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

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Abstract

The structure of pristine AgFeO₂ and phase makeup of Ag_{0.2}FeO_{1.6} (a one-pot composite comprised of nanocrystalline stoichiometric AgFeO₂ and amorphous γ -Fe₂O₃ phases) was investigated using synchrotron x-ray diffraction. A new stacking-fault model was proposed for AgFeO₂ powder synthesized using the co-precipitation method. The lithiation/de-lithiation mechanisms of silver ferrite, AgFeO₂ and Ag_{0.2}FeO_{1.6} were investigated using *ex-situ*, *in-situ*, and *operando* characterization techniques. An amorphous γ -Fe₂O₃ component in the Ag_{0.2}FeO_{1.6} sample is quantified. *Operando* XRD of electrochemically reduced AgFeO₂ and Ag_{0.2}FeO_{1.6} composites demonstrated differences in the structural evolution of the nanocrystalline AgFeO₂ component. As complimentary techniques to XRD, *ex-situ* x-ray Absorption Spectroscopy (XAS) provided insight into the short-range structure of the (de)lithiated nanocrystalline electrodes, and a novel in-situ high energy x-ray fluorescence nanoprobe (HXN) mapping measurement was applied to spatially resolve the progression of discharge. Based on the results, a redox mechanism is proposed where the full reduction of Ag⁺ to Ag⁰ and partial reduction of Fe³⁺ to Fe²⁺ occur on reduction to 1.0 V, resulting in a Li_{1+y}Fe^{III}Fe^{II}_yO₂ phase. The Li_{1+y}Fe^{III}Fe^{II}_yO₂ phase can then reversibly cycle between Fe³⁺ and Fe²⁺ oxidation states, permitting good capacity retention over 50 cycles. In the Ag_{0.2}FeO_{1.6} composite, a substantial amorphous γ -Fe₂O₃ component is observed which discharges to rock salt LiFe₂O₃ and Fe⁰ metal phase in the 3.5 – 1.0 V voltage range (in parallel with the AgFeO₂ mechanism), and reversibly reoxidizes to a nanocrystalline iron oxide phase.

Introduction

Silver ferrite, AgFeO₂, belongs to the delafossite mineral group which consists of ternary transition metal oxides with the chemical formula ABO₂. Typically, ABO₂ oxides are layered materials where monovalent and trivalent cations occupy the A and B sites, respectively, and are viable electrode materials for rechargeable lithium-based batteries owing to the robust layered framework which facilitates lithium intercalation and 2-D transport of ions. Investigations regarding delafossite oxides in lithium-based batteries include CuFeO₂¹ and

CuCrO₂² as anodes in lithium-ion batteries, AgNiO₂ in alkaline³ and zinc⁴ batteries, and AgCuO₂, AgCu_{0.5}Mn_{0.5}O₂⁵ and CuFeO₂⁶ as cathodes in lithium batteries. Silver delafossites (AgBO₂ where B = 3+ transition metal) are interesting model electrode materials. Their layered structure is of interest for investigation owing to the reduction displacement of Ag⁺ cations, within the layered structure, to metallic Ag⁰ nanoparticles. The formation of Ag metal is expected to provide performance enhancement in the form of an *in-situ* conductive network, as has been observed in some layered materials.⁷

The first reported powder XRD pattern of silver ferrite described a rhombohedral ($R\bar{3}m$) or 3R-AgFeO₂ phase, also referred to as α -AgFeO₂⁸ and the first single crystal structure refinement of 3R-AgFeO₂ was later performed.⁹ In addition to the rhombohedral α -AgFeO₂ phase, it was shown that AgFeO₂ could also crystallize in a hexagonal structure.¹⁰ Refinement of a single crystal of the new hexagonal phase, denoted as 2H-AgFeO₂, showed that it crystallized in the *P63/mmc* space group.¹¹ The 3R and 2H structures are both composed of alternating FeO₆ and Ag layers, but differ in the plane stacking sequence, **Figure 1**.

AgFeO₂ has been prepared by both reflux and hydrothermal techniques.^{8, 12} In 2012, the first low-temperature co-precipitation of AgFeO₂ was reported.¹³ Imaging of the low-temperature prepared material indicated acicular particles with uniform crystallites with an average size of 31 nm.¹³ More recently, the same co-precipitation synthesis using a non-stoichiometric combination of reagents was found to produce composite materials comprised of crystalline AgFeO₂ and amorphous maghemite, γ -Fe₂O₃, which has been defined as Ag_xFeO_y (**Equation 1**).¹⁴

The composite nature of Ag_xFeO_y prepared via a one-pot synthesis has been established as a mixture of crystalline AgFeO₂ and amorphous γ -Fe₂O₃ using x-ray absorption near edge structure (XANES) and Raman spectroscopic analyses.¹⁴⁻¹⁵ In a previous report, high resolution transmission electron microscopy (HRTEM) of a Ag_xFeO_y ($x = 0.2$, $y = 1.6$) composite material showed crystalline acicular AgFeO₂ nanoparticles uniformly dispersed among irregularly-shaped, poorly crystalline and porous γ -Fe₂O₃ particles.¹⁵ Furthermore, analysis of powder XRD data illustrated that both the 2H-AgFeO₂ and 3R-AgFeO₂ phases appeared to be present in the Ag_xFeO_y composite.¹⁴ The mixture of both hexagonal and rhombohedral phases in the material has precedence in the literature, with reports of other synthesized delafossite materials AgGaO₂,¹⁶ AgScO₂,¹⁷ as well as a previous study on AgFeO₂¹⁸ all indicating the presence of both hexagonal and rhombohedral AgMO₂ (M = Ga, Sc, or Fe) phases.

The electrochemistry of Ag_xFeO_y composites, AgFeO₂, and γ -Fe₂O₃ was recently investigated;¹⁵ however, the lithiation and delithiation mechanism is not well understood. Reduced Ag_xFeO_y composites are expected to have improved conductivity relative to the pristine material due to the *in-situ* generation of conductive Ag⁰ nanoparticles; this paradigm was extended from the silver containing phosphate material silver vanadium phosphorous oxide (Ag₂VO₂PO₄)¹⁹. In the previous study on Ag_xFeO_y composites, a Ag_{0.2}FeO_{1.6} composite displayed enhanced cycling efficiency and 100% higher delivered capacity than stoichiometric AgFeO₂ over 50 cycles¹⁵.

In the current study the lithiation and de-lithiation mechanisms of both $\text{Ag}_{0.2}\text{FeO}_{1.6}$ and stoichiometric AgFeO_2 are investigated. Both *operando* and *ex-situ* XRD, as well as *ex-situ* X-ray absorption spectroscopy (XAS), and *in-situ* X-ray fluorescence nanoprobe mapping (HXN1, HXN2, HXN3) techniques²⁰ were used to probe several (de)lithiation states of the materials. XRD and XAS are complimentary methods, with XRD well suited to observe changes in crystalline phases and XAS sensitive to the local structure of atoms within the sample. XAS has been used previously to elucidate the evolution of the oxidation state of lithiated transition metal oxides and determine mechanisms during electrochemical cycling.²¹ Both X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) regions of Fe and Ag K-edge XAS spectra were analyzed, with XANES providing oxidation state information and EXAFS offering quantitative information regarding interatomic distances and the coordination environment to the absorbing Fe and Ag atoms. A novel *in-situ* x-ray fluorescence nanoprobe mapping measurement was also applied to evaluate the reduction process at 0.3 V, providing spatial information regarding the discharge progression.

