Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Insight into the charging-discharging of magnetite electrodes: *In situ*XAS and DFT study

C. Nayak*[,1], Abharana N.[1], B. Modak[2], K. Halankar[3], S. N. Jha[1] and D. Bhattacharyya[1]

[1]*Atomic and Molecular Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai, INDIA.*

[2]*Theoretical Chemistry Section, Bhabha Atomic Research Centre, Trombay, Mumbai, INDIA.*

[3]*Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai, INDIA.*

**Corresponding Author Email: nayakc@barc.gov.in*

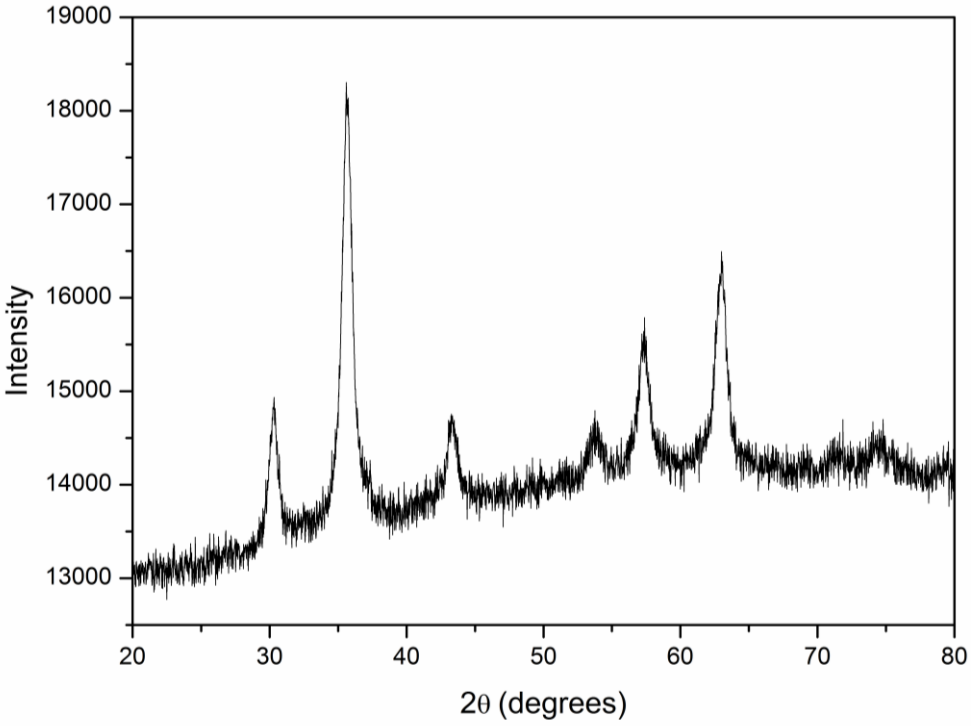

Fig. S1: XRD spectrum of the as-prepared Fe_3O_4 nanoparticles

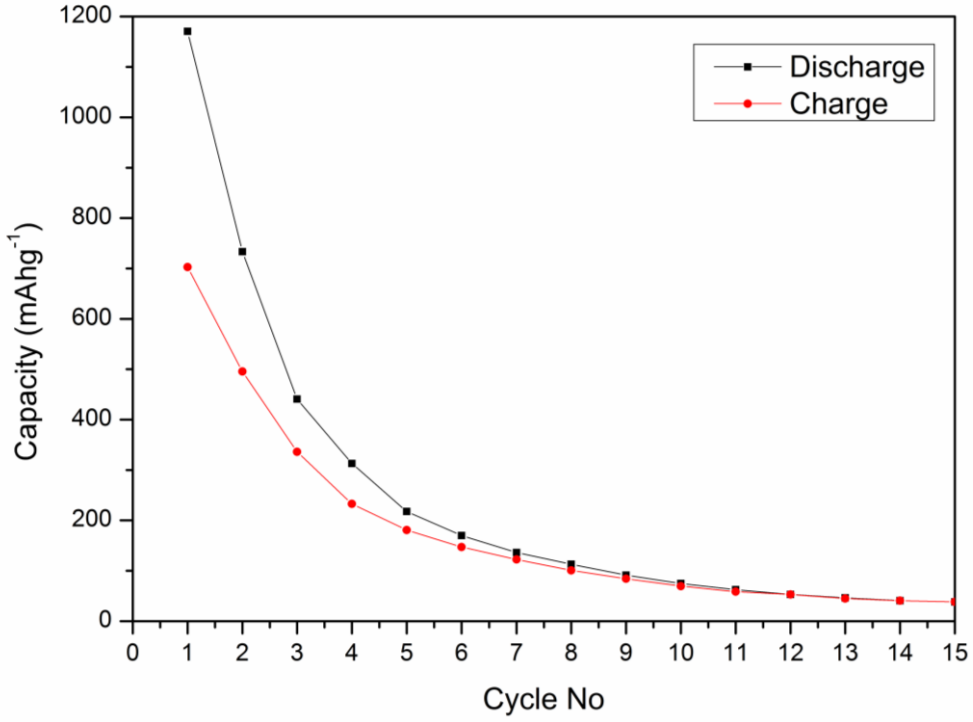

Fig. S2: Galvanostatic cycling performance of Fe_3O_4 nanoparticle electrode at the rate of 100 mAg^{-1}in the voltage range of 0.03-3.0 V.

