_4	671	Li_2FeO_3	516	$\text{Li}_3\text{Fe}_2\text{O}_4$	458	$\text{Li}_2\text{Fe}_2\text{O}_3$	336
Li_2FeO_4	447	LiFeO_3	258	LiFeO_2	305	LiFe_2O_3	168
LiFeO_4	223	LiFe_2O_6	129	LiCoO_2	180	LiFePO_4	140

Energy density is the product of voltage and capacity:

The area under the curve



A Problem with Iron Oxides

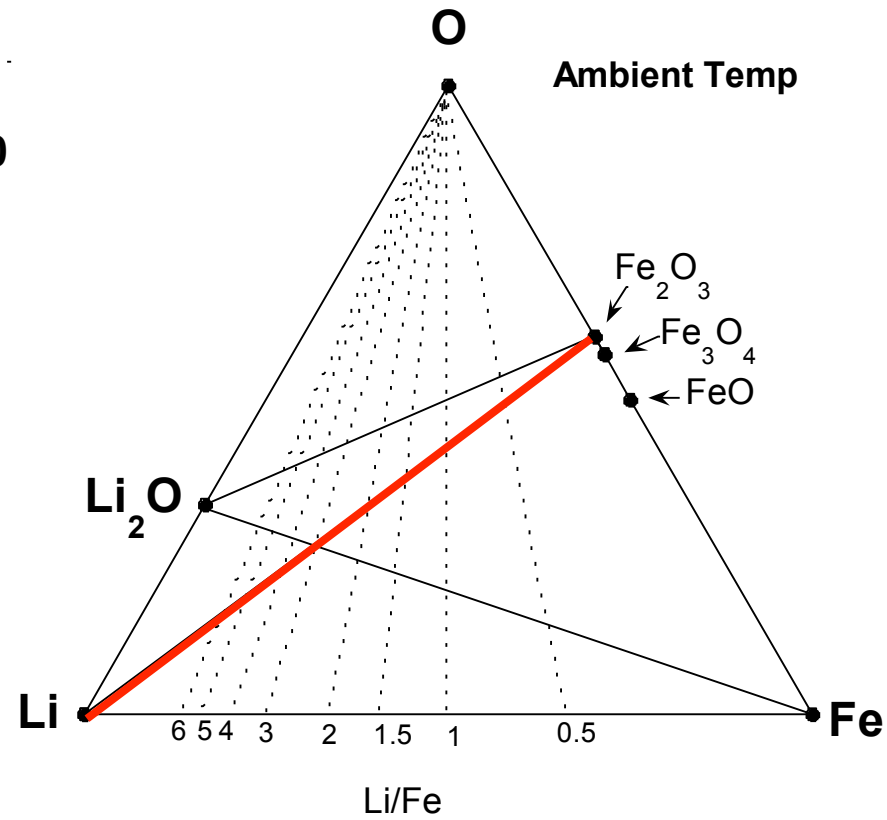
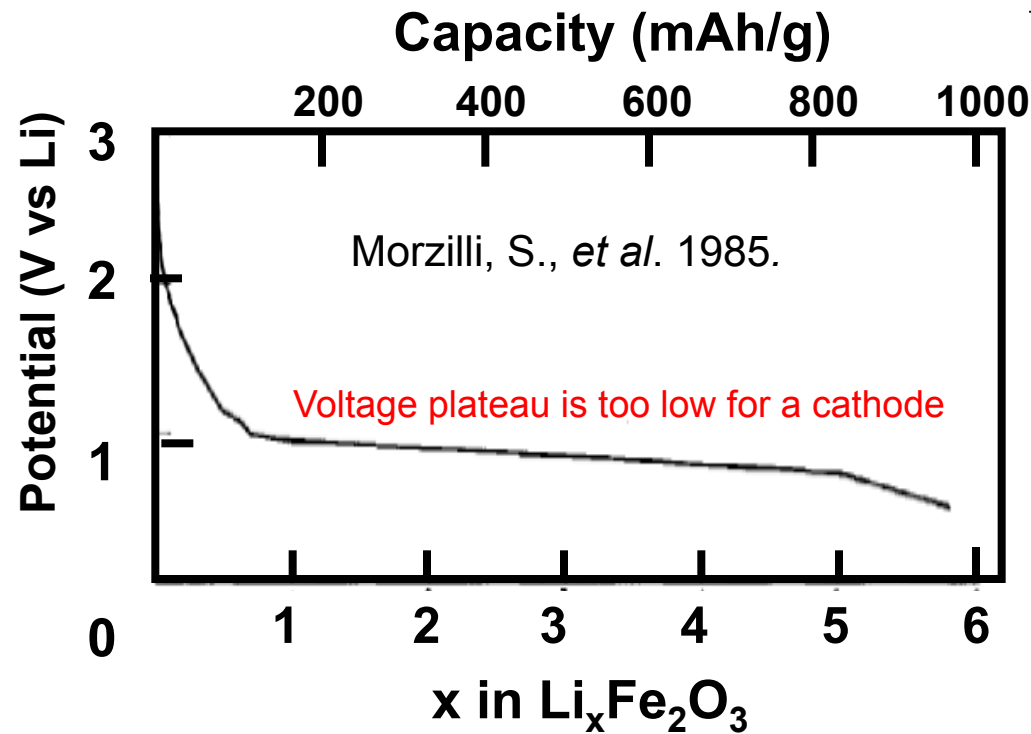


Iron oxide seems an obvious choice as an electroactive material...why aren't we using it in modern batteries?

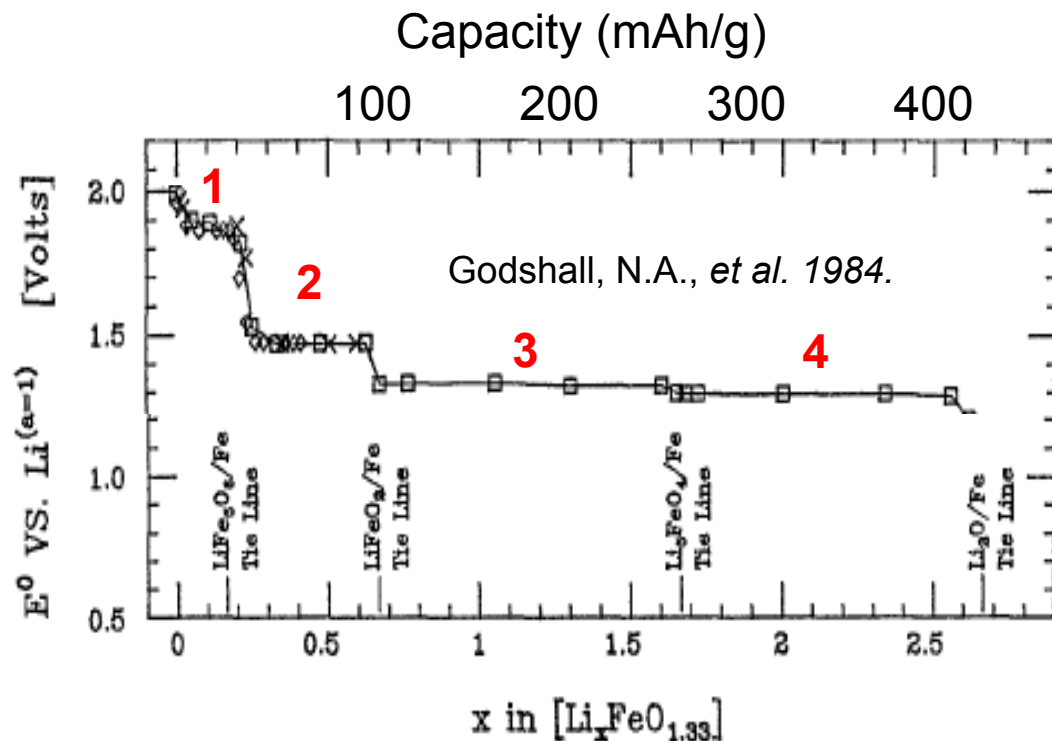
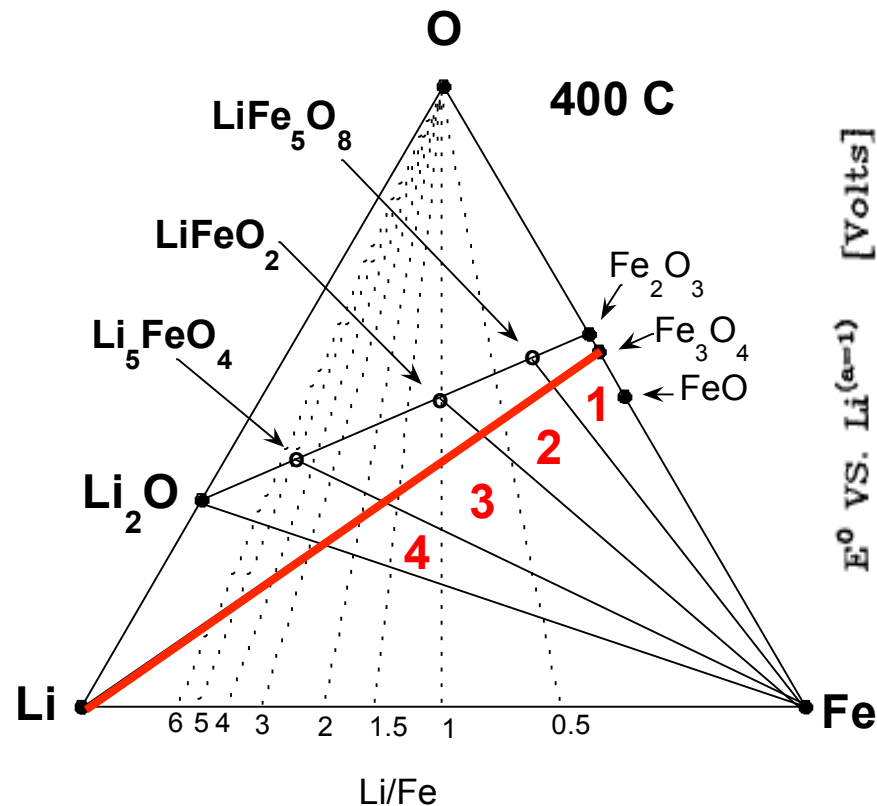
Low voltage plateau

Poor (virtually non-existent!) cyclability

Slow kinetics (electrically and ionically diffusion limited)



