

SUPPLEMENTARY INFORMATION

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

Christina A. Cama^a, Christopher J. Pelliccione^b, Alexander B. Brady^c, Jing Li^c, Eric A. Stach^b, Jiajun Wang^b, Jun Wang^b, Esther S. Takeuchi^{a,b,c,*}, Kenneth J. Takeuchi^{a,c,*}, Amy C. Marschilok^{a,c,*}

a. Department of Chemistry, Stony Brook University, Stony Brook, NY 11794

b. Energy Sciences Directorate, Brookhaven National Laboratory, Upton, NY 11973

c. Department of Materials Science and Engineering, Stony Brook University, Stony Brook, NY 11794

*corresponding authors: (EST) esther.takeuchi@stonybrook.edu, (KJT) kenneth.takeuchi.1@stonybrook.edu, (ACM) amy.marschilok@stonybrook.edu

Table S1: Atomic positions from Rietveld refinement of synchrotron XRD data.

Atom	X	Y	Z	Uiso
Cu (oct)	0	0	0.5	0.000(10)
Fe (oct)	0	0	0.5	0.01(2)
Fe (tet)	0	0.75	0.125	0.011(1)
O	0	0.010(1)	0.2479(8)	0.008(1)

Table S2: LCF Results of TXM samples.

State	Fe K - edge					Cu K - edge			
	R-factor cutoff	% Fe(III)	%Fe (II)	%Fe(0)	Reduced χ^2	R-factor cutoff	%Cu (II)	%Cu(0)	Reduced χ^2
As synthesized	0.03	96	3.8	0	4E-3	0.07	100	0	3E-3
Partially discharged (1.5V, 2.1e-)	0.007	72	17	10	9E-4	0.03	21	79	4E-4
Fully discharged (0.5V, 7.3e-)	0.01	28	12	60	1E-3	0.04	13	87	5E-3
Discharged, then Charged (3.5 V, 3.4 e-)	0.01	55	22	23	3E-4	0.03	10	90	4E-4

Figure S1: Electrochemical Data for Electrode C. Discharged at 80 mA/g to 1.0 V, then charged to 3.5 V, held at 3.5V for 2 hours.

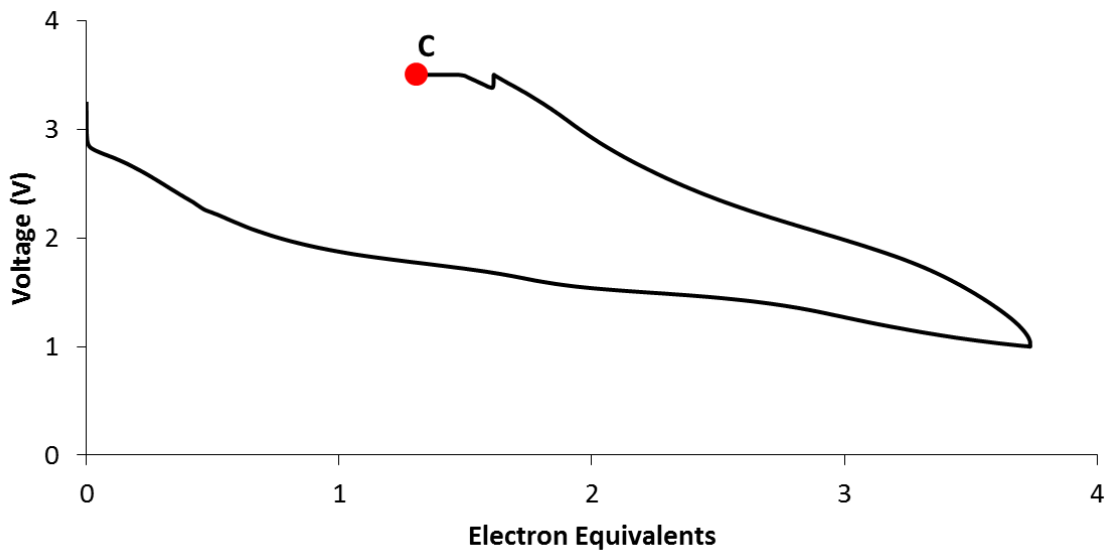


Figure S2: Electrochemical Data for Electrode D. Discharged at 80 mA/g to 1.0 V, then charged to 3.5 V, held at 3.5 V for 2 hours, then discharged again to 1.0 V