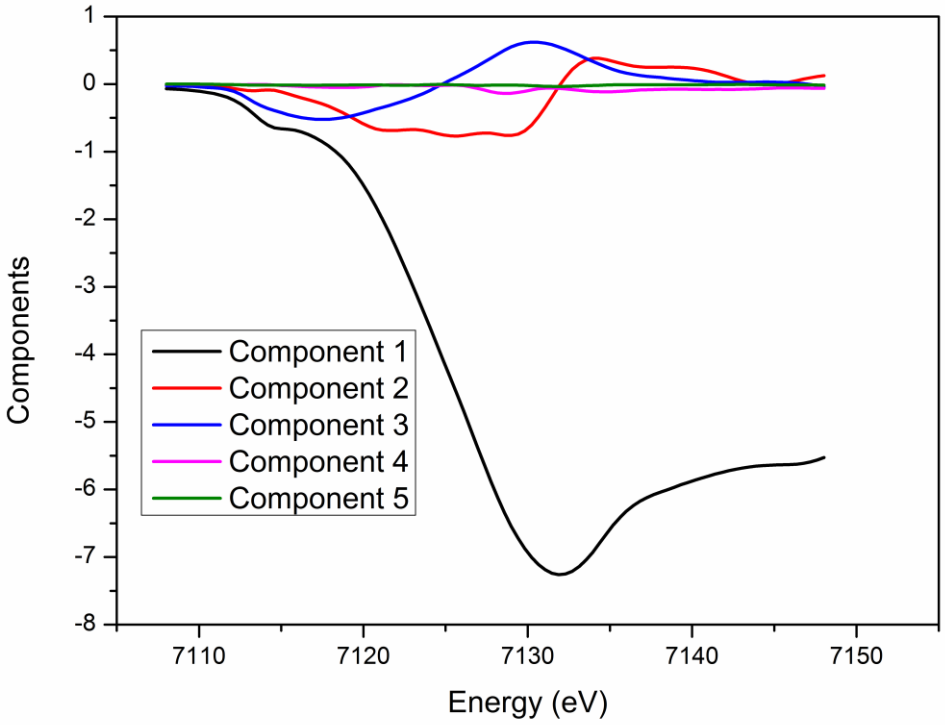

Fig. S3: First five components as obtained from PCA analysis of the *in situ* XANES spectra recorded during the first discharge of Fe_3O_4 electrode.

