



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

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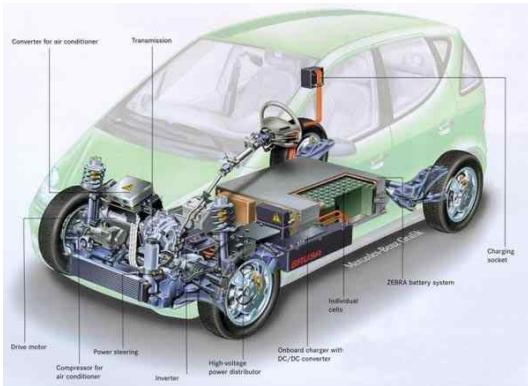
# Why Batteries?

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

Solar energy



Vehicle electrification



Utility infrastructure



Wind power



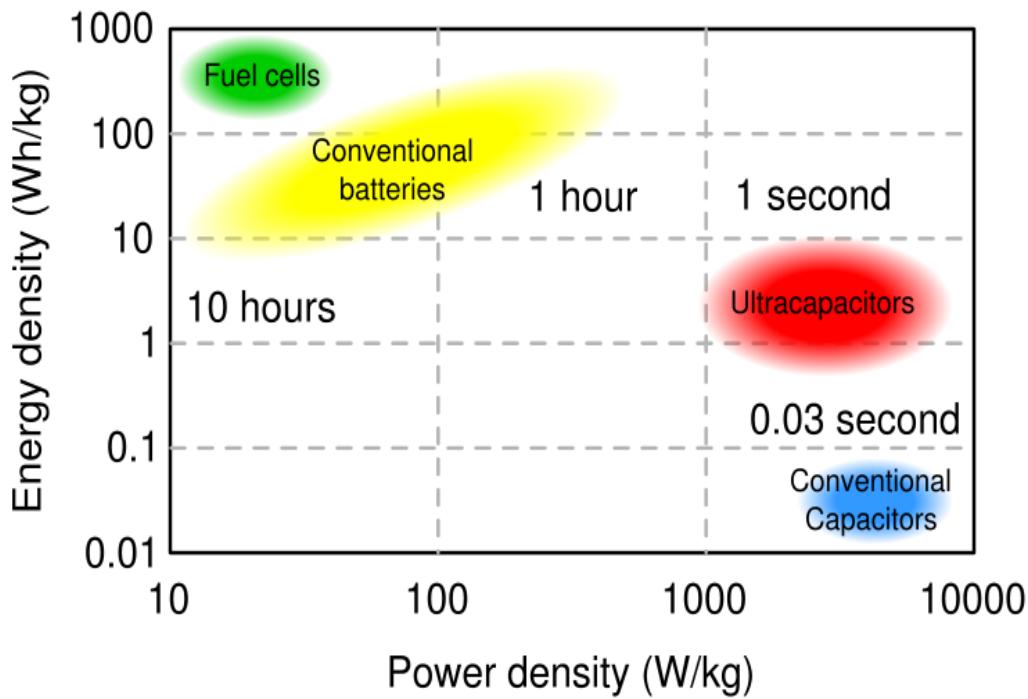
Portable electronics



# Battery Materials Motivation



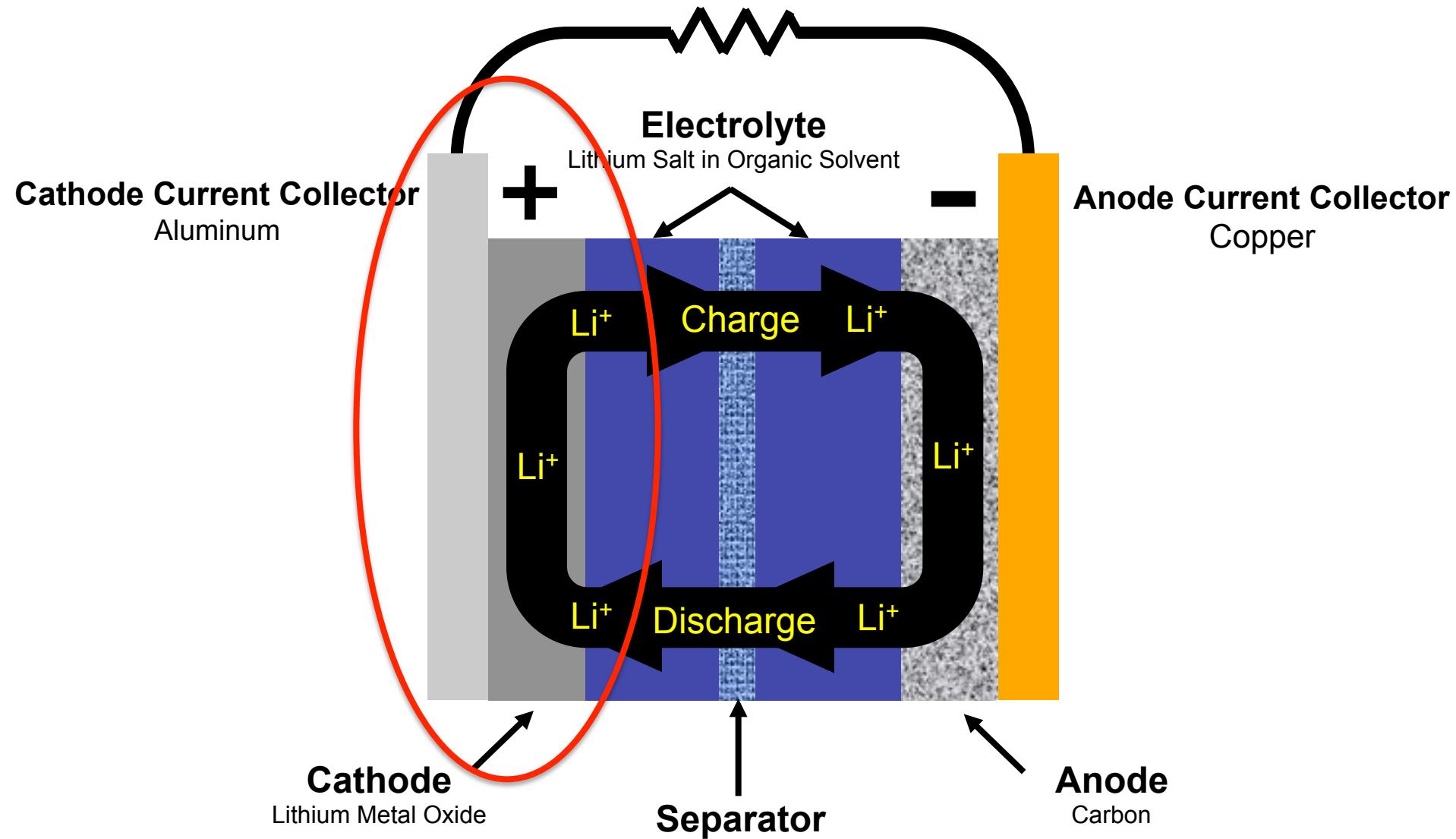
What are the focal points of modern battery research?



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



# Battery Basics: A Lithium Ion Cell

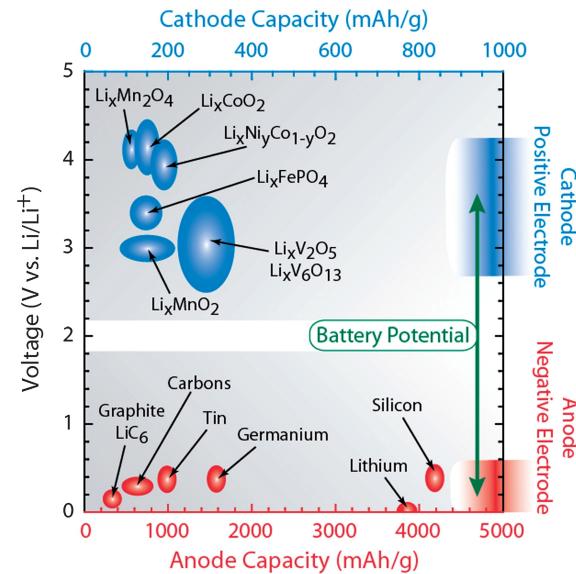




# Candidate Cathodes

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

Cathode Material	Average Voltage	Gravimetric Capacity
$\text{LiCoO}_2$	3.7 V	140 mAh/g
$\text{LiMn}_2\text{O}_4$	4.0 V	100 mAh/g
$\text{LiNiO}_2$	3.5 V	180 mAh/g
$\text{LiFePO}_4$	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

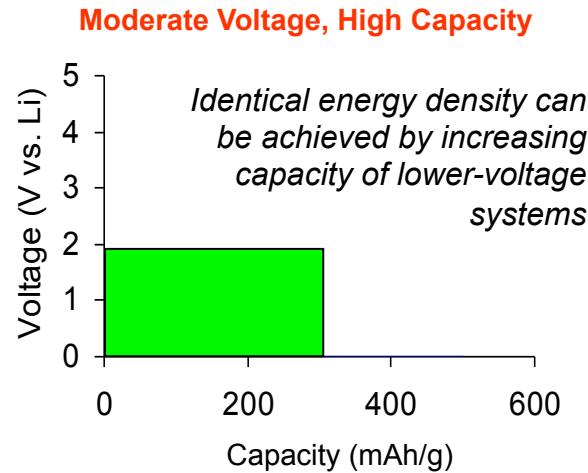
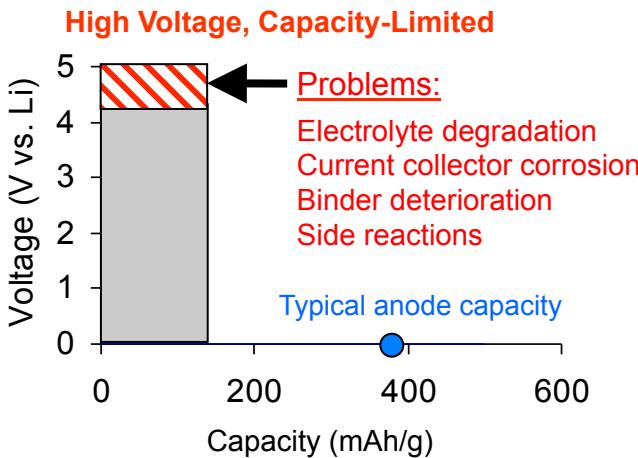
- High energy density
- High power density
- Low cost
- Safe (related to cost)
- Lightweight

Volume  
mentally friendly

Phase	(mAHR/g)	Phase	(mAHR/g)	Phase	(mAHR/g)	Phase	(mAHR/g)
$\text{Li}_5\text{FeO}_4$	1118	$\text{Li}_3\text{FeO}_3$	774	$\text{Li}_2\text{FeO}_2$	610	$\text{Li}_2\text{O} + \text{Fe}$	1007
$\text{Li}_3\text{FeO}_4$	671	$\text{Li}_2\text{FeO}_3$	516	$\text{Li}_3\text{Fe}_2\text{O}_4$	458	$\text{Li}_2\text{Fe}_2\text{O}_3$	336
$\text{Li}_2\text{FeO}_4$	447	$\text{LiFeO}_3$	258	$\text{LiFeO}_2$	305	$\text{LiFe}_2\text{O}_3$	168
$\text{LiFeO}_4$	223	$\text{LiFe}_2\text{O}_6$	129	$\text{LiCoO}_2$	180	$\text{LiFePO}_4$	140