Extending Voltage Plateaus to Enhance Capacity

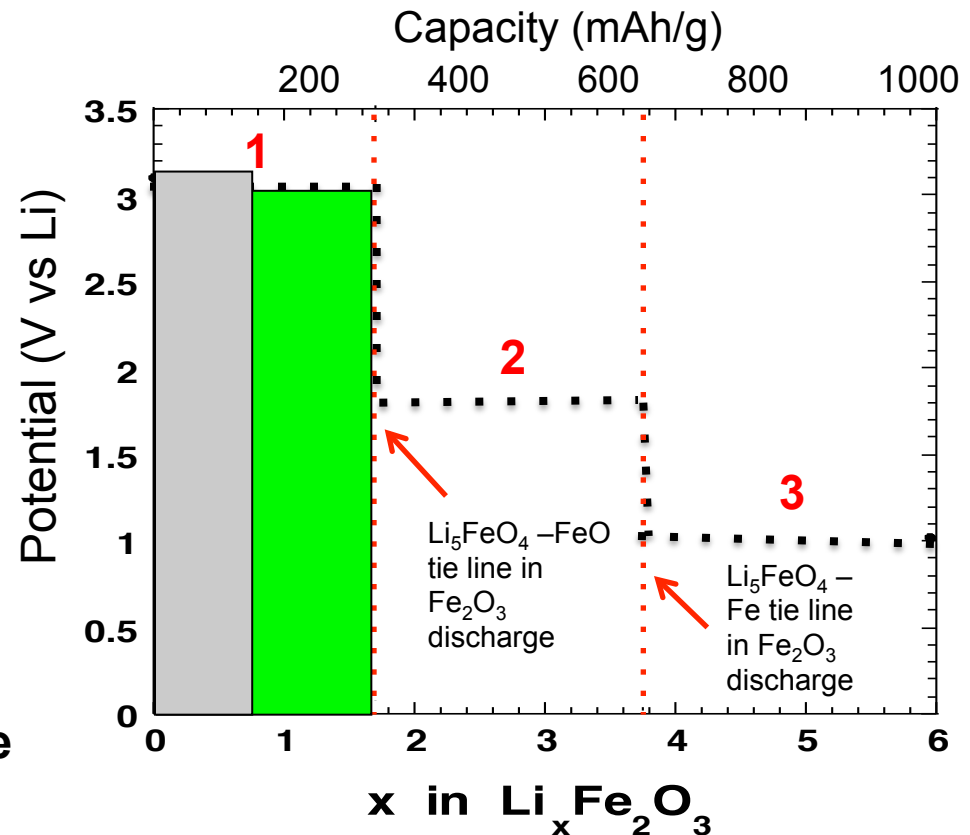
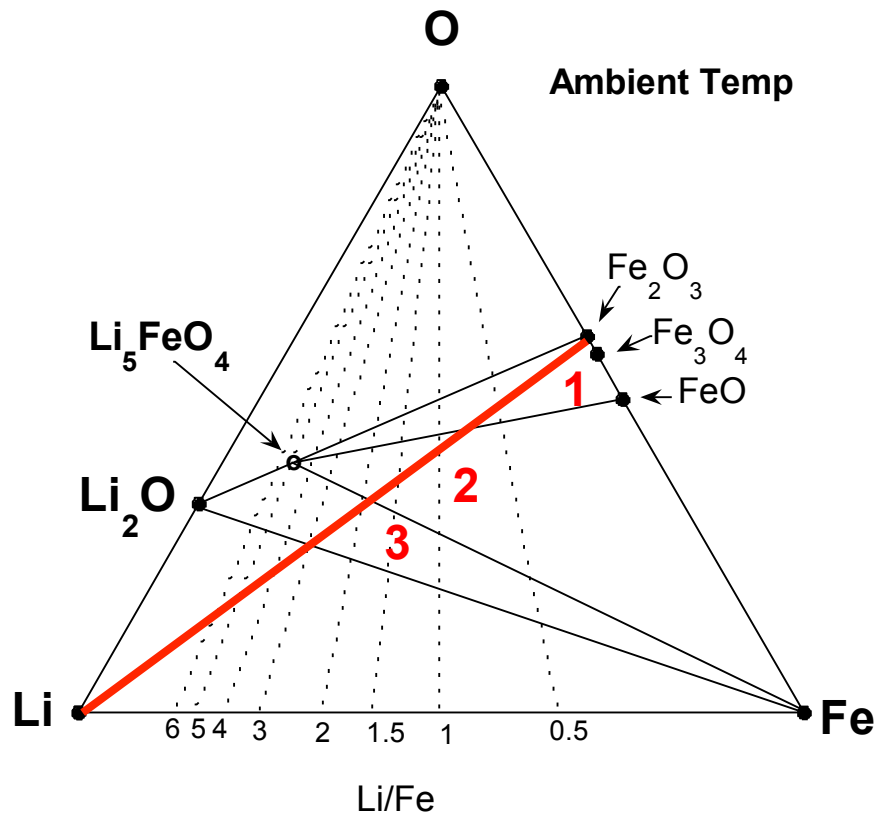


At 400°C “new” phases in the Li-Fe-O phase diagram are stable. These phases result in the formation of “Voltage Plateaus” that enhance capacity.

Extending Voltage Plateaus at Room Temperature



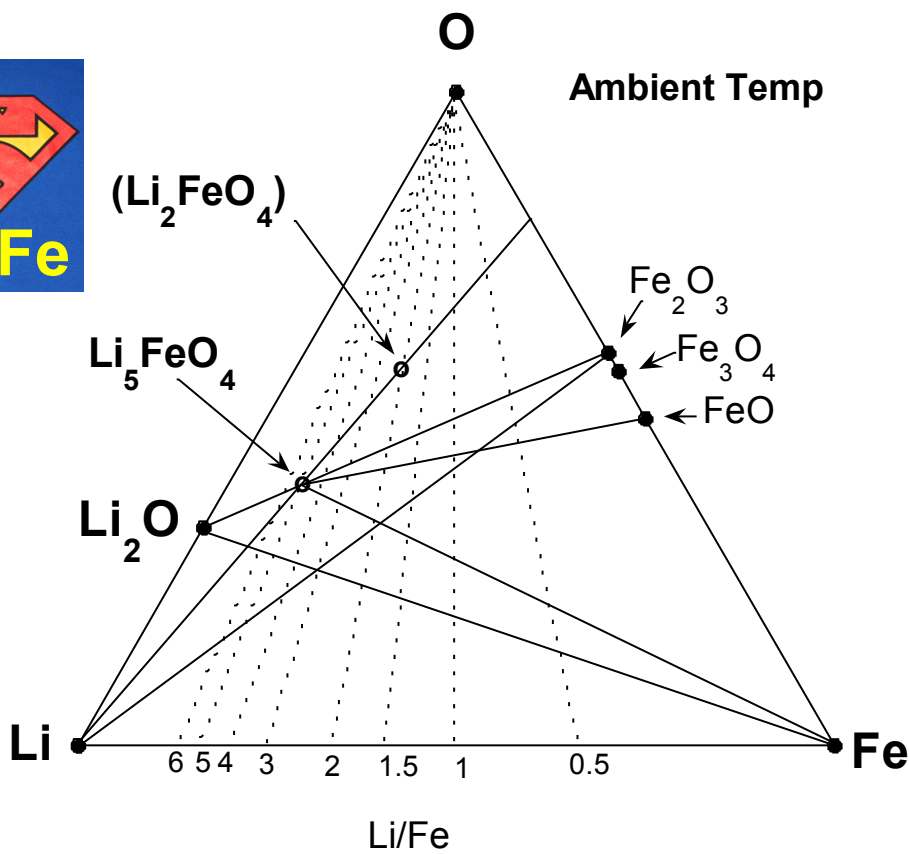
Controlling phase conversion behavior stands to impact energy density



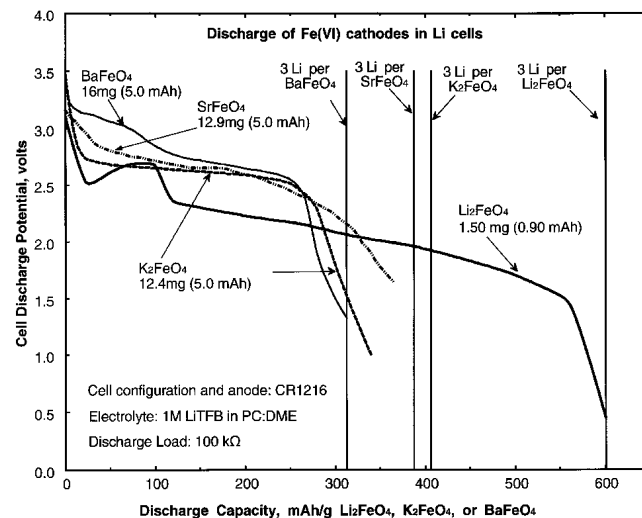
Continuing to Explore Li-Fe-O Phase Space



Understanding the relationships between materials phase and electrochemical behavior may facilitate access increased capacity at higher potentials



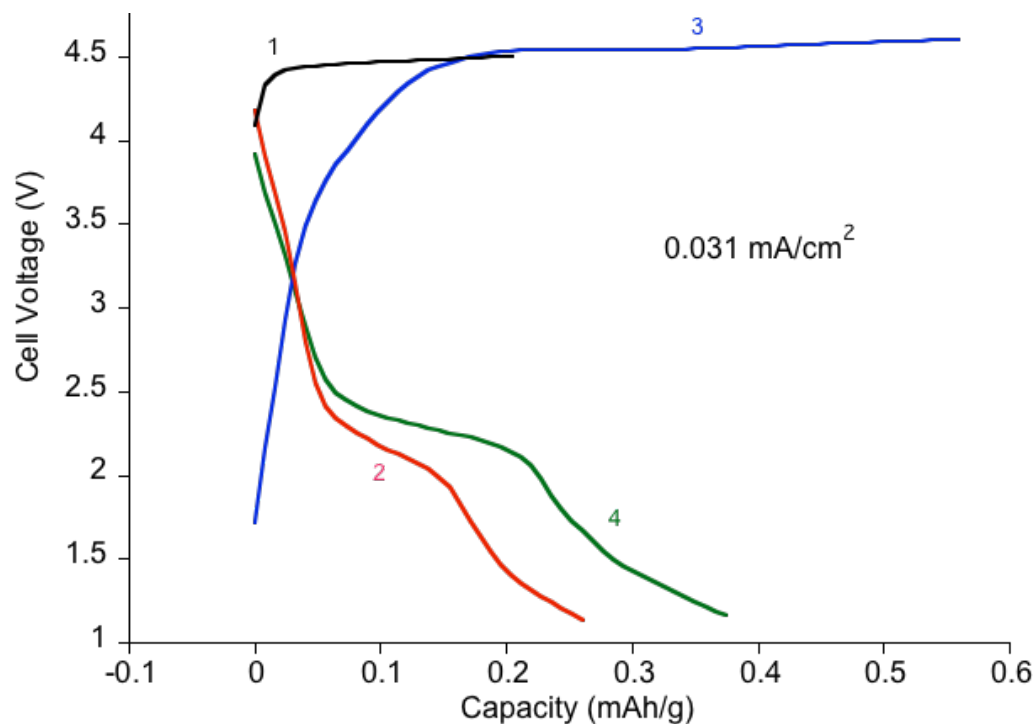
New phases of lithium iron oxide, such as those containing “Superiron” (Fe^{6+}), promise higher voltages.



Superiron – Not So Super?

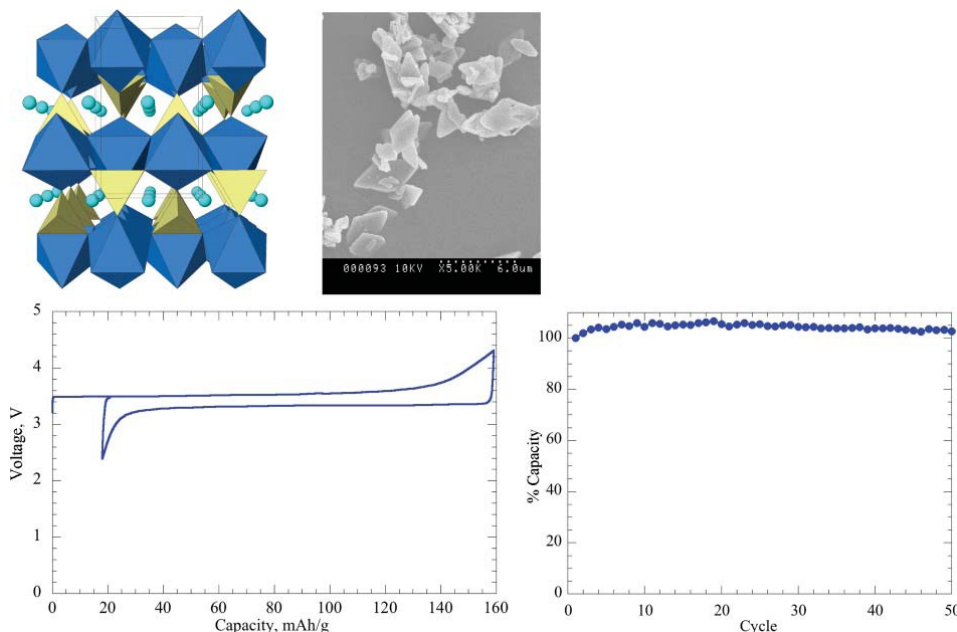


Superiron (Fe^{6+}) ferrates proved electrochemically inactive or synthetically impractical.