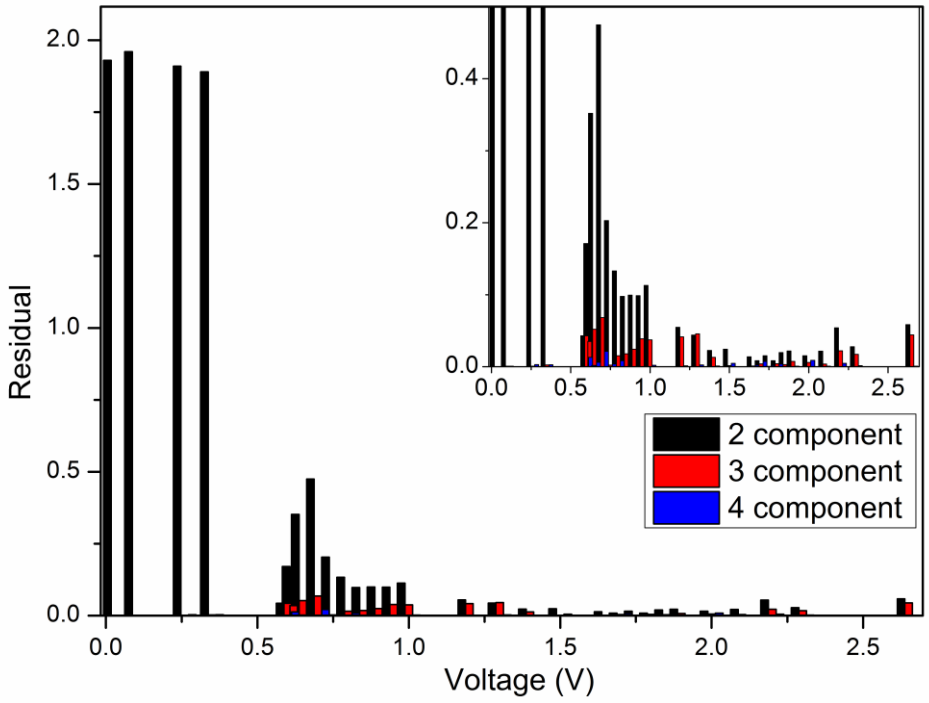

Fig. S4: Residuals of the LCF fittings of the *in situ* XANES spectra recorded during the first discharge of Fe_3O_4 electrode, with two, three and four PCA components. Inset: Enlarged view of the figure.

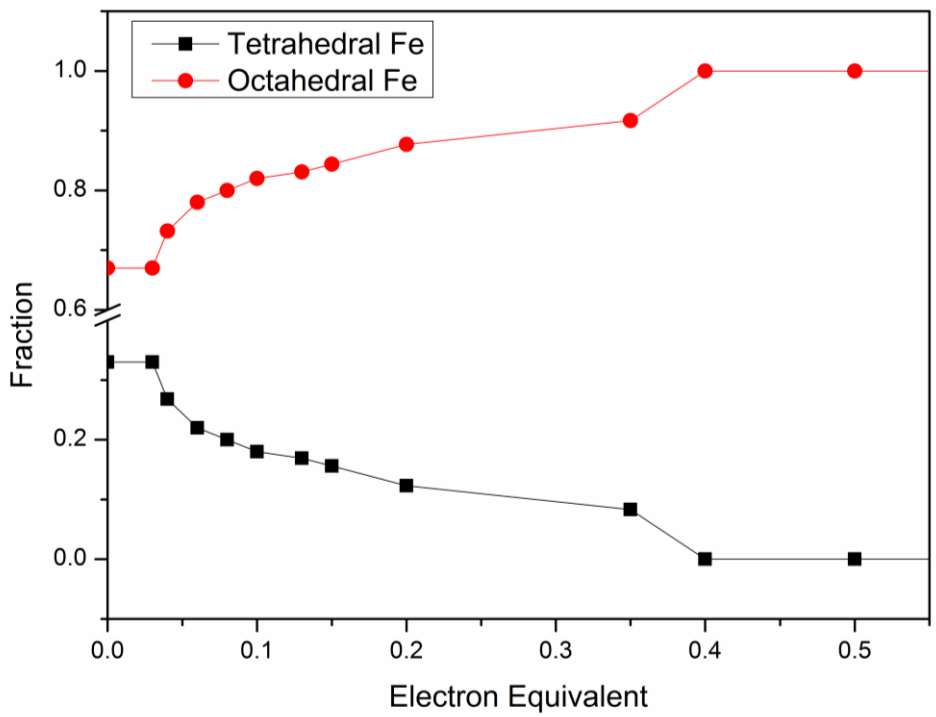

Fig. S5: The variation of tetrahedral and octahedral Fe during the first discharge of Fe_3O_4 electrode.

