Electrochemical (de)lithiation of silver ferrite and composites: Mechanistic insights from *ex-situ, in-situ,* and *operando* x-ray techniques

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Figure S1. Powder X-ray diffraction (XRD) of a Ag_{0.2}FeO_{1.6} composite (0.2) and AgFeO₂ (1.0) with 2H-AgFeO₂ (PDF 01-070-1452) and 3R-AgFeO₂ (PDF 01-075-2147) reference patterns.



Figure S2. Rietveld fitting of powder diffraction data from a Rigaku SmartLab laboratory diffractometer: (a) $AgFeO_2$ fit using a mixed phase model, (b) $AgFeO_2$ fit with a model based on an extended unit cell comprised of 100 stacked lattice planes, and (c) a $Ag_{0.2}FeO_{1.6}$ composite fit using a mixed phase model.



Figure S3. Rietveld of synchrotron XPD data from a $Ag_{0.2}FeO_{1.6}$ silver ferrite/maghemite composite using a combination of hexagonal (2H-AgFeO₂) and rhombohedral (3R-AgFeO₂) phases.

Variable	Ag _{0.2} FeO _{1.6} Composite	AgFeO ₂	Variable	AgFeO₂
Rhombohedral A	3.037(2) Å	3.035(2) Å	A and B	3.0369(4) Å
Rhombohedral C	18.603(9) Å	18.654(3) Å	Plane Spacing	6.2181(4) Å
Rhombohedral Crystal Size	21 nm	9.6 nm	Crystal Size	97 nm (<i>a</i> & <i>b</i>) 45 nm (<i>c</i> -axis)
Rhombohedral Weight %	4.9%	56%	Weight %	100
Hexagonal A	3.044(3) Å	3.031(1) Å	-	-
Hexagonal C	12.52(1) Å	12.46(1) Å	-	-
Hexagonal Crystal Size	13 nm	45 nm	-	-
Hexagonal Weight %	8.6%	44%	-	-
Maghemite A	8.441(8) Å	-	-	-
Maghemite Crystal Size	1.7 nm	-	-	-
Maghemite Weight %	86%	-	-	-
Rwp	10.32%	18.19%	Rwp	7.58%

Table S1. Rietveld fitting parameters of AgFeO₂ (mixed phase and (1 0 0) layer models) and a Ag_{0.2}FeO_{1.6} composite (mixed phase model) diffraction data from a Rigaku SmartLab instrument.



Figure S4. XANES spectra of pristine AgFeO₂, a Ag_{0.2}FeO_{1.6} composite, and amorphous γ -Fe₂O₃.



Figure S5. Ex-situ XANES (Fe K-edge) spectra of electrochemically cycled (a) AgFeO₂ and (b) a $Ag_{0.2}FeO_{1.6}$ composite with FeO and Fe metal standards.



Figure S6. Fluorescence maps and normalized absorption spectrum of Li/AgFeO₂ cell discharged to 0.3 V (Cell B). The normalized absorption spectrum of Cell B is compared to the normalized absorption spectrum of iron metal powder standard.



Figure S7: EXAFS fit of the undischarged AgFeO₂ electrode in $|\chi(R)|$ at the Ag K-edge.



Figure S8: EXAFS fit of the partially discharged AgFeO₂ electrode in $|\chi(R)|$ at the Ag K-edge.



Figure S9: EXAFS fit of the 1^{st} discharge AgFeO₂ electrode in $|\chi(R)|$ at the Ag K-edge.



Figure S10: EXAFS fit of the undischarged AgFeO₂ electrode in $|\chi(R)|$ at the Fe K-edge.



Figure S11: EXAFS fit of the partially discharged AgFeO₂ electrode in $|\chi(R)|$ at the Fe K-edge.



Figure S12: EXAFS fit of the 1st discharge AgFeO₂ electrode in $|\chi(R)|$ at the Fe K-edge.



Figure S13: EXAFS fit of the 1^{st} charge AgFeO₂ electrode in $|\chi(R)|$ at the Fe K-edge.



Figure S14: EXAFS fit of the undischarged Ag_{0.2}FeO_{1.6} electrode in $|\chi(R)|$ at the Fe K-edge.



Figure S15: EXAFS fit of the partially discharged Ag_{0.2}FeO_{1.6} electrode in $|\chi(R)|$ at the Fe K-edge.



Figure S16: EXAFS fit of the 1st discharge Ag_{0.2}FeO_{1.6} electrode in $|\chi(R)|$ at the Fe K-edge.



Figure S17: EXAFS fit of the 1^{st} charge Ag_{0.2}FeO_{1.6} electrode in $|\chi(R)|$ at the Fe K-edge.