LiFePO₄: A “small” success

LiFePO₄ has emerged as a very promising, very fast lithium intercalation cathode



- Excellent intercalation – virtually no lattice change on Li⁺ insertion or removal.
- The oxygen is tied up in the phosphate, so it will not react with electrolyte (*safer*)
- Reasonable voltage and capacity

- But...packing density drops dramatically
- Higher surface area means you need more binder – you lose active material.
- LiFePO₄ is a poor electrical conductor

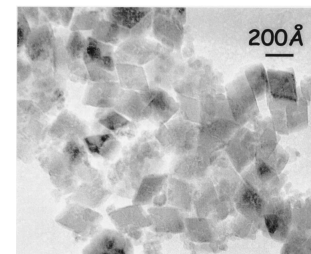
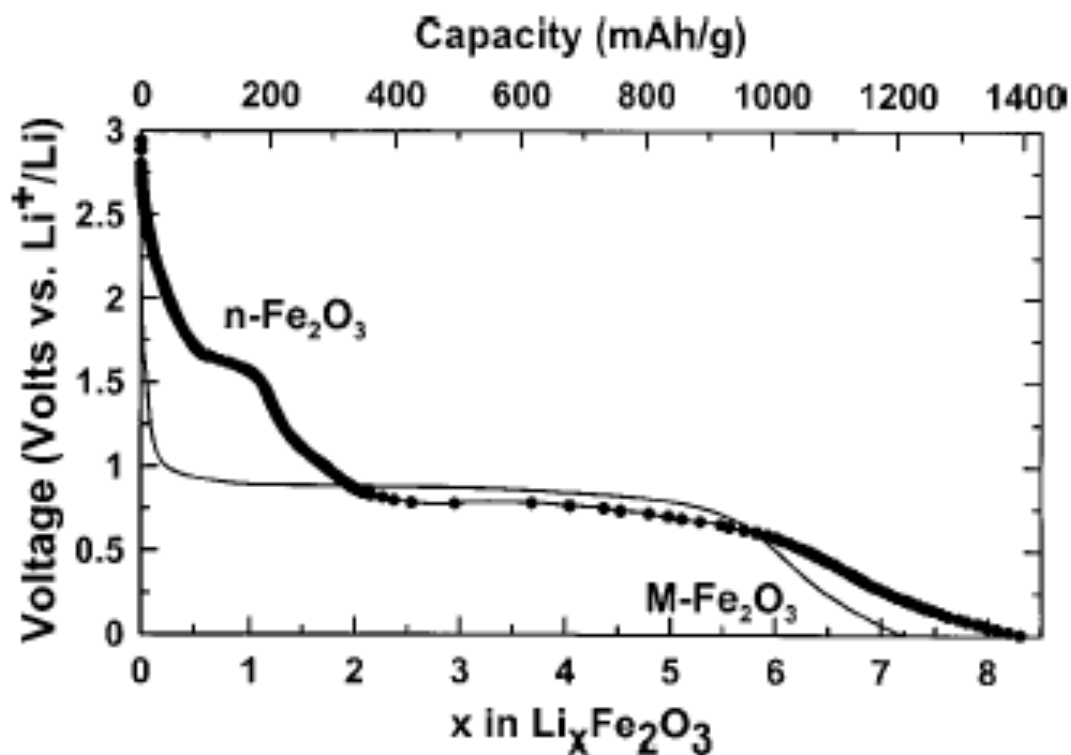
Largely resolved by doping or integrating with nanoconductive carbons

SWNTs have also been considered – high electrical conductivity (5×10^5 S/m)

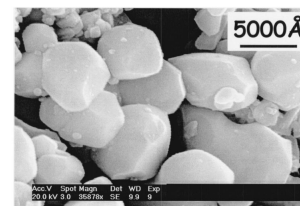
Nano-Enabled Fe_2O_3 Cathodes



Nanoscale morphology of iron oxide structures have been shown to extend voltage plateaus!



n- Fe_2O_3
60 m^2/g



M- Fe_2O_3
2 m^2/g

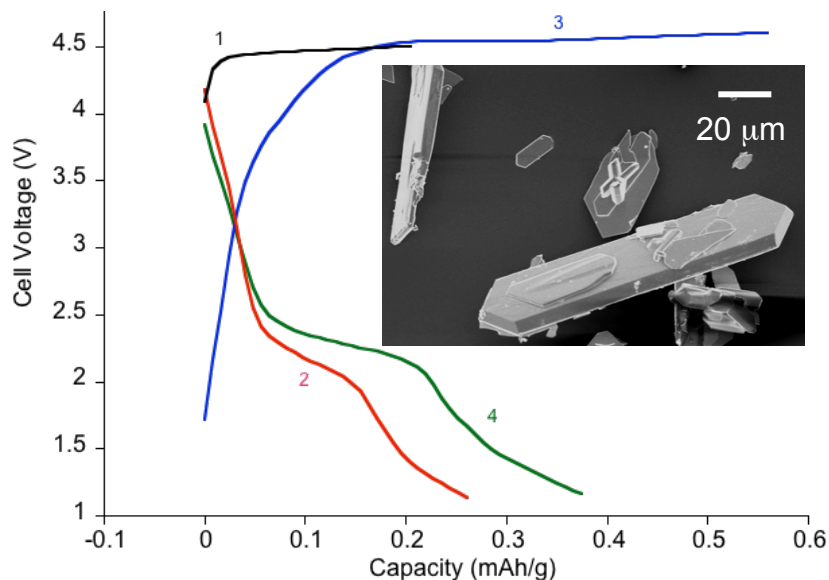
Size-Dependent Cathode Enhancement



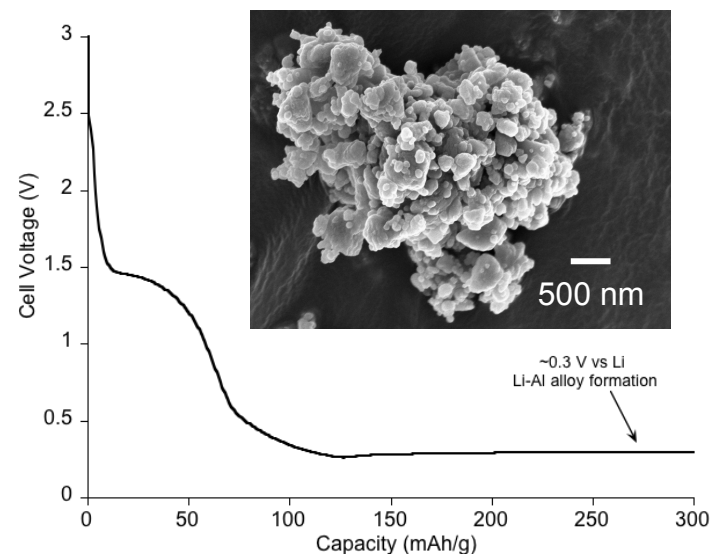
Reducing particle size can produce extended voltage plateaus.

Consider K_2FeO_4

Large Particle Size



Submicron Particle Size



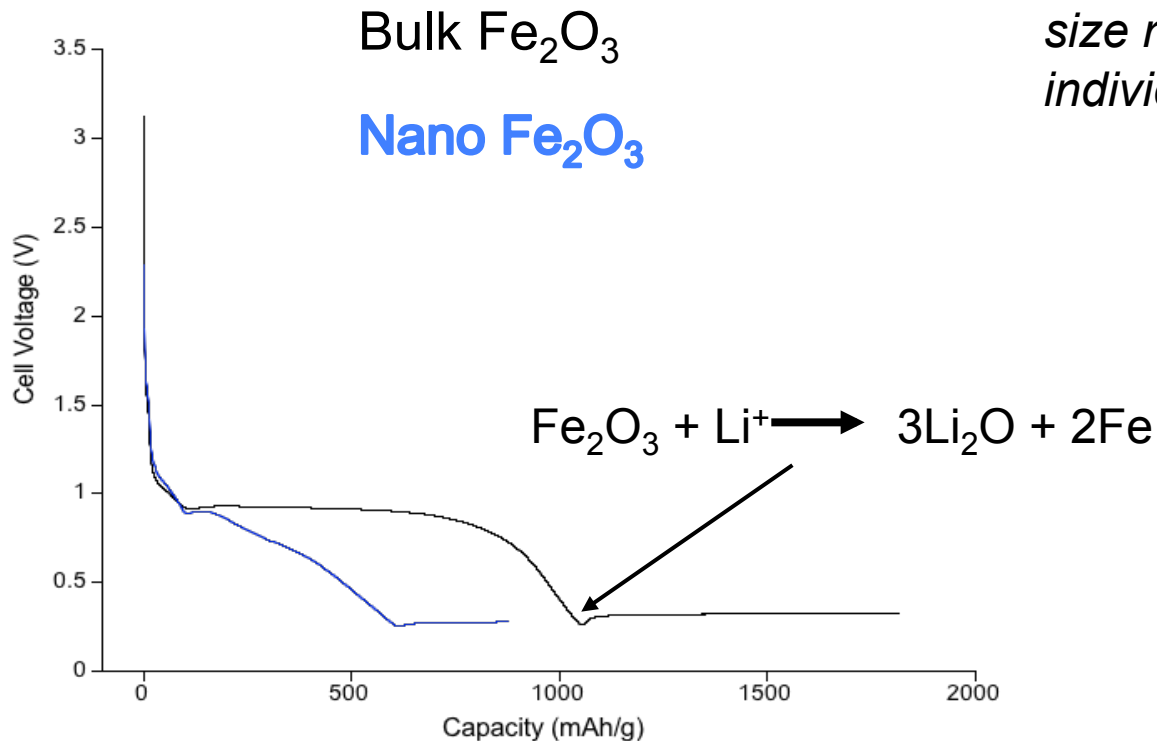
Is “Nano” Universally Beneficial?



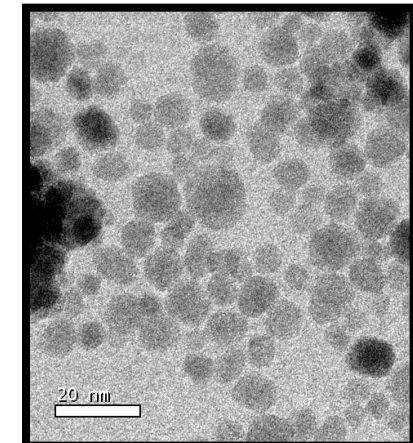
Reducing particles to nanoscale only improves performance in select phases...

- Introduces new processing challenges (binder/active material interfaces)
- Reduces effective active material content

The effect of reducing particle size must be considered on an individual materials basis.



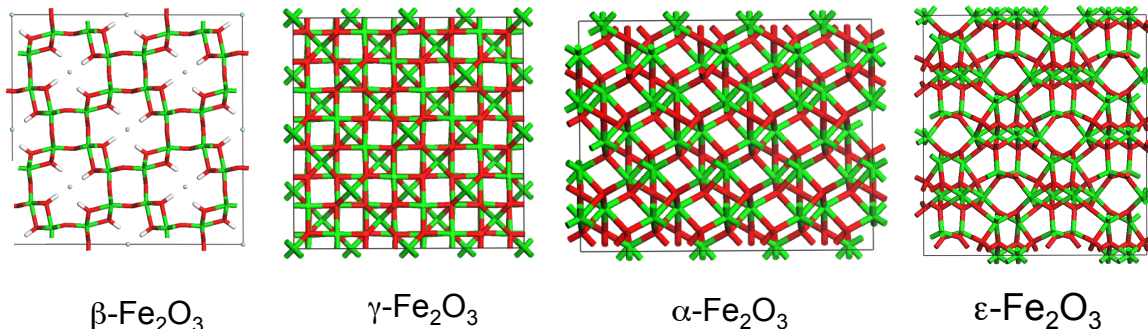
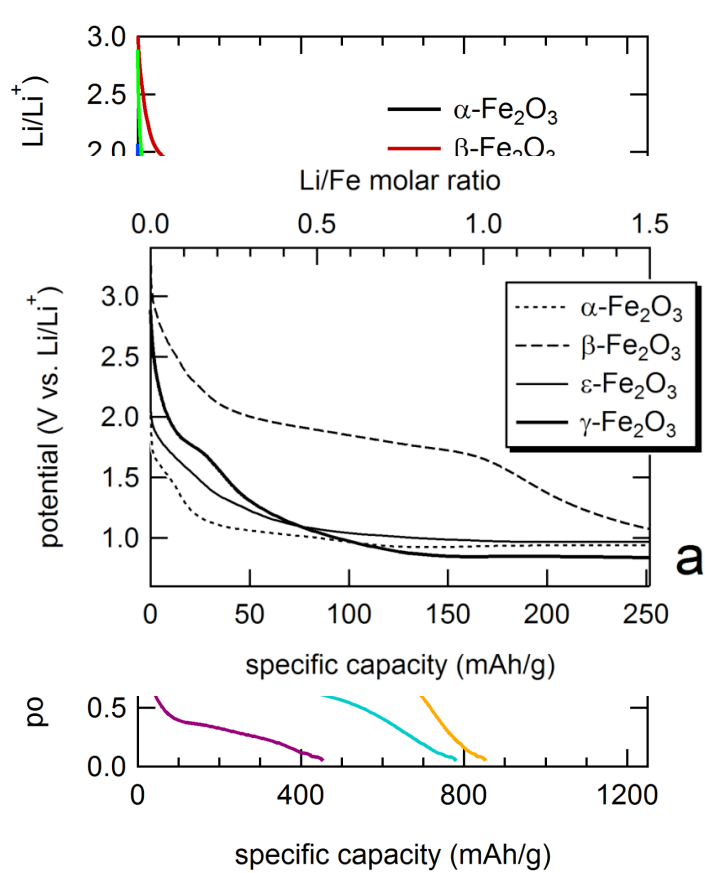
Nano Fe_2O_3