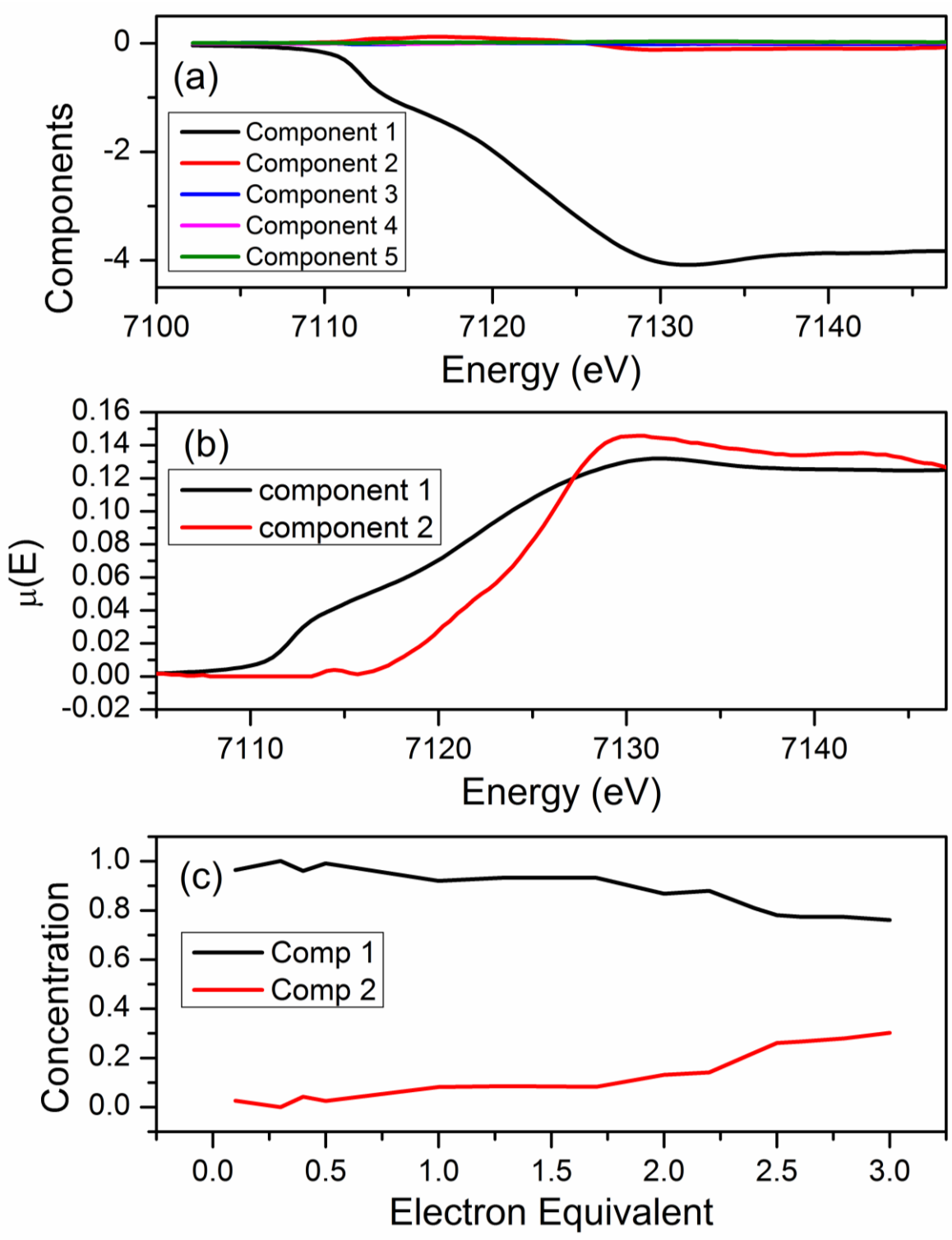

Fig. S6: (a) First five components as obtained from PCA analysis of the *in situ* XANES spectra recorded during the first charge of Fe_3O_4 electrode. (b) XANES spectra of the two species present during the first charge of Fe_3O_4 electrodes as obtained from the MCR-ALS analysis. (c) Concentration profile of the two species obtained from the MCR-ALS analysis during the first charge cycle of Fe_3O_4 electrodes.

