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**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**

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Redox chemistry of a binary transition metal oxide (AB₂O₄): A study of the Cu²⁺/Cu⁰ and Fe³⁺/Fe⁰ interconversions observed upon lithiation in a CuFe₂O₄ battery using X-ray Absorption Spectroscopy

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Abstract

Copper ferrite, CuFe₂O₄, is a promising candidate for application as a high energy electrode material in lithium based batteries. Mechanistic insight on the electrochemical reduction and oxidation processes was gained through the first x-ray absorption spectroscopic study of lithiation and delithiation of CuFe₂O₄. A phase pure tetragonal CuFe₂O₄ material was prepared and characterized using laboratory and synchrotron x-ray diffraction, Raman spectroscopy, and transmission electron microscopy. Ex-situ x-ray absorption spectroscopy (XAS) measurements were used to study the battery redox processes at the Fe and Cu K-edges, using x-ray absorption near-edge structure (XANES), extended X-ray absorption fine structure (EXAFS), and transmission x-ray microscopy (TXM) spectroscopies. EXAFS analysis showed upon discharge, an initial conversion of 50% of the copper(II) to copper metal positioned outside of the spinel structure, followed by a migration of tetrahedral iron(III) cations to octahedral positions previously occupied by copper(II). Upon charging to 3.5 V, the copper metal remained in the metallic state, while iron metal oxidation to iron(III) was achieved. The results provide new mechanistic insight regarding the evolution of the local coordination environments at the iron and copper centers upon discharging and charging.

Introduction

Copper ferrite, CuFe₂O₄ has two crystal structures determined by the crystallographic sites occupied by Fe ions: cubic CuFe₂O₄ (c-CuFe₂O₄), a normal spinel structure with all Fe³⁺ cations located on octahedral B-sites and all Cu²⁺ cations on tetrahedral A-sites; and tetragonal CuFe₂O₄ (t-CuFe₂O₄), an inverse spinel structure with all Cu²⁺ occupying B-sites and the Fe³⁺ cations distributed evenly between A-sites and B-sites.¹

In recent years, binary transition metal oxides such as copper ferrite, CuFe₂O₄, have gained significant interest as electrodes for lithium based batteries.²⁻¹⁰ One reason in particular is their high theoretical capacities, which allow them to store more energy than typical insertion materials. For the CuFe₂O₄ material, up to 8 Li⁺ ions can be

transferred through a combined insertion and conversion mechanism, resulting in a high theoretical capacity of 893 mAh/g. Equation 1 depicts the overall electrochemical reduction of the CuFe_2O_4 material upon lithiation.²⁻⁴

Cyclic voltammetry (CV) of both the cubic (c- CuFe_2O_4) and tetragonal (t- CuFe_2O_4) structures was reported at a scan rate of 0.1 mV/s in the voltage range of 0.01-3 V vs. Li^+/Li .^{5, 6} In addition to phase differences, recent literature has shown that CuFe_2O_4 electrochemistry can be affected by particle size,^{2, 3, 7} morphology,^{8, 9} and the use of conductive coatings.^{5, 10}

⁵⁷Fe Mössbauer spectroscopy and ex-situ x-ray diffraction have been used to monitor the discharge process.^{2, 11} Upon appropriate electrochemical reduction conditions, copper metal formation has been observed via x-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM) studies; however, after just one electron equivalent of discharge, phase identification of the reduced product by XRD was not possible.^{2, 3}

Thus, analysis of conversion mechanisms for CuFe_2O_4 materials can be challenging, since diffraction methods may not provide structural information towards conversion intermediates. In this paper, the complex redox processes associated with the lithiation of CuFe_2O_4 are investigated for the first time using several x-ray absorption spectroscopy (XAS) techniques. XAS provides a direct probe of the electronic and local atomic configurations of elements within a sample, and can be used to accurately characterize both crystalline and highly disordered materials. Specifically, x-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopies are powerful techniques that can be used to determine both the oxidation state and local atomic geometry of an atom respectively. Further, transmission x-ray microscopy (TXM) can be used to map oxidation state distributions over a large sample area via XANES.^{12, 13} In this manner, both reduced and oxidized species were identified and quantified via Fe and Cu K-edge XAS measurements to map CuFe_2O_4 electrodes that had been discharged and charged to various electrochemical states. In total, all of the XAS data combine to describe the evolution of the local coordination environments at the copper and iron centers during the reduction and oxidation processes, providing mechanistic insight regarding the battery-relevant electrochemistry of phase pure, nanocrystalline CuFe_2O_4 material.