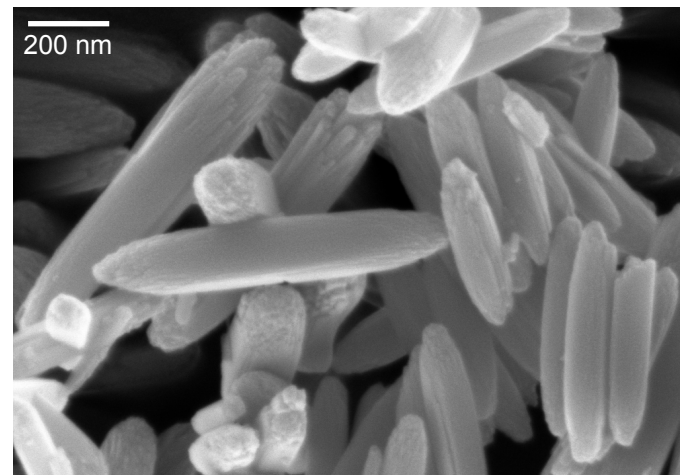
Discharge Behavior of Iron Oxides



Iron oxides show consistent* voltage plateaus around 1V



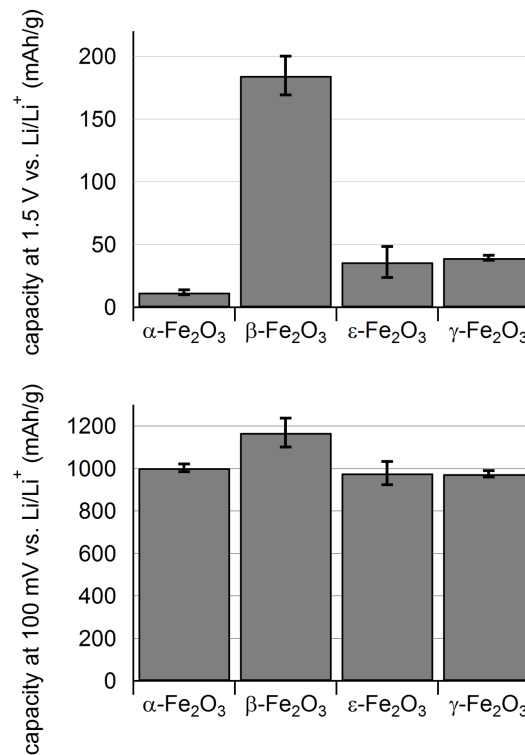
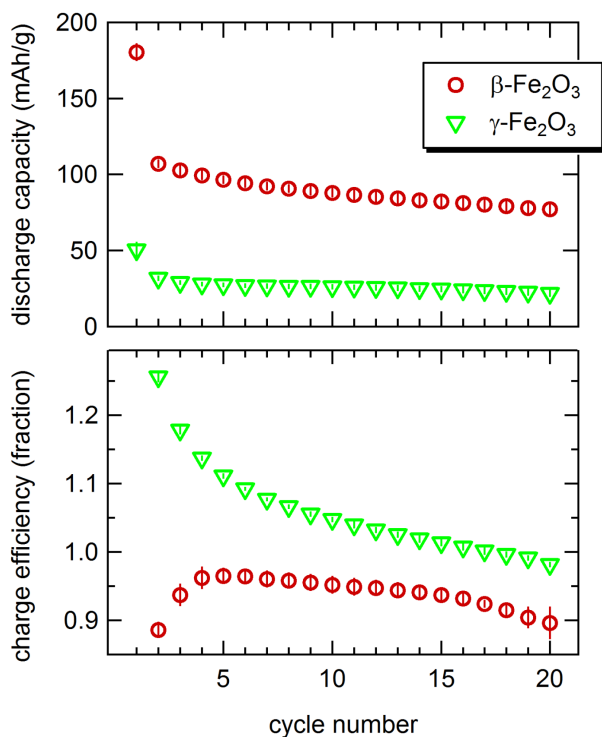
* $\beta\text{-Fe}_2\text{O}_3$ (image right) shows unique extended capacity and good cyclability near 2V.



Electrochemical Cycling of Iron Oxides



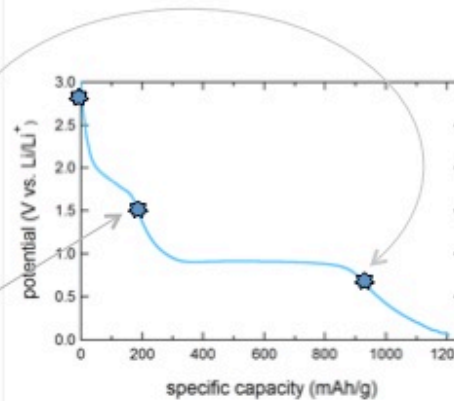
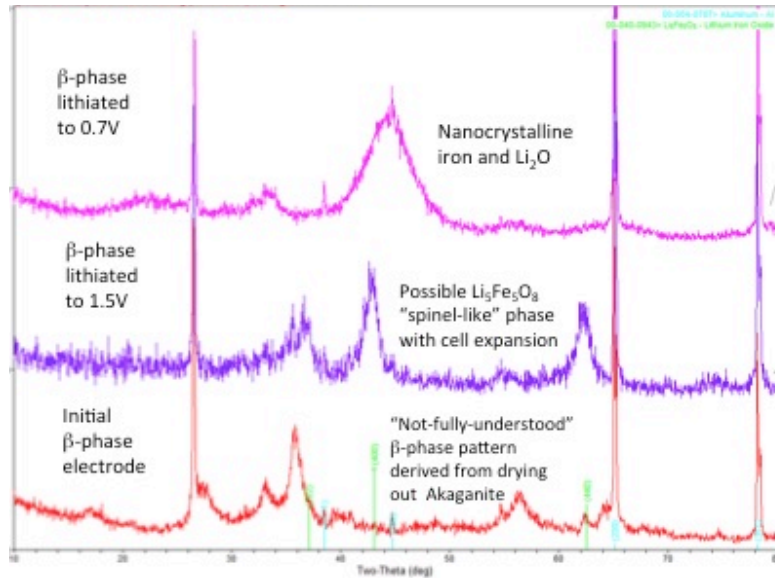
β - Fe_2O_3 cycling, charge efficiency, and capacity are all enhanced relative to other Fe_2O_3 polymorphs



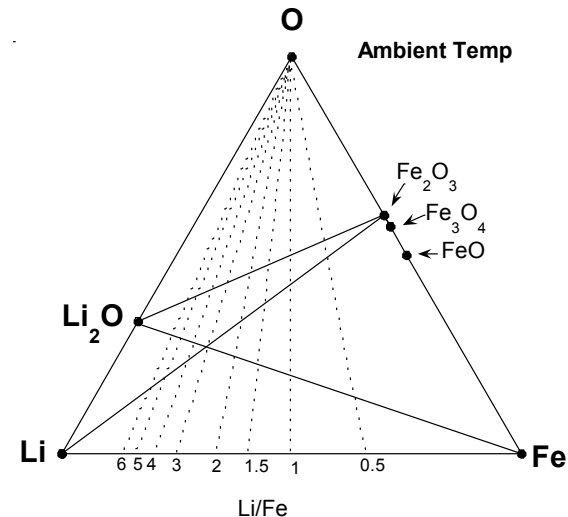
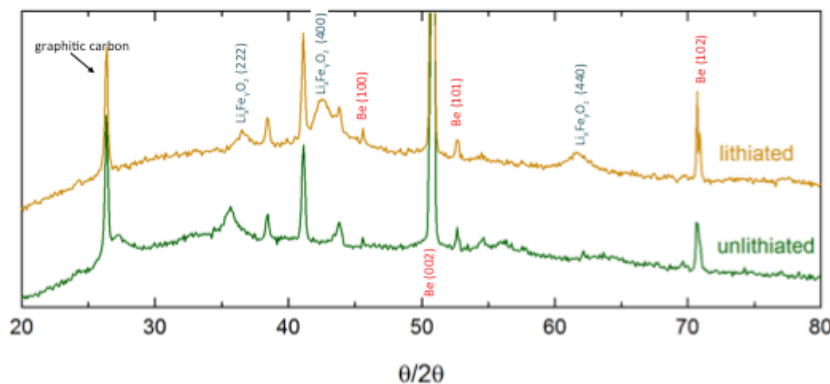
Understanding β -Fe₂O₃



Ex-situ and *in-situ* X-ray diffraction shows there is a phase transformation during discharge



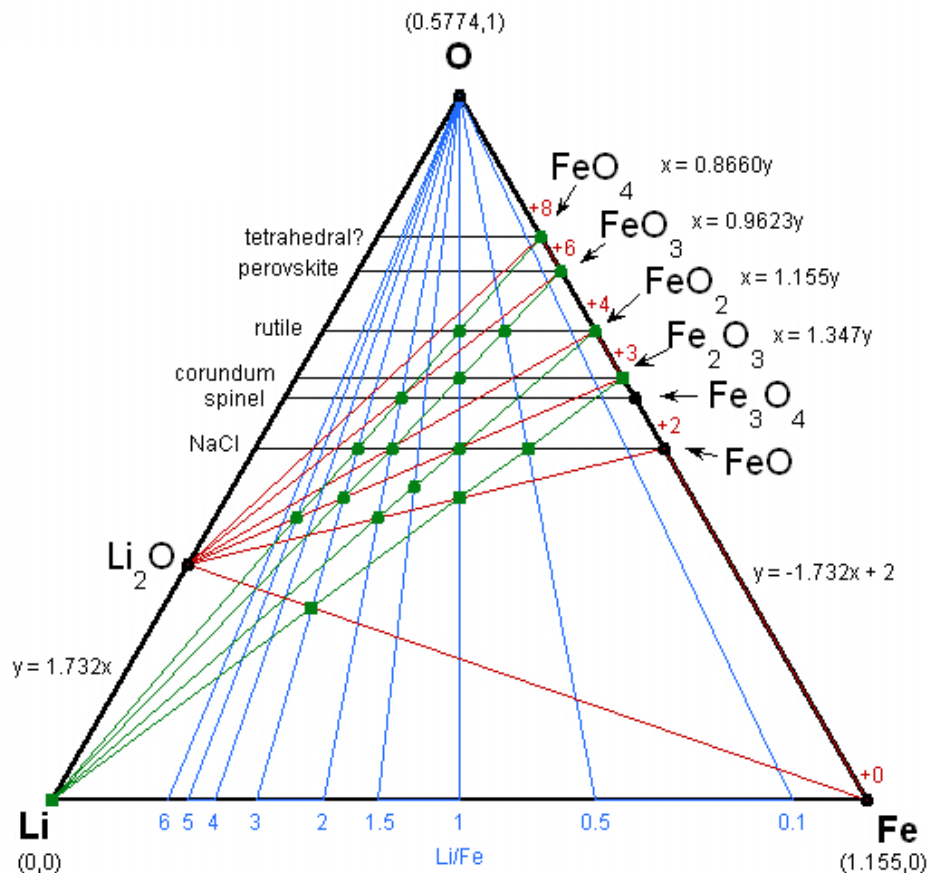
Cycling at 1.5V is related to formation of a spinel-like phase with a composition of $\text{Li}_x\text{Fe}_5\text{O}_8$



Phase Change Kinetics



Phase transformations in Fe_2O_3 will be kinetically slow...



LiFePO_4 is kinetically fast in part because reversible Li intercalation does not change crystal structure.