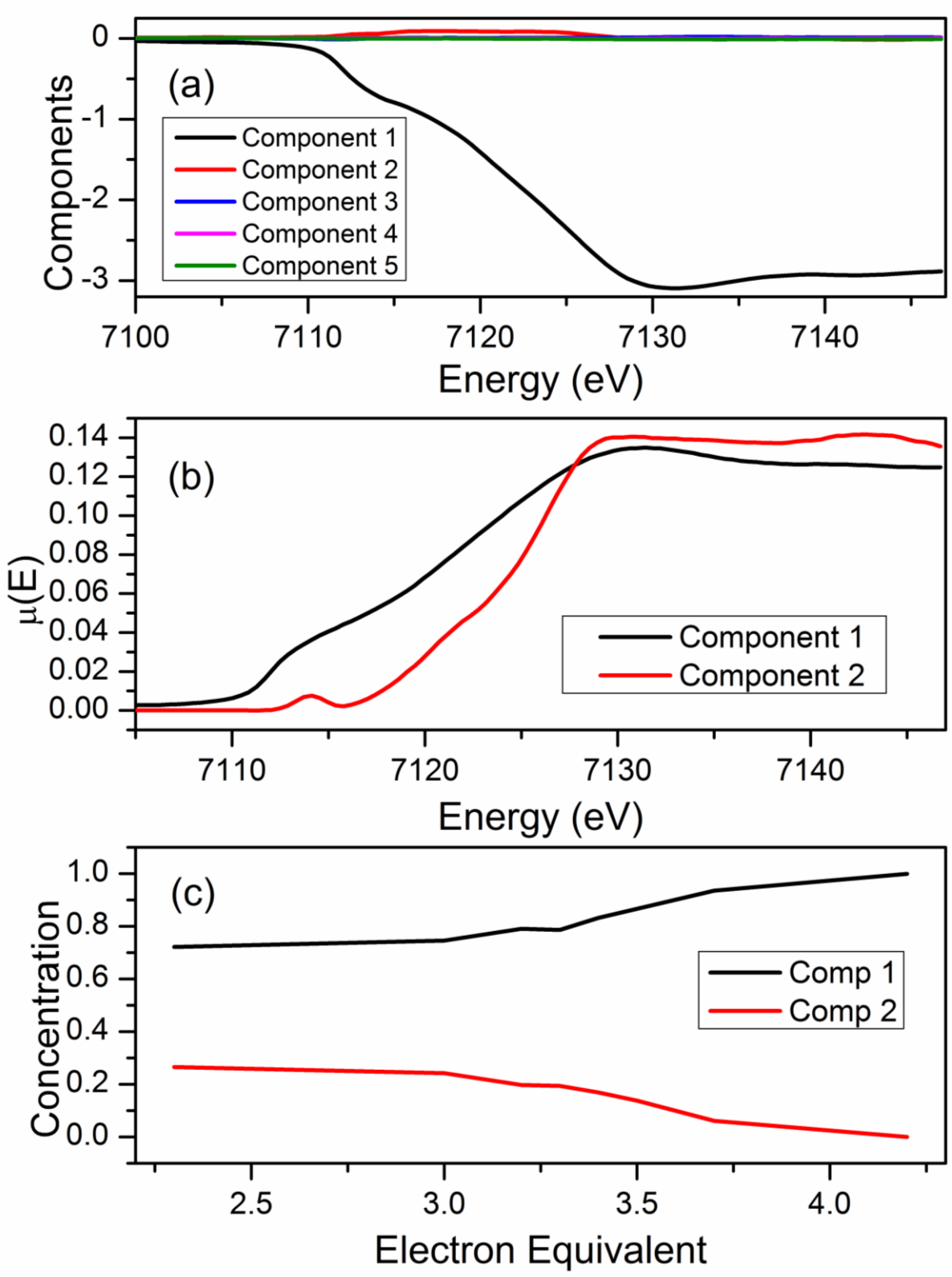

Fig. S7: (a) First five components as obtained from PCA analysis of the *in situ* XANES spectra recorded during the second discharge of Fe_3O_4 electrode. (b) XANES spectra of the two species present during the second discharge of Fe_3O_4 electrodes as obtained from the MCR-ALS analysis. (c) Concentration profile of the two species obtained from the MCR-ALS analysis during the second discharge cycle of Fe_3O_4 electrodes.