Experimental:

Synthesis of copper ferrite, CuFe_2O_4

Copper ferrite, CuFe_2O_4 was synthesized via a co-precipitation reaction adapted from prior reports.^{14, 15} An aqueous solution with stoichiometric equivalents of copper(II) nitrate hemipentahydrate, $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$ and iron(III) nitrate nonahydrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added to an aqueous solution of sodium hydroxide, NaOH. The mixture was washed, refluxed, washed again and dried under vacuum at 80°C.

Characterization of copper ferrite material and electrodes

Material purity and crystallite size were characterized using a Rigaku Smartlab X-ray Diffractometer using Cu K α radiation and Bragg-Brentano geometry. Crystallite size was estimated using the Scherrer equation after correcting for instrument broadening with LaB $_6$.^{16, 17}

Synchrotron level x-ray powder diffraction data was collected in a sealed Kapton capillary at the NSLS-II XPD 1 beamline. The x-ray wavelength was calibrated at 0.1899 Å. Detection was performed using a 16-inch CsI scintillator. The two-dimensional data was integrated to simulate a one-dimensional pattern using Fit2D software.¹⁸ Rietveld Refinement was carried out using GSAS II.¹⁹ Instrumental parameters were fit using the LaB6 standard. The empty Kapton tube was used for an initial background subtraction. A 20-term polynomial background was fit, along with lattice parameters, a uniaxial microstrain model, and atomic positions and Debye-Waller factors.

Surface area was measured using a Quantachrome NOVA BET (Brunauer, Emmet, and Teller) surface area analyzer via a multi – point BET method. The copper and iron concentrations in each sample were verified using Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP – OES) with a Thermo Scientific iCAP 6000 series spectrometer. Raman spectra were collected using a Horiba ExploRA Raman microscope with a 532 nm laser at 10% laser power, between 100 and 1000 cm⁻¹, grating 1200 cm⁻¹, slit and hole were 200 and 500 μ m, respectively.

The as-synthesized CuFe $_2$ O $_4$ nanoparticle samples were dispersed in ethanol and sonicated for 2 minutes to ensure a uniform dispersion. One drop of the solution was evaporated onto a 300 mesh Cu grid, which was coated with a lacey carbon film. TEM characterizations, including high-resolution TEM and selected area electron diffraction, were performed using a JEOL-2100F TEM equipped with a field-emission electron gun operated at 200 kV, and a point-to-point spatial resolution of 0.19 nm can be achieved.

Electrochemical Testing

Electrodes were composed of 90% active material, 5% Super P carbon and 5% polyvinylidene fluoride (PVDF) binder. Three electrode cells with Li metal foil as both the reference and counter electrodes, 1 M LiBF $_4$ in PC/DMC (1:1) as electrolyte were used for the voltammetry studies. Voltammetry studies were conducted between 0.3 and 3.5 V at a rate of 0.05 mV/s. Coin type cells used lithium electrodes and the same electrolyte as in the voltammetry studies. All galvanostatic charge and discharge experiments were conducted at 0.1C rate at 30°C.

X – ray Absorption Spectroscopy

Ex situ XAS measurements were conducted at X11 A at the National Synchrotron Light Source I (NSLS I) at Brookhaven National Laboratory to measure the Cu K-edge (8.979 keV) and at Sector 12 – BM at Argonne National Laboratory for the Fe K-edge (7.112 keV) both in transmission geometry with incident and transmitted X-ray flux monitored with ionization chambers. A Fe or Cu foil was utilized for initial X-ray beam energy calibration, and were measured simultaneously with any sample at the respective

element edge for proper energy alignment of multiple scans. FeO, Fe₂O₃, Fe₃O₄ and Cu(NO₃)₂ standards were measured in addition to the metal foils for comparison of relative oxidation state changes observed as shifts in the XANES region (ca. 30 eV below and above the absorption edge) of the XAS spectra.

Each XAS scan was aligned, merged, deglitched and normalized in Athena.^{20, 21} The built in AUTOBK algorithm was used to minimize the contribution of background below $R_{\text{bkg}} = 1.0 \text{ \AA}$. Linear combination fitting of the XANES region at both the Fe and Cu K –edges was completed in Athena as well. The Fe and Cu K-edge EXAFS spectra were modeled using Artemis with theoretical models created by FEFF6.²¹⁻²³ The undischarged state in both the Fe and Cu K-edge spectra were modeled based on the *I 4₁/amd* CuFe₂O₄ crystal structure.²⁴ Other electrochemical states of the electrode were modeled with a combination of Fe₃O₄,²⁵ Cu metal²⁶ and the original CuFe₂O₄ structure. All fits were conducted in a k-range of 2 – 10 $\text{\AA}^{-1}$ using a Hanning window with a $dk = 3$ in k, k^2 and k^3 k-weightings simultaneously. Most fits were conducted in an R-range of 1.0 – 3.0 $\text{\AA}$, however the range was expanded to 3.5 $\text{\AA}$ for a few spectra to fully encompass the second shell peaks.