**Energy density is the product of voltage and capacity:**

***The area under the curve***





# A Problem with Iron Oxides

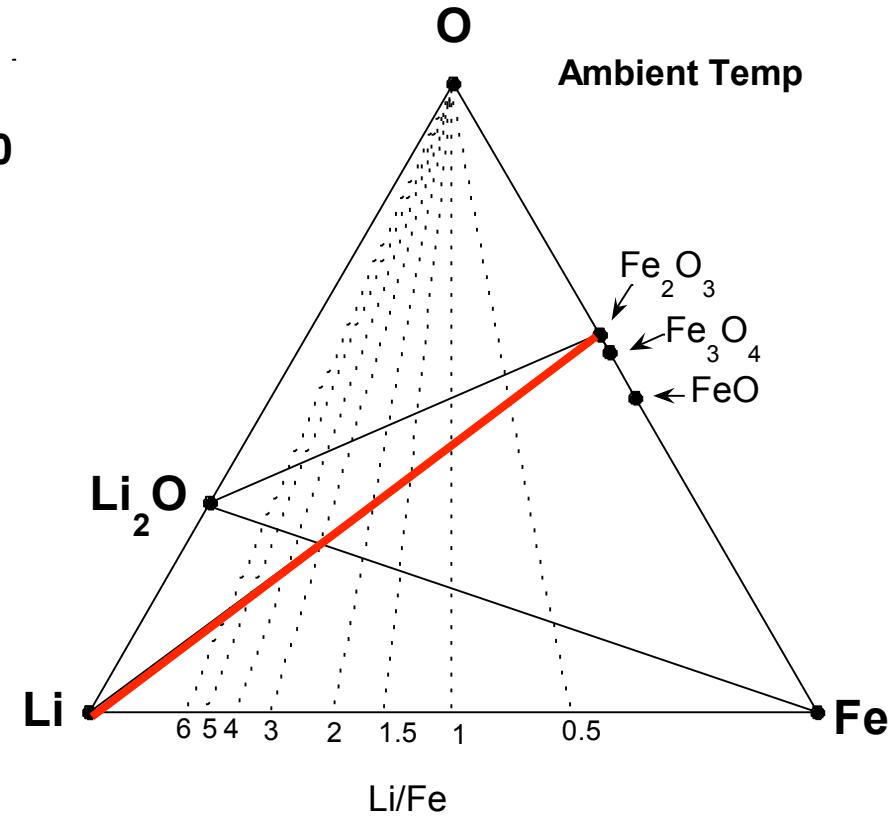
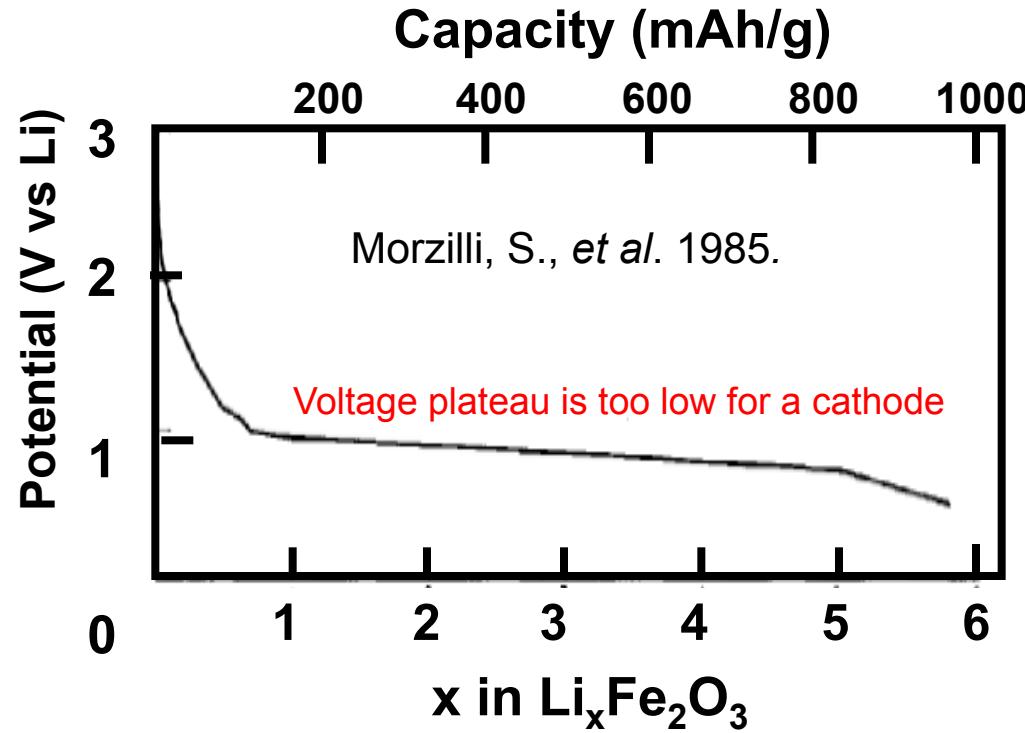


Iron oxide seems an obvious choice as an electroactive material...why aren't we using it in modern batteries?

Low voltage plateau

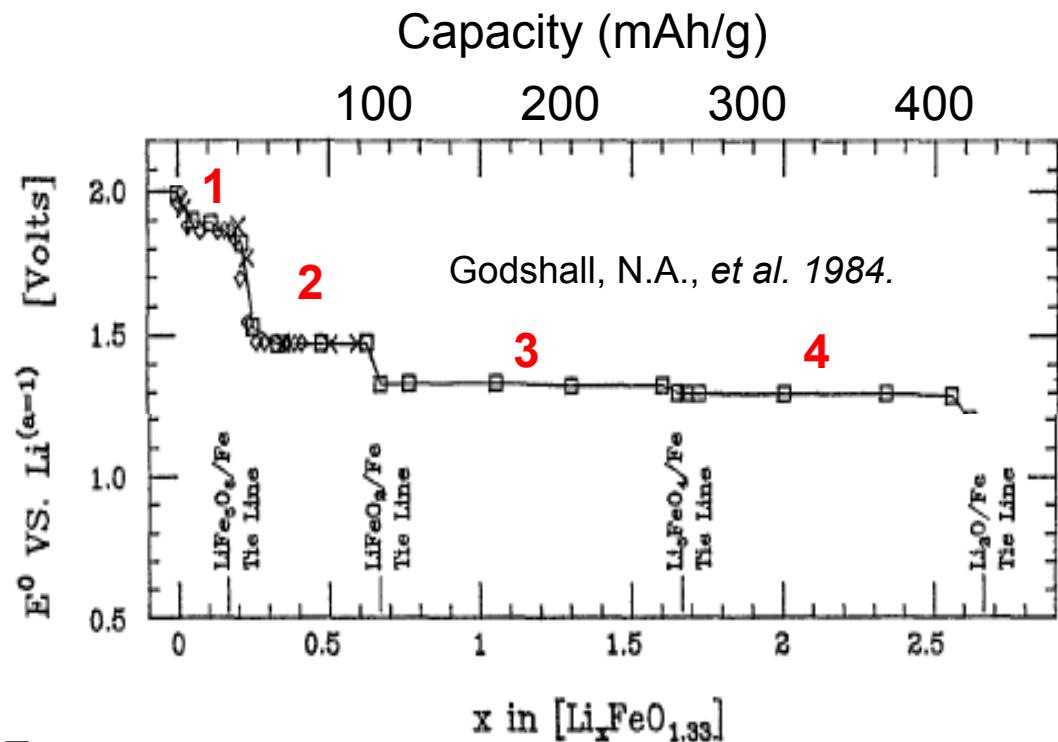
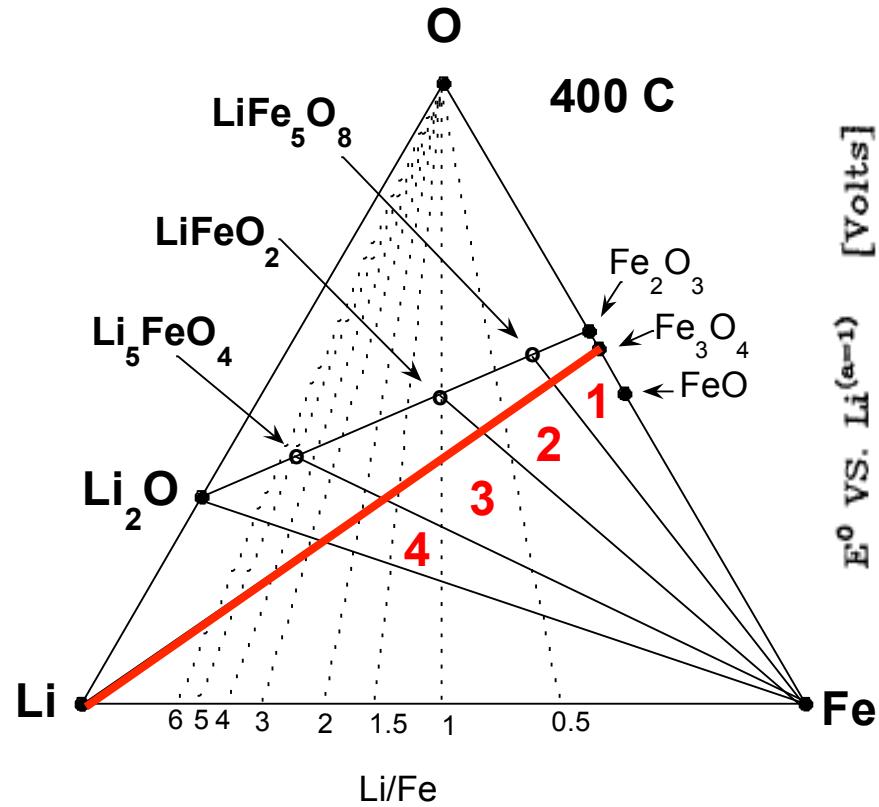
Poor (virtually non-existent!) cyclability

Slow kinetics (electrically and ionically diffusion limited)





# Extending Voltage Plateaus to Enhance Capacity



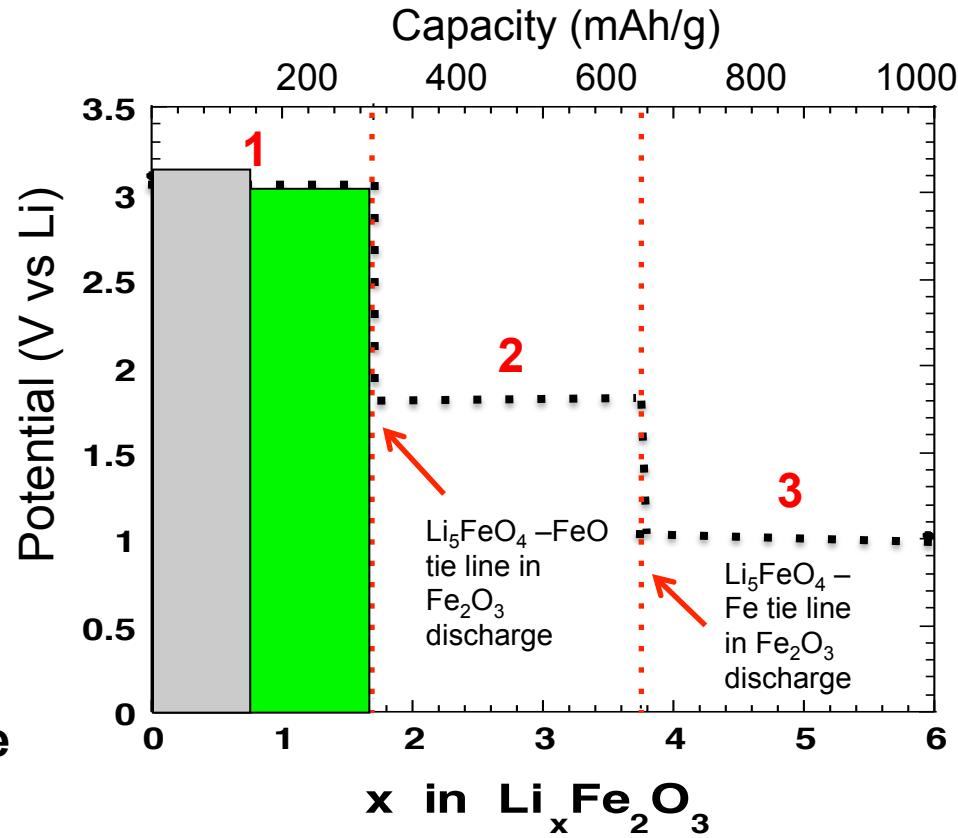
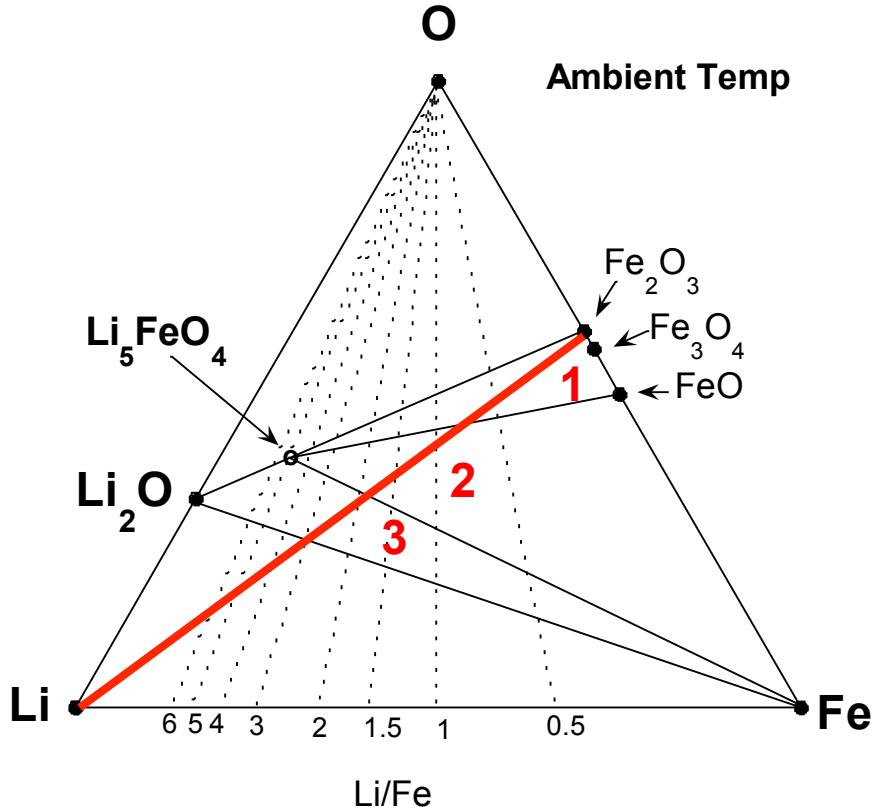
At 400°C “new” phases in the Li-Fe-O phase diagram are stable. These phases result in the formation of “Voltage Plateaus” that enhance capacity.