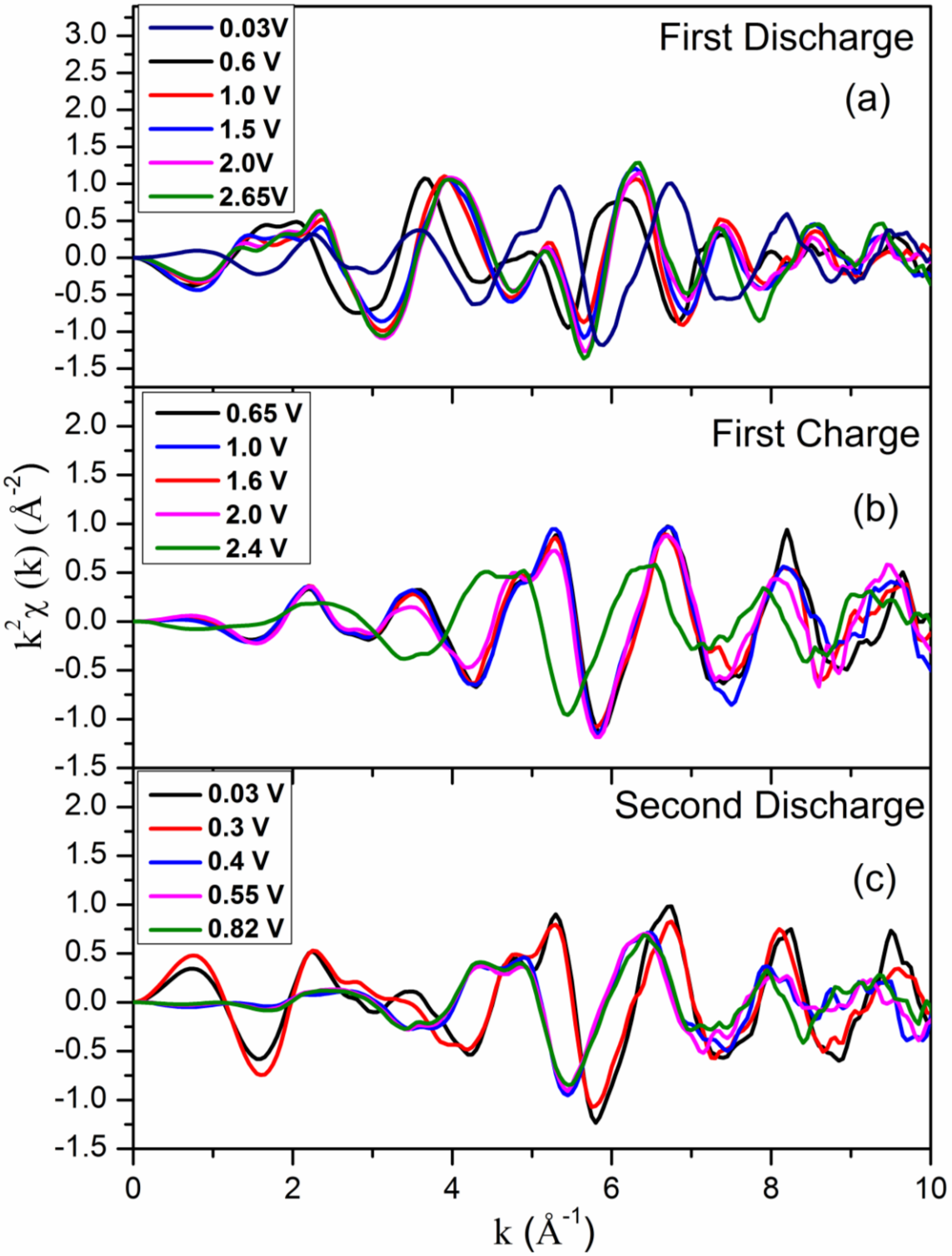

Fig.S8: EXAFS $\chi(k)$ versus k spectra at few selected points during the first discharge, first charge and second discharge of Fe_3O_4 electrode.

Table S1: EXAFS fitting results during the first discharge of Fe_3O_4electrode

0 ee	x(tet)=0.341±0.022		
	R (Å)	N	σ^2 (Å^2)
Fe-O1	1.922 ±0.008	4	0.0005 ±0.0007
Fe-O2	2.084 ±0.007	6	0.0226 ±0.0012
Fe-Fe1	3.029 ±0.006	4.4 ±0.3	0.0129 ±0.0007
Fe-Fe2	3.511 ±0.008	3.9 ±0.4	0.0096 ±0.0009
0.03 ee	x(tet)=0.335±0.018		
	R (Å)	N	σ^2 (Å^2)
Fe-O1	1.934 ±0.005	4	0.0005 ±0.0007
Fe-O2	2.042 ±0.006	6	0.0226 ±0.0015
Fe-Fe1	3.007 ±0.005	4.5 ±0.3	0.0129 ±0.0008
Fe-Fe2	3.516 ±0.007	3.6 ±0.3	0.0096 ±0.0007
0.04 ee	x(tet)=0.268±0.019		
	R (Å)	N	σ^2 (Å^2)
Fe-O1	1.937 ±0.007	4	0.0007 ±0.0005
Fe-O2	2.032 ±0.007	6	0.0209 ±0.0009
Fe-Fe1	3.013 ±0.008	5.4 ±0.5	0.0130 ±0.0009
Fe-Fe2	3.519 ±0.006	2.3 ±0.8	0.0049 ±0.0007
0.06 ee	x(tet)=0.224±0.018		
	R (Å)	N	σ^2 (Å^2)
Fe-O1	1.906 ±0.009	4	0.0008 ±0.0005
Fe-O2	2.009 ±0.008	6	0.0210 ±0.0010
Fe-Fe1	3.010 ±0.008	4.6 ±0.5	0.0116 ±0.0008
Fe-Fe2	3.522 ±0.006	2.0 ±0.7	0.0030 ±0.0007
0.08 ee	x(tet)=0.204±0.016		
	R (Å)	N	σ^2 (Å^2)
Fe-O1	1.941 ±0.007	4	0.0007 ±0.0004
Fe-O2	2.047 ±0.007	6	0.0220 ±0.0009
Fe-Fe1	3.024 ±0.009	4.6 ±0.3	0.0115 ±0.0010
Fe-Fe2	3.528 ±0.007	3.2 ±0.5	0.0092 ±0.0006
0.1 ee	x(tet)=0.186±0.018		