Transmission X – ray Microscopy

Transmission X – ray microscopy (TXM) was measured at the X8C beamline in NSLS-I. XANES mapping was collected on a 40 x 40 μm region of the electrode. Each sample was collected at the Fe and Cu K –edges between 7091 and 7191 eV and 8958 to 9058 eV with a 2eV step size, respectively. The Fe K –edge maps were collected with 5s exposure time for a full field of 40 x 40 μm with binning 4 x 4 pixels. Each pixel in the Fe K – edge maps is approximately 19.5 x 19.5 nm^2 . The Cu – K edge maps were collected under similar conditions; however the binning was 8 x 8 pixels; Utilizing a custom Matlab program, with Fe foil, FeO, Fe₂O₃, Cu foil and Cu(NO₃)₂ as standards, a colored 2D image of oxidation states was produced, with each color corresponding to a specific oxidation state. This technique allows visualization of the distribution of copper and iron particles, as well as spatially resolved oxidation states. Further image analysis was done using ImageJ.²⁷

Results:

Synthesis & Characterization

Figure 1. Characterization of as-synthesized CuFe_2O_4 . (A) X-ray diffraction (XRD), from laboratory diffractometer (Cu K- α radiation, $\lambda = 1.54 \text{ \AA}$) compared to reference patterns of tetragonal CuFe_2O_4 (t- CuFe_2O_4) (PDF# 01-072-1174), cubic CuFe_2O_4 (c- CuFe_2O_4) (PDF # 01-077-0010), CuO (PDF# 01-070-6829), and $\alpha\text{-Fe}_2\text{O}_3$ (PDF# 00-033-0664), (B) Raman spectrum compared with, CuO , and $\alpha\text{-Fe}_2\text{O}_3$. (C) Synchrotron based XRD ($\lambda = 0.1899 \text{ \AA}$), fit (blue), background (red), and difference (green). (D) Octahedral geometry around the copper and iron centers (B- sites) and (E) Tetrahedral geometry around the iron centers (A- sites) based on Rietveld Refinement.

Copper ferrite, CuFe_2O_4 was synthesized in aqueous media via a co-precipitation technique. As shown in the XRD pattern depicted in **Figure 1A**, the as – synthesized material is phase pure CuFe_2O_4 , with no evidence of the CuO or Fe_2O_3 impurities commonly found in CuFe_2O_4 samples.²⁸⁻³² Further, Raman spectroscopy is capable of distinguishing between CuO , CuFe_2O_4 , and $\alpha\text{-Fe}_2\text{O}_3$. **Figure 1B** depicts the collected Raman patterns. The as synthesized CuFe_2O_4 was consistent with previously published data³³⁻³⁵ and did not exhibit evidence of CuO or $\alpha\text{-Fe}_2\text{O}_3$ phases. The copper to iron ratio was calculated to be 2.02 ± 0.01 from ICP – OES analysis. Further characterization of the particles using the BET method indicated that the surface area was $90 \pm 10 \text{ m}^2/\text{g}$.

The structure of CuFe_2O_4 exists in an inverse spinel configuration which can possess either cubic or tetragonal symmetry, such that the corresponding space groups are $\text{Fd}\bar{3}m$ and $\text{I}4_1/\text{amd}$, respectively. The two phases are very similar; however, in the tetragonal phase, Cu^{2+} ions occupy octahedral sites, resulting in the elongation of the c – axis due to Jahn – Teller distortion. In both phases Fe^{3+} ions are evenly distributed amongst the tetrahedral and octahedral sites.³⁶⁻³⁸ Rietveld refinement was performed on synchrotron based x-ray powder diffraction data **Figure 1C**. The appearance of the data and difference pattern resulting from the fit were consistent with prior reports for synchrotron based x-ray powder diffraction of other nanocrystalline bimetallic oxides.³⁹ The CuFe_2O_4 structure was fit with a single, tetragonal phase (space group $\text{I}4_1/\text{amd}$).²⁴ The lattice parameters are slightly distorted from the reference phase, with a slight expansion in the A-B plane and a slight contraction along the C-axis, as shown in **Table 1**. Atomic positions are in **Table S1**. These results confirm a tetragonal distortion at the octahedral site, likely due to Cu^{2+} (d^9). A rotation in the orientation at the octahedral site is also observed, as well as a slight distortion in the bond angles. The tetrahedral site is compressed and rotated, though near the standard bond angles are maintained at $\sim 109.5^\circ$. Scherrer analysis was done on the (211) and (422) peaks, using both the laboratory and synchrotron XRD data after correcting for instrumental broadening. The crystallite size was estimated to be ~ 25 nm (211 peak) and ~ 38 nm (422 peak). Transmission electron microscopy showed the CuFe_2O_4 to form aggregated particles with a range of particle sizes, with smaller particles ~ 4 nm clustered around larger particles of ~ 60 nm, providing an average particle size ~ 40 nm, **Figure 2a-c**. Selected area diffraction confirmed the tetragonal disordered spinel structure, **Figure 2d**, consistent with the bulk XRD results.