# Extending Voltage Plateaus at Room Temperature

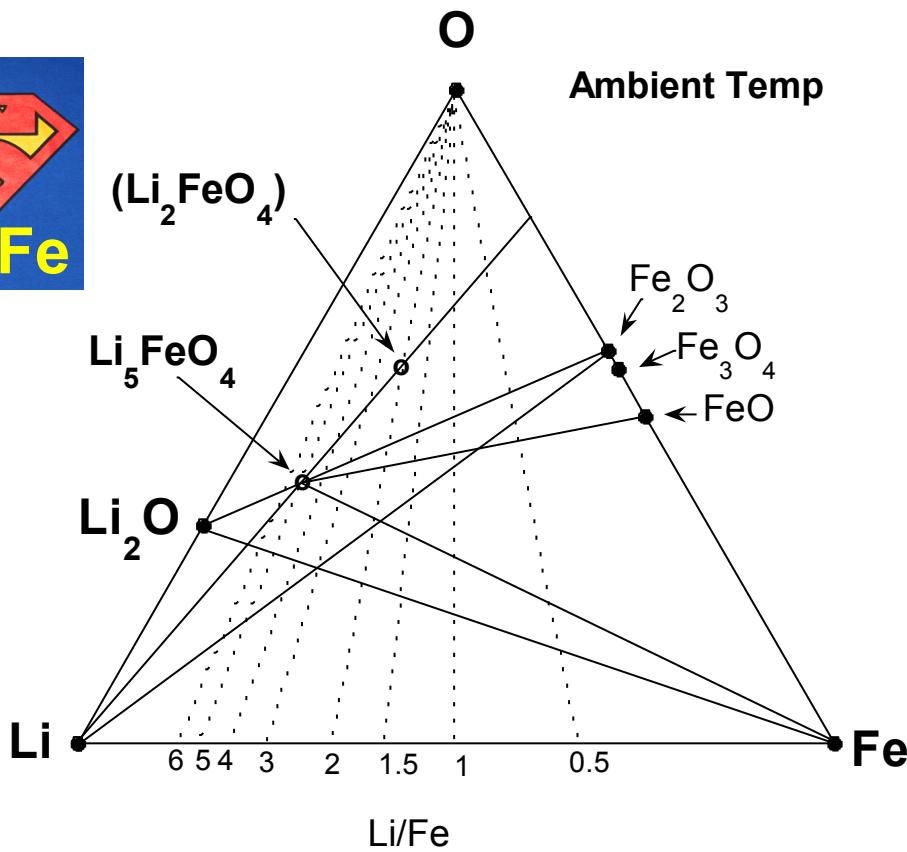


Controlling phase conversion behavior stands to impact energy density

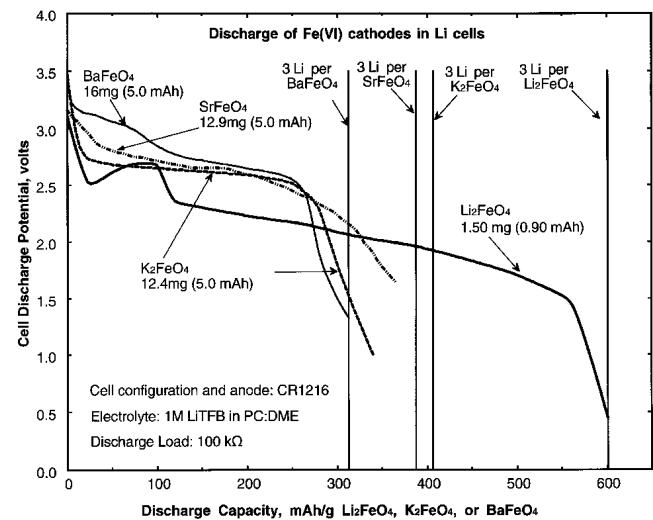


# Continuing to Explore Li-Fe-O Phase Space

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



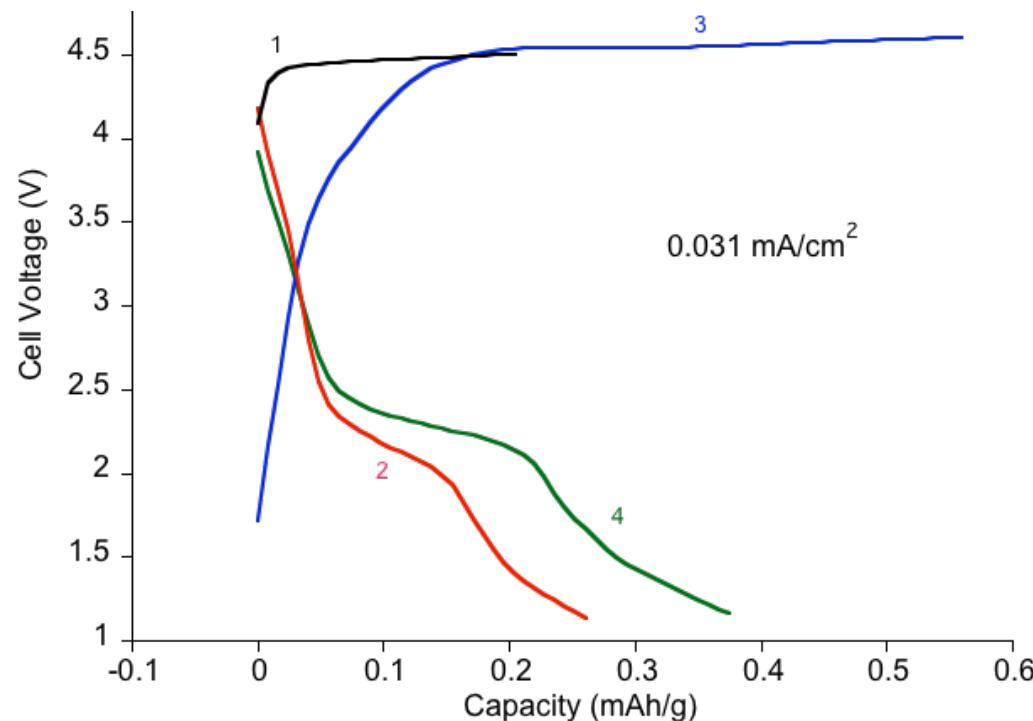
New phases of lithium iron oxide, such as those containing “Superiron” ( $\text{Fe}^{6+}$ ), promise higher voltages.





# Superiron – Not So Super?

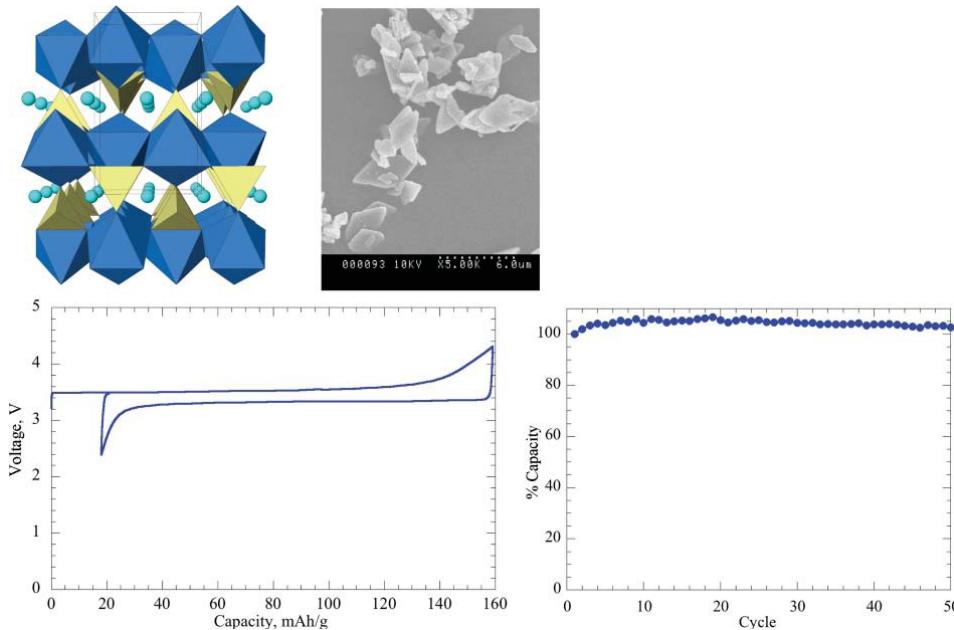
*Superiron ( $Fe^{6+}$ ) ferrates proved electrochemically inactive or synthetically impractical.*





# LiFePO<sub>4</sub>: A “small” success

LiFePO<sub>4</sub> has emerged as a very promising, very fast lithium intercalation cathode



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

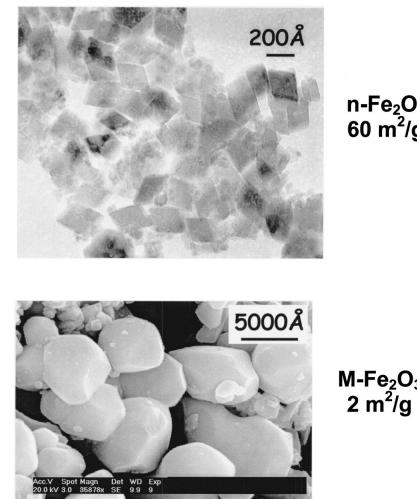
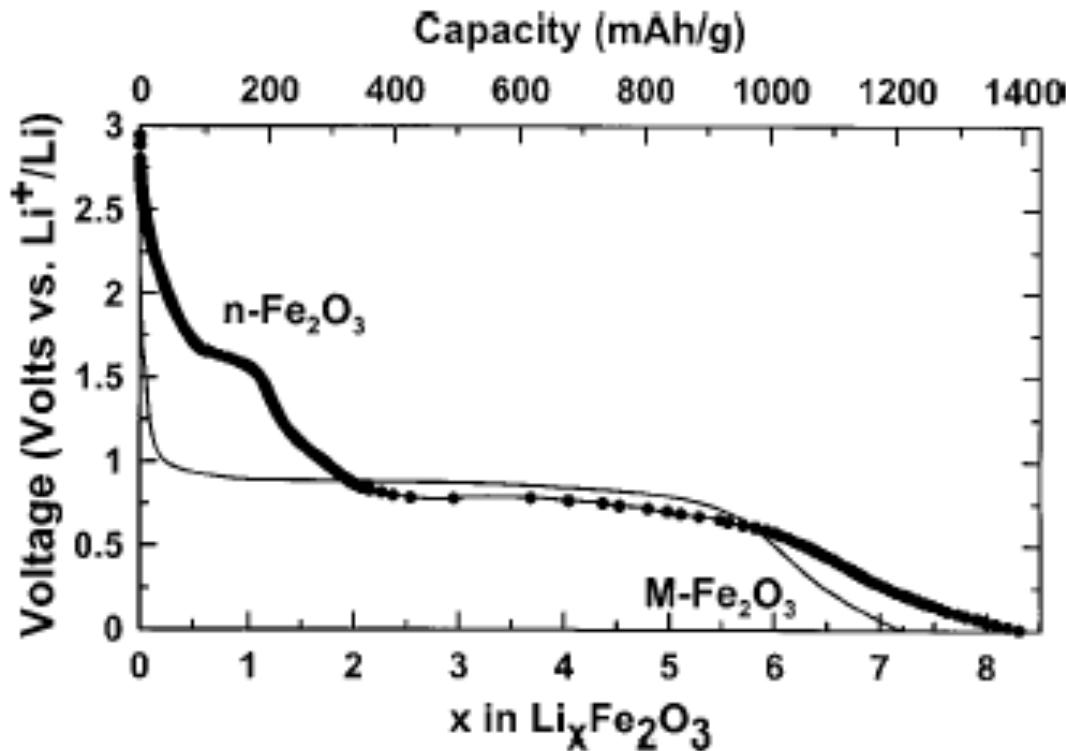
- But...packing density drops dramatically
- Higher surface area means you need more binder – you lose active material.
- LiFePO<sub>4</sub> is a poor electrical conductor

Largely resolved by doping or integrating with nanoconductive carbons  
SWNTs have also been considered – high electrical conductivity ( $5 \times 10^5$  S/m)



# Nano-Enabled $\text{Fe}_2\text{O}_3$ Cathodes

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



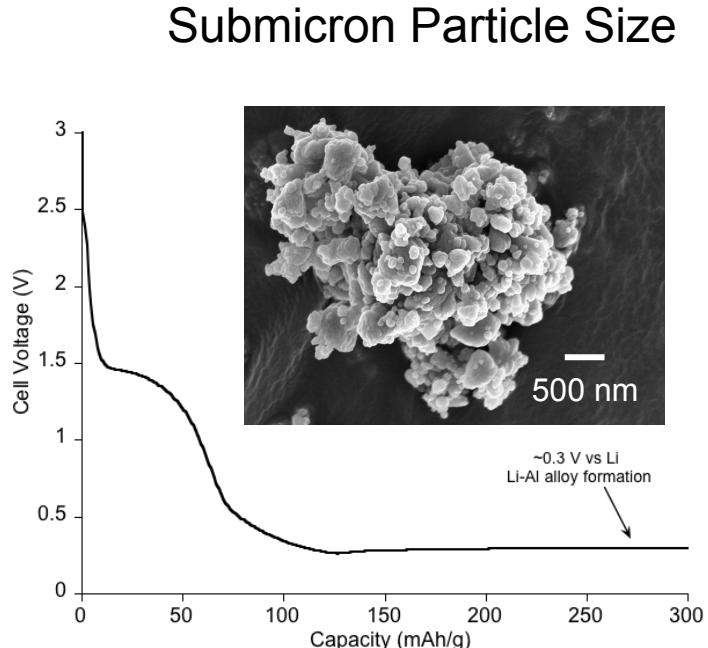
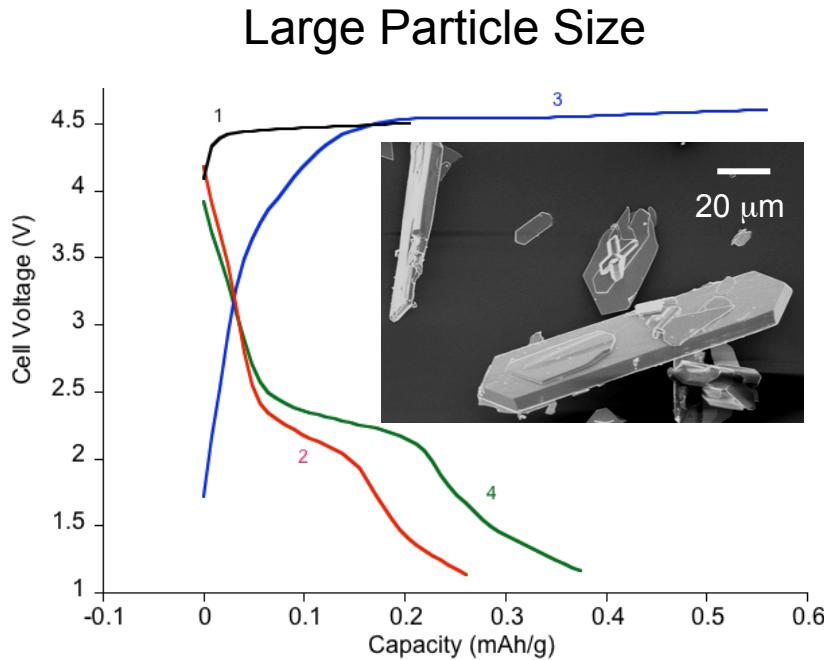