	R (Å)	N	σ^2 (Å^2)
Fe-O1	1.948 ±0.006	4	0.0007 ±0.0004
Fe-O2	2.033 ±0.008	6	0.0228 ±0.0009
Fe-Fe1	3.026 ±0.007	6.0 ±0.2	0.0148 ±0.0009
Fe-Fe2	3.519 ±0.008	2.7 ±0.4	0.0066 ±0.0006
0.13 ee	x(tet)=0.169±0.019		
	R (Å)	N	σ^2 (Å^2)
Fe-O1	1.910 ±0.009	4	0.0006 ±0.0005
Fe-O2	2.036 ±0.007	6	0.0187 ±0.0010
Fe-Fe1	3.028 ±0.006	6.2 ±0.4	0.0156 ±0.0008
Fe-Fe2	3.505 ±0.006	2.4 ±0.5	0.0048 ±0.0007
0.15 ee	x(tet)=0.156±0.015		
	R (Å)	N	σ^2 (Å^2)
Fe-O1	1.921 ±0.008	4	0.0007 ±0.0005
Fe-O2	2.037 ±0.008	6	0.0199 ±0.0010
Fe-Fe1	3.029 ±0.007	6.1 ±0.2	0.0150 ±0.0008
Fe-Fe2	3.511 ±0.006	3.0 ±0.3	0.0084 ±0.0008
0.2 ee	x(tet)=0.123±0.015		
	R (Å)	N	σ^2 (Å^2)
Fe-O1	1.924 ±0.005	4	0.0008 ±0.0006
Fe-O2	2.027 ±0.007	6	0.0205 ±0.0008
Fe-Fe1	3.029 ±0.006	6.1 ±0.2	0.0147 ±0.0009
Fe-Fe2	3.514 ±0.007	2.4 ±0.4	0.0061 ±0.0006
0.35 ee	x(tet)=0.083±0.014		
	R (Å)	N	σ^2 (Å^2)
Fe-O1	1.929 ±0.007	4	0.0007 ±0.0006
Fe-O2	2.011 ±0.008	6	0.0196 ±0.0008
Fe-Fe1	3.023 ±0.008	6.2 ±0.3	0.0151 ±0.0009
Fe-Fe2	3.491 ±0.007	4.4 ±0.2	0.0116 ±0.0007
0.4 ee	x(tet)=0		
	R (Å)	N	σ^2 (Å^2)
Fe-O	2.003 ±0.005	6	0.0181 ±0.0012

Fe-Fe1	3.026 ±0.006	6.1 ±0.3	0.0155 ±0.0008
Fe-Fe2	3.498 ±0.006	3.4 ±0.5	0.0085 ±0.0009
0.5 ee	x(tet)=0		
	R (Å)	N	σ^2 (Å^2)
Fe-O	2.019 ±0.007	6	0.0208 ±0.0010
Fe-Fe1	3.061 ±0.009	6.1 ±0.2	0.0139 ±0.0007
Fe-Fe2	3.509 ±0.008	2.7 ±0.3	0.0091 ±0.0008
0.7 ee	x(tet)=0		
	R (Å)	N	σ^2 (Å^2)
Fe-O	2.016 ±0.007	6	0.0190 ±0.0009
Fe-Fe1	3.015 ±0.005	6.3 ±0.3	0.0145 ±0.0008
Fe-Fe2	3.493 ±0.009	3.1 ±0.5	0.0017 ±0.0008
1 ee	x(tet)=0		
	R (Å)	N	σ^2 (Å^2)
Fe-O	2.087 ±0.006	6	0.0214 ±0.0007
Fe-Fe1	2.977 ±0.006	6.1 ±0.3	0.0165 ±0.0006
Fe-Fe2	3.431 ±0.007	3.9 ±0.4	0.0083 ±0.0009
1.7 ee	x(tet)=0		
	R (Å)	N	σ^2 (Å^2)
Fe-O	2.095 ±0.008	6	0.0186 ±0.0007
Fe-Fe1	2.956 ±0.007	5.9 ±0.4	0.0164 ±0.0008
FeFe2	3.424 ±0.007	2.7 ±0.3	0.0054 ±0.0007
2 ee	x(tet)=0		
	R (Å)	N	σ^2 (Å^2)
Fe-O	2.076 ±0.009	5.9 ±0.3	0.0197 ±0.0009
Fe-Fe	3.069 ±0.009	7.1 ±0.5	0.0137 ±0.0008
4.1 ee	x(tet)=0		
	R (Å)	N	σ^2 (Å^2)
Fe-O	2.084 ±0.008	6.1 ±0.2	0.0171 ±0.0011
Fe-Fe	3.043 ±0.009	11.2 ±0.5	0.0128 ±0.0009
6 ee	x(tet)=0		
	R (Å)	N	σ^2 (Å^2)
Fe-O	2.064 ±0.007	6.2 ±0.3	0.0149 ±0.0009
Fe-Fe	3.025	12.1	0.0177

	±0.008	±0.2	±0.0007
Data fitted with Fe metal structure			
	R (Å)	N	σ^2 (Å^2)
7.2 ee	2.420 ±0.009	5.0 ±0.2	0.0099 ±0.0009
7.6 ee	2.415 ±0.007	5.4 ±0.3	0.0097 ±0.0008
8.7 ee	2.422 ±0.008	5.4 ±0.3	0.0096 ±0.0007
9.5ee	2.421 ±0.007	5.5 ±0.2	0.0112 ±0.0008