Parameter		Value
Material		CuFe_2O_4
Space Group		$\text{I}4_1/\text{amd}$
Lattice Parameters	A	5.87417(4) Å
	B	5.87417(4) Å
	C	8.558(1) Å
Crystallite Size		44(2) nm
Microstrain	A-B plane	1.4(8)%
	C-axis	4(2)%
Data Points		1897
Contributing Reflections		170
R_{wp}		7.27%

R_{exp}	6.80%
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Table 1. Lattice parameters and related values from Rietveld refinement of synchrotron XRD data. Crystallite size value based on whole pattern fit.

Figure 2. Morphology and phase characterization of CuFe_2O_4 nanoparticle. (a, b, c) representative morphology and high resolution transmission electron microscopy (HRTEM) image. (d) Selected area electron diffraction patterns corresponding with the tetragonal structure, space group $I4_1/amd$.

Electrochemical Testing

The as synthesized material was used to assemble both three and two electrode cells for electrochemical analysis. Cyclic voltammetry for 4 cycles was conducted on the three – electrode cells between 0.3 and 3.5 V at a rate of 0.05 mV/s, **Figure 3**. Cycle 1 is notable and displays large cathodic current peaks at 0.67, 1.3, and 1.6 V and a large anodic peak which can be deconvoluted to two peaks at 2.20 and 2.69 V. The relative peak areas of the cathodic peaks at 0.67, 1.3 and 1.6 V are 6:2:1, respectively. After the first cycle the peak observed at 1.6 V is no longer observed and the peaks at 1.3 and 0.67 V decrease in intensity.

Figure 3: Cyclic voltammetry of CuFe_2O_4 versus Li metal at a scan rate of 0.05 mV/s.

CuFe_2O_4 electrodes were also tested under galvanostatic conditions under three voltage ranges, **Figure 4**. In the first experiment, **Figure 4A**, the cells were discharged between 3.5 and 1.5 V at 80 mA/g for 5 cycles. In the first cycle, a plateau is observed at 1.7 V. At 1.5 V, 1.3 electrons are discharged into the structure. Upon charging 54% of the capacity is recovered. During further cycling, the discharge and charge curves are featureless where the degree of polarization remains unchanged, however, the capacity continues to decrease. Reversibility was also tested between 3.5 and 1.0 V, **Figure 4B**. In the first cycle, the discharge profile exhibits two plateaus at 1.8 and 1.5 V, as was observed in **Figure 3** and **Figure 4A**. On charging, only one plateau was observed consistent with the CV profile. In the third experiment, the voltage window was extended to incorporate the entire conversion process for lithiation of CuFe_2O_4 . **Figure 4C** depicts the discharge – charge profiles between 3.0 and 0.1 V at 153 mA/g. In the first discharge profile, plateaus are observed at 1.7, 1.4 and 0.88 V, similar to the previously discussed experiments. As was observed in **Figure 4B**, the plateaus occurring above 1.0 V are not as distinct as they were in the first cycle. The plateau at 0.88 V appears in each cycle; however, the length of the plateau significantly decreases as cycling progresses.

Figure 4: Galvanostatic discharge – charge profiles for Li/CuFe₂O₄ for different voltage ranges: (A) 3.5 – 1.5 V at 80 mA/g, (B) 3.5 – 1.0 V at 80 mA/g, and (C) 3.0 – 0.1 at 153 mA/g.

Transmission X – ray microscopy

Figure 5: Galvanostatic curves depicting sample selection for TXM analysis.

Transmission X – ray microscopy is an advantageous technique that was used to measure XANES over an entire 40 x 40 μm region, thereby, measuring the distribution of species present at various states of discharge. This technique has been used previously to study both the mechanism and efficiency of redox processes in Li/CuO⁴⁰ and Li/Fe₃O₄⁴¹ systems. **Figure 5** depicts the depth of discharge and charge for the samples selected for TXM study. The DODs are indicated by electron equivalents which are calculated from the CuFe₂O₄ capacity and converted to the moles of electrons in the material. The TXM images collected at the Cu and Fe K – edges are depicted in **Figure 6**. Each image was analyzed with a minimum R – factor, indicated in **Table S2** as R – factor cutoff. The corresponding Linear Combination Fitting (LCF) results are depicted in **Table S2**.