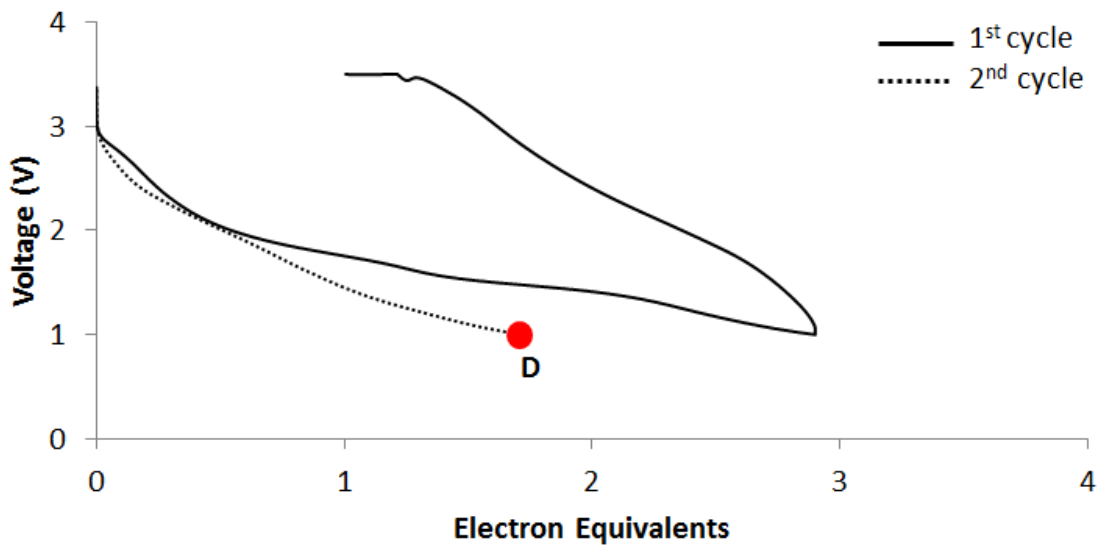


Table S3: XAFS Fitting parameters at Cu K – edge:

Sample	R-factor	E(0)	S0 ²	Path	N	N _{nano}	R
As-synthesized	0.013	-1 ± 1	0.6 ± 0.1	Cu – O	4	2.4 ± 0.4	1.96 ± 0.02
			0.2 ± 0.2	Cu – O	2	0.4 ± 0.4	2.20 ± 0.02
			6 ± 2	Cu – Fe	1	6 ± 2	2.97 ± 0.02
1.8 V	0.048	8 ± 1	0.4 ± 0.2	Cu – Cu	12	5 ± 2	2.56 ± 0.02
			2.4 ± 0.5	Cu – O	1	2.4 ± 0.5	1.94 ± 0.03
			6 ± 2	Cu - Fe	1	6 ± 2	2.95 ± 0.03
3.0 V	0.031	2 ± 2	0.3 ± 0.2	Cu - Cu	12	4 ± 2	2.52 ± 0.03
			1.5 ± 0.5	Cu – O	1	1.5 ± 0.5	1.89 ± 0.03
3.0 V, cycled	0.022	4 ± 1	0.4 ± 0.1	Cu - Cu	12	5 ± 1	2.52 ± 0.01
			1.1 ± 0.3	Cu – O	1	1.1 ± 0.3	1.87 ± 0.03

Table S4: XAFS Fitting parameters at Fe K – edge, for samples discharged within first cycle.