# Size-Dependent Cathode Enhancement



*Reducing particle size can produce extended voltage plateaus.*

Consider  $\text{K}_2\text{FeO}_4$



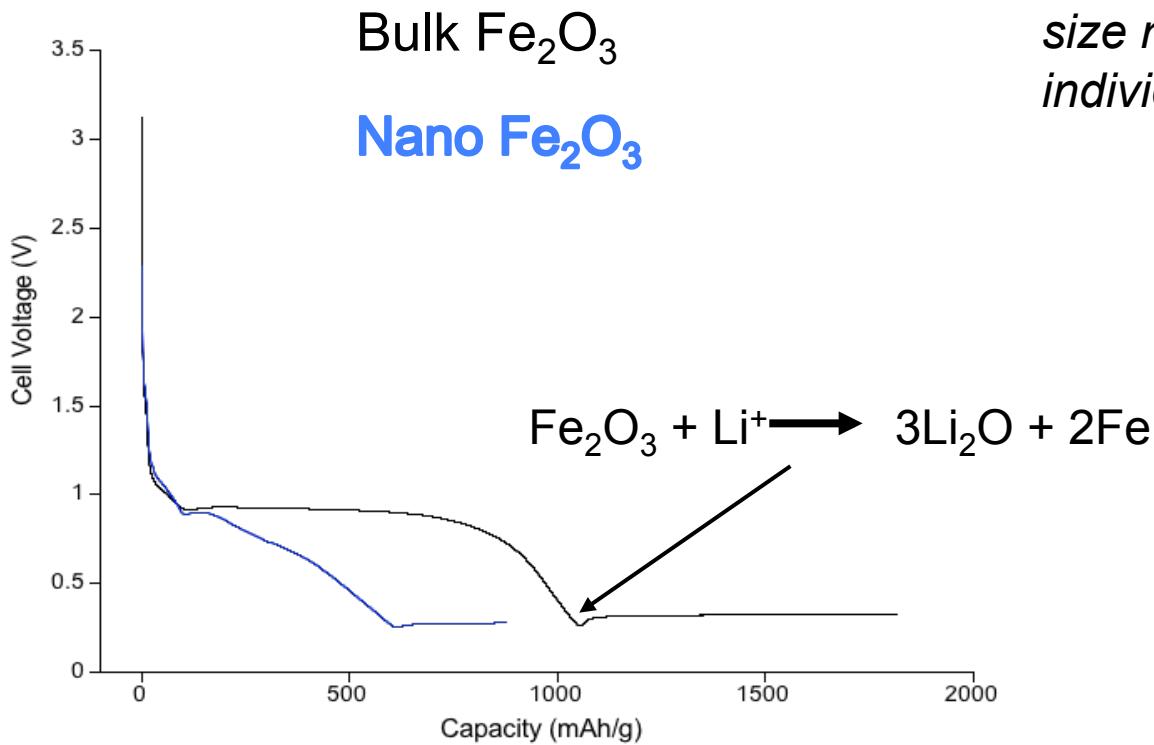


# Is “Nano” Universally Beneficial?

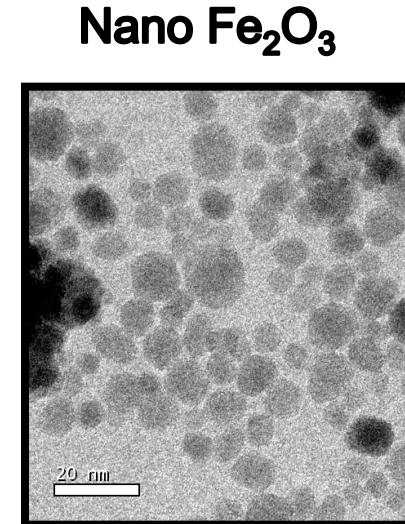


Reducing particles to nanoscale only improves performance in select phases...

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



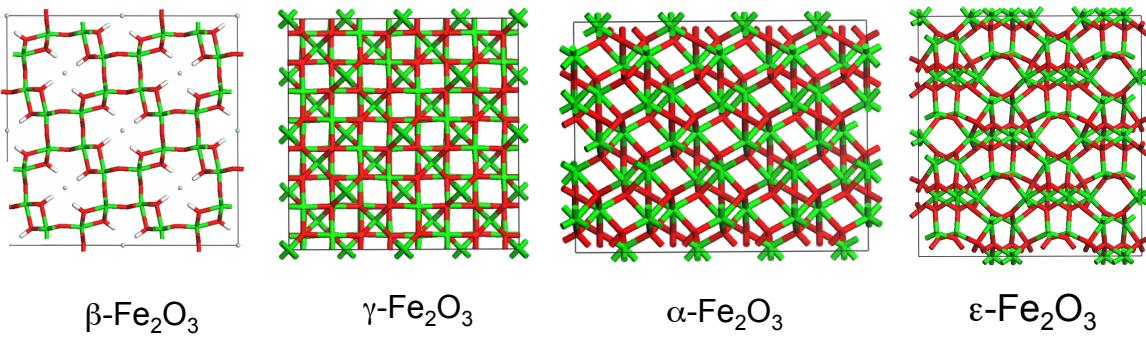
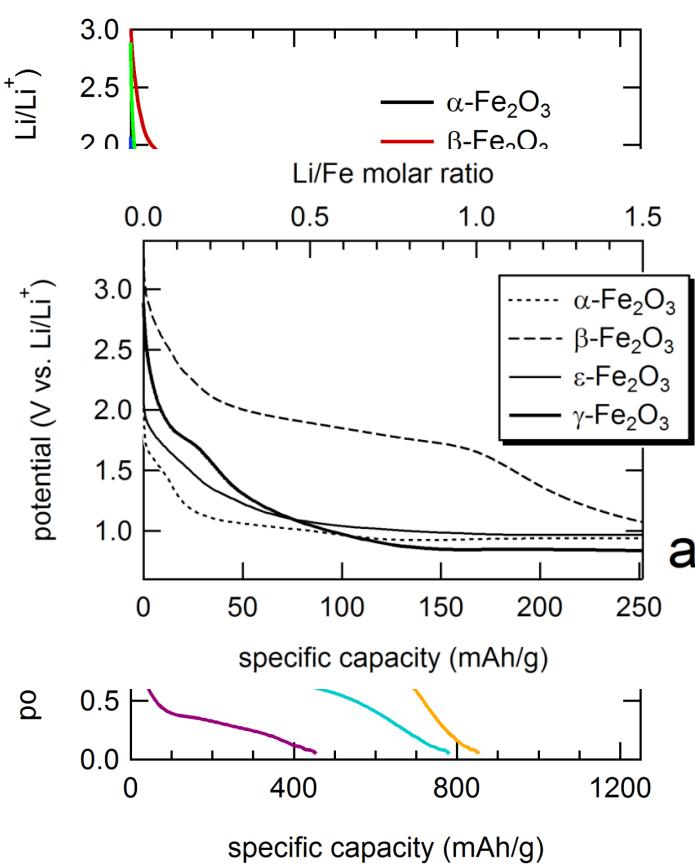
*The effect of reducing particle size must be considered on an individual materials basis.*



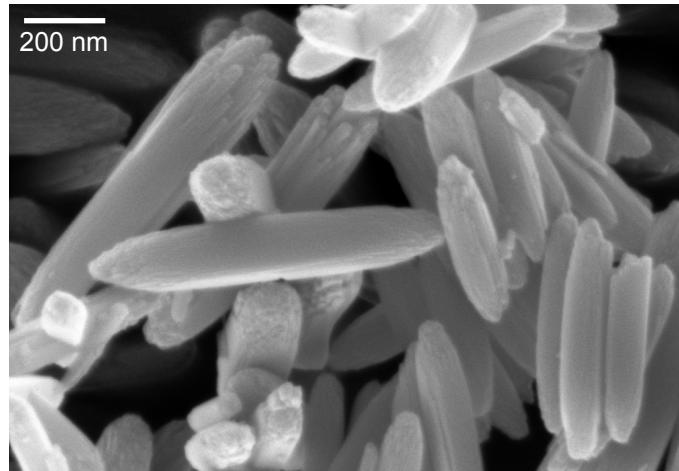
# Discharge Behavior of Iron Oxides



Iron oxides show consistent\* voltage plateaus around 1V



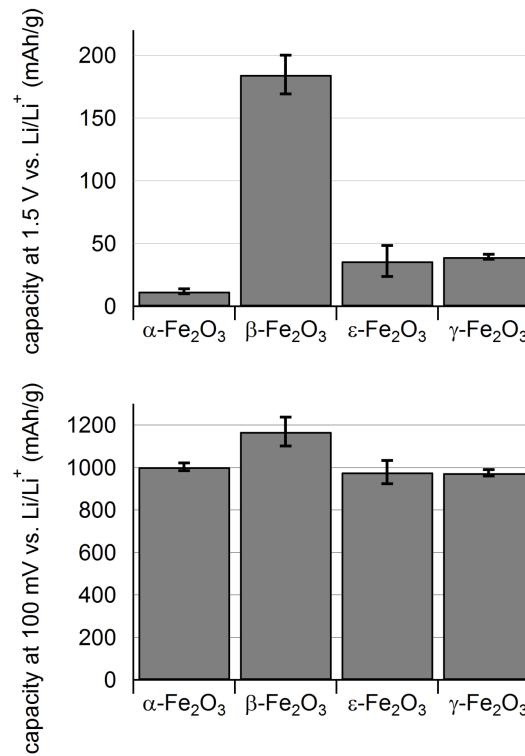
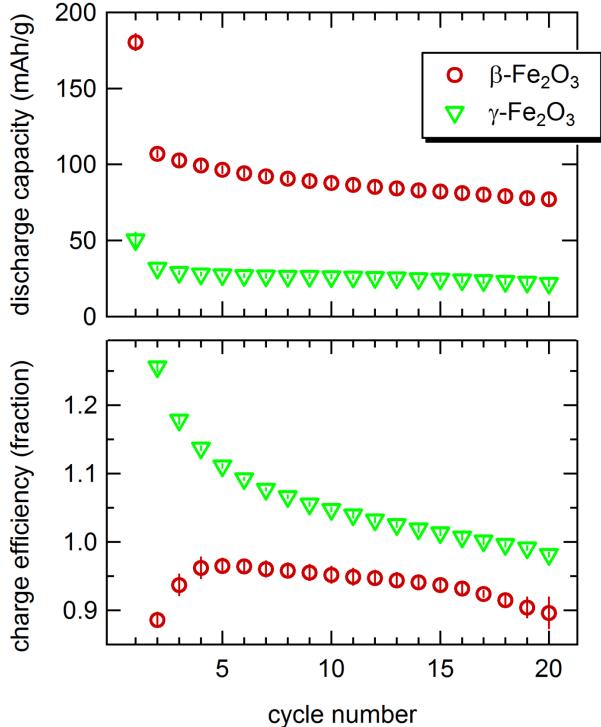
\*  $\beta\text{-Fe}_2\text{O}_3$  (image right) shows unique extended capacity and good cyclability near 2V.