For the as – synthesized sample, a pristine, non - discharged CuFe₂O₄ electrode was used. As depicted in **Figure 6-B1, and D1**, the as – synthesized material is composed of Cu(II) and Fe(III). Upon discharge to 1.5 V, a large shift in the Cu K – edge is observed from 8985 to 8978 eV, **Figure 6-B2** and **Figure 6-E**, consistent with the edge energy of copper metal (8979 eV). The TXM results upon discharge to 1.5 V show the electrode to be composed of copper metal, matching the edge energy of Cu metal, **Figures 6-A2** and **6-B2**. While some regions evidence Cu²⁺, Region i in **Figure 6-B2** and **Figure 6-E**, the data are dominated by Cu metal, Region ii in **Figure 6-B2** and

Figure 6-E. Upon discharge to 1.5 V, the iron K – edge exhibited a slight decrease in edge energy, resulting in ~30% reduction of the Fe(III), consistent with **Figure 6-D2** which depicts a mixture of Fe(III) and Fe(II) species. Further discharge to 0.5 V resulted in formation of copper and iron metal, **Figures 6-B3** and **D3**. LCF estimated that ~60% of the electrode was reduced to metallic iron, indicating an incomplete conversion reaction as expected since the depth of discharge (~ 7.3 electron equivalents) was not sufficient for full electrochemical reduction to iron metal. Upon charging, **Figure 6-B4**, copper metal was not oxidized where ~90% of the electrode exhibited XANES spectra consistent with Cu metal. In fact, at the Cu K – edge, the charged electrode looked very similar to copper metal, as shown in **Figure 6F**. The Fe K – edge did show evidence of iron oxidation upon charge, **Figure 6-D4**, where LCF estimated the electrode to be composed of ~80% oxidized iron, with a mixture of Fe(III) and Fe(II), **Table S2**.

As - synthesized

1.5 V

0.5 V

3.5 V

Figure 6: (A) TXM microscope images of the 40 x 40 μm areas chosen for study at the Cu K – edge. (B) Cu K – edge XANES results for the areas depicted in (A). Regions (i) and (ii) correspond to areas where LCF was done. (C) TXM microscope images of the 40 x 40 μm areas chosen for study at the Fe K – edge. (D) Fe K – edge XANES results for the areas depicted in (B). Chosen electrodes were (1) as – synthesized electrode, (2) discharged to 1.5 V, (3) 0.5 V, and (4) charged to 3.5 V. Cu – K edge XANES spectra for regions i and ii (E) and iii (F).

Ex – Situ X – ray Absorption Spectroscopy

Table 1: Electrode labeling & corresponding final electron counts.

Electrode	Final Electron Count
A	1.07
B	7.02
C	1.28
D	2.72
E	7.16
F	2.63

Figure 7: (I) Select discharge and charge curves for electrodes studied using XAS. Electrodes were tested at 80 mAh/g to various states of discharge and charge. See Figures S1 and S2 for electrochemical data for electrodes C and D, respectively.

Bulk XANES and EXAFS were analyzed to characterize the structure and composition of the electrode at various points during discharge and charge. Electrodes were discharged and charged at 80 mA/g to various states, as described in **Table 1** with **Figure 7** depicting the corresponding discharge-charge curves for selected electrodes. As in the TXM study, the depths of discharge are also indicated by electron equivalents and are calculated from the CuFe_2O_4 capacity. **Figures S1 and S2** depict the electrochemical data for the remaining electrodes.

The Cu and Fe K – edge XANES and $|\chi(R)|$ (Fourier transform of $\chi(k)$) are depicted in **Figures 8 and 9**, respectively. Resulting EXAFS fits are included in **Tables S3 – S5**. The as – synthesized CuFe_2O_4 showed similar edge energies to the Cu(II) and Fe(III) standards $\text{Cu}(\text{NO}_3)_2$ and $\alpha - \text{Fe}_2\text{O}_3$, respectively. Further EXAFS analysis confirmed that the as – synthesized material is tetragonal CuFe_2O_4 . The EXAFS fits of

both Cu and Fe K – edges showed a slight reduction in amplitudes from the standard bulk crystal, as is expected for nanomaterials due to the higher degree of disorder and higher surface to bulk ratio. The EXAFS fit at the Cu K – edge showed Cu^{2+} coordinated to 2.4 ± 0.4 oxygens at $1.96 \pm 0.02 \text{ \AA}$ and $2.20 \pm 0.02 \text{ \AA}$. These distances are consistent with the tetragonally distorted geometry expected for Cu^{2+} in the CuFe_2O_4 structure. At $2.97 \pm 0.02 \text{ \AA}$, 6 ± 2 iron and/ or copper atoms surround the absorber. The EXAFS model of the Fe K – edge of the undischarged material used a convolution of Fe in two different coordination schemes due to the inability of the fit to differentiate between Fe and Cu atoms. The ratio between tetrahedral and octahedral iron occupancy was consistent with an inverse spinel structure.