Sample	R-factor	E(0)	S0 ²	Path	N	N _{nano}	R
As-synthesized	0.008	-4.0 ± 0.9	0.34 ± 0.05	Fe – O	4	1.4 ± 0.2	1.93 ± 0.05
			0.34 ± 0.05	Fe – Fe	12	4.1 ± 0.6	3.46 ± 0.01
			0.34 ± 0.05	Fe – O	12	4.1 ± 0.6	3.55 ± 0.05
			0.34 ± 0.05	Fe – O	6	2.0 ± 0.3	1.95 ± 0.02
			0.34 ± 0.05	Fe – Fe	3	1.0 ± 0.2	2.99 ± 0.02
			0.34 ± 0.05	Fe – Fe	6	2.0 ± 0.3	3.46 ± 0.01
			0.34 ± 0.05	Fe – Cu	3	1.0 ± 0.2	2.99 ± 0.02
1.8 V	0.016	-2 ± 1	0.24 ± 0.05	Fe – O	4	1.0 ± 0.4	1.93
			0.24 ± 0.05	Fe – Fe	12	3 ± 1	3.46
			0.24 ± 0.05	Fe – O	12	3 ± 1	3.54
			0.45 ± 0.02	Fe – O	6	2.7 ± 0.2	1.99
			0.45 ± 0.02	Fe – Fe	3	1.4 ± 0.1	3.01
			0.24 ± 0.05	Fe – Fe	6	1.4 ± 0.5	3.52
			0.22 ± 0.02	Fe – Cu	3	0.66 ± 0.1	3.01
			0.24 ± 0.05	Fe – Fe	4	1.0 ± 0.4	3.56
0.3 V	0.012	3.5 ± 0.5	0.4 ± 0.1	Fe – Fe	8	3.2 ± 0.8	2.48 ± 0.01
			0.11 ± 0.07	Fe – O	4	0.4 ± 0.3	1.85 ± 0.07
			0.08 ± 0.09	Fe – O	6	0.5 ± 0.5	2.46 ± 0.2
3.0 V	0.018	-2 ± 1	0.09 ± 0.05	Fe – O	4	0.4 ± 0.2	1.95 ± 0.02
			0.09 ± 0.05	Fe – Fe	12	1 ± 0.6	3.20 ± 0.07
			0.09 ± 0.05	Fe – O	12	1 ± 0.6	3.56 ± 0.02
			0.7 ± 0.1	Fe – O	6	4.2 ± 0.6	1.99 ± 0.02
			0.7 ± 0.1	Fe – Fe	6	4.2 ± 0.6	3.00 ± 0.03
			0.09 ± 0.05	Fe – Fe	6	0.5 ± 0.3	3.20 ± 0.07

Table S5: XAFS Fitting parameters at Fe K – edge for samples discharged within second cycle.

Sample	R-factor	E(0)	Amplitude	Path	N	N _{nano}	R
1.0 V	0.017	-3 ± 0.9	0.06 ± 0.05	Fe – O	4	0.2 ± 0.2	1.95 ± 0.08
			0.06 ± 0.05	Fe – Fe	12	0.7 ± 0.6	3.15 ± 0.03
			0.06 ± 0.05	Fe – O	12	0.7 ± 0.6	3.56 ± 0.08
			0.49 ± 0.06	Fe – O	6	2.9 ± 0.4	2.04 ± 0.01
			0.49 ± 0.06	Fe – Fe	6	2.9 ± 0.4	3.00 ± 0.02
			0.06 ± 0.05	Fe – Fe	6	0.4 ± 0.4	3.52 ± 0.02
			0.06 ± 0.05	Fe – Fe	4	0.2 ± 0.2	3.62 ± 0.01
			0.49 ± 0.06	Fe – O	6	2.9 ± 0.4	3.69 ± 0.02
0.3 V	0.018	5 ± 4	0.27 ± 0.07	Fe – O	4	1.1 ± 0.3	1.88 ± 0.04
			0.14 ± 0.08	Fe – O	6	0.8 ± 0.4	2.43 ± 0.08
			1.6 ± 0.7	Fe - Fe	1	1.6 ± 0.7	2.49 ± 0.03
3.0 V, cycled	0.031	-2 ± 1	0.10 ± 0.08	Fe – O	4	0.4 ± 0.3	1.94 ± 0.02
			0.10 ± 0.08	Fe – Fe	12	1.0 ± 1.0	3.89 ± 0.07
			0.10 ± 0.08	Fe – O	12	1.0 ± 1.0	3.55 ± 0.02
			0.7 ± 0.1	Fe – O	6	4.2 ± 0.6	2.00 ± 0.02
			0.7 ± 0.1	Fe – Fe	6	4.2 ± 0.6	3.02 ± 0.02
			0.10 ± 0.08	Fe – Fe	6	0.6 ± 0.5	3.89 ± 0.07