Table S2: EXAFS fitting results during the first charge of Fe_3O_4electrode

Electron Equivalent	Fe-Fe (Fe metal)			Fe-O (FeO)		
	r (Å)	N	σ^2	r (Å)	N	σ^2
0.1	2.421 ±0.005	4.5 ±0.2	0.0075 ±0.0008	-	-	-
0.3	2.431 ±0.008	4.5 ±0.3	0.0083 ±0.0009	-	-	-
0.4	2.421 ±0.007	4.4 ±0.2	0.0075 ±0.0007	-	-	-
0.5	2.424 ±0.005	4.3 ±0.2	0.0076 ±0.0007	-	-	-
1.0	2.435 ±0.008	4.1 ±0.4	0.0079 ±0.0009	2.063 ±0.006	1.5 ±0.3	0.0101 ±0.0007
1.3	2.441 ±0.007	4.1 ±0.3	0.0075 ±0.0008	2.133 ±0.008	1.6 ±0.2	0.0099 ±0.0007
1.7	2.442 ±0.007	3.9 ±0.2	0.0077 ±0.0008	2.122 ±0.005	1.6 ±0.2	0.0098 ±0.0008
2.0	2.442 ±0.006	3.8 ±0.3	0.0075 ±0.0007	2.125 ±0.008	2.9 ±0.3	0.0108 ±0.0009
2.2	2.452 ±0.008	3.4 ±0.3	0.0068 ±0.0006	2.082 ±0.008	3.8 ±0.4	0.0143 ±0.0011
2.4	2.460 ±0.005	3.1 ±0.2	0.0056 ±0.0008	2.094 ±0.007	5.4 ±0.2	0.0147 ±0.0010
2.5	2.454 ±0.007	2.8 ±0.2	0.0052 ±0.0005	2.101 ±0.007	5.4 ±0.2	0.0126 ±0.0009
2.6	2.450 ±0.008	2.5 ±0.4	0.0054 ±0.0008	2.106 ±0.005	5.8 ±0.3	0.0122 ±0.0008
2.8	2.459 ±0.006	2.4 ±0.2	0.0054 ±0.0009	2.101 ±0.008	6.0 ±0.2	0.0123 ±0.0009

Table S3: Results of linear combination fitting of the XANES data recorded during the seconddischarge cycle of Fe_3O_4electrode

Voltage(V)	Electron Equivalent	R factor	FeO	Fe
0.03	4.2	0.00367	0.05717	0.94283
0.2	3.7	0.00245	0.08501	0.91499
0.3	3.5	0.00357	0.12509	0.87491
0.35	3.4	0.00477	0.13538	0.86462
0.4	3.3	0.00960	0.1066	0.8934
0.46	3.2	0.00878	0.12944	0.87056
0.55	3.0	0.01211	0.13801	0.86199
0.82	2.3	0.01454	0.1445	0.8555

Table S4: EXAFS fitting results during the second discharge of Fe_3O_4electrode

Electron Equivalent	Fe-Fe (Fe metal)			Fe-O (FeO)		
	r (Å)	N	σ^2	r (Å)	N	σ^2
4.2	2.497 ±0.006	1.7 ±0.2	0.0060 ±0.0007	2.173 ±0.008	5.9 ±0.3	0.0094 ±0.0005
3.7	2.481 ±0.008	2.0 ±0.3	0.0083 ±0.0006	2.184 ±0.009	5.9 ±0.2	0.0103 ±0.0008
3.5	2.434 ±0.005	2.1 ±0.3	0.0047 ±0.0008	2.193 ±0.008	5.9 ±0.3	0.0126 ±0.0008
3.4	2.469 ±0.006	2.1 ±0.2	0.0062 ±0.0007	2.179 ±0.006	5.8 ±0.2	0.0095 ±0.0007
3.3	2.452 ±0.006	3.0 ±0.2	0.0059 ±0.0008	2.085 ±0.007	5.8 ±0.1	0.0101 ±0.0006
3.2	2.454 ±0.007	3.1 ±0.3	0.0054 ±0.0009	2.071 ±0.006	5.5 ±0.2	0.0117 ±0.0007
3.0	2.452 ±0.006	3.1 ±0.2	0.0052 ±0.0008	2.085 ±0.005	4.1 ±0.3	0.0122 ±0.0008
2.3	2.442 ±0.007	3.3 ±0.2	0.0051 ±0.0007	2.089 ±0.006	3.8 ±0.2	0.0106 ±0.0007