Figure 8: (I) XANES at Cu K –edge of discharged & charged coatings, (II) EXAFS (R-space) for discharged coatings, dotted line represents Cu – metal.

Figure 9: Fe K – edge of (I) XANES of electrodes discharged in first cycle (II) EXAFS of electrodes discharged in first cycle, (III) XANES of electrodes discharged in second cycle and beyond, (IV) XAFS of electrodes discharged in second cycle and beyond.

As discharge progresses to 1.8 V, 1.07 electrons are discharged, as depicted in **Figure 7I** and **Table 2** for Electrode A. Cu metal formation is evident by the large shift in edge energy from 8992 to 8977 eV, as depicted in **Figure 8I**. The Fe K – edge energy does not change from the as – synthesized edge energy of 7126 eV for Electrode A, as shown in **Figure 9I**, although, LCF analysis estimated about 13% of the Fe(III) and 50% of the Cu²⁺ was reduced.

The Cu atoms in Electrode A appear to form very small Cu metal nanoparticles, as evidenced from the interatomic distance between Cu atoms of 2.55 ± 0.03 Å, which is within estimated standard deviation of the Cu-Cu distance of 2.55 Å in bulk fcc copper (12 Cu-Cu near neighbors at 2.55 Å). This observed interatomic distance is well short of the expected Cu-Cu distance in the CuO (2.88 Å) and Cu₂O (3.02 Å) crystal structures. The Cu K – edge EXAFS estimated that the copper atoms, when discharged to 1.8 V, is coordinated to 5 ± 2 Cu atoms. The reduced coordination compared to bulk Cu metal

suggests that the size of the metallic species that forms is disordered and very small. Using this ratio, the size of the copper was estimated to be on the order of several nm.⁴²

At the Fe K – edge, the conversion of Cu(II) to copper metal is evidenced by the loss in coordination of copper to iron from 1.0 ± 0.2 to 0.66 ± 0.1 copper atoms coordinated to iron, in Electrode A. Thus, ~34% of copper(II) is estimated to have left the structure. Concomitant with the decrease of copper in the structure is a ~ 40% decrease in occupancy of iron tetrahedral sites and ~ 40% increase in iron octahedral sites. Although there is no evidence of iron reduction, the EXAFS suggests a reordering of iron from tetrahedral sites to octahedral sites. The tetrahedral iron may be occupying octahedral sites that are left vacant from Cu extraction from the structure. This is similar to the discharge mechanism of magnetite, Fe_3O_4 , in which when discharged to low lithiation concentrations, lithium is inserted into vacant octahedral sites until a critical Li^+ concentration is reached, forcing tetrahedral Fe^{3+} to migrate to octahedral positions.⁴³

As the sample further discharges to 0.3 V, 7.02 electrons are discharged, as depicted in **Figure 7** for Electrode B. A significant change in the Fe K – edge XANES suggests that iron metal has formed, **Figure 9I**. LCF of the XANES region estimated that ca. 94% of the electrode was converted to iron metal. EXAFS fitting further supported this observation, as the Fe – Fe interatomic distance was determined to be 2.48 ± 0.01 Å, consistent with iron metal (2.48 Å) with 3.2 ± 0.8 Fe atoms surrounding each iron atom.²⁵ In bulk Fe metal, Fe-Fe coordination is 8, and since the observed number of neighboring Fe atoms is significantly smaller, it suggests the size of the metallic iron which forms is estimated to be on the order of several nm.⁴² EXAFS also estimates a small amount of iron is coordinated to oxygen and is likely due to surface oxide surrounding the iron metal nanoparticles. Based on electron count, there should also be a small concentration of oxidized iron that is not directly observed in EXAFS or XANES analysis. As XAS is a bulk technique, the likely small concentration of oxidized iron is difficult to differentiate from the primarily metallic Fe local environment across the entire electrode.

After discharging to 1.0 V and then charging to 3.5 V, the Cu K – edge increases from 8977 (Electrode A) to 8979 eV for Electrode C, still far from the as – synthesized edge energy of 8992 eV. **Figure S1** depicts the electrochemical data for Electrode C. Analysis of the XANES spectra using LCF estimated the electrode to be composed of 62% copper metal after charging. The EXAFS modeling results were similar to what was observed for the 1.8 V discharged electrode, thus, most of the Cu^0 did not oxidize. The observation of 1.5 ± 0.5 oxygen atoms at 1.89 ± 0.03 Å and the low number of neighboring Cu atoms (4 ± 2 copper atoms vs. the expected 12 in the copper metal crystal structure) suggests that the Cu metal nanoparticles are still very small, on the order of several nm, with a surface oxide. The presence of Cu metal agrees with the electron count of the electrode, since 1.28 electrons remain unaccounted for after charging, suggesting the entire electrode does not return to the pristine crystal state.