Experimental

Synthesis. Silver ferrite was synthesized using a reaction adapted from previously reported schemes based on co-precipitation.^{13-14, 22} In brief, solutions of silver nitrate, iron(III) nitrate, and sodium hydroxide in deionized water were combined yielding a dark precipitate. Stoichiometric amounts of silver nitrate and iron (III) nitrate were added to synthesize AgFeO_2 , while for the “one pot” synthesis of $\text{Ag}_{0.2}\text{FeO}_{1.6}$, the mass of iron (III) nitrate was kept constant and the mass of silver nitrate was reduced to achieve a 1:5 Ag/Fe ratio.

X-Ray Diffraction (XRD). Diffraction patterns of the materials were collected at the 28-ID beamline at the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory, NY. The samples were sealed in Kapton tubes for measurement. The X-ray beam was calibrated to 0.1899 Å and a 16-inch CsI scintillation detector was used. LaB_6 was used as a standard and each two-dimensional pattern was integrated using GSAS-II.²³ Data were analyzed using GSAS-II²³ and DIFFaX.²⁴ XRD data for AgFeO_2 and $\text{Ag}_{0.2}\text{FeO}_{1.6}$ samples were also collected at room temperature on a Rigaku SmartLab system with $\text{Cu-K}\alpha$ radiation and Bragg-Brentano geometry.

Operando XRD. *Operando* XRD measurements were conducted using a custom electrochemical cell with a Rigaku Miniflex diffractometer utilizing a D/tex 1D Si strip detector. AgFeO_2 and $\text{Ag}_{0.2}\text{FeO}_{1.6}$ electrodes were discharged at a 45 mA/g rate using a Bio-Logic multichannel potentiostat/galvanostat. XRD spectra were collected repeatedly during electrochemical reduction in a 2θ region of 25-85° after an initial scan at open circuit voltage (OCV). Each XRD scan took approximately 20 minutes.

Electrochemistry. Two electrode coin type cells were used to electrochemically reduce and oxidize AgFeO_2 and the $\text{Ag}_{0.2}\text{FeO}_{1.6}$ composite material. Electrodes were prepared by mixing silver ferrite with conductive carbon black and polyvinylidene fluoride (PVDF) binder for a composition of 85% active material, 10% conductive carbon black, and 5% binder and casting on an aluminum foil substrate. An electrolyte solution of 1 M LiPF_6 in 30/70 (v/v) ethylene carbonate/dimethyl carbonate was used for electrochemical testing. Galvanostatic cycling over 50 cycles was performed from 1.0 V to 3.5 V using a current of 45 mA/g of active material using a Maccor Series 4000 Battery Test System with temperature chamber maintained at 30°C.

Ex-situ XAS. AgFeO₂ and Ag_{0.2}FeO_{1.6} electrodes for XAS analysis were prepared by electrochemically discharging and charging within a standard coin-type cell to specified depths of discharge/charge. The depths of discharge targeted for the EXAFS study were undischarged, partially discharged (defined as 1 molar electron equivalent; 137 mAh/g and 260 mAh/g for AgFeO₂ and Ag_{0.2}FeO_{1.6}, respectively), 1st discharge (defined as 2 molar electron equivalents, 274 mAh/g and 520 mAh/g for AgFeO₂ and Ag_{0.2}FeO_{1.6}, respectively), and 1st charge (recharged to 3.5 V after discharge to 2 electron equivalents). The samples were recovered and sealed between polyimide tape and stored within an inert atmosphere until XAS data were collected. XAS measurements of the Fe K-edge (7.112 keV) were acquired at Sector 12-BM at the Advanced Photon Source (APS) at Argonne National Laboratory, IL. The Ag K-edge (25.514 keV) spectra were collected at the X18C beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, NY. Both Fe and Ag K-edge measurements were collected in transmission geometry with the incident and transmitted X-ray flux monitored with ionization chambers. For both Fe and Ag K-edge measurements, Fe and Ag metal reference foils were utilized, respectively, for proper initial beam energy calibration. The reference foils were also measured simultaneously with each sample spectrum to ensure proper alignment of multiple scans during data normalization and analysis.

The extended X-ray absorption fine structure (EXAFS) spectra were aligned, merged and normalized using Athena.²⁵ The background was removed below 1.0 Å using the standard AUTOBK algorithm. Both the Fe and Ag K-edge measurements were fit in Artemis with theoretical models generated from known crystal structures of rhombohedral AgFeO₂,²⁶ inverse-spinel γ-Fe₂O₃,²⁷ Fe metal,²⁸ and Ag metal²⁹ using FEFF6.^{25a, 30} All spectra were fit using a k range of 2-11 Å⁻¹ using a Hanning Fourier transform window with dk = 2 and were fit simultaneously using k, k², and k³ weighting. An R-range was used to fully encompass the first and second coordination shells, typically between 1-3.2 Å or 1-3.6 Å. Initially, an S₀² value of ~0.85 was determined from fitting Fe and Ag metal standards, and this term was utilized in all fits to account for intrinsic losses in the electron propagation and scattering process caused by core-hole effects.³¹

The undischarged spectra of AgFeO₂ were fit using the rhombohedral AgFeO₂ crystal structure for both the Ag and Fe K-edge measurements. The Ag_{0.2}FeO_{1.6} composite data was modeled using a combination of the AgFeO₂ structure combined with the structure of γ-Fe₂O₃. The discharged and subsequent charged electrochemical states were modeled using a combination of metallic (Ag or Fe) or the original AgFeO₂ structure. The data and subsequent fitting results dictated which phases that were included or excluded from each model. If a specific phase resulted in a small relative amplitude (near 0 with estimated standard deviations) or fitting variables were unrealistic and/or statistically insignificant, it was excluded from further models at that electrochemical state.

In-situ X-ray fluorescence nanoprobe mapping. Specially designed electrochemical cells with polypropylene based housing and pouch cell construction were assembled under dry room atmosphere, with lithium foil, polypropylene separator, and a AgFeO₂ working electrode with 1M LiPF₆ ethylene carbonate:dimethylcarbonate (EC:DMC) (3:7 v/v) electrolyte. The working electrode was composed of 60% AgFeO₂, 30% Super P carbon, and 10% PVDF on a carbon substrate. Two cells were prepared (A and B), where Cell A was kept at open circuit voltage (OCV), and Cell B was galvanostatically discharged at C/2 rate to 0.3 V.

Fe K-edge fluorescence maps were collected on the cells at the Hard X-ray Nanoprobe (HXN) Beamline at NSLS-II. A nanofocused x-ray beam with a 60 nm spot size was produced using an x-ray zoneplate. For each cell, fluorescence maps were collected at energies of 7100, 7113, 7116, 7118, 7120, 7123, 7126, 7128, 7130, 7132, 7134, 7138, 7150, and 7200 eV using a step size of 200 nm and acquisition time of 0.1 s per step, utilizing continuous fly-scans. Maps were collected from areas of 30 x 30 μm and 20 x 20 μm for cells A and B, respectively. Absorption maps were then generated in PyXRF software by fitting fluorescence spectra, dividing the integrated fluorescence intensity by incident beam intensity and were aligned in ImageJ using the JavaSIFT plugin. Following alignment, images were cropped to dimensions of 24 x 24 μm and 18.6 x 18.6 μm , respectively. The intensities for each map in a set (Cell A, Cell B) were normalized against the intensity of the map measured at 7200 eV for that set.

