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Redox Chemistry of a Potential Solid State Battery Cathode – Discuss!

Read this article before class:

"Redox chemistry of a binary transition metal oxide (AB_2O_4): a study of the Cu^{2+}/Cu^0 and Fe^{3+}/Fe^0 interconversions observed upon lithiation in a $CuFe_2O_4$ battery using X-ray absorption spectroscopy." Cama, C.A.; Pelliccione, C.J.; Brady, A.B.; Li, J.; Stach, E.A.; Wang, J.; Wang, J.; Takeuchi, E.S.; Takeuchi, E.J.; Marschilok, A.C. *Phys. Chem. Chem. Phys.*, **2016**, *18*, 16930-16940.

Guide to acronyms of analytical techniques discussed in this paper:

Acronym	Name
XAS	X-ray Absorption Spectroscopy
EXAFS	Extended X-ray Absorption Fine Structure
XANES	X-ray Absorption Near Edge Structure
XRD	X-ray Diffraction
TXM	Transmission X-ray Microscopy
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
LCF	Linear Combination Fitting
SEI	Solid Electrolyte Interphase (Layer)
DOD	Depth of Discharge
SAED	Selected Area Electron Diffraction
CV	Cyclic Voltammetry

Questions

1. The binary transition metal oxide, copper ferrite: $CuFe_2O_4$, used in this research, is a mixed metal oxide. Identify the charges of the metal cations based on the formula. Show how this conforms to the general formula of a spinel: AB_2O_4.
2. Since copper ferrite, $CuFe_2O_4$ has a crystal structure in the spinel family, draw the general unit cell of a spinel, and explain the structure. A spinel structure has a face-centered cubic lattice of oxide anions with ⅛ of the tetrahedral holes occupied by A cations and ½ of the octahedral holes occupied by B cations. Next, compare this unit cell to that of an inverse spinel in which half of the B cations are in the ⅛ of the tetrahedral holes, and both A and B cations are in the ½ of the octahedral holes. What would be the cations' placements if $CuFe_2O_4$ has a normal spinel or inverse spinel structure? Which structure, normal spinel or inverse spinel, did the authors find for $CuFe_2O_4$, and what evidence did they use to come to their conclusion?
3. Magnetite, Fe_3O_4 is a cubic inverse spinel where the unit cell lengths are equal ($a = b = c$, $\alpha = \beta = \gamma = 90°$). Copper ferrite has a tetragonal unit cell ($a = b \neq c$, $\alpha = \beta = \gamma = 90°$). What is unique for copper ferrite that the structure is not cubic like magnetite? Consider the electron configuration of Cu^{2+} and its potential to undergo Jahn-Teller distortion.
4. Write a balanced equation of reaction for the formation of copper ferrite. What is the role of sodium hydroxide in this reaction? Propose a reason for why the crude product was heated under vacuum at 80°C. What size particles were created? Give a range and an average. Assuming a unit cell volume

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of 294 Å^3 for copper ferrite and the 60 nm size for the large particles seen in TEM, how many formula units of copper ferrite are in a 60 nm cubic nanoparticle?

5. Many X-ray techniques were used in this research. What are the basic principles of X-ray absorption and X-ray fluorescence in atoms? What are the Cu K_α and Fe K_α absorption/emission lines due to? What standards were chosen for comparison and why?
6. Draw a picture or diagram of the composition of the battery; identify the parts, lithium ion flow and electron flow. Identify the anode and cathode, and how charging, discharging, lithiation and de-lithiation are interrelated.
7. What are the critical voltages at which reduction of Cu^{II} and Fe^{III} could be occurring, according to the CV results? Compare these to the standard $E°_B$ values for $Cu^{II} \rightarrow Cu$, $Fe^{III} \rightarrow Fe^{II}$, $Fe^{II} \rightarrow Fe$ and $Fe^{III} \rightarrow Fe$. Why are standard basic conditions the most relevant comparison?
8. Examine Figure 6. The first column of TXM results are labeled "As-synthesized." The three subsequent columns only have voltage values listed. Determine what was happening in the battery for each of these columns, either charging or discharging, and explain.
9. More on Figure 6. Refer back to your answers for Q#7. After the experiment at 1.5 V, how has the composition of the copper ferrite changed? After 0.5 V, how has the composition of copper ferrite changed? After charging at 3.5 V, how has the composition changed? Does the copper ferrite discharge and charge reversibly? Provide evidence for your conclusion.
10. Read about EXAFS and XANES in the supplement provided. How did EXAFS help determine the geometry and oxidation states of copper and iron in the battery before and after each experiment?
11. Expand Table 2. Add in descriptions of relevant experiments and a description of what happens to the copper ferrite as a result, using the discussion in the paper as a guide.

Electrodes	Experiment	Final (net) electron count	Cu and/or Fe reduction and movement
A	*Discharge to 1.8V*	1.07	*Reduction of 50% Cu^{2+} to Cu^0, and migration of Cu out of $CuFe_2O_4$*
B		7.02	
C		1.28	
D		2.72	
E		7.16	
F		2.63	

12. What was known about copper ferrite as a cathode material before and after this paper, i.e. what new results were found?