# Electrochemical Cycling of Iron Oxides



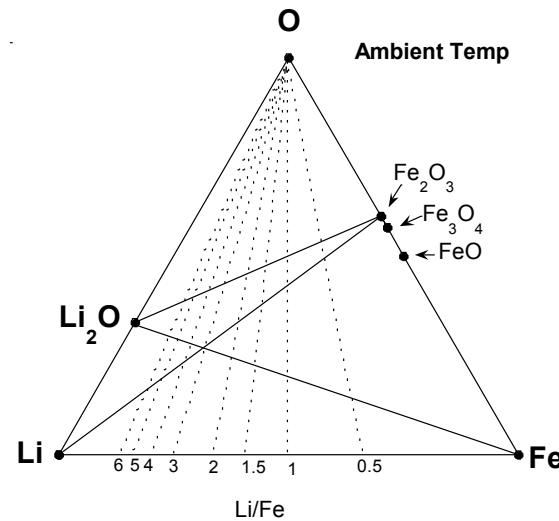
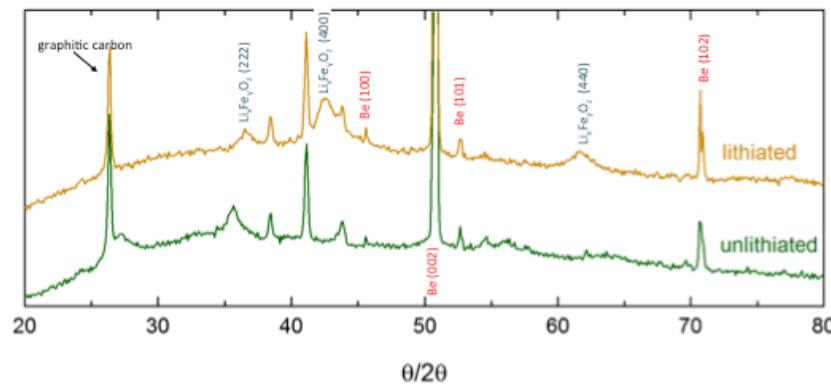
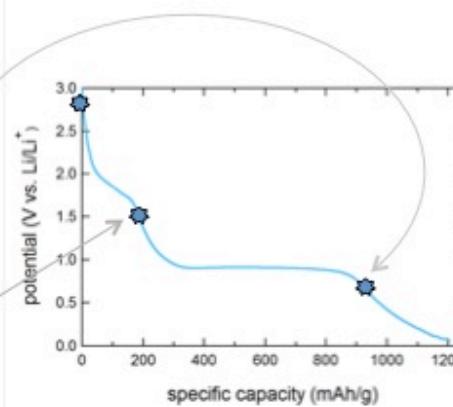
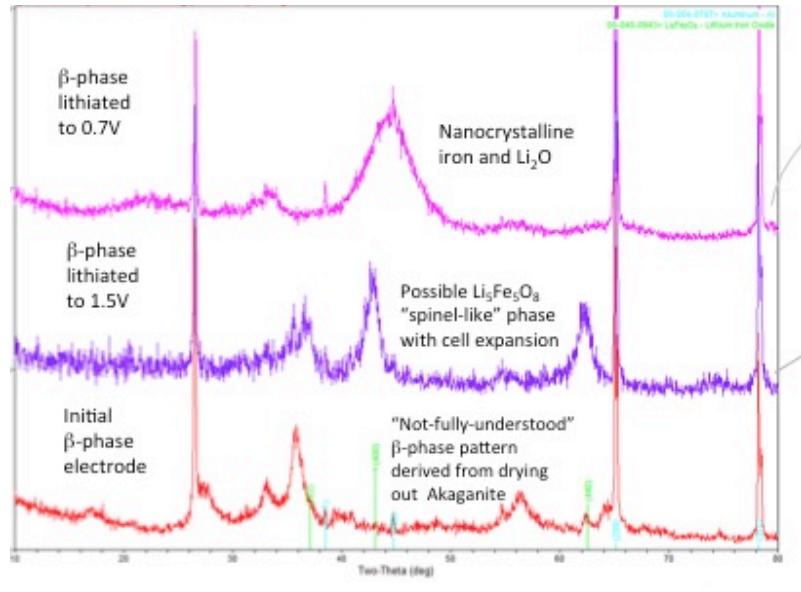
$\beta\text{-Fe}_2\text{O}_3$  cycling, charge efficiency, and capacity are all enhanced relative to other  $\text{Fe}_2\text{O}_3$  polymorphs





# Understanding $\beta$ -Fe<sub>2</sub>O<sub>3</sub>

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

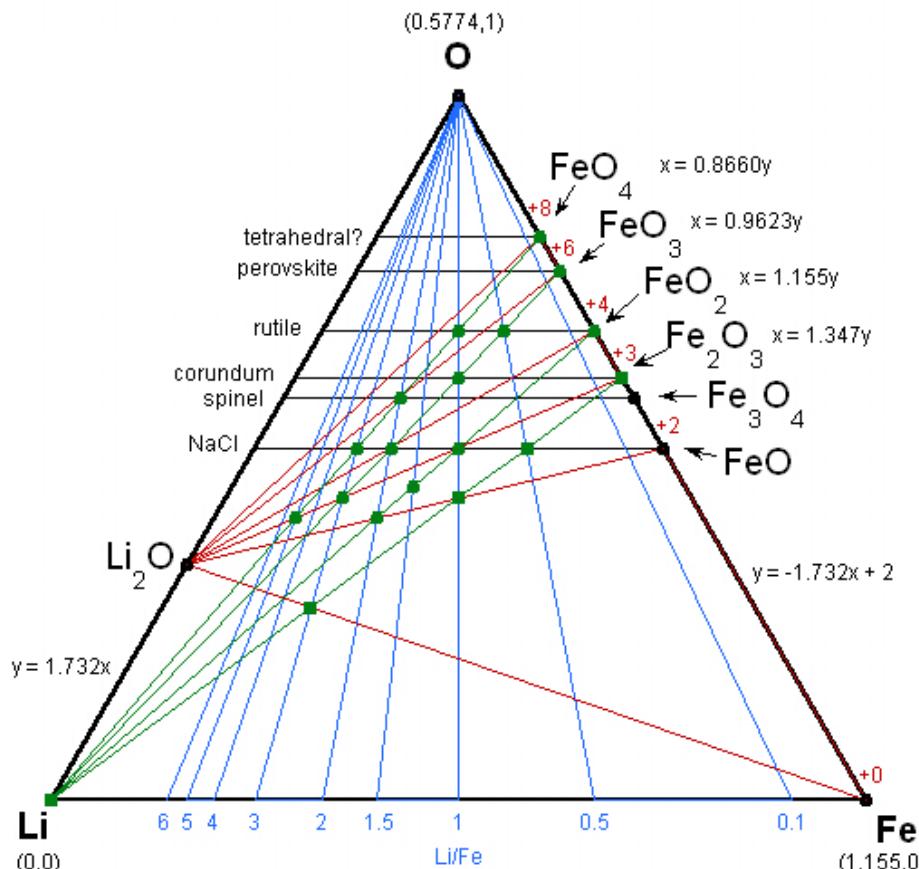




# Phase Change Kinetics



Phase transformations in  $\text{Fe}_2\text{O}_3$  will be kinetically slow...



$\text{LiFePO}_4$  is kinetically fast in part because reversible Li intercalation does not change crystal structure.

$\text{LiFePO}_4$  (triphylite) and  $\text{FePO}_4$  (heterosite) are both olivine-like orthorhombic crystal structures.

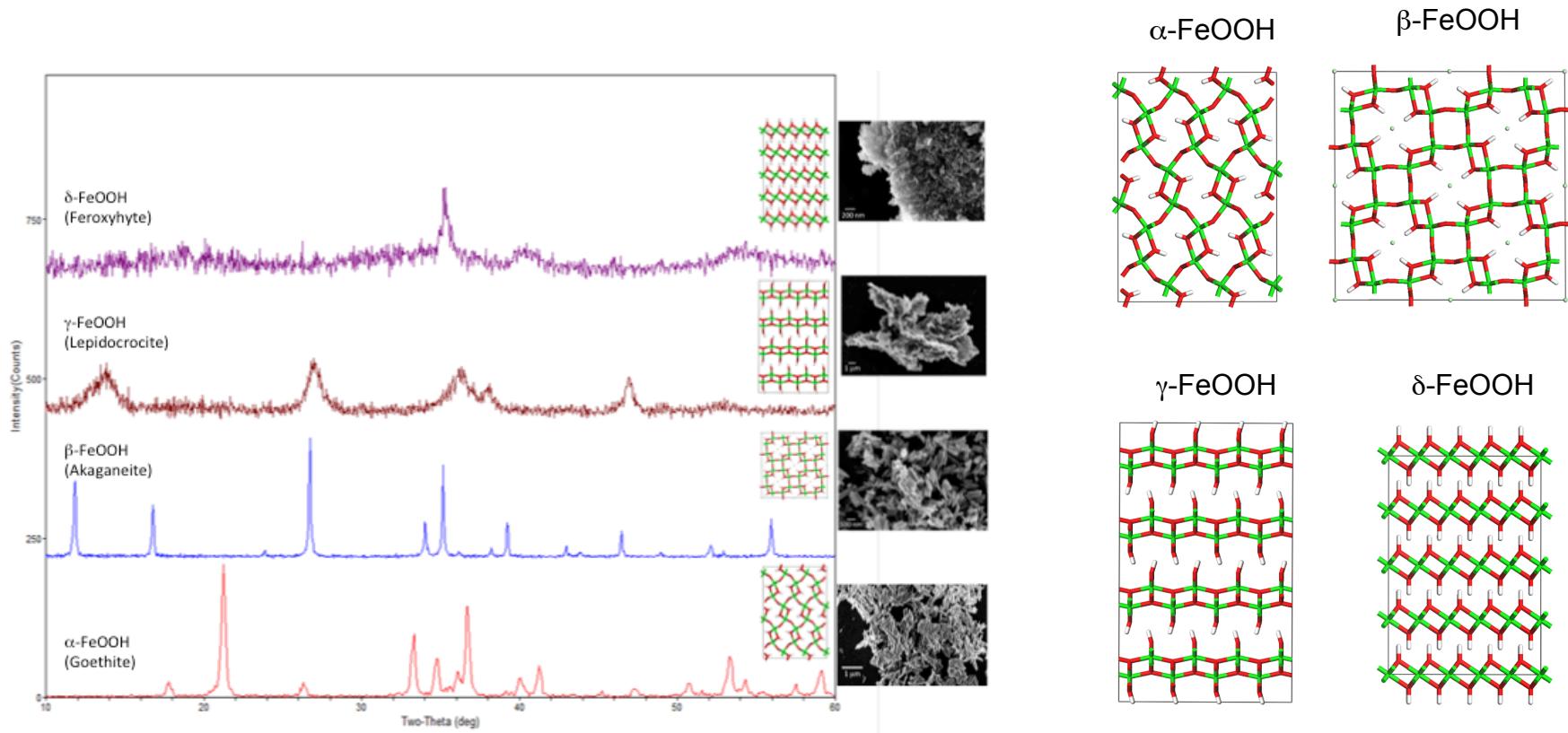
Iron oxides may have significantly greater crystallographic change during cycling.



# Open Lattices: FeOOH Polymorphs



Taking a cue from the  $\beta$ -Fe<sub>2</sub>O<sub>3</sub> work, consider FeOOH polymorphs

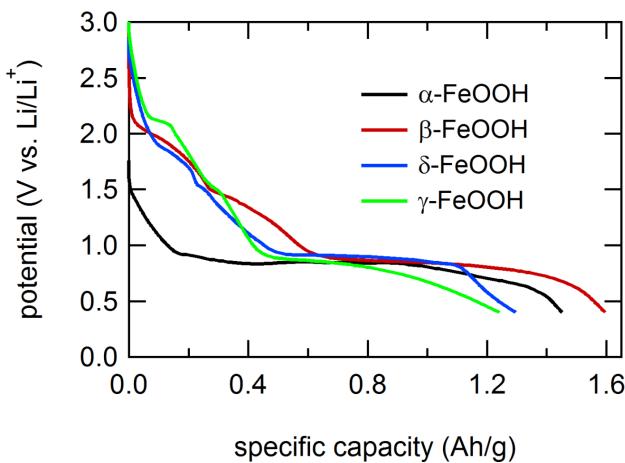
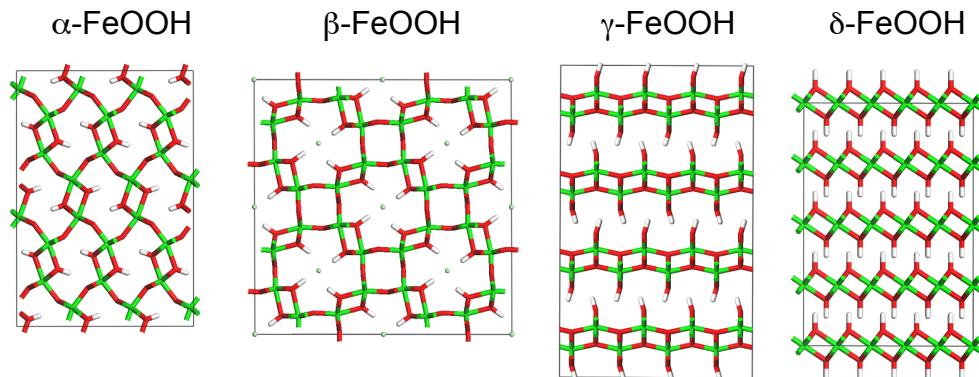




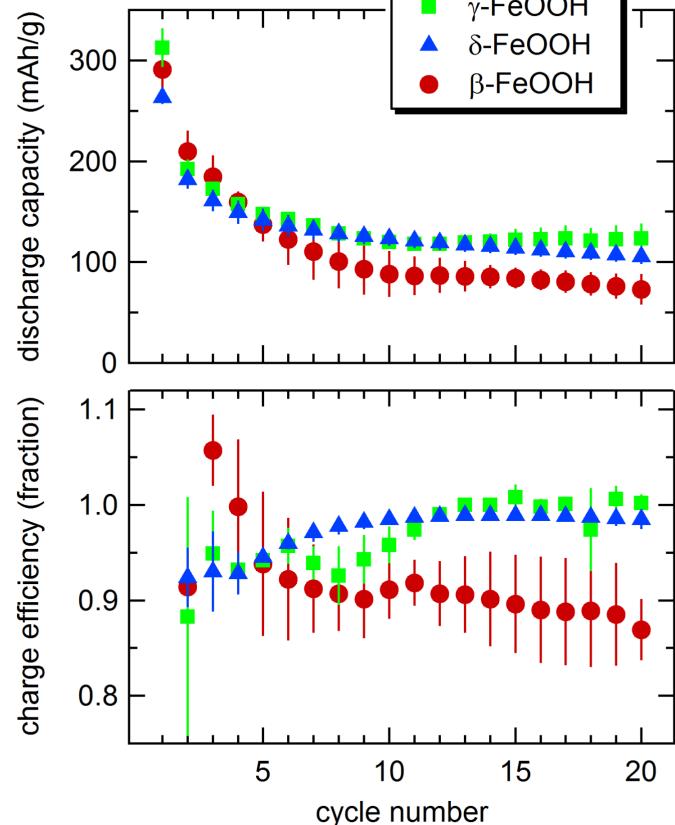
# Electrochemistry of FeOOH



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



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



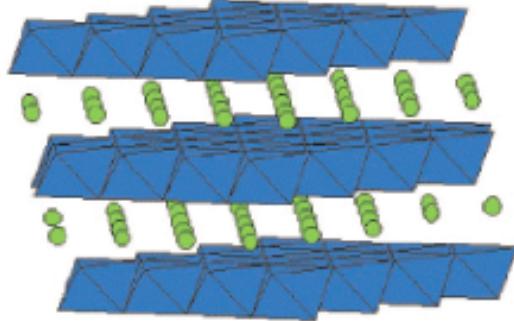


# Ion Pathways in Cathodes

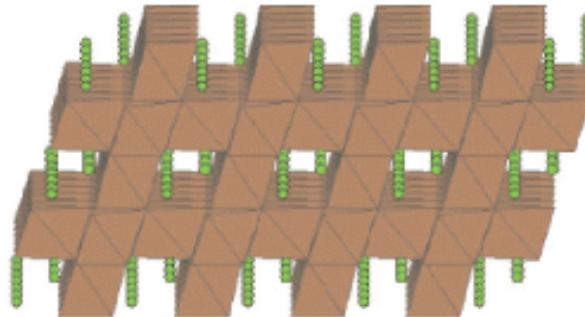


Other layered materials are known to be effective cathodes owing to excellent ion transport properties.