Results and Discussion

X-Ray Diffraction (XRD). **Figure 1** shows synchrotron based X-ray powder diffraction (XPD) stoichiometric AgFeO_2 while **Figure S1** shows diffraction data collected using a laboratory diffractometer. **Figure S3** shows diffraction data of the $\text{Ag}_{0.2}\text{FeO}_2$ sample. Detailed analysis of the data reveals that a combination of hexagonal and rhombohedral phases does not fit the observed diffraction patterns of stoichiometric AgFeO_2 well, most notably in the shoulder region from 4.3 to 4.9° 2-theta and near the broad, asymmetric reflection centered at 6.3° (**Figure S2a**). Simulations using DIFFaX software²⁴ in **Figures 1b** and **S2c** show that the observed diffraction patterns are better matched by a stacking fault model. The hexagonal (2H) and rhombohedral (3R) AgFeO_2 phases differ from each other due to stacking of alternating layers of edge-shared FeO_6 octahedra and close-packed Ag^+ metal cations (**Figure 1c**). 2H- AgFeO_2 follows an XYXYXY pattern where X can be envisioned as the repeating combination of A (Ag) and B (Fe) lattice planes while Y is defined as the repeating combination of C (Ag) and B (Fe) layers in **Figure 1g**. Conversely, 3R- AgFeO_2 follows an XYZXYZ pattern where the A (Ag), B (Fe), and C (Ag) layers comprise the repeating XYZ unit.

Prior to building a stacking fault model, the geometry of each plane in AgFeO_2 was examined. Iron atoms form a hexagonal lattice with a plane of oxygen atoms above and below (**Figure 1f**) where the iron atoms are octahedrally coordinated to oxygen atoms. In the iron oxide (FeO_6) layers, the iron and the oxygen atoms are offset from each other (**Figure 1d**). Between FeO_6 layers, silver atoms are linearly coordinated between oxygen atoms (**Figure 1e**) which geometrically constrains silver planes to be offset from the nearest iron planes. Furthermore, since oxygens above and below each iron plane are offset from each other, the silver planes must be offset from the next nearest silver plane as well. Because there are only three choices of plane type (A, B, or C) in **Figure 1f and g**, each silver lattice plane is fully constrained by the two planes previous (one Fe and one Ag). Therefore, the only plane that can vary is the iron lattice plane, which can either match the previous iron plane (resulting in hexagonal XYXYXY stacking behavior) or mismatch both the previous iron and silver planes (resulting in rhombohedral XYZXYZ stacking behavior). While the authors are not aware of a previous report of this model for ferrite materials, the model bears some similarities to that reported for CuScO_2 .³²

Using the DIFFaX software package, the structure was simulated assuming the iron atoms would stack either hexagonally or rhombohedrally with a 50% probability. The DIFFaX

simulation in **Figure 1b**, using a 100 layer random stacking model, illustrates a reasonable match to the synchrotron XPD data. To obtain lattice parameters and crystallite size, the AgFeO₂ structure was further simulated using GSAS-II. We generated an extended unit cell comprised of 100 stacked lattice planes in Matlab. The structure was then imported into GSAS II, where it provided a reasonable fit. A likely limitation to this fitting method is that it may overestimate the peak widths and underestimate the crystallite sizes.

The XPD pattern of a Ag_{0.2}FeO_{1.6} composite in **Figure S3** demonstrates broad peaks over 2 θ value ranges of 3.7-4.8° and 6.5-7.6°, situated below the AgFeO₂ diffraction pattern, which are indicative of a poorly crystalline maghemite (γ -Fe₂O₃) phase. The Ag_{0.2}FeO_{1.6} composite appears to be represented as a mixture of rhombohedral and hexagonal phases, especially with respect to minor peak splitting at 4.1° and separated peaks at 6.0° and 6.2°. However, the peaks at 6.6° and 3.9° do not correspond with any of the structures used for refinement and could represent an impurity phase or a lower-symmetry structure. The maghemite structure was simulated with a small crystallite size, 1.7 nm, to estimate the weight percent of this phase. The Ag_{0.2}FeO_{1.6} composite material has a much smaller crystallite size than for the AgFeO₂ material (**Table 1**) which is also observed as decreased intensity of the Ag_{0.2}FeO_{1.6} composite diffraction pattern in **Figure S1** and has been reported previously.¹⁴⁻¹⁵ The lattice parameters for the rhombohedral (3R-AgFeO₂) and hexagonal (2H-AgFeO₂) phase are split, above and below the lattice parameters for the stacking fault phase. The lattice parameters of the maghemite phase are significantly distorted from an ideal crystal structure (8.33 Å).²⁷ In the refinement, the Ag_{0.2}FeO_{1.6} composite is dominated by the maghemite (γ -Fe₂O₃) contribution, nearly 77% by weight in the Rietveld fit. This is similar to, though not quite the same, as the weight ratio suggested by stoichiometry of approximately 62%.

Table 1. Rietveld fitting results for a Ag_{0.2}FeO_{1.6} composite using a mixed phase model and AgFeO₂ using a randomly generated (1 0 0) layer model.

Variable	Ag _{0.2} FeO _{1.6} Composite	Variable	AgFeO ₂
Rhombohedral A	3.039(1) Å	A and B	3.0394(3) Å
Rhombohedral C	18.655(7) Å	Plane Spacing	6.226(1) Å
Rhombohedral Crystal Size	15 nm	Crystal Size	72 nm (<i>a</i> & <i>b</i>) 48 nm (<i>c</i> -axis)
Rhombohedral Weight %	18.4%	Weight %	100%
Hexagonal A	3.038(4) Å	-	-
Hexagonal C	12.46(1) Å	-	-
Hexagonal Crystal Size	18 nm	-	-
Hexagonal Weight %	5.0%	-	-
Maghemite A	8.418(6) Å	-	-
Maghemite Crystal Size	2.0 nm	-	-

Maghemite Weight %	76.6%	-	-
Rwp	6.97%	Rwp	5.26%

Operando XRD. The structural evolution of AgFeO₂ and Ag_{0.2}FeO_{1.6} electrodes was monitored as a function of lithiation via *operando* X-ray diffraction (XRD) as shown in **Figures 2** and **3**, respectively. Intense diffraction peaks located at ~36°, 52°, and 65° correlate to the (1 1 0), (2 0 0), and (2 1 1) Li metal Bragg reflections, respectively.³³ Peaks at ~35°, 61°, and 68° are from the (1 0 1), (1 0 10) and (2 -1 6) lattice planes of the nominal AgFeO₂ crystal structure.²⁶ All other small, unchanging diffraction peaks are related to other components of the cell materials.