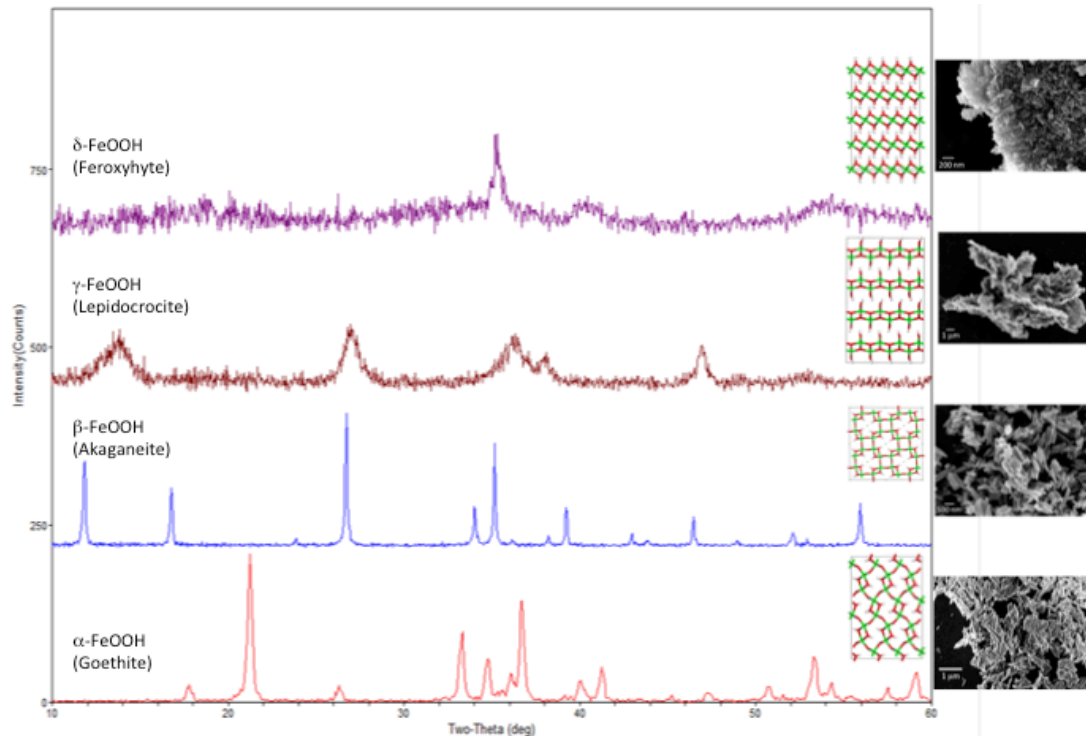
LiFePO_4 (triphylite) and FePO_4 (heterosite) are both olivine-like orthorhombic crystal structures.

Iron oxides may have significantly greater crystallographic change during cycling.

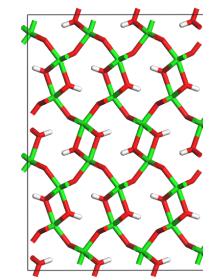
Open Lattices: FeOOH Polymorphs



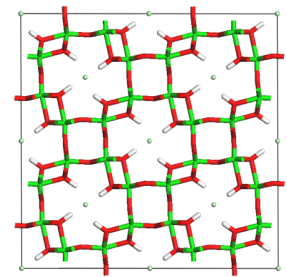
Taking a cue from the β -Fe₂O₃ work, consider FeOOH polymorphs



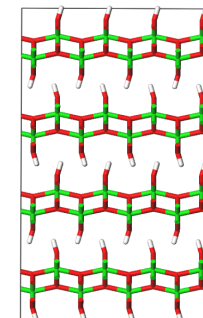
α -FeOOH



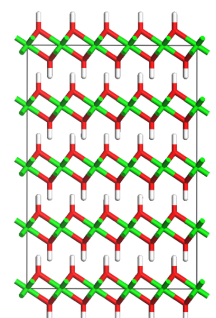
β -FeOOH



γ -FeOOH



δ -FeOOH

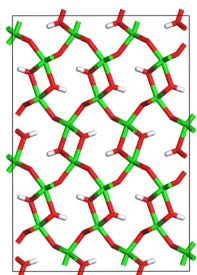


Electrochemistry of FeOOH

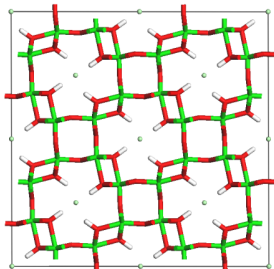


Oxy-hydroxides show promising cycling behavior with good capacity near 2V.

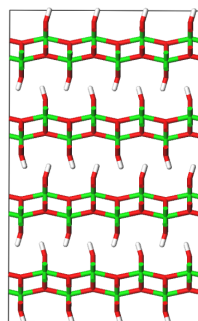
α -FeOOH



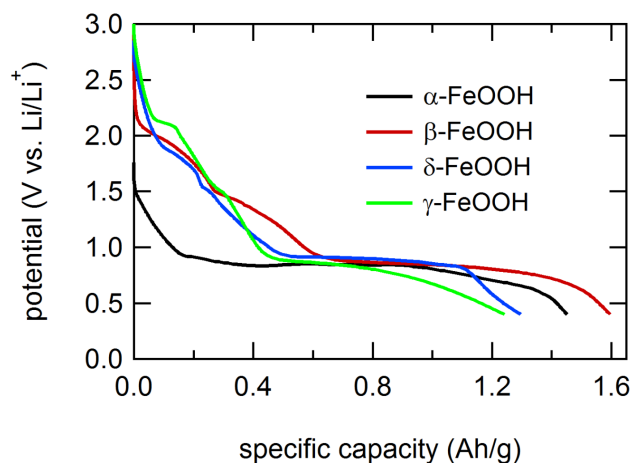
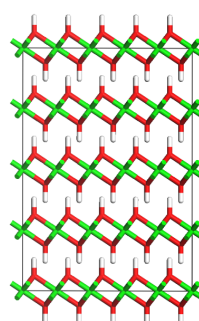
β -FeOOH



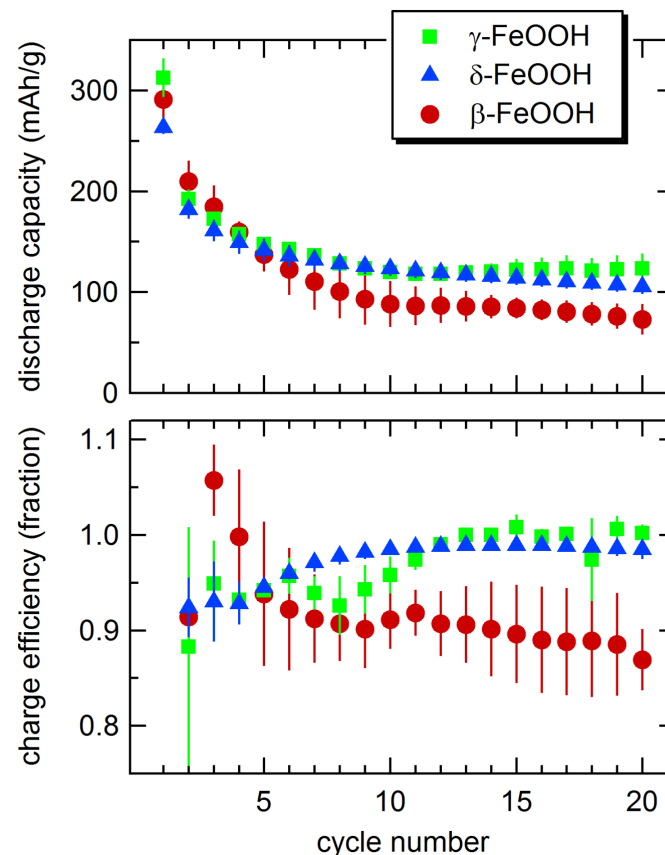
γ -FeOOH



δ -FeOOH



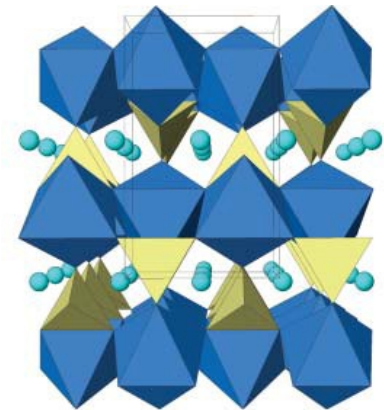
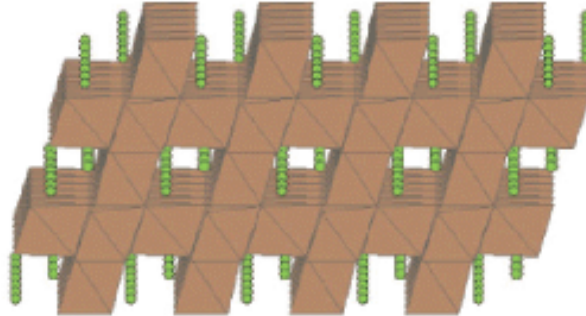
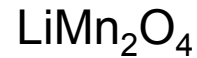
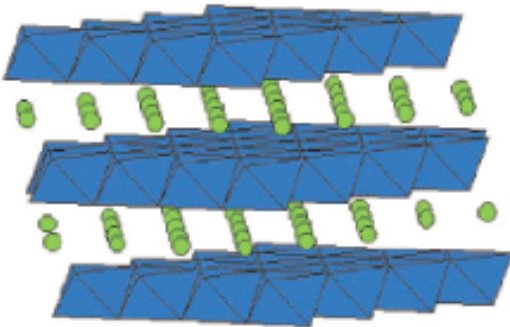
Open lattices,
particularly
with layered
morphology
provide good
structure for
Li-intercalation



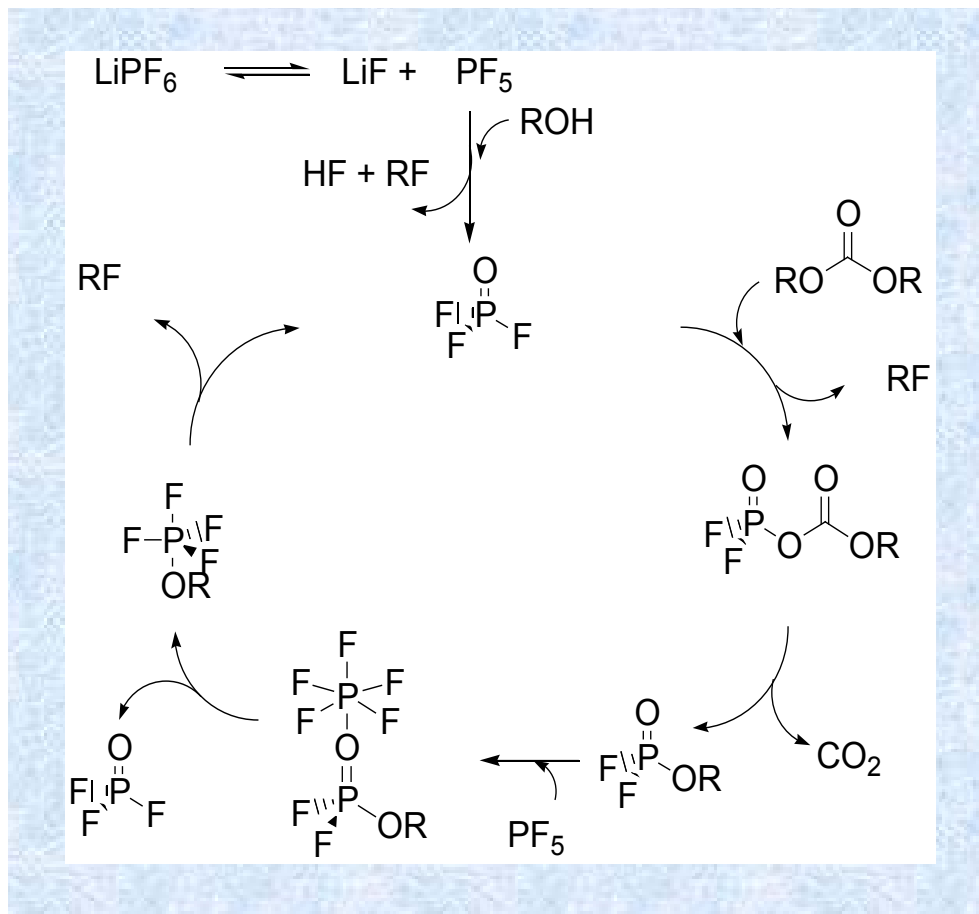
Ion Pathways in Cathodes



Other layered materials are known to be effective cathodes owing to excellent ion transport properties.



A Problem with FeOOH



Hydroxides can restructure, liberating water.

Trace water or alcohol impurities catalyze the thermal decomposition of electrolytes.

Produces:

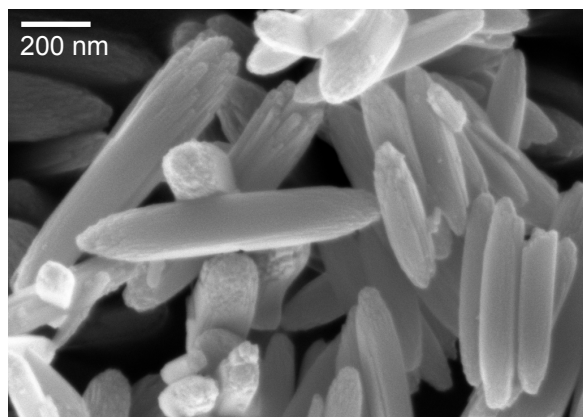
- ✧ Fluorinated organic contaminants
- ✧ HF!