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State	Edge	Combined R-factor
AgFeO ₂ undischarged	Ag	3.5
AgFeO ₂ partial discharge	Ag	2.9
AgFeO₂1st discharge	Ag	2.2
AgFeO₂ undischarged	Fe	3.3
AgFeO ₂ partial discharge	Fe	1.1
AgFeO₂1st discharge	Fe	1.4
AgFeO₂ 1st charge	Fe	1.4
$Ag_{0.2}FeO_{1.6}$ undischarged	Fe	1.0
Ag _{0.2} FeO _{1.6} partial discharge	Fe	1.3
Ag _{0.2} FeO _{1.6} 1st discharge	Fe	0.9
Ag _{0.2} FeO _{1.6} 1st charge	Fe	1.3

Table S2. Combined R-factor from EXAFS fits of k, k^2 and k^3 k-weights for all fits.

State	Edge	E _o (eV)
AgFeO ₂ undischarged	Ag	3.33 ± 1.54
AgFeO ₂ partial discharge	Ag	2.37 ± 0.64
AgFeO ₂ 1st discharge	Ag	2.59 ± 0.56
AgFeO ₂ undischarged	Fe	-0.08 ± 1.42
AgFeO ₂ partial discharge	Fe	-0.25 ± 1.33
AgFeO ₂ 1st discharge	Fe	0.30 ± 0.96
AgFeO₂ 1st charge	Fe	0.30 ± 0.51
Ag _{0.2} FeO _{1.6} undischarged	Fe	-0.38 ± 2.76
Ag _{0.2} FeO _{1.6} partial discharge	Fe	-5.63 ± 2.19
Ag _{0.2} FeO _{1.6} 1st discharge	Fe	-4.29 ± 0.13
Ag _{0.2} FeO _{1.6} 1st charge	Fe	-2.44 ± 2.25

 $\label{eq:table_state} \textbf{Table S3.} \ E_0 \ values \ for \ all \ fits.$

		Debye Waller Factor (Å ⁻²)			
		r	leighboring atom		
State	Core atom	O Ag Fe			
AgFeO ₂ undischarged	Ag	0.012 ± 0.006	0.015 ± 0.004	0.015 ± 0.004	
AgFeO ₂ partial discharge	Ag	-	0.014± 0.002	-	
AgFeO ₂ 1st discharge	Ag	-	0.013±0.001	-	
AgFeO ₂ undischarged	Fe	0.006 ± 0.002	0.006 ± 0.002	0.006 ± 0.003	
AgFeO ₂ partial discharge	Fe	0.006 ± 0.002	-	0.011 ± 0.002	
AgFeO ₂ 1st discharge	Fe	0.005 ± 0.002	-	0.011 ± 0.002	
AgFeO ₂ 1st charge	Fe	0.005 ± 0.002	-	0.011 ± 0.002	
Ag _{0.2} FeO _{1.6} undischarged	Fe	0.005 ± 0.004	0.008 ± 0.003	0.008 ± 0.003	
Ag _{0.2} FeO _{1.6} partial discharge	Fe	0.006 ± 0.002	-	0.015 ± 0.004	
Ag _{0.2} FeO _{1.6} 1st discharge	Fe	0.013 ± 0.004	-	0.014 ± 0.005	
Ag _{0.2} FeO _{1.6} 1st charge	Fe	0.008 ± 0.002		0.013 ± 0.002	

 Table S4. Debye-Waller factor values for all fits.

	State			
Path	AgFeO ₂ undischarged	AgFeO ₂ partial discharge	AgFeO ₂ 1st discharge	
Ag-O (AgFeO ₂)	1.2 ± 0.3	-	-	
Ag-Ag (AgFeO ₂)	3.7 ± 0.8	-	-	
Ag-Fe (AgFeO ₂)	3.7 ± 0.8	-	-	
Ag-O (AgFeO ₂)	7.4 ± 1.6	-	-	
Ag-Ag (Ag metal)	-	8.4 ± 1.0	8.9 ± 0.8	

Table S5. Number of near neighbors EXAFS fitting results for AgFeO₂ electrodes at the Ag K-edge.

Path	AgFeO ₂ undischarged	AgFeO ₂ partial discharge	AgFeO ₂ 1st discharge
Ag-O (AgFeO ₂)	2.07 ± 0.03 Å	-	-
Ag-Ag (AgFeO ₂)	2.89 ± 0.03 Å	-	-
Ag-Fe (AgFeO ₂)	3.65 ± 0.08 Å	-	-
Ag-O (AgFeO ₂)	3.47 ± 0.04 Å	-	-
Ag-Ag (Ag metal)	-	2.86 ± 0.01 Å	2.85 ± 0.01 Å

Table S6. Interatomic distances EXAFS fitting results for AgFeO₂ electrodes at the Ag K-edge.