The AgFeO₂ electrode undergoes crystalline changes during lithium insertion (**Figure 2a**). As the material is discharged, some amorphization is observed by the end of the discharge plateau at ~1.7 V (0.9 electrons) as indicated by a reduction in the diffraction peak intensity which is particularly evident in the (1 1 0) reflection at approximately 60.8° (**Figure 2b**) and continues until the end of the discharge near 1.0 V or 1.83 electrons. The FWHM of the (1 1 0) reflection did not change significantly as a function of discharge, remaining at a value of about 0.8 ± 0.03°. However, a slight peak shift from 60.96° to 60.83° is observed (**Figure 2c**) due to the expansion of the lattice parameters from the insertion of lithium ions into the layered AgFeO₂ crystal structure. The *operando* XRD data suggests that the AgFeO₂ material has experienced a minor transformation, but the overall layered crystal structure remains intact after the 1st discharge.

The structural evolution of the Ag_{0.2}FeO_{1.6} electrode is more difficult to definitively assess via *operando* XRD measurements due to the small crystallite size (10 nm), however, differences with respect to the AgFeO₂ electrode are obvious. Specifically, as lithium is intercalated into the layered structure, the broad and low intensity Bragg reflections related to the initial AgFeO₂ structure disappear rapidly, by approximately 0.6 electrons or 1.4 V (**Figure 3**). As the diffraction peaks disappear, no new peaks are discernible suggesting that the Ag_{0.2}FeO_{1.6} composite has become highly amorphous/nanocrystalline during lithiation and cannot be detected with laboratory XRD measurements. Continued discharge of the Ag_{0.2}FeO_{1.6} electrode shows no change in the XRD pattern, indicating the phases formed during discharge continue to be primarily amorphous/nanocrystalline.

Ex-Situ XAS. X-ray absorption near edge structure (XANES) spectra of representative AgFeO₂, γ-Fe₂O₃, and Ag_{0.2}FeO_{1.6} composite samples are illustrated in **Figure S4**. Linear combination fitting of the Ag_{0.2}FeO_{1.6} composite was performed, using AgFeO₂ and amorphous γ-Fe₂O₃ as standards, to elucidate the composite nature of the one-pot prepared material and provide quantitative details (**Figure 4**). The fit indicates that the iron component of the Ag_{0.2}FeO_{1.6} composite is composed of 79 ± 0.6% γ-Fe₂O₃ and 21 ± 0.6% AgFeO₂ which was expected per **Equation 1**.

To investigate the redox processes that occur during discharge and charge, Ag_{0.2}FeO_{1.6} and AgFeO₂ electrodes were recovered at specific depths of discharge or charge (**Figure 5**) and XAS data (**Figure S5**) was collected with particular focus on the EXAFS region. With regard to EXAFS, k²-weighted |χ(R)| (Fourier transform of χ(k)) of AgFeO₂ (Ag and Fe K-edge) and the Ag_{0.2}FeO_{1.6} composite (Fe K-edge) are shown in **Figure 6**. The depths of discharge targeted for the XAS study are indicated by yellow diamonds in **Figure 5** and include undischarged, partially discharged (defined as 1 molar electron equivalent; 137 mAh/g and 260 mAh/g for AgFeO₂ and

Ag_{0.2}FeO_{1.6}, respectfully), 1st discharge (defined as 2 molar electron equivalents, 274 mAh/g and 520 mAh/g for AgFeO₂ and Ag_{0.2}FeO_{1.6}, respectfully), and 1st charge (recharged to 3.5 V after discharge to 2 electron equivalents).

The Ag K-edge of the AgFeO₂ electrode in **Figure 6** displays a sudden shift from the undischarged AgFeO₂ crystal structure to what qualitatively appears to be Ag metal (in comparison with Ag metal reference foil shown). This suggests that during the initial discharge of AgFeO₂, Ag⁺ ions within the original structure are displaced when lithium is inserted and reduced to metallic Ag⁰ nanoparticles. The Ag⁰ particles do not appear to change significantly as a function of electrochemical state due to the similar $|\chi(R)|$ of the partially and fully discharged electrochemical states of AgFeO₂. This agrees with previous electrochemical data for AgFeO₂ where the voltage plateau at 1.9 V (**Figure 5a**) during the 1st discharge was assigned to the reduction of Ag⁺ to Ag⁰ and simultaneous partial reduction of Fe³⁺.¹⁴⁻¹⁵

The Fe K-edge of the AgFeO₂ electrode material also suggests that a portion of the Ag⁺ ions are removed from the structure, as the small defined double-peak at ~3.2 Å in **Figure 6** dissipates and is due to Ag atom contributions. It should be noted that the distance of ~3.2 Å is uncorrected for phase shifts associated with the electron scattering process and are ~0.4 Å shorter than the actual interatomic distances determined through theoretical modeling. When AgFeO₂ is partially discharged, the double-peak disappears aligning well with the formation of Ag metal observed from the Ag K-edge. However, as the AgFeO₂ is further lithiated, the original Fe-O/Fe-Fe framework of the initial crystal structure appears to remain intact as the 1st shell peak at ~1.4 Å (Fe-O contribution) and the 2nd shell peak at ~2.5 Å (Fe-Fe contribution) do not significantly change. This data agrees with the *operando* XRD measurements of AgFeO₂ where a slight broadening of the initial AgFeO₂ Bragg reflections and reduction in peak intensity is observed. Notably, these AgFeO₂ reflections are still present when the electrode is fully discharged to 1.0 V.

The Fe K-edge of the Ag_{0.2}FeO_{1.6} electrode in **Figure 6**, which includes contributions from both AgFeO₂ and γ-Fe₂O₃ phases undergoes considerable structural changes during the first discharge. As the material is partially discharged, the distinct 2nd shell peak between 2.5 and 3.0 Å, which includes both Fe-O and Fe-Fe contributions, converts to a broad feature that encompasses the entire range between 2.0 and 3.0 Å. This peak becomes significantly broader upon the full discharge of the Ag_{0.2}FeO_{1.6} electrode material. During charge or de-intercalation, it appears as if an iron environment analogous to the initial structure is restored, owing to the observation of a similar, distinct 2nd shell peak relative to the undischarged Ag_{0.2}FeO_{1.6} composite Fe K-edge spectrum.

To quantify structural changes at the atomic-level, AgFeO₂ and Ag_{0.2}FeO_{1.6} EXAFS spectra were modeled using a mixture of AgFeO₂, γ-Fe₂O₃, and Fe metal crystal structures. The EXAFS fitting results, which include the interatomic distance and number of neighboring atoms, from the Fe K-edge spectra are shown in **Figure 7**. Full detailed fitting parameters results are presented in the Supplemental Information, **Figures S7 – S17** and **Tables S2 – S10**. The modeling results for AgFeO₂ align with the *operando* XRD data and the observations of the $|\chi(R)|$ spectra in **Figure 6**. In the undischarged state, the AgFeO₂ phase was used to model the data, and fitted Fe-O, Fe-Fe, Fe-O and Fe-Ag distances at 2.02 ± 0.01 Å, 3.05 ± 0.01 Å, 3.64 ± 0.01 Å, and 3.55 ± 0.05 Å are in good agreement with respective theoretical distances of 2.04 Å, 3.04 Å, 3.66 Å, and 3.58 Å. No significant change in the Fe-O or Fe-Fe interatomic distances of