Not Good!

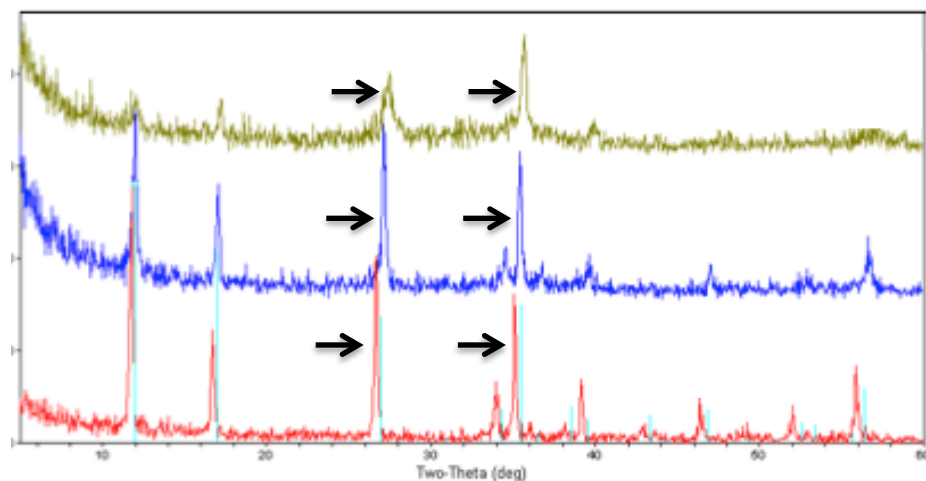
Solving the Problem with FeOOH?



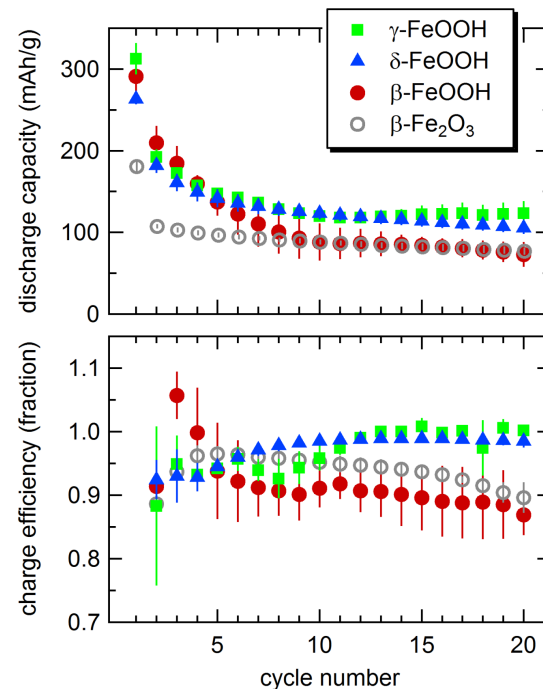
Take out the water!



Measured weight loss of water at 10.6% (vs. 10.1% theoretical) and x-ray diffraction show a decrease in lattice parameter (but retention of crystal structure) confirming:



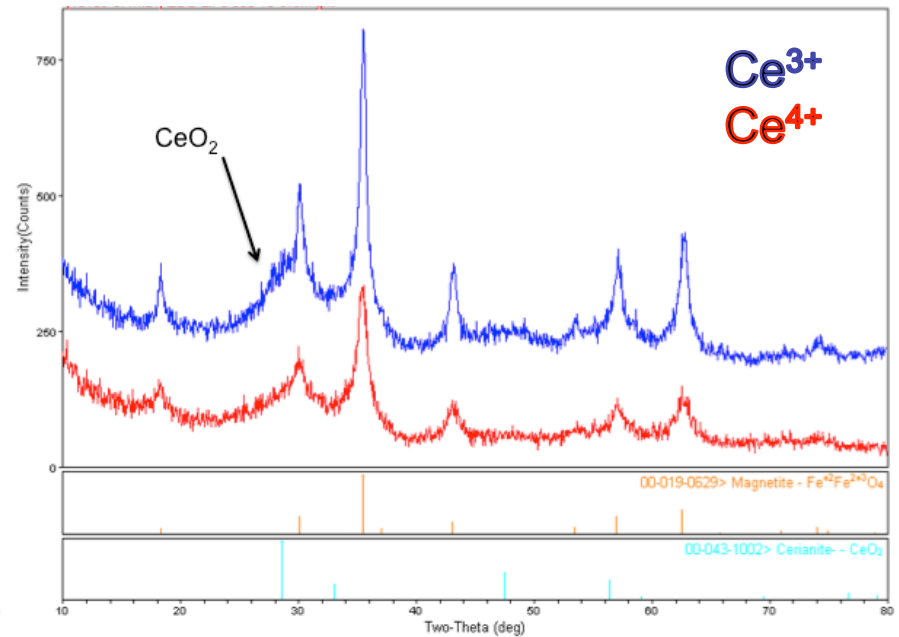
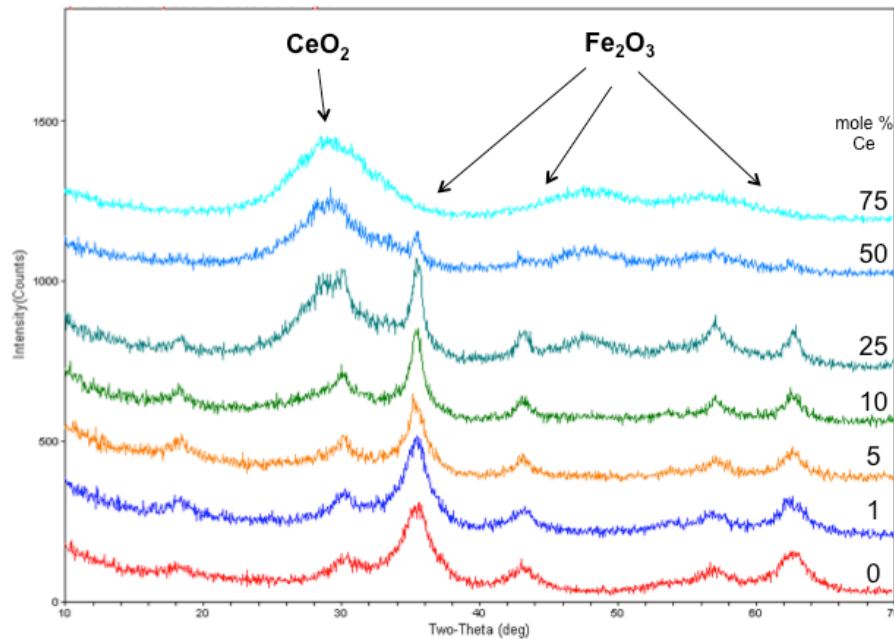
Decreasing H₂O



Cationic Doping Maghemite



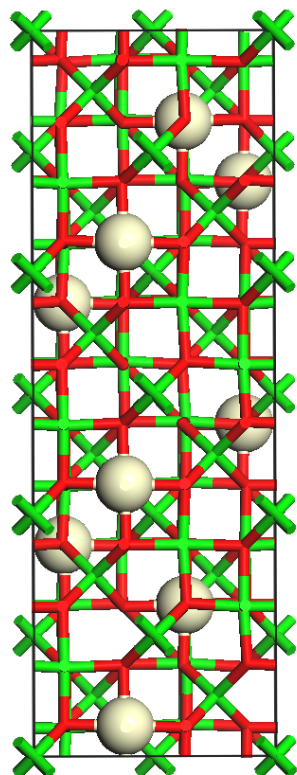
Ce^{4+} shows good solubility in the $\gamma\text{-Fe}_2\text{O}_3$ lattice



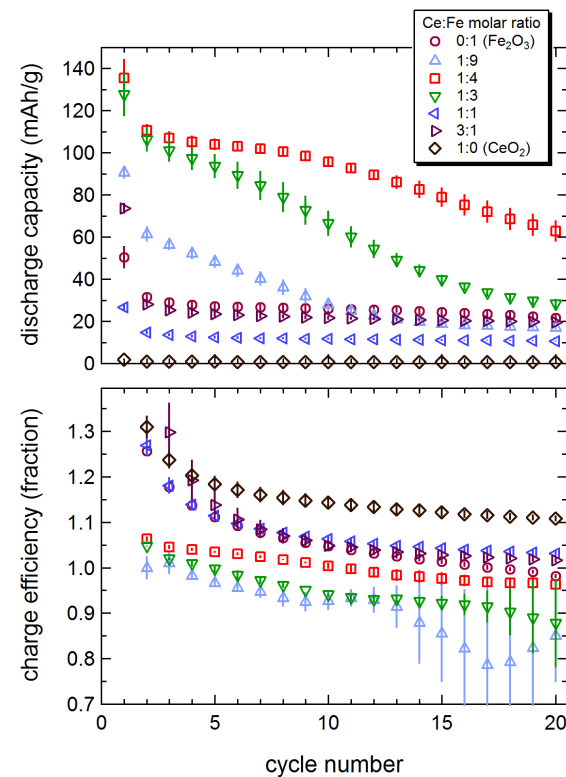
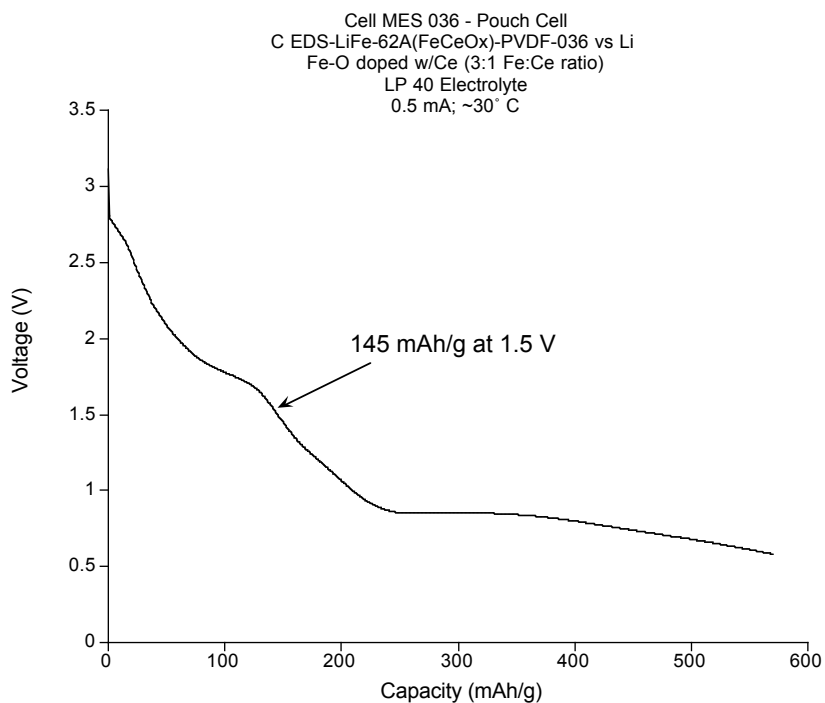
Electrochemistry of Ce- γ -Fe₂O₃



Doping the γ -Fe₂O₃ crystal lattice with large cations improves electrochemical behavior



Ce-doped γ -Fe₂O₃

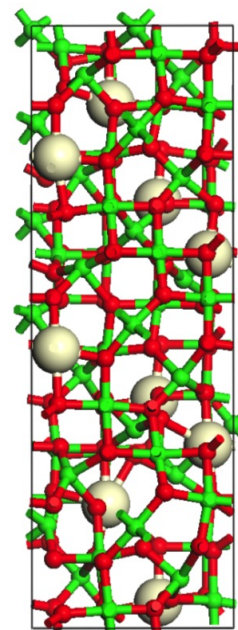
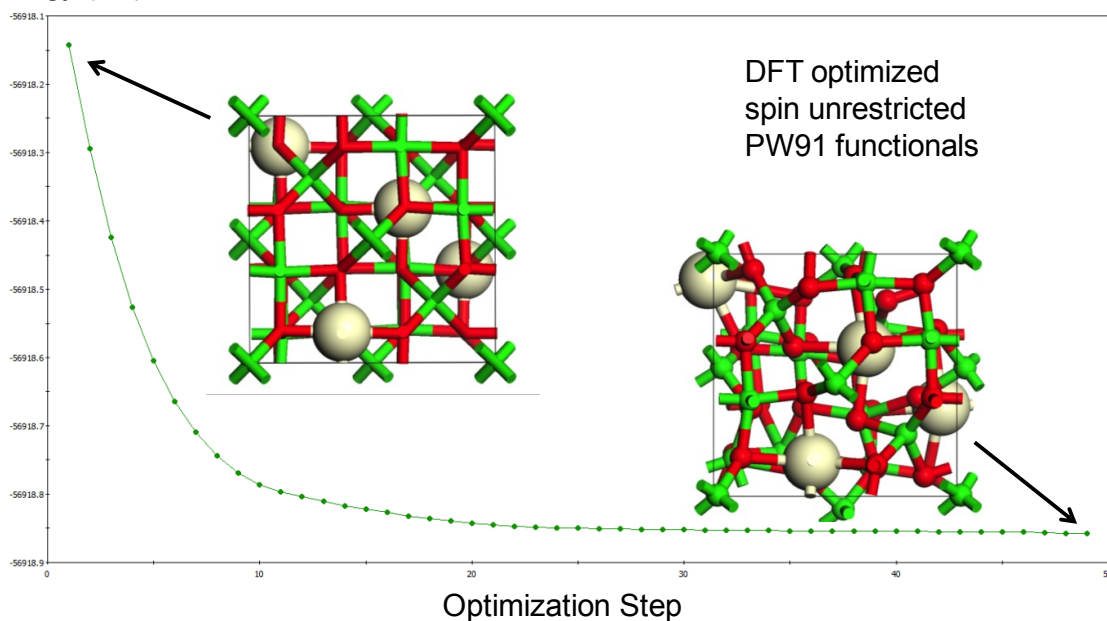


Modeling Cerium Doping

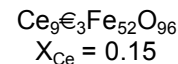


Potential energy convergence and structures for the DFT optimization of highly defective Ce-doped γ -Fe₂O₃ shows significant lattice distortion.