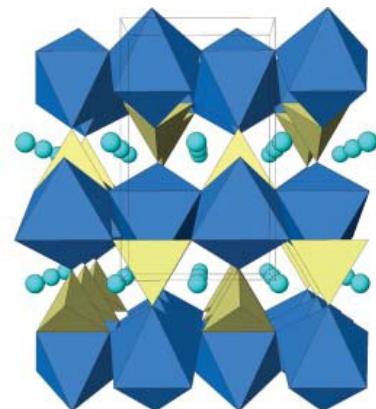
$\text{LiCoO}_2$



$\text{LiMn}_2\text{O}_4$

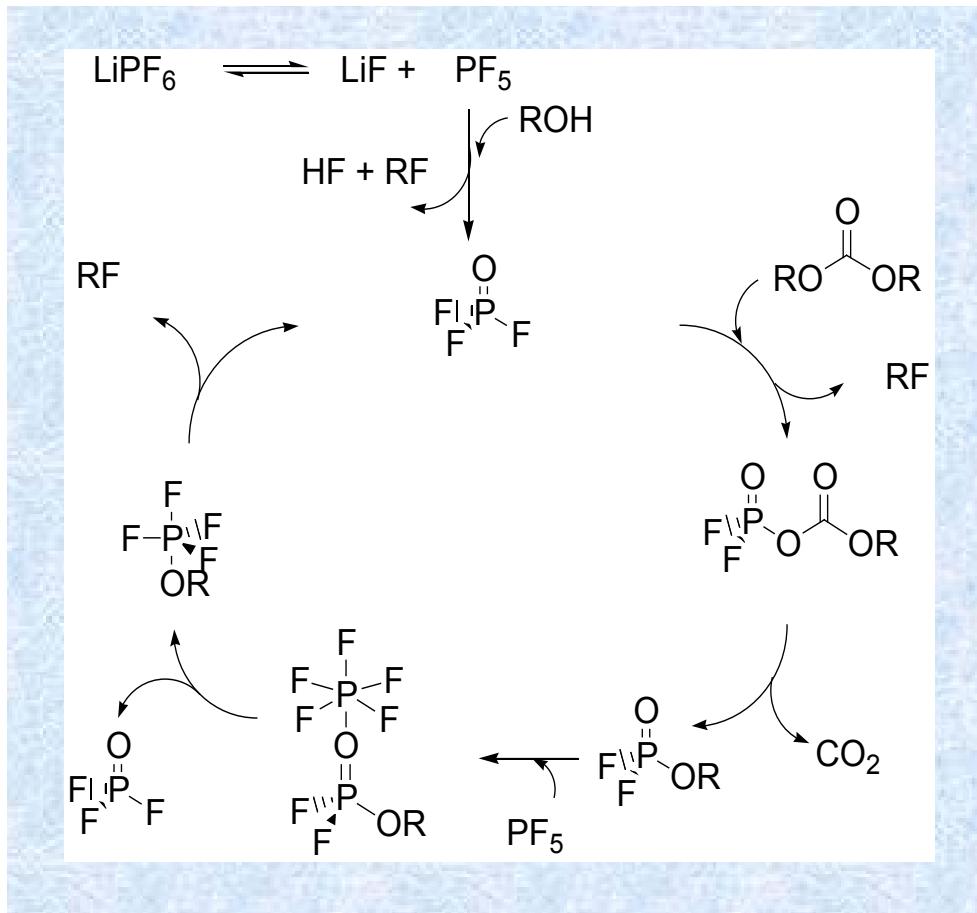


$\text{LiFePO}_4$





# 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!

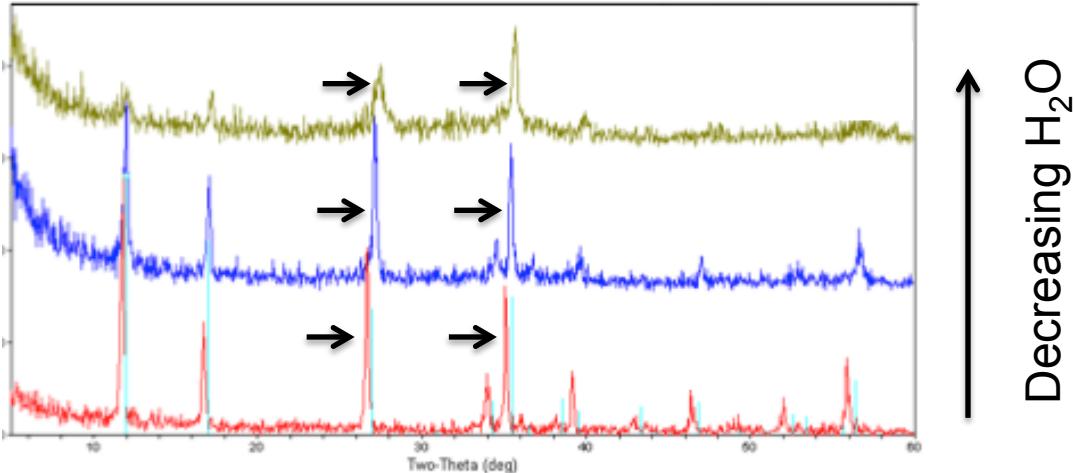
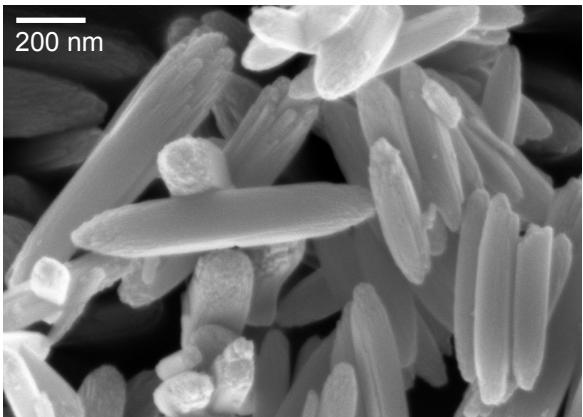
**Not Good!**



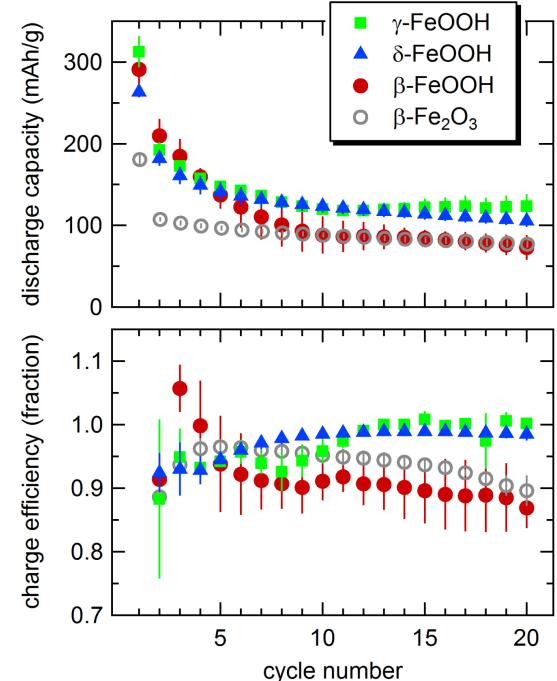
# Solving the Problem with FeOOH?



## 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:

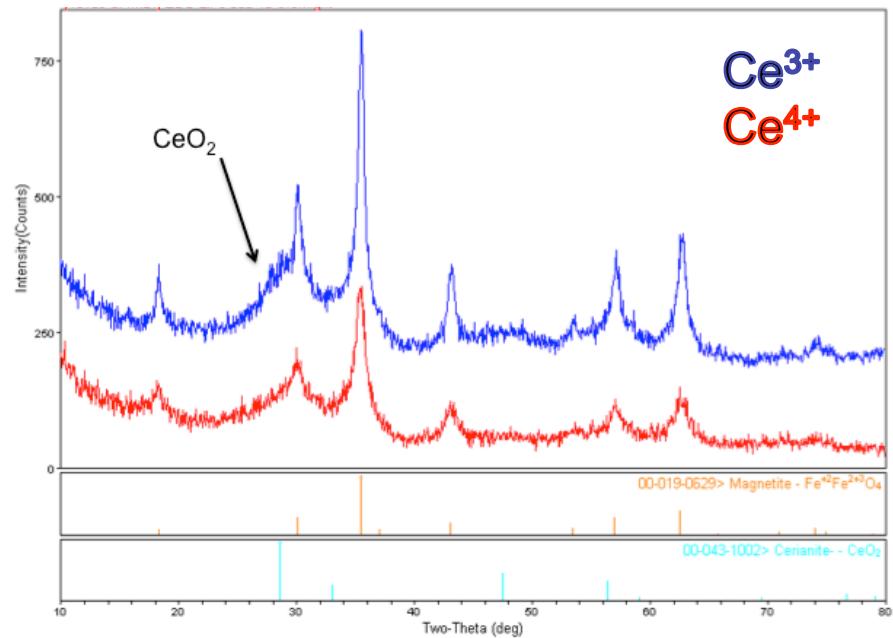
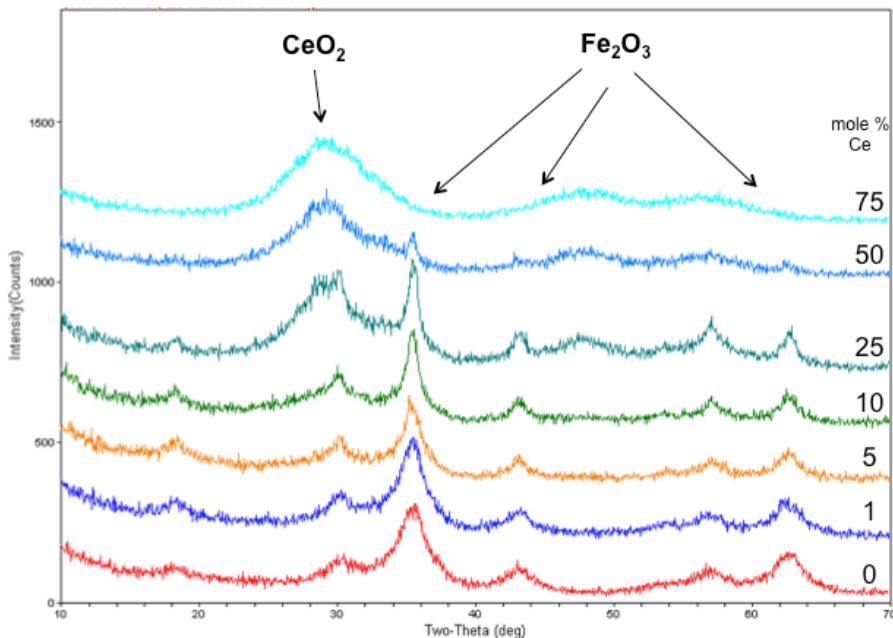