AgFeO₂ are observed upon discharge, with the exception of the contraction in the long-range Fe-O contribution from 3.64 ± 0.01 Å to 2.95 ± 0.03 Å (**Figure 7**). The migration of Ag atoms out of the AgFeO₂ crystal structure were clearly observed in **Figure 6** as the partially discharged spectrum resulted in limited Fe-Ag neighboring atoms, which cause the Fe-O contraction within the discharged AgFeO₂ structure. Once the contraction of the long-range Fe-O contributions has occurred in the partially discharged AgFeO₂ state, no statistically significant changes in interatomic distances in either the fully discharged or charged states are observed **Figure 7**. This finding is significant because it indicates that Ag⁰ does not reoxidize to Ag⁺ ions during recharge of the material. Additionally, the number of neighboring atoms of the closest Fe-O and Fe-Fe contributions decreases from the initial value of 4.8 ± 0.2 atoms to 3.5 ± 0.3 atoms when fully discharged. The reduction in observed neighboring atoms in discharge AgFeO₂ is likely due to either a decrease in particle size, leading to an increase in the ratio of surface terminated atoms to bulk atoms,³⁴ or amorphization of the crystal phase, as the number of neighboring atoms and the Debye-Waller factor, which accounts for thermal and structural disorder, are highly correlated (as high as 90% in these fitting models). The Debye Waller factor for Fe-Fe paths increases from 0.006 ± 0.003 in the undischarged material to 0.011 ± 0.002 in the material after 1st discharge, providing further evidence that the material becomes more disordered as it is discharged. The EXAFS fitting results agree with the *operando* XRD measurements, as a broadening of the crystalline peaks is observed with continued lithiation and is indicative of reduced crystallite size or amorphization of the crystal structure. The Ag K-edge modeling results of the AgFeO₂ electrode confirm the formation of metallic Ag⁰ upon discharge. In particular, the reduced number of neighboring Ag-Ag atoms from the expected value of 12, based on the standard fcc crystal structure and assuming a spherical particle morphology, to 8.4 ± 1.0 neighboring atoms allows for the estimation of particle size, on the order of several nanometers in diameter. The particle size can be estimated due to surface termination effects which artificially reduce the average number of neighboring atoms.^{34a}

EXAFS analysis of the Ag_{0.2}FeO_{1.6} composite in **Figure 7** is more complex due to the presence of both AgFeO₂ and γ-Fe₂O₃ phases in the pristine material. The EXAFS region of the pristine Ag_{0.2}FeO_{1.6} composite more closely resembles γ-Fe₂O₃ (**Figure 4b**) when compared directly to AgFeO₂ in **Figure 6**. In the Ag_{0.2}FeO_{1.6} composite, AgFeO₂ and γ-Fe₂O₃ phases display distinct Fe-Fe distances, shown in **Figure 7**, which permits the direct observation of each phase (specifically, Fe-Fe_{AgFeO2} is 3.10 ± 0.02 Å while Fe-Fe_{γ-Fe2O3} distances are 2.97 ± 0.05 Å and 3.48 ± 0.05 Å for Fe atoms in octahedral and tetrahedral coordination environments, respectively). The partially discharged and 1st discharge states could not be modeled using the initial AgFeO₂ and γ-Fe₂O₃ phases; rather a rock-salt FeO model³⁵ was adopted. Excellent agreement between the model and the data were observed, with combined R-factors < 2.0. From this structure, two Fe-O contributions and one Fe-Fe contribution were used. Fitted distances of 2.01 ± 0.01 Å and 3.04 ± 0.01 Å were found for nearest neighbor Fe-O and Fe-Fe paths respectively when discharged to 2 electron equivalents, which indicates a contraction relative to the standard FeO structure (theoretical Fe-O distance of 2.17 Å and Fe-Fe distance of 3.06 Å in FeO³⁵). The deviation from the standard structure of FeO is expected due to the presence of Li atoms in the structure which are also present from the lithiation reaction, but which are not directly observed via EXAFS because of weak X-ray scattering from Li. An additional Fe-O path at Fe-O at ca. 2.7 Å was also necessary to yield an acceptable fit due to residual signal in the second

coordination shell. The extra Fe-O path is thought to be attributable to surface oxide species and the nanocrystalline nature of the discharging particle, since (a) a significant percentage of the total Fe atoms on the discharging nanoparticle are surface atoms, and (b) the surface iron atoms are expected to be coordinated with oxygen.

Because EXAFS modeling clearly indicates the presence of a rock-salt type phase, we hypothesize that the lithiated structure is that of rock-salt LiFeO_2 . The presence of LiFeO_2 phase has been previously observed in other $\gamma\text{-Fe}_2\text{O}_3$ electrodes cycled above 1.0 V.³⁶ XANES results also support the existence of LiFeO_2 rather than rock-salt FeO , as the collected spectra are significantly different than that of the FeO reference. (Figure S5(b)). In addition to the LiFeO_2 phase, an Fe metal contribution was observed in the partially discharged state of the $\text{Ag}_{0.2}\text{FeO}_{1.6}$ composite material. The Fe metal phase was easily resolved due to the distinct interatomic distance, fit to 2.53 ± 0.01 Å. Upon recharge to 3.5 V, the Fe metal formed during discharge oxidizes, as there is no evidence of it in the EXAFS spectra. Further, it appears that the recharged structure reorganizes into an iron oxide structure with a Fe-O and Fe-Fe distances similar to the LiFeO_2 rock-salt type phase. This structure is also similar to that of AgFeO_2 , which also contains a single Fe-O and Fe-Fe contribution in the first two coordination shells. Therefore, it is uncertain from this analysis whether the material returns to the original layered AgFeO_2 type structure, or reverts to a more disordered iron oxide phase where iron remains in a similar environment.

The Fe K-edge EXAFS data indicate that metal Fe was formed in the partially or 1st discharge $\text{Ag}_{0.2}\text{FeO}_{1.6}$ electrode but not in the AgFeO_2 electrode. Consideration of the depths of discharge provides insight, where partial discharge and 1st discharge are defined as 1 electron equivalent and 2 electron equivalents, respectfully. In the $\text{Ag}_{0.2}\text{FeO}_{1.6}$ electrode, only 0.2 moles of Ag^+ are available for reduction; thus a minimum of 0.8 electron equivalents and 1.8 electron equivalents are available for reduction of Fe^{3+} at 1 and 2 electron equivalents of discharge, respectively. Because reduction of Fe^{3+} beyond 1 equivalent must result in a mixture of Fe^{2+} and Fe^0 , it is expected that Fe^0 would be present at 2 electrons of reduction for the $\text{Ag}_{0.2}\text{FeO}_{1.6}$ composite. since Fe^0 metal is observed at 1 electron equivalent, some Fe^0 must be reduced before full reduction of Fe^{3+} to Fe^{2+} has occurred, though it is unclear from the XAS data whether the reduction to Fe^0 metal is primarily associated with reduction of the AgFeO_2 phase or the $\gamma\text{-Fe}_2\text{O}_3$ phase reduction to Fe^0 metal is primarily associated with reduction of the AgFeO_2 phase or the $\gamma\text{-Fe}_2\text{O}_3$ phase that together constitute the $\text{Ag}_{0.2}\text{FeO}_{1.6}$ composite material. Upon further discharge to 2 electron equivalents, the amount of Fe^0 metal observed increases only marginally (Fe-Fe near neighbors for Fe metal component are 2.4 ± 0.7 and 2.5 ± 0.8 for 1 electron equivalent and 2 electron equivalents, respectively), thus additional reduction of Fe^{3+} to Fe^{2+} occurs during the second equivalent of reduction. In contrast, the AgFeO_2 electrode contains 1 molar equivalent of Ag^+ ions per formula unit, compared to 0.2 molar equivalents of Ag^+ ions per formula unit in $\text{Ag}_{0.2}\text{FeO}_{1.6}$. EXAFS modeling indicates that by 2 electron equivalents, the majority of Ag^+ has been reduced to Ag^0 , since there is no evidence of Ag-Fe or Ag-O paths from the original starting AgFeO_2 structure. Assuming all Ag^+ has been reduced, only 1 electron equivalent remains to reduce Fe^{3+} and likely results in the reduction of Fe^{3+} to Fe^{2+} . Thus, it is unlikely that Fe^0 metal would be reduced in the 1st discharge state (2 electron equivalents) of AgFeO_2 .