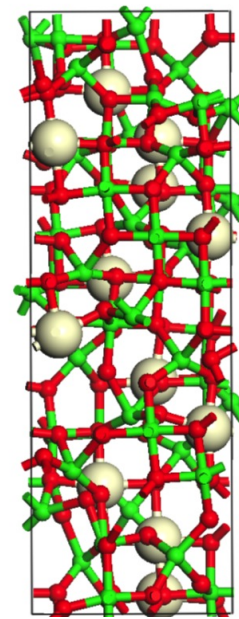
Energy (Ha)



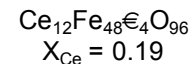
$$r_{\text{Ce}4+} = 1.01 \text{ \AA}$$



$$E = -2722 \text{ kcal/mol}$$



$$r_{\text{Ce}4+} = 1.01 \text{ \AA}$$

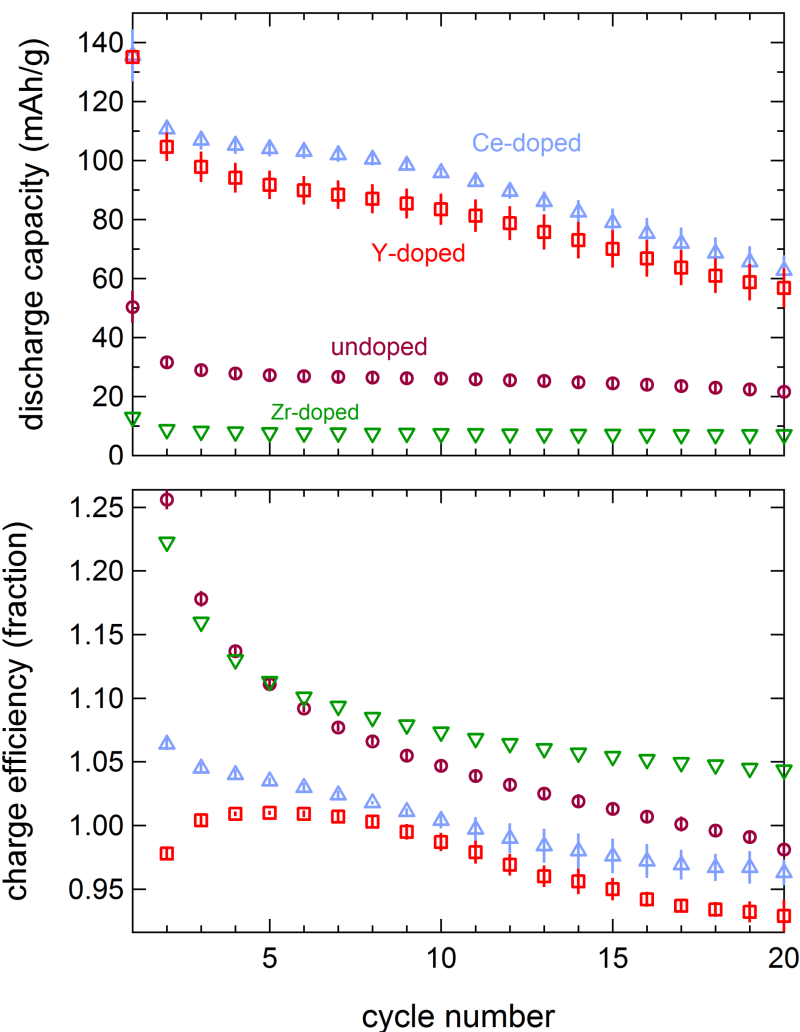
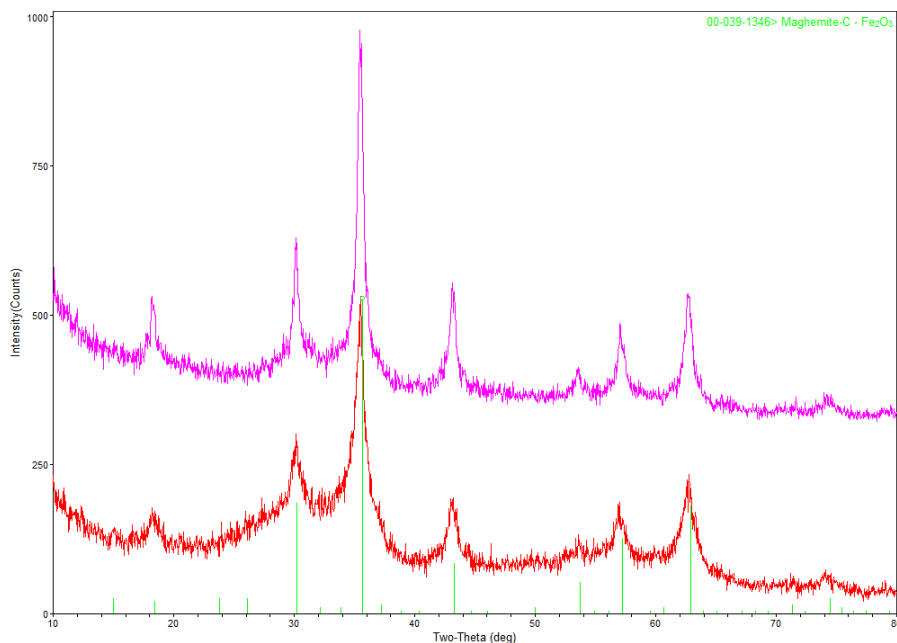


$$E = -2698 \text{ kcal/mol}$$

Size Matters

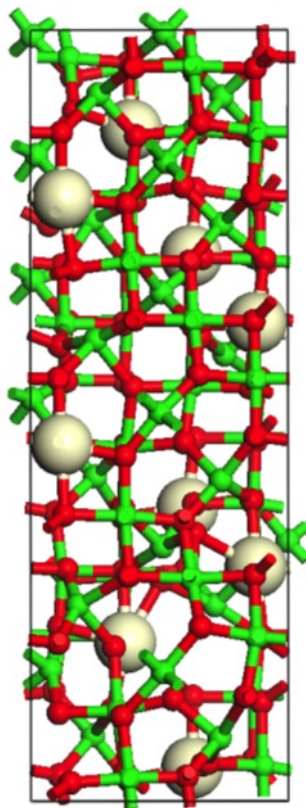


Improved electrochemical performance is tied to the size, not the charge of the dopant.

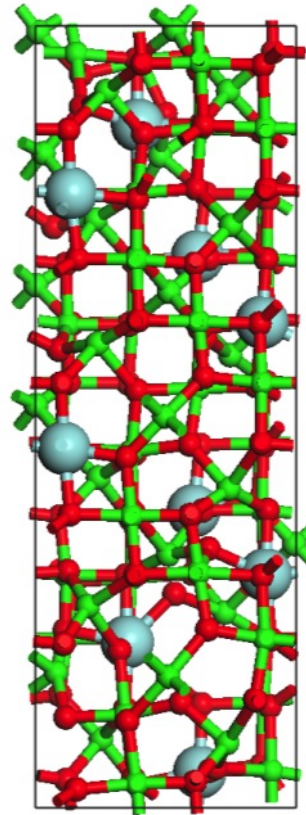
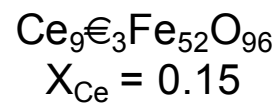


$$*r_{\text{Ce(IV)}} = 1.01\text{\AA}, r_{\text{Y(III)}} = 1.04\text{\AA}, r_{\text{Zr(IV)}} = 0.86\text{\AA}$$

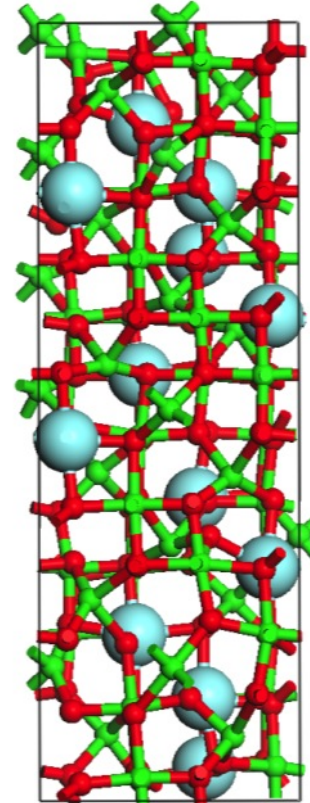
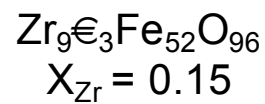
Comparing Cationic Doping



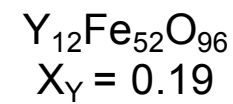
$$r_{\text{Ce}4+} = 1.01 \text{ \AA}$$



$$r_{\text{Zr}4+} = 0.86 \text{ \AA}$$



$$r_{\text{Y}3+} = 1.04 \text{ \AA}$$





Acknowledgements



Collaborators

Nick Hudak
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Mark Rodriguez

Randy Cygan

Holly Zarick
Jill Wheeler
Tim Boyle

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Sandia's Laboratory Directed Research
and Development Program



Thanks!