At the Fe K – edge, Electrode C did not depict any appreciable change in XANES from the as – synthesized and Fe(III) standard; however, the EXAFS does reveal a reordering of the iron, similar to that observed for Electrode A. The Fe atoms transition from distinct tetrahedral and octahedral coordination geometries in the as-synthesized state to only a octahedral-like coordination with 4.2 ± 0.6 oxygen atoms at 1.99 ± 0.02 Å and 4.2 ± 0.6 iron atoms at 3.00 ± 0.03 Å. This coordination environment is similar to the

expected distances and relative ratio of coordination numbers for the 16d octahedral sites in magnetite, Fe_3O_4 (nominally 6 oxygen atoms at 2.06 Å and 6 iron atoms at 2.97 Å).

On second discharge to 1.0 V, the Fe K – edge for Electrode D is shifted toward lower energies, indicating some reduction of iron. **Figure S3** depicts the electrochemical data for Electrode D, which has a final electron count of 2.72 electrons. LCF estimated about 25% of Fe(III) was reduced to Fe(II). EXAFS analysis did not show a significant change in structure from the charged structure discussed previously.

On discharging further to 0.3 V, the capacity achieved decreases significantly from the first cycle, as shown in **Figure 7I** for Electrode E. XANES shows significant iron metal formation; however, an increase in the oxide layer is observed in both the XANES and EXAFS. LCF estimated about 73% of the electrode was converted to iron metal and EXAFS depicted Fe – O distances of 1.88 ± 0.04 Å and 2.43 ± 0.08 Å.

After five cycles between 3.5 and 1.0 V, the structure of the Fe atoms and Cu atoms in Electrode F is nearly unchanged from the first charged state. As shown in **Figure 7II** and **Table 1**, Electrode F still retains 2.63 electrons, despite being charged. Although the Cu is still reduced, the iron valence has oxidized to near the as – synthesized state. According to EXAFS analysis, the Cu atoms remain with 1.1 oxygen atoms at 1.87 ± 0.03 Å and 5 ± 1 copper atoms at 2.52 ± 0.01 Å while the Fe atoms remain in a mostly octahedral-like orientation with the number of oxygen and iron atoms within estimated standard deviation of the charged state. A minor amount of iron atoms occupy tetrahedral sites according to EXAFS fits at the Fe K – edge.

Discussion

Previous studies of the redox mechanisms of lithiation and delithiation of CuFe_2O_4 have used various techniques including XRD, TEM, SEM, and Mössbauer spectroscopy. From these methods researchers have observed the change in structure and oxidation states throughout discharge. According to these studies, CuFe_2O_4 is electrochemically reduced upon lithiation through a conversion mechanism to form Cu^0 and Fe^0 . The authors also report that the reduction of Cu^{2+} and Fe^{3+} occur simultaneously below 1.0 V. Any reduction prior to 1.0 V has been attributed to CuO impurities and SEI formation.^{2, 3, 11}

The as synthesized CuFe_2O_4 nanoparticles described in this study were investigated using TXM and XAS to understand the mechanism during electrochemical oxidation and reduction on a local atomic scale around both Fe and Cu atoms. To our knowledge, this is the first study of the lithiation of CuFe_2O_4 using XAS as the primary investigational method.

As lithiation of CuFe_2O_4 progresses, there is a noticeable shift in the Cu K – edge, such that by 1.8 V, 1.07 electrons are used to convert 50% of the Cu^{2+} to copper metal outside of the spinel structure, **Figure 8**. Interestingly, although the Fe K – edge energy did not change from the as – synthesized energy, the EXAFS fit showed a migration of tetrahedral iron atoms to octahedral positions previously occupied by copper, **Figure 9**. As discharge continues to 1.5 V, 2.08 electrons are discharged and all of the Cu^{2+} is converted to copper metal. The Fe K – edge is shifted slightly to lower energies, implying that the Fe(III) in the electrode is partially reduced, **Figure 9**.

The XAS analysis implies that the reduction of copper and iron does not take place as a fully concerted processes. Previous research using Mössbauer spectroscopy

indicated that Fe^{3+} reduction occurred throughout discharge after 2.0 electrons. The authors believed that the initial 2.0 electrons were used for SEI formation and the reduction of CuO impurities.² The data presented here also indicate that iron reduction is not initiated until 2.0 electrons; however, the copper edge XAS data indicated that the initial reduction to 2.0 electron equivalents resulted in the reduction of Cu^{2+} to Cu^0 metal and not primarily SEI formation.