Figure 8 shows the wavelet modulus spectra of both the AgFeO_2 and $\text{Ag}_{0.2}\text{FeO}_{1.6}$ spectra of the undischarged, partially discharged, and fully discharged electrochemical states. These images provide elemental contrast of the $|\chi(R)|$ spectra as high-Z elements tend to contribute more significantly at higher k-values, and vice versa for low-Z elements. The heat maps depict the k-dependence of the $|\chi(R)|$ peak and thus provide some qualitative indication of the elemental contributions to the peaks. The undischarged AgFeO_2 electrode shows a broad feature in the heat map at ca. $k = 10 \text{ \AA}^{-1}$ and $R = \text{ca. } 3.5 \text{ \AA}$. Due to the large k-value along with the appropriate interatomic distance for the Fe-Ag contribution to the spectrum, it can be concluded that this feature is attributed to Ag atoms within the original AgFeO_2 crystal structure. As the material is partially discharged, this feature clearly dissipates again confirming the loss of Ag atoms from the original layered iron oxide framework of the AgFeO_2 crystal structure. However, this is the only change observed with no specific changes observed in the 1st or 2nd shell contributions between the undischarged and fully discharged spectra, again in agreement with the *operando* XRD and EXAFS fits which illustrate minor structural changes once Ag atoms are removed in the AgFeO_2 electrode. The $\text{Ag}_{0.2}\text{FeO}_{1.6}$ electrode however clearly undergoes significant structural changes from the undischarged state as evidenced by the large shift in the 2nd shell environment in the partially discharged state from a distinct peak to a broad feature. Continued lithiation to the fully discharged state shows the evolution of a distinct peak in the 2nd shell coordination. Combined with the EXAFS modeling results, this peak is a mixture of Fe-Fe from a disordered iron oxide phase as well as contributions from Fe metal.

***In-situ* x-ray Fluorescence Nanoprobe mapping.** *In-situ* x-ray fluorescence nanoprobe mapping measurements were collected at the Fe K-edge on electrochemical Li/ AgFeO_2 cells to spatially resolve the progression of discharge in the AgFeO_2 active material. The stoichiometric AgFeO_2 material was selected for the *in-situ* x-ray fluorescence nanoprobe mapping measurements due to the larger crystallite size of the material. Maps were collected for two cells, the first measured at open circuit voltage (Cell A), the second measured after discharge to 0.3 V (Cell B). **Figure 9a** shows the voltage profile for Cell B, which was discharged to 0.3V at a C/2 rate. Discharge to 0.3 V resulted in ca. 4.5 electron equivalents of discharge capacity. The fluorescence maps were collected at 14 energy levels ranging from 7100 to 7200 eV (Fe K-edge = 7112 eV), with 200 nm pixel resolution. Selected maps collected on cells A and B are shown in **Figure 10** to illustrate the changes in fluorescence intensity with respect to energy. Additional maps are depicted in **Figure S6**. For cell A, at incident photon energies of 7113 and 7120 eV, very little signal is observed and the map is largely blue, indicating little X-ray absorption and corresponding fluorescence occurs at these energies; however, at energies above the Fe oxide white lines, the intensity increases and a clear map of AgFeO_2 agglomerates emerges, predominantly arranged as large particles up to $\sim 15 \text{ }\mu\text{m}$ in size. The centers of the agglomerates exhibit the highest signal intensities on the map due to greater AgFeO_2 thickness in these areas. For maps collected on Cell B, similar size aggregates are observed at 7200 eV. Notably, higher levels of signal intensity occur at lower incident energy for Cell B as compared to Cell A indicating that the Fe absorption edge has shifted to lower energy for the discharged cell, consistent with the reduction of the Fe oxidation state of the material. To further explore the changes in oxidation state between the undischarged and discharged cells, XANES spectra were generated from the average absorption intensity of all pixels within a map, for maps collected at the 14 energies between 7110 and 7200 eV (**Figures 9b, S6**). The

resulting spectrum for Cell A has similar edge energy to that of a hematite, α – Fe_2O_3 standard indicating the oxidation state of the iron center at OCV is Fe^{3+} . The generated XANES spectra for Cell A also includes a pre-edge peak and a rising absorption edge at ~ 7124 eV, consistent with spectra reported in the literature for AgFeO_2 .^{15, 37} For cell B, a significant shift in the XANES spectra to lower edge energy is observed. The spectrum exhibits an edge energy of 7112 eV, consistent with that of an Fe metal standard (**Figure S6**). Furthermore, the general profile of the sample spectrum is analogous to that of the standard, indicating that by 0.3V, the majority of the iron centers in AgFeO_2 have been reduced to Fe metal. In contrast to the ex-situ XAS experiment, where the 1st discharge of AgFeO_2 was defined as 2 electron equivalents, for the in-situ X-ray fluorescence nanoprobe mapping experiment the AgFeO_2 electrode was discharged to 4.5 electron equivalents, with final discharge voltage of 0.3 V. The additional 2.5 electron equivalents of reduction for the *in-situ* cell resulted in the reduction of most Fe ions to Fe metal.

Redox Mechanism. The XAS results can be used to provide insight into the discharge mechanisms of AgFeO_2 and $\text{Ag}_{0.2}\text{FeO}_{1.6}$ composite. EXAFS modeling illustrates that AgFeO_2 experiences displacement of Ag^+ ions from the crystal structure, also referred to as a reduction-displacement reaction. The reduction-displacement of Ag^+ to Ag^0 , within transition metal oxide electrode materials, is a paradigm well established with silver vanadium oxide ($\text{Ag}_2\text{V}_4\text{O}_{11}$),³⁸ then later with silver vanadium phosphorous oxide ($\text{Ag}_2\text{VO}_2\text{PO}_4$)¹⁹ and recently to $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ ³⁹ and silver ferrite (AgFeO_2).¹³⁻¹⁴ XAS data of partially discharged AgFeO_2 samples at both the Fe K-edge and Ag K-edge indicate that Ag^+ reduction and Fe^{3+} reduction occur in parallel during the first discharge to one electron equivalent. In particular, the appearance of Ag^0 peaks in the EXAFS spectra (**Figure 6**) as well as shifting of the Fe K-edge edge position to lower energies (**Figure S5**) in the partially discharged sample indicate that Fe and Ag reduction is occurring concurrently.