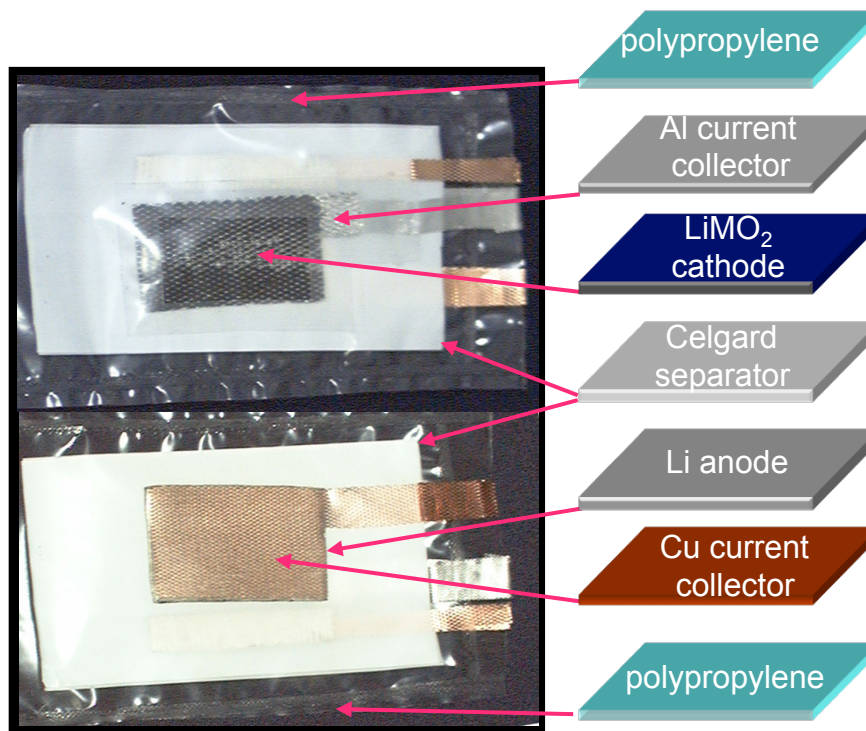


Backup Slides

In situ Diffraction Coupled with Electrochemical Testing



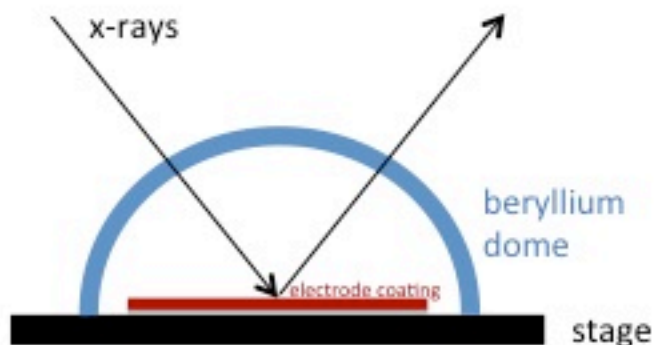
Electrochemical “pouch” cells can be used to perform “in situ” diffraction analysis during electrochemical cycling



Comparing *Ex-Situ* and *In-Situ* Methods

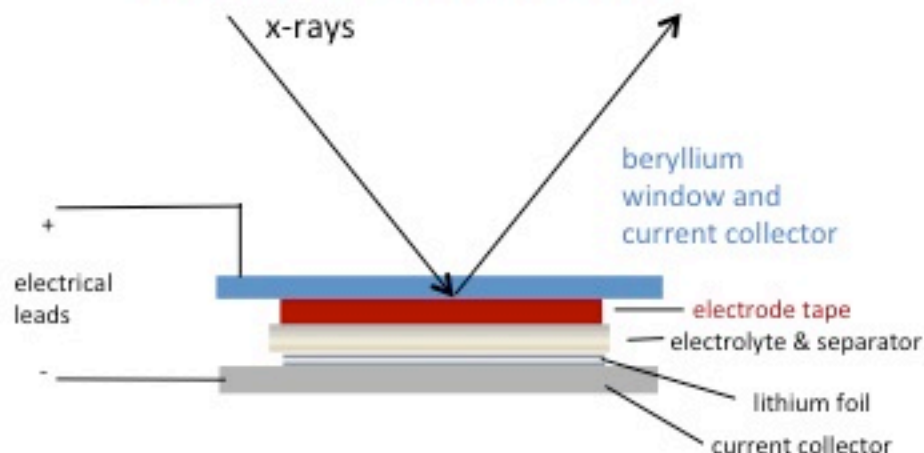


Ex Situ Measurements



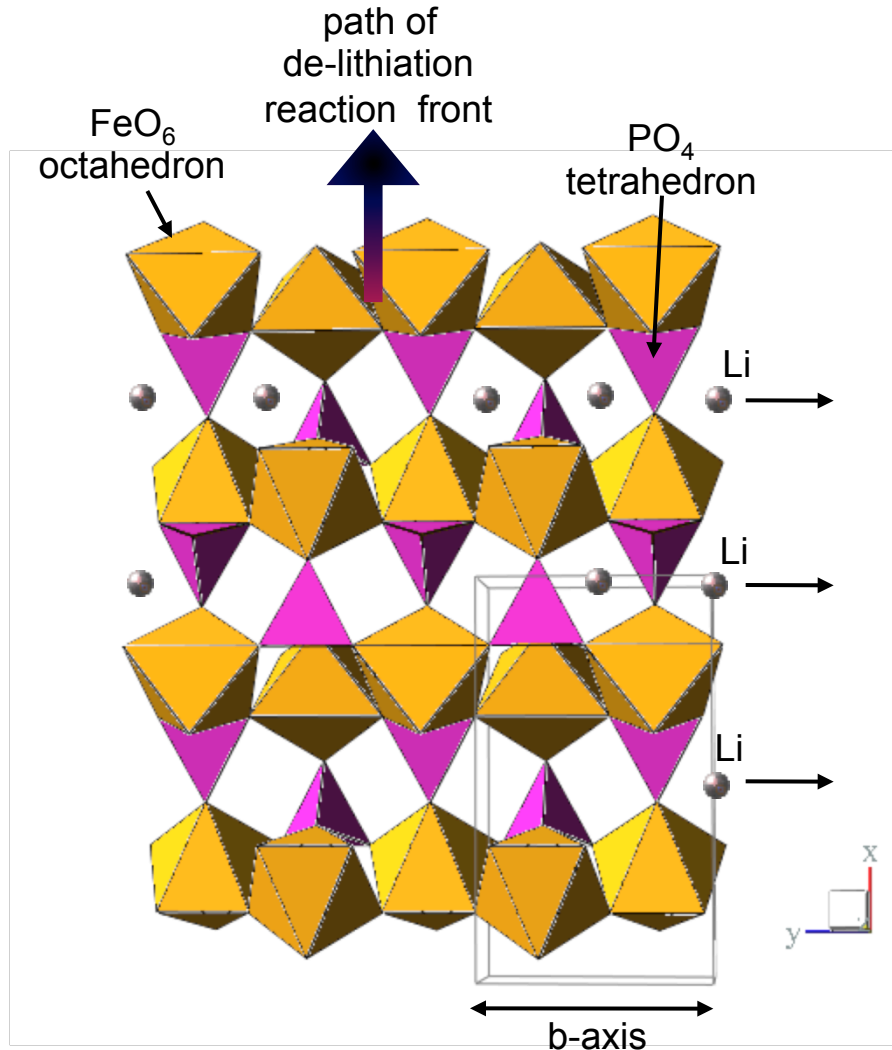
- after cell discharge or cycling, electrode is removed in dry room or glove box
- electrode coating is sealed in Be dome fixture in the glove box or dry room
- limitation: many cells must be assembled, tested, disassembled to get full picture

In Situ Measurements



- new CINT capability: battery cell attachment for Rigaku XRD
- Be window allows simultaneous electrochemistry and XRD
- **free-standing electrode tape (not coating) must be made**
- challenges: many cell components reduce signal-to-noise ratio, additional peaks due to beryllium

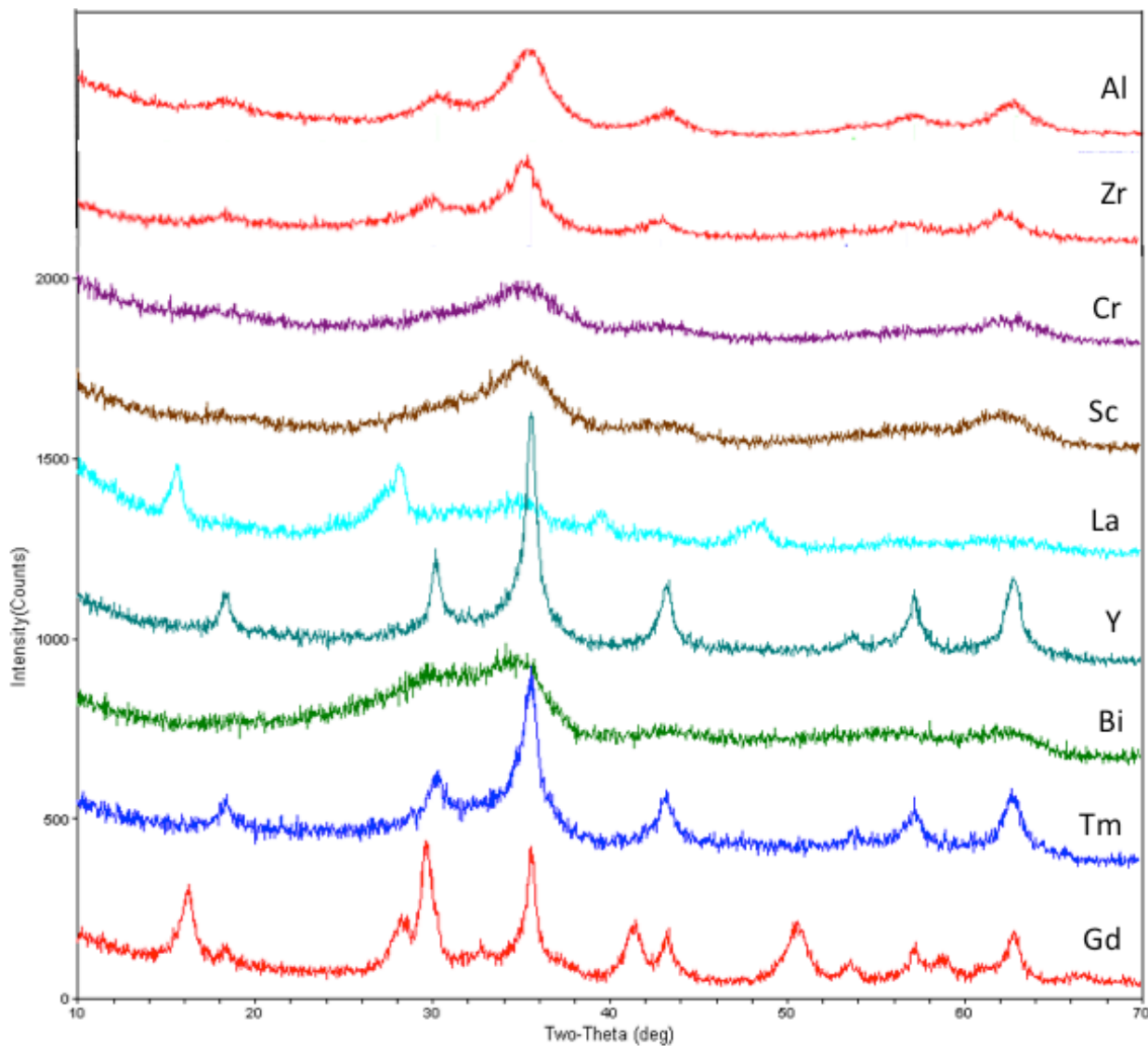
Interfacial transport theory of Li in LiFePO_4



- Laffont, et. al* has suggested that Li transport occurs by “unzipping” the Triphylite LiFePO_4 phase.
- Li atoms are thought to propagate out of the host lattice via the b-axis, leaving behind the Heterosite FePO_4 compound
- Intercalation of Li occurs in the reverse fashion.

*L. Laffont, et. al, *Chem. Mater.*, **18** 5520-5529 (2006).

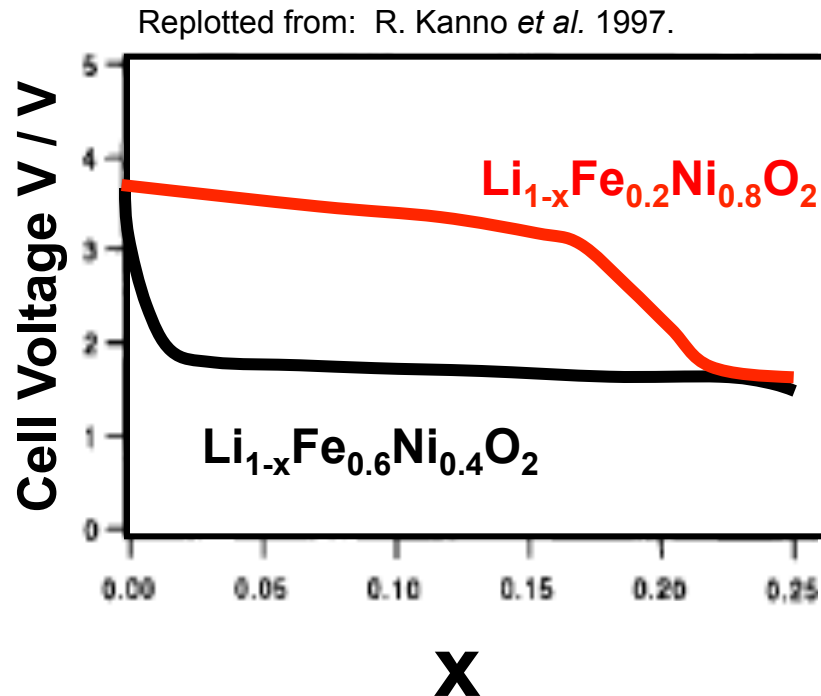
Doping with a Wide Range of Cations



Cation Doping to Enhance Capacity



Cationic substitution has also been shown to improve capacity at higher voltages in iron-based oxides



Potential candidate dopants:

Structural stabilization: **Al, Ni**

Electroactive dopants: **Co, Mn**

Computational Modeling will be used to guide experimental dopant studies

Iron Oxide Electrochemistry