	State			
Path	AgFeO ₂ undischarged	AgFeO₂ partial discharge	AgFeO ₂ 1st discharge	AgFeO₂ 1st charge
Fe-O (AgFeO ₂)	4.8 ± 0.2	3.5 ± 0.3	3.5 ± 0.3	3.5 ± 0.2
Fe-Fe (AgFeO ₂)	4.8 ± 0.3	3.5 ± 0.3	3.5±0.3	3.5 ± 0.3
Fe-O (AgFeO ₂)	4.8 ± 0.2	2.0 ± 0.5	1.8 ± 0.5	1.6 ± 0.3
Fe-Ag (AgFeO ₂)	1.4 ± 0.7	-	-	-

Table S7. Number of near neighbors EXAFS fitting results for AgFeO2 electrodes at the Fe K-
edge.

	State			
Path	AgFeO ₂ undischarged	AgFeO₂ partial discharge	AgFeO₂ 1st discharge	AgFeO ₂ 1st charge
Fe-O (AgFeO ₂)	2.02 ± 0.01 Å	2.01 ± 0.01 Å	2.02 ± 0.01 Å	1.99 ± 0.01 Å
Fe-Fe (AgFeO ₂)	3.05 ± 0.01 Å	3.05 ± 0.01 Å	3.05± 0.02 Å	3.06 ± 0.01 Å
Fe-O (AgFeO ₂)	3.64 ± 0.01 Å	2.95 ± 0.03 Å	2.95 ± 0.04 Å	2.94 ± 0.03 Å
Fe-Ag (AgFeO ₂)	3.55 ± 0.05 Å	-	-	-

Table S8. Interatomic distances EXAFS fitting results for AgFeO₂ electrodes at the Fe K-edge.

	State			
Path	Ag _{0.2} FeO _{1.6} undischarged	Ag _{0.2} FeO _{1.6} partial discharge	Ag _{0.2} FeO _{1.6} 1st discharge	Ag _{0.2} FeO _{1.6} 1st charge
Fe-O (AgFeO ₂)	4.1 ± 1.1	-	-	-
Fe-Fe (AgFeO ₂)	4.1 ± 1.1	-	-	-
Fe-O (AgFeO ₂)	1.4 ± 0.5	-	-	-
Fe-Ag (AgFeO ₂)	0.3 ± 0.2	-	-	-
$Fe_{tetrahedral}$ -O (γ -Fe ₂ O ₃)	0.3 ± 0.1	-	-	-
$Fe_{tetrahedral}$ -Fe (γ -Fe ₂ O ₃)	1.2 ± 0.5	-	-	-
$Fe_{tetrahedral}$ -O (γ -Fe ₂ O ₃)	1.4 ± 0.5	-	-	-
$Fe_{tetrahedral}$ -Fe (γ -Fe ₂ O ₃)	1.4 ± 0.5	-	-	-
Fe-O (rock salt FeO)	-	1.4 ± 0.3	2.8 ± 0.7	4.1 ± 0.7
Fe-Fe (rock salt FeO)	-	1.4 ± 0.3	2.8 ± 0.7	4.1 ± 0.7
Fe-O (rock salt FeO)	-	3.1 ± 0.5	3.2 ± 0.7	1.6 ± 0.5
Fe-Fe (Fe metal)	-	2.4 ± 0.7	2.5 ± 0.7	-

Table S9. Number of near neighbors EXAFS fitting results for Ag_{0.2}FeO_{1.6} electrodes at the Fe K-edge.

	State			
Path	AgFeO₂ undischarged	AgFeO₂ partial discharge	AgFeO ₂ 1st discharge	AgFeO₂ 1st charge
Fe-O (AgFeO ₂)	1.98 ± 0.01 Å	-	-	-
Fe-Fe (AgFeO ₂)	3.10 ± 0.02 Å	-	-	-
Fe-O (AgFeO ₂)	3.71 ± 0.05 Å	-	-	-
Fe-Ag (AgFeO ₂)	3.59 ± 0.05 Å	-	-	-
$Fe_{tetrahedral}$ -O (γ -Fe ₂ O ₃)	1.90 ± 0.04 Å	-	-	-
$Fe_{tetrahedral}$ -Fe (γ -Fe ₂ O ₃)	3.48 ± 0.05 Å	-	-	-
$Fe_{tetrahedral}$ -O (γ -Fe ₂ O ₃)	2.16 ± 0.04 Å	-	-	-
Fe _{tetrahedral} -Fe (γ-Fe ₂ O ₃)	2.97 ± 0.05 Å	-	-	-
Fe-O (rock salt FeO)	-	1.93 ± 0.01 Å	2.01 ± 0.01 Å	1.96 ± 0.01 Å
Fe-Fe (rock salt FeO)	-	3.08 ± 0.02 Å	3.04 ± 0.01 Å	3.04 ± 0.01 Å
Fe-O	-	2.73 ± 0.02 Å	2.68 ± 0.02 Å	2.84 ± 0.04 Å
Fe-Fe (Fe metal)	-	2.53 ± 0.01 Å	2.51 ± 0.01 Å	-

Table S10. Interatomic distance EXAFS fitting results for $Ag_{0.2}FeO_{1.6}$ electrodes at the Fe K-edge.