On the first discharge of AgFeO_2 , it is likely that Fe^{3+} only partially reduces to Fe^{2+} since the AgFeO_2 *operando* XRD pattern showed a decrease in the crystallinity of AgFeO_2 and no evidence of a new iron oxide phase (**Figure 2**). Further, the XANES (Fe K-edge) of AgFeO_2 electrodes in **Figure S5** does not illustrate full reduction of Fe^{3+} to Fe^{2+} . In contrast, in the $\text{Ag}_{0.2}\text{FeO}_{1.6}$ composite material, the XANES data show more significant edge position shifts to lower energy (**Figure S5**), indicating greater reduction of Fe^{3+} to Fe^{2+} . Thus, during the electrochemical reduction of the $\text{Ag}_{0.2}\text{FeO}_{1.6}$ composite, a greater level of Fe reduction occurs relative to the stoichiometric AgFeO_2 material. The reduction of a portion of Fe^{3+} to Fe^0 in $\text{Ag}_{0.2}\text{FeO}_{1.6}$ is also validated by the XANES Fe K-edge where the edge shift of the fully discharge composite material remains between metallic Fe^0 and the undischarged material with an oxidation state of Fe^{3+} . For the AgFeO_2 material, XANES spectra generated from *in-situ* nano-fluorescence mapping measurements on a cell discharged to 0.3 V (ca. 4.5 electron equivalents) indicate that full discharge of AgFeO_2 does result in the eventual reduction of most Fe ions to Fe^0 . Fe^0 metal has been observed for a number of ferrite materials, and has even been previously reported for silver ferrite^{15, 40}. Fe^0 has also been observed in a number of similar ferrite materials, including ZnFe_2O_4 ⁴¹, NiFe_2O_4 ⁴², MnFe_2O_4 ⁴³ and CuFe_2O_4 ⁴⁴.

Upon charging from 1.0 V to 3.5 V, the oxidation of iron in the AgFeO_2 and $\text{Ag}_{0.2}\text{FeO}_{1.6}$ electrodes is reversible in both materials returning to nearly a 3+ oxidation state indicated by

the XANES results (**Figure S5**). The reversibility of the redox mechanism is also demonstrated by the cycling efficiency of AgFeO₂ and Ag_{0.2}FeO_{1.6} electrodes, which demonstrates little to no capacity fade over 50 cycles. EXAFS modeling in **Figure 8** shows that the iron environment of AgFeO₂ upon charge is similar to that of the initial AgFeO₂ structure; however, it is notable that XAS results show that the contraction of long range Fe-O contributions in AgFeO₂ does not expand during recharge of the material, indicating that Ag⁰ does not oxidize and reinsert into the Li_xFeO₂ structure. For Ag_{0.2}FeO_{1.6}, it is unclear as to the exact nature of the recharged iron oxide phase, since the iron oxide structure has Fe-O and Fe-Fe distances similar to both a rock-salt type phase as well as AgFeO₂. Nonetheless, the recharged phase is highly nanocrystalline and cannot be detected by diffraction.

Taking into consideration the electrochemical data and the results obtained from the advanced characterization techniques, a generalized redox mechanism is proposed in **Equations 2-4** for the AgFeO₂ component. The reduction displacement of Ag⁺ ions in AgFeO₂ is represented in **Equation 2** where Li⁺ ions, up to 1 electron equivalent, are inserted into the crystal structure and Ag⁺ is reduced to metallic Ag⁰. The reduction-displacement of Ag⁺ to Ag⁰ is an irreversible process which occurs concurrently with the partial reduction of Fe³⁺ in **Equation 3** where the oxidation state of iron remains above Fe²⁺. The reversible reduction and oxidation of iron in the AgFeO₂ component is shown in **Equation 4** where Li⁺ ions are intercalated and de-intercalated within the lithiated AgFeO₂ (LiFeO₂) structure. A second generalized redox mechanism is proposed in **Equation 5** for the γ-Fe₂O₃ component where Li⁺ is intercalated into the inverse-spinel structure to afford a rock salt LiFe₂O₃ structure, as suggested by EXAFS modeling and observed in other γ-Fe₂O₃ electrodes cycled above 1.0 V.³⁶ Reduction of Ag_{0.2}FeO_{1.6} also results in the formation of Fe metal (**Equation 6**), which reoxidizes upon discharge to an iron oxide phase. Thus, in Ag_xFeO_y composites, **Equations 4, 5, and 6** are expected to occur where the full reduction of Ag⁺ to Ag⁰ is observed initially, and is accompanied by the reversible reduction and oxidation of Fe³⁺ in AgFeO₂ and γ-Fe₂O₃.

Conclusion

Synchrotron X-Ray diffraction was used to characterize pristine AgFeO₂ and Ag_{0.2}FeO_{1.6}. A stacking-fault model was shown to match well with diffraction data for AgFeO₂. A method was shown to fit the stacking fault model to the data using GSAS II, a Rietveld Refinement software. The amount of the amorphous γ-Fe₂O₃ impurity in the Ag_{0.2}FeO_{1.6} sample was quantified, and matched well with expectations. A combination of advanced *ex-situ*, *in-situ*, and *operando* techniques were utilized to investigate electrochemically reduced (discharged) and oxidized (charged) electrodes and provided meaningful insight into the lithiation/de-lithiation mechanism of a Ag_{0.2}FeO_{1.6} composite (AgFeO₂ + γ-Fe₂O₃) and stoichiometric AgFeO₂. *Operando* XRD monitored the structural evolution of AgFeO₂ and a Ag_{0.2}FeO_{1.6} composite, as a function of depth of discharge, and demonstrated different mechanisms where crystal

structure of AgFeO_2 remained intact after discharge to 1.0 V while the diffraction pattern of the $\text{Ag}_{0.2}\text{FeO}_{1.6}$ composite amorphized. XAS data of partially discharged AgFeO_2 samples at both the Fe K-edge and Ag K-edge indicate that Ag^+ reduction and Fe^{3+} reduction occur concurrently during the first discharge. On charge, the formed Ag^0 was not observed to oxidize to Ag^+ , while the Fe^{2+} oxidized to Fe^{3+} . Furthermore, the XAS data show more reduction of Fe^{3+} occurs in the $\text{Ag}_{0.2}\text{FeO}_{1.6}$ composite relative to AgFeO_2 in the utilized voltage range (3.5 V to 1.0V). Based on the XAS results, a redox mechanism is proposed where the full reduction of Ag^+ to Ag^0 and partial reduction of Fe^{3+} to Fe^{2+} occur initially, resulting in a $\text{Li}_{1+y}\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}\text{O}_2$ phase. The $\text{Li}_{1+y}\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}\text{O}_2$ phase can be reversibly cycled, between Fe^{3+} and Fe^{2+} oxidation states, resulting in reversible capacity delivery over 50 cycles. Upon further electrochemical reduction to 0.3V (ca. 4.5 electron equivalents), the majority of the iron centers in AgFeO_2 have been reduced to Fe metal, as indicated by an *in-situ* x-ray fluorescence nanoprobe mapping measurement. In the $\text{Ag}_{0.2}\text{FeO}_{1.6}$ composite, a substantial amorphous $\gamma\text{-Fe}_2\text{O}_3$ component is observed which discharges to rock salt LiFe_2O_3 and Fe^0 metal phase in the 3.5 – 1.0 V voltage range (in parallel with the AgFeO_2 mechanism), and reoxidizes to a nanocrystalline iron oxide phase.