# Cationic Doping Maghemite



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

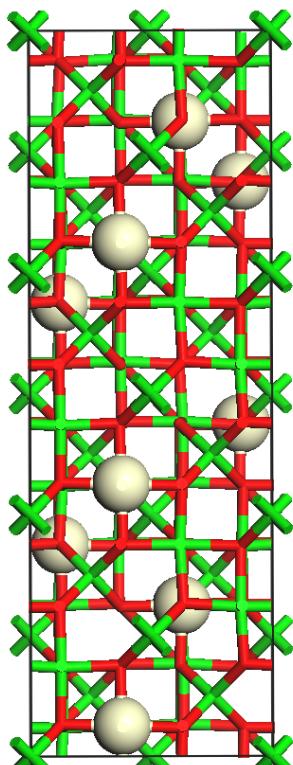




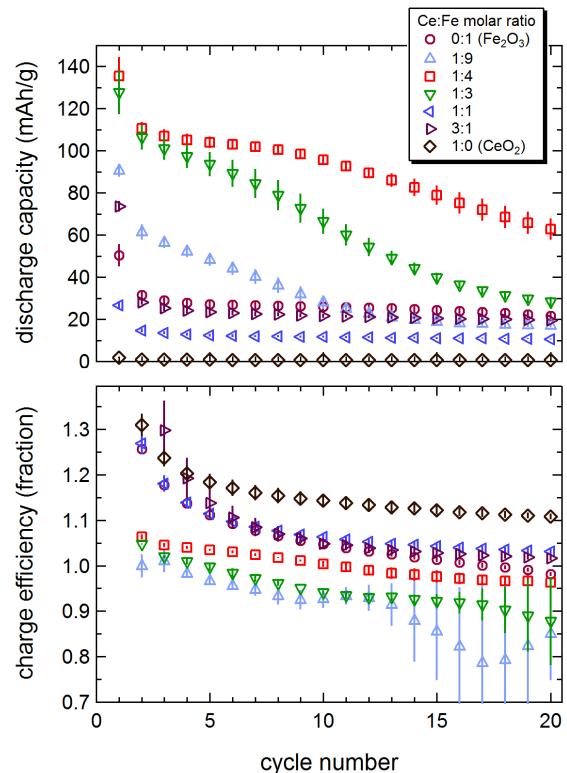
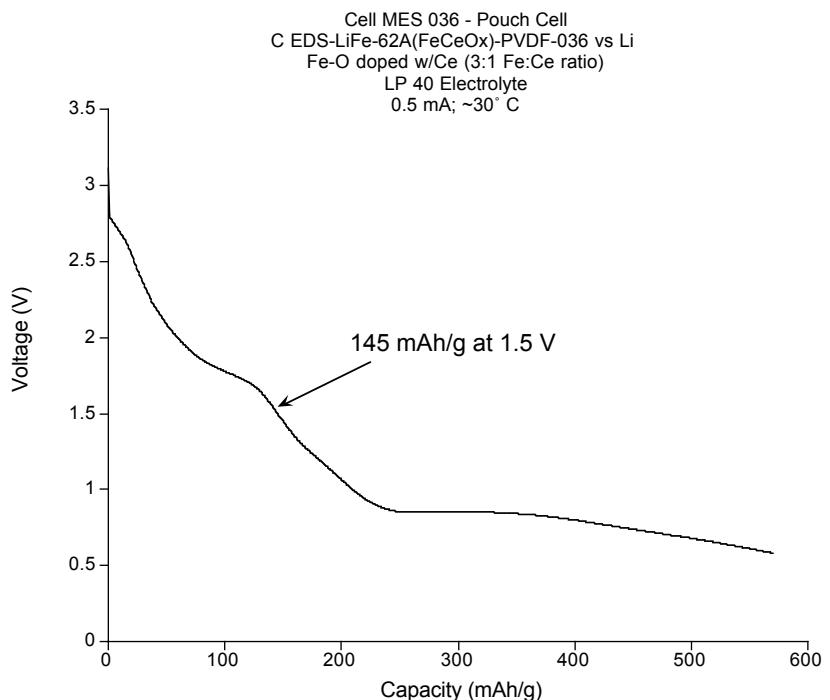
# Electrochemistry of Ce- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>



Doping the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> crystal lattice with large cations improves electrochemical behavior



Ce-doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>



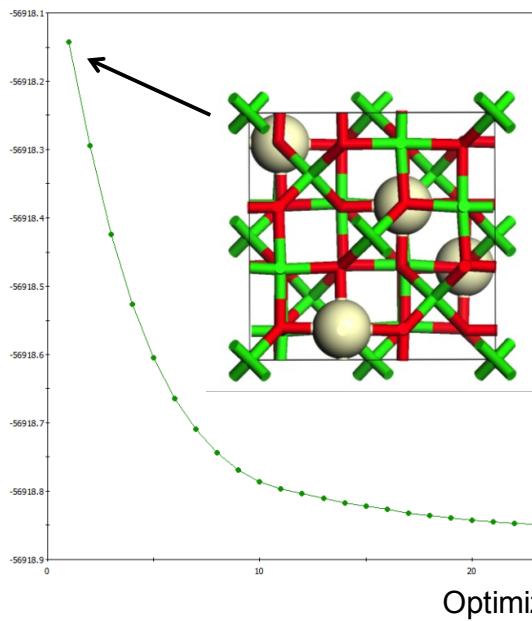


# Modeling Cerium Doping

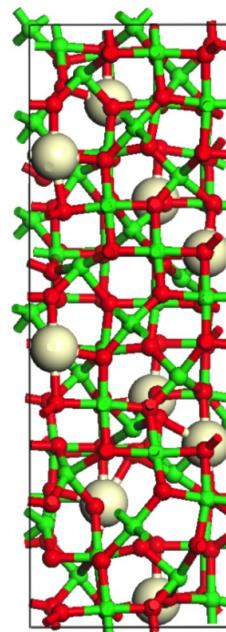
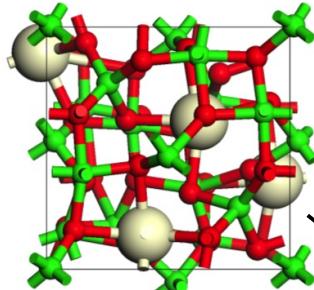


Potential energy convergence and structures for the DFT optimization of highly defective Ce-doped  $\gamma\text{-Fe}_2\text{O}_3$  shows significant lattice distortion.

Energy (Ha)

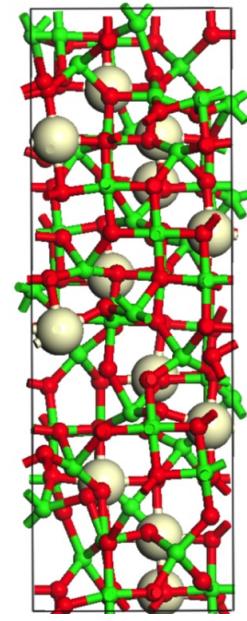


DFT optimized  
spin unrestricted  
PW91 functionals



$r_{\text{Ce}4+} = 1.01 \text{ \AA}$   
 $\text{Ce}_9\text{Fe}_{52}\text{O}_{96}$   
 $X_{\text{Ce}} = 0.15$

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



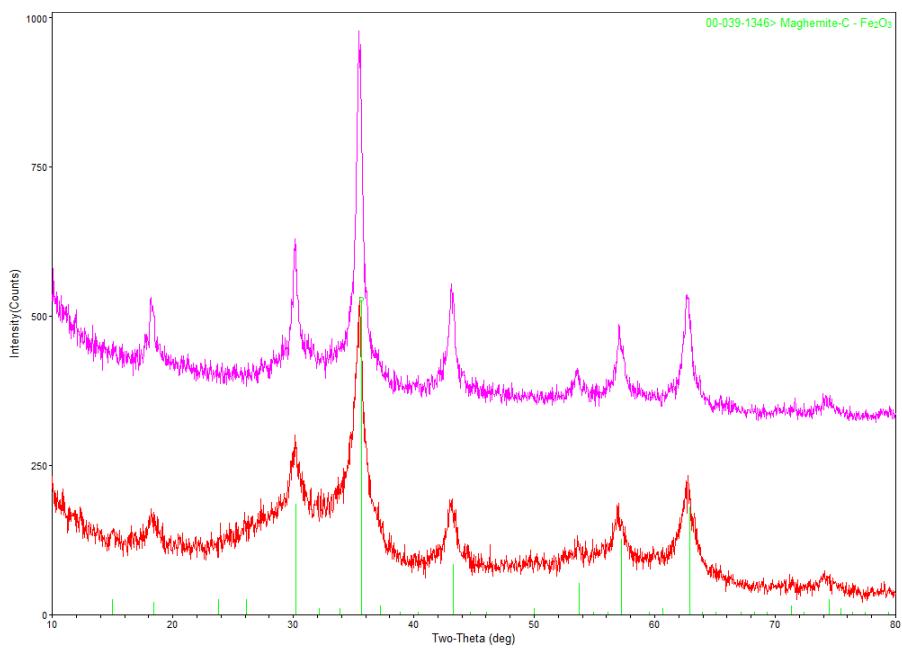
$r_{\text{Ce}4+} = 1.01 \text{ \AA}$   
 $\text{Ce}_{12}\text{Fe}_{48}\text{O}_{96}$   
 $X_{\text{Ce}} = 0.19$

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

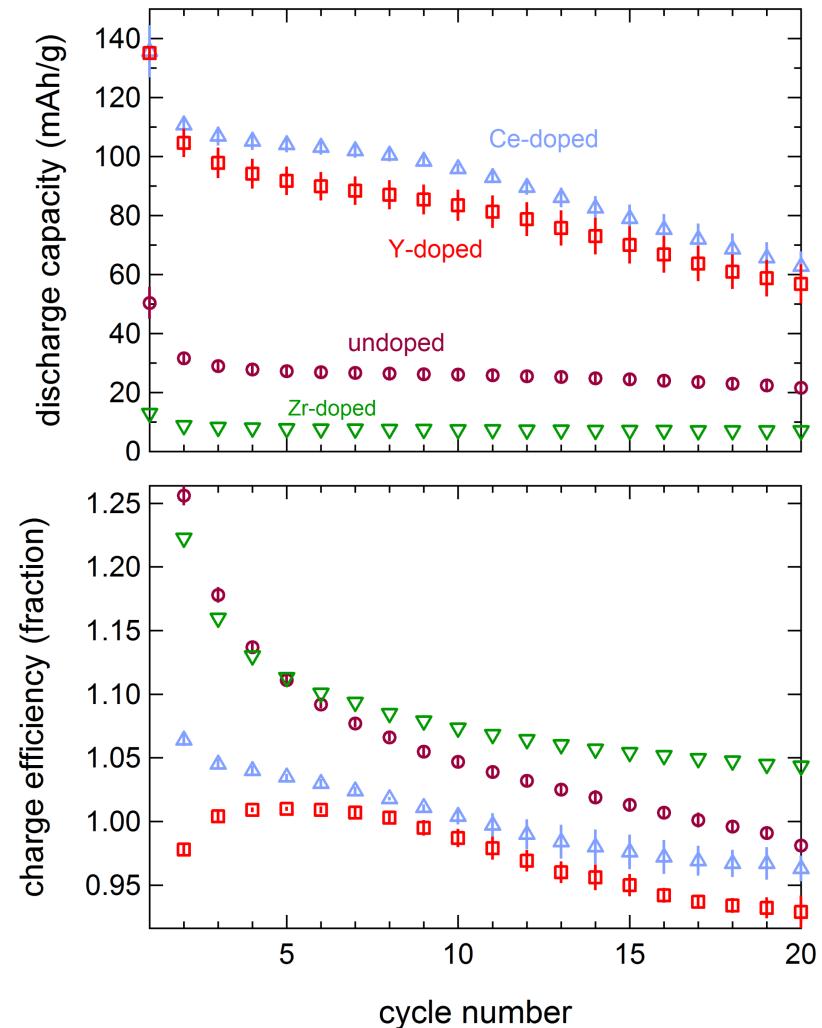


# Size Matters

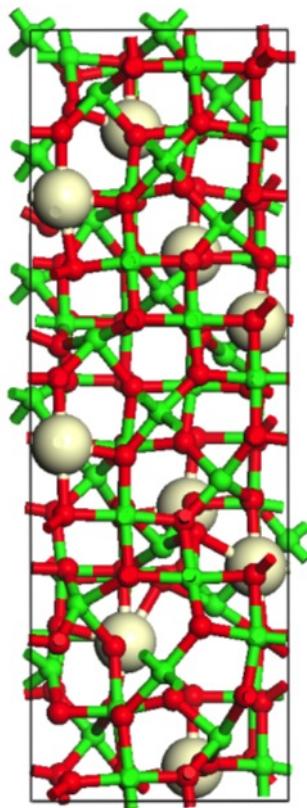
Improved electrochemical performance is tied to the size, not the charge of the dopant.



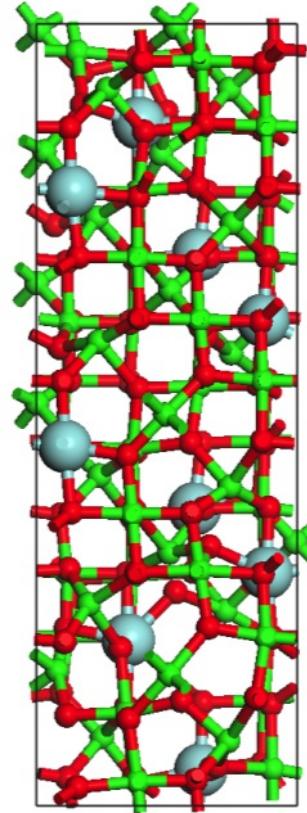
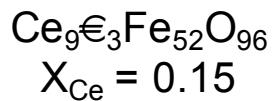
$$^*r_{\text{Ce(IV)}} = 1.01\text{\AA}, r_{\text{Y(III)}} = 1.04\text{\AA}, r_{\text{Zr(IV)}} = 0.86\text{\AA}$$



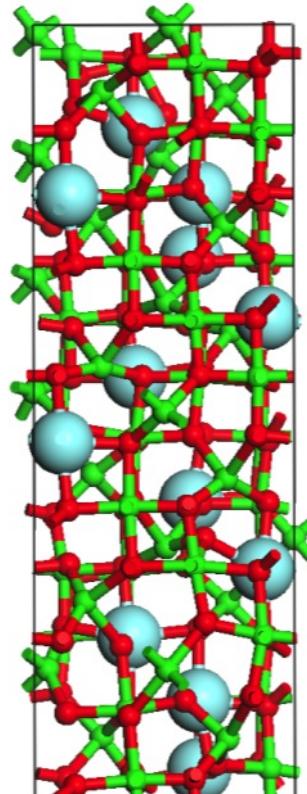
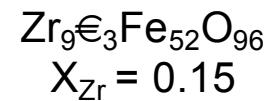
# Comparing Cationic Doping



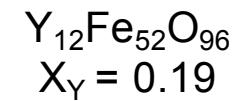
$$r_{\text{Ce}^{4+}} = 1.01 \text{ \AA}$$



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



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





# Acknowledgements

## Collaborators

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Frank Delnick  
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Mike Stoll