As the discharge continues, Fe^0 nanoparticles begin to form. At 0.5 V, 7.34 electron equivalents of reduction have taken place, where the electroactive material is now composed of primarily iron and copper metal nanoparticles, as shown in **Figure 6**. In a previous study, SEM – EDS was used to characterize an electrode discharged to 0V. The study observed both Cu^0 and Fe^0 , as expected; however, the study also revealed that Cu^0 and Fe^0 were not found in the same site on the electrode. The authors inferred that as the metallic species formed they segregated resulting in copper and iron rich regions observed using EDS.³ In **Figure 6**, the electrode discharged to 0.5 V appears as a homogenous mixture of copper and iron. In **Figure 8**, EXAFS analysis indicates copper leaving the spinel structure to form copper metal at 1.8 V, Electrode A.

Similar to the electrode studied at 0.5 V, Electrode B was discharged by 7.02 electron equivalents to 0.3 V. Iron nanoparticles can be detected and appear to be surrounded by a surface oxide, as observed in the EXAFS of the Fe, **Figure 9**. This observation is consistent with the prior Mössbauer spectroscopy studies that indicated metallic iron nanoparticles were embedded in a Li_2O matrix where the surface iron atoms were in closer proximity to Li_2O than the core.¹¹

After 1 cycle between 3.5 and 0.1 V, the TXM of the charged electrode showed 55% Fe^{3+} and 94% Cu^0 , **Figure 6**. The final electron count of the electrode is 3.38 electrons, accounting for the presence of Cu^0 and the distribution of oxidized iron species according to the LCF results in **Table S2**. This was also observed in Electrode C, which was discharged to 1.0 V and then charged to 3.5 V. The EXAFS data indicated that oxidation of iron did occur, however the spinel structure was not maintained. In fact, the iron atoms occupied only octahedral sites, as observed in the geometry when the cell was discharged to 1.8V. This is similar to the $\text{Li}/\text{Fe}_3\text{O}_4$ system, where upon charging, a migration of iron atoms from tetrahedral sites to empty octahedral sites is observed.^{43, 44}

The reversibility of $\text{Fe}^{3+}/\text{Fe}^0$ was further investigated. During the second cycle, Electrode D was discharged to 1.0 V with a total reduction of 2.72 electron equivalents and showed 25% reduction of Fe^{3+} to Fe^{2+} , with no change in structure from the charged state, Electrode C. Further discharge to 0.3 V, Electrode E, exhibited iron metal nanoparticles. From the EXAFS analysis, two Fe – O distances are required to fit the spectrum. The shorter Fe – O distance is due to an oxide layer surrounding the iron nanoparticles ($1.88 \pm 0.04 \text{ \AA}$). The longer Fe – O distance ($2.43 \pm 0.08 \text{ \AA}$) is likely due to Li_2O which surrounds the coated nanoparticles, as was observed in Electrode B after the first discharge to 0.3 V.

After 5 cycles between 3.5 and 1.0 V, the charged, Electrode F, **Figure 7II** was investigated where XAS shows that the Fe K – edge is similar in energy to the Fe(III) standard, **Figure 9**. LCF indicate that the ~90% of the electrode is in the Fe(III) state. XAFS fitting implied that the structure is very similar to the initial charged state, Electrode C. The Cu K –edge, depicted in **Figure 8I**, shows that the copper form is most similar to Cu metal, further supporting the irreversibility of copper metal. The copper

metal that forms during the conversion process is estimated from the EXAFS to be on the order of several nm.⁴² Thus, this study shows that while the reduction of Cu^{2+} can occur readily, the oxidation of Cu^0 does not occur efficiently.

Conclusion

Synthesis of phase pure tetragonal copper ferrite (CuFe_2O_4) was verified by laboratory and synchrotron XRD, Raman spectroscopy, and TEM based SAED. The redox mechanism associated with lithiation of CuFe_2O_4 was investigated using several ex-situ x-ray absorption spectroscopy (XAS) techniques, including XANES, EXAFS, and TXM. The combined XAS analyses at both K-edges indicate that Fe and Cu atoms are not reduced concurrently. EXAFS analysis showed an initial conversion of 50% of the Cu^{2+} to copper metal outside of the spinel structure, followed by a migration of tetrahedral iron atoms to octahedral positions previously occupied by copper ions. As discharge continues the remaining Cu^{2+} is converted to copper metal. Upon charging to a voltage of 3.5 V, our study showed that while the copper remains in its reduced form, the iron can be oxidized back to near its as-synthesized 3+ valence state. Analysis of the charged electrode showed that the original spinel structure was not restored, as the Fe atoms remained in an octahedral coordination environment, with no tetrahedrally-coordinated Fe detected.

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