Conflicts of Interest

There are no conflicts of interest to declare.

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Figure 2. (a) *Operando* XRD of AgFeO_2 electrodes where red lines indicate diffraction patterns of the non-lithiated electrode, the electrode lithiated to ca. 1 electron equivalents (partial discharge), and the electrode lithiated to 2.0 electron equivalents (full discharge). These three electrode compositions were also analyzed by XAS. (b) Evolution of the **normalized intensity** and peak position of the (1 1 0) reflection as a function of discharge. (c) Expanded view of *operando* XRD data corresponding to (1 1 0) reflection region. (d) View of AgFeO_2 crystal structure, where arrow indicates the (1 1 0) lattice direction. (e) View of crystal structure along [1 1 0].

Figure 3. *Operando* XRD of $\text{Ag}_{0.2}\text{FeO}_{1.6}$ electrodes where red lines indicate diffraction patterns of the non-lithiated electrode, the electrode lithiated to ca. 1 electron equivalent (partial discharge), and the fully lithiated electrode (ca. 2.0 electron equivalents). These three lithiation compositions were also analyzed by XAS.

Figure 4. (a) Linear combination fitting of pristine $\text{Ag}_{0.2}\text{FeO}_{1.6}$ composite material using AgFeO_2 and amorphous $\gamma\text{-Fe}_2\text{O}_3$ as standards. (b) k^2 -weighted $|\chi(R)|$ of a $\text{Ag}_{0.2}\text{FeO}_{1.6}$ composite (black line) and nanocrystalline $\gamma\text{-Fe}_2\text{O}_3$ (green line) at the Fe K-edge.

Figure 5. Discharge and charge profiles of (a) AgFeO_2 and (b) a $\text{Ag}_{0.2}\text{FeO}_{1.6}$ composite, with yellow diamonds indicating *ex-situ* XAS samples. Yellow diamonds indicate the depths of (dis)charge targeted for the EXAFS study and include undischarged, partially discharged (defined as 1 molar electron equivalent; 137 mAh/g and 260 mAh/g for AgFeO_2 and $\text{Ag}_{0.2}\text{FeO}_{1.6}$, respectively), 1st discharge (defined as 2 molar electron equivalents, 274 mAh/g and 520 mAh/g for AgFeO_2 and $\text{Ag}_{0.2}\text{FeO}_{1.6}$, respectively), and 1st charge (defined as charged to 3.5 V).

Figure 6. k^2 -weighted $|\chi(R)|$ of AgFeO_2 (Ag and Fe K-edge) and a $\text{Ag}_{0.2}\text{FeO}_{1.6}$ composite (Fe K-edge) in undischarged (black line), partially discharged (red line), 1st discharge (blue line), and 1st charge (pink line) electrochemical states. An Ag metal reference foil is also shown (dashed black line) for comparison. The depths of discharge for the tested electrodes are indicated in Figure 5.

Figure 7. EXAFS modeling results of interatomic distance (top) and number of near neighbors (bottom) for AgFeO_2 (left) and a $\text{Ag}_{0.2}\text{FeO}_{1.6}$ composite (right) with Fe-O (black lines), Fe-Fe contributions from oxide structures (red lines) and Fe-Fe contributions from Fe metal (blue lines).

Figure 8. k^3 -weighted continuous wavelet analysis of AgFeO_2 (left) and $\text{Ag}_{0.2}\text{FeO}_{1.6}$ (right) electrodes. The heat map indicates the k -dependence of the R -space peaks. Red regions on the heat map indicate high magnitude of $|\chi(R)|$ while blue regions indicate low magnitude of $|\chi(R)|$.

Figure 9. (a) Discharge profile of Li/AgFeO₂ cell used for *in-situ* nano-fluorescence mapping measurement. Labeled points indicate state of discharge of for cell A (measured at OCV) and cell B (measured at 0.3 V). (b) Normalized absorption spectra in the Fe K-edge region, generated from the average absorption intensity of all pixels within a map, for maps collected at 14 energies between 7110 and 7200 eV.

Figure 10. Fluorescence maps at 7113 eV, 7120 eV, and 7200 eV collected from *in-situ* cells at open circuit voltage (Cell A) and discharged to 0.3 V (Cell B).

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Supplementary Information

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 $\text{Ag}_{0.2}\text{FeO}_{1.6}$ composite (0.2) and AgFeO_2 (1.0) with 2H-AgFeO_2 (PDF 01-070-1452) and 3R-AgFeO_2 (PDF 01-075-2147) reference patterns.

Figure S2. Rietveld fitting of powder diffraction data from a Rigaku SmartLab laboratory diffractometer: (a) AgFeO₂ fit using a mixed phase model, (b) AgFeO₂ 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 $\text{Ag}_{0.2}\text{FeO}_{1.6}$ silver ferrite/maghemite composite using a combination of hexagonal (2H-AgFeO_2) and rhombohedral (3R-AgFeO_2) phases.

Variable	$\text{Ag}_{0.2}\text{FeO}_{1.6}$ Composite	AgFeO_2	Variable	AgFeO_2
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 AgFeO_2 (mixed phase and (1 0 0) layer models) and a $\text{Ag}_{0.2}\text{FeO}_{1.6}$ composite (mixed phase model) diffraction data from a Rigaku SmartLab instrument.

Figure S4. XANES spectra of pristine AgFeO_2 , a $\text{Ag}_{0.2}\text{FeO}_{1.6}$ composite, and amorphous $\gamma\text{-Fe}_2\text{O}_3$.

Figure S5. *Ex-situ* XANES (Fe K-edge) spectra of electrochemically cycled (a) AgFeO_2 and (b) a $\text{Ag}_{0.2}\text{FeO}_{1.6}$ 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 1st 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 1st 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 1st charge Ag_{0.2}FeO_{1.6} electrode in $|\chi(R)|$ at the Fe K-edge.

State	Edge	Combined R-factor
AgFeO ₂ undischarged	Ag	3.5
AgFeO ₂ partial discharge	Ag	2.9
AgFeO ₂ 1st discharge	Ag	2.2
AgFeO ₂ undischarged	Fe	3.3
AgFeO ₂ partial discharge	Fe	1.1
AgFeO ₂ 1st discharge	Fe	1.4
AgFeO ₂ 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
AgFeO ₂ 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

Table S3. E₀ values for all fits.

State	Core atom	Debye Waller Factor (Å ⁻²)		
		Neighboring 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	AgFeO ₂ partial discharge	AgFeO ₂ 1st discharge	AgFeO ₂ 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	AgFeO ₂ partial discharge	AgFeO ₂ 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	AgFeO ₂ undischarged	AgFeO ₂ partial discharge	AgFeO ₂ 1st discharge	AgFeO ₂ 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.