**Mark Rodriguez**

Randy Cygan

**Holly Zarick**  
Jill Wheeler  
Tim Boyle

## Funding

Sandia's Laboratory Directed Research and Development Program



# Thanks!



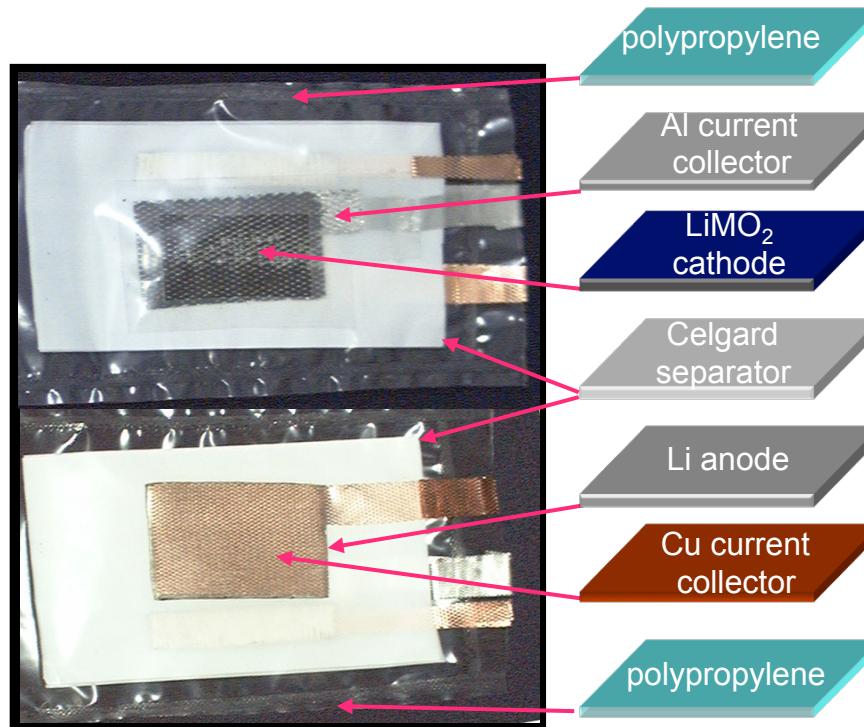
# Backup Slides



# *In situ* Diffraction Coupled with Electrochemical Testing



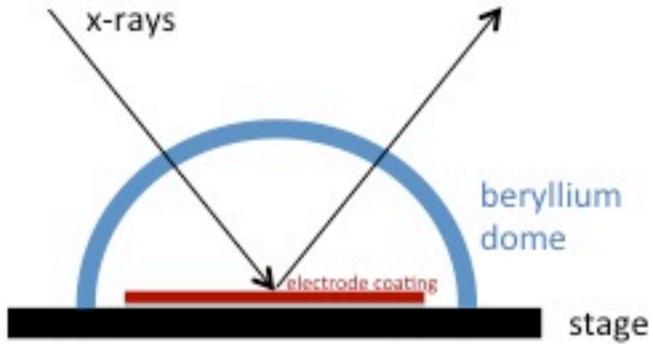
*Electrochemical “pouch” cells can be used to perform “in situ” diffraction analysis during electrochemical cycling*



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

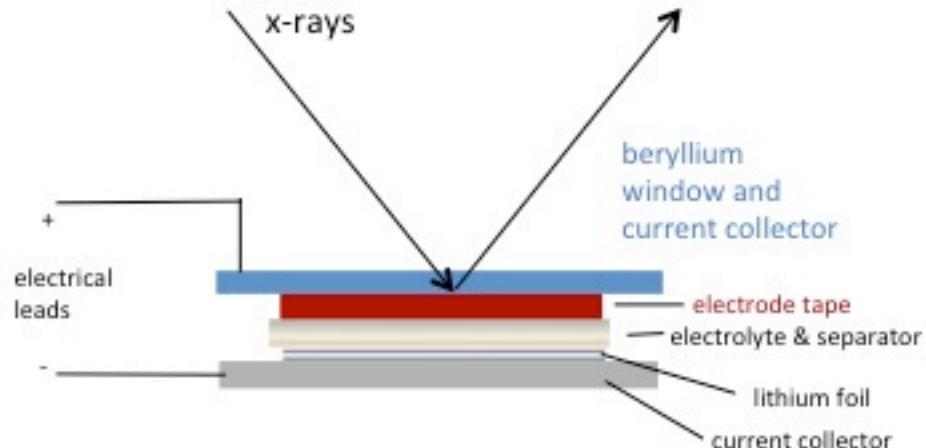


## *Ex Situ* Measurements



- 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

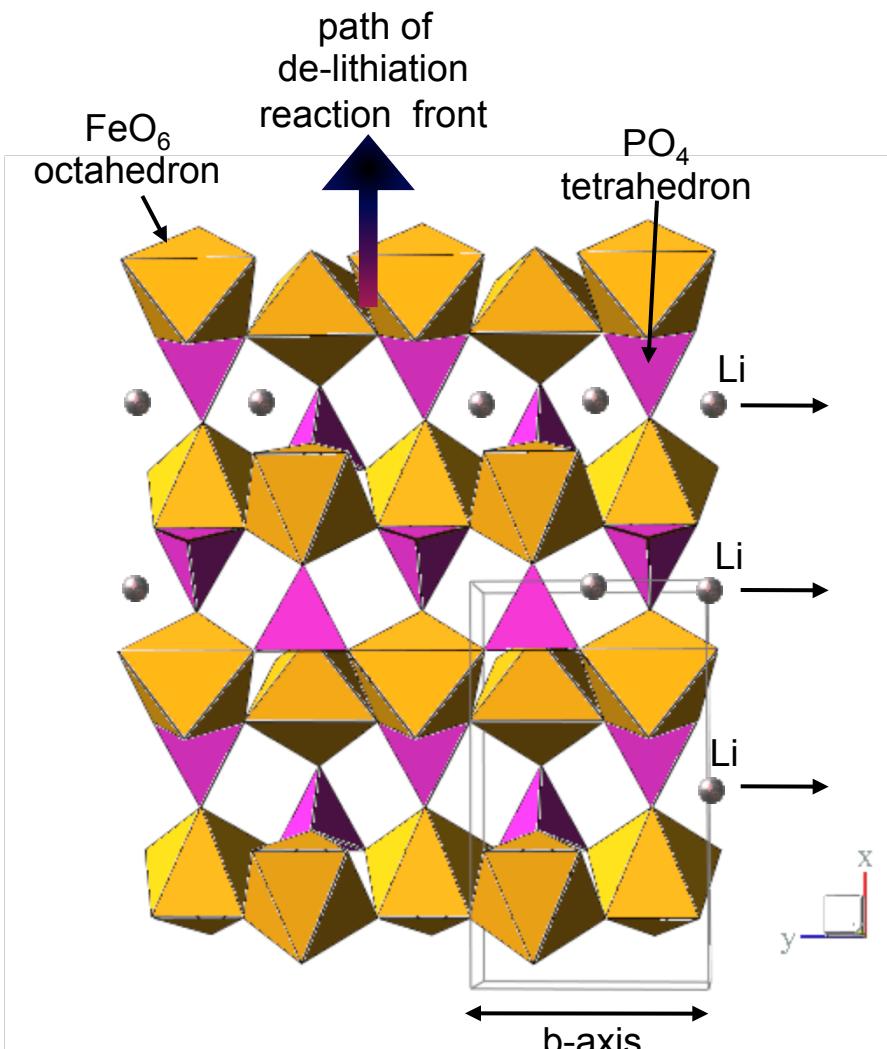
## *In Situ* Measurements



- 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<sub>4</sub>

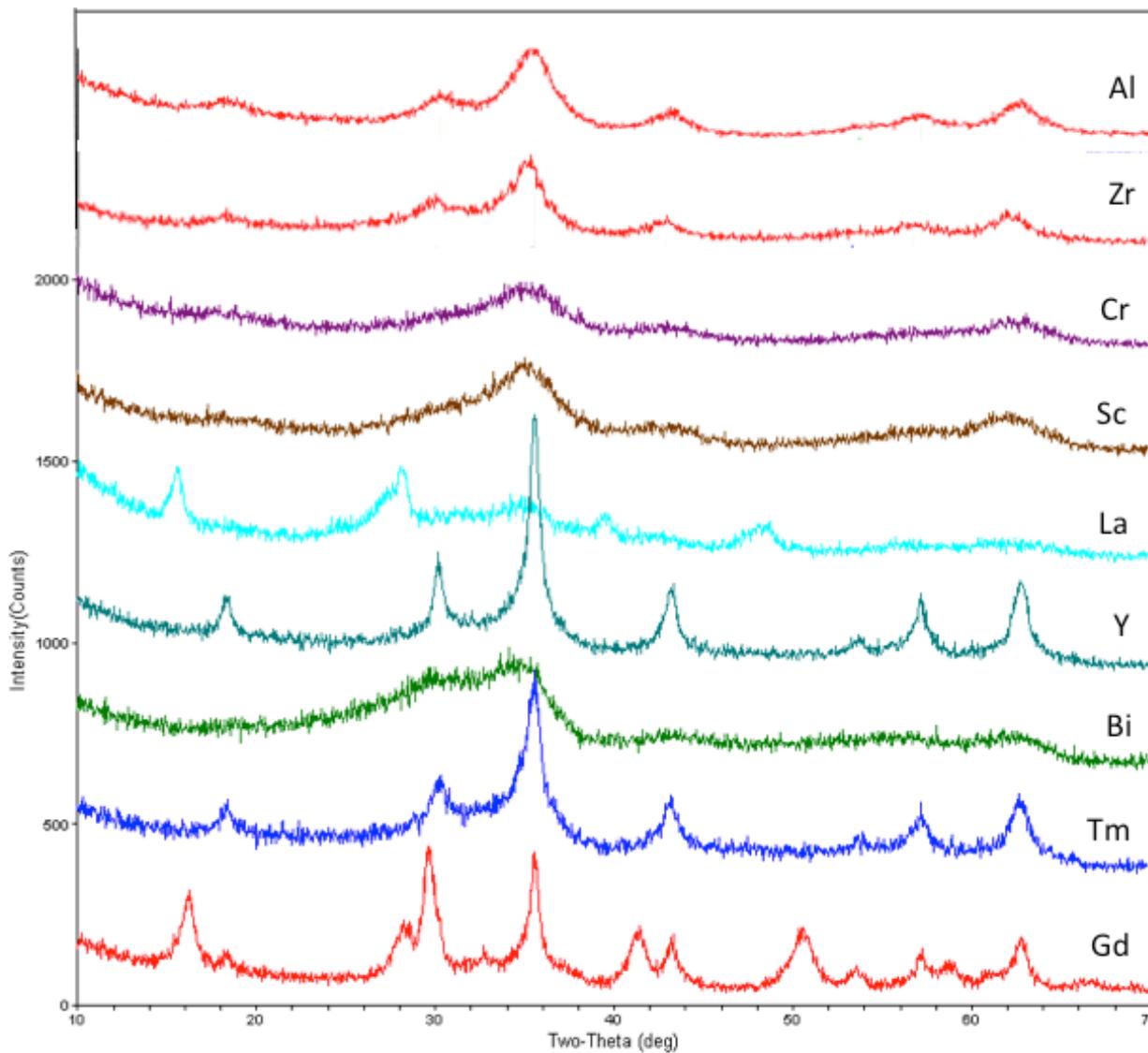


- Laffont, et. al\* has suggested that Li transport occurs by “unzipping” the Triphylite  $\text{LiFePO}_4$  phase.
- Li atoms are thought to propagate out of the host lattice via the *b*-axis, leaving behind the Heterosite  $\text{FePO}_4$  compound
- Intercalation of Li occurs in the reverse fashion.

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



# Doping with a Wide Range of Cations



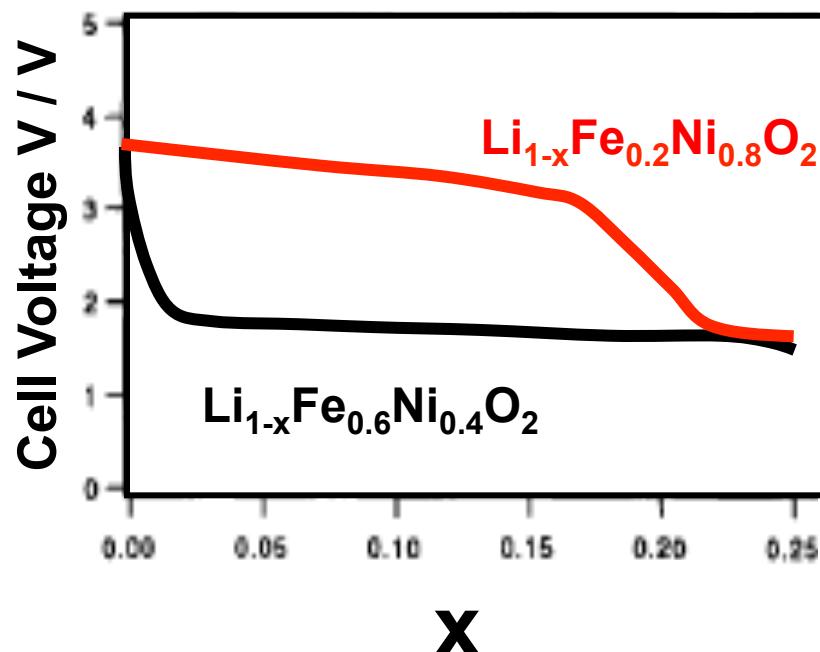


# Cation Doping to Enhance Capacity



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

Replotted from: R. Kanno et al. 1997.



Potential candidate dopants:

Structural stabilization: **Al, Ni**  
Electroactive dopants: **Co, Mn**

*Computational Modeling will be used to guide experimental dopant studies*



# Iron Oxide Electrochemistry

