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Selective Synthesis of Iron Oxide-Hydroxides

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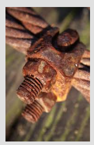
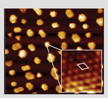
Background and Motivation

- Iron oxides comprise a rich class of materials that is chemically, structurally, and functionally diverse.
  - Oxides → FeO_x
  - Hydroxides → $Fe(OH)_x$
  - Oxide-Hydroxides → FeO(OH)
- Iron oxides are found all around us, forming naturally and spontaneously (if not always desirably!).



- Laboratory synthesis is inexpensive and has become increasingly important as these green materials have found applications ranging from pigment to catalysis. The multiple oxidation states of iron have even made iron oxides attractive candidates for electrical energy storage.

Iron oxide pigments

Nanoscale iron oxide catalyst

- Each of these applications, however, is dependent on being able to synthesize iron oxide phases with the desired morphological, crystallographic, magnetic, and chemical characteristics.
- The focus here is on the formation of specific crystallographic polymorphs of iron oxide-hydroxide (FeOOH):
  - α-FeOOH → Goethite
  - β-FeOOH → Akaganeite
  - γ-FeOOH → Lepidocrocite
  - δ-FeOOH → Feroxyhyte

Our Challenge

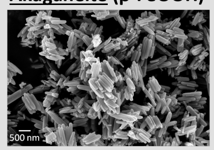
Can we control the selective synthesis of FeOOH polymorphs and evaluate the influence of these structures on their electrochemical activity?

Synthesis Methods

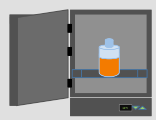
General Preparation Method: Oxidation of an aqueous iron salt solution

Experimental Parameters:
- Oxidizing Agent
- Temperature
- Iron Salt
- Reagent Concentration
- Reaction Rate
- pH

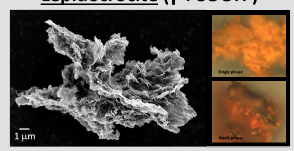
Akaganeite (β-FeOOH)



- $FeCl_3$ solution, 1:60 weight to water ratio
- Overnight oven incubation at 60ºC

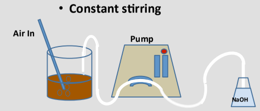


Lepidocrocite (γ-FeOOH)

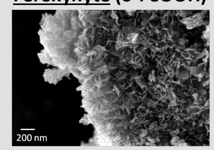


- 50 mM $FeCl_2$ solution
- 0.05 M NaOH to pH 7
- Slow base addition with peristaltic pump
  - Air bubbling
  - Constant stirring

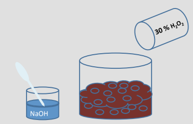
Subtle processing changes lead to second phase (magnetite) formation.



Feroxyhyte (δ-FeOOH)



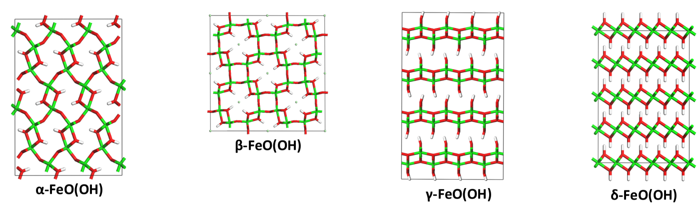
- 100 mM $FeCl_2$ solution
  - 10 M NaOH to pH 8
- Simultaneous H_2O_2 addition
  - Constant stirring

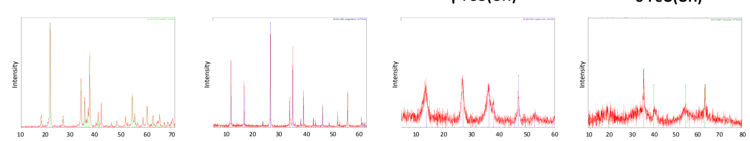


*α-Fe_2OOH (Goethite) was purchased phase-pure commercially from Alpha Aesar®

Crystallography

Each polymorph of FeOOH is compositionally identical, but structurally very different.

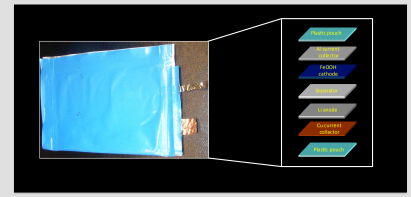


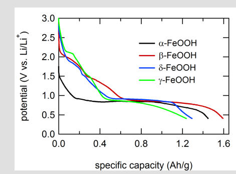


Powder X-ray diffraction confirms the phase-pure synthesis of each polymorph.

Electrochemical Performance

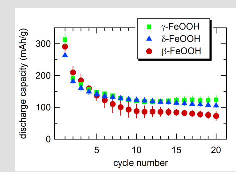
FeOOH powders were mixed with binder and conductive carbon, coated onto aluminum foil and assembled as cathodes into lithium half-cell test pouches or coin cells.





The galvanostatic discharge of these cells (71 µA cm^{-2}) shows that electrochemical lithiation of FeOOH varies with the structural form of the FeOOH.

Porous or layered structures produce extended capacities (more charge storage) at higher voltages (above 1V).



Although all samples showed significant capacity loss initially, with repeated charges and discharge cycles(1.5-4V), the porous and layered structures showed stable capacity at 1.5V.

These studies show that the structure of each FeOOH polymorph affects both the energy density (the product of voltage *and* capacity) and the cyclability of these materials as lithium ion electrodes.

Conclusions and Future Directions

- Careful control over synthetic processes can produce phase pure iron oxide-hydroxides.
- Crystallographically diverse polymorphs demonstrate distinct electrochemical responses.
- Future work will explore mechanisms of lithium intercalation into iron oxide-hydroxides, and will investigate other materials with similar polymorphic influences.

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