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Operando Synchrotron XRD Investigation of Silver Metal Formation upon Electrochemical Reduction of Silver Iron Pyrophosphate ($\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$)

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ABSTRACT: The formation of conductive metallic silver upon electrochemical reduction and lithiation of $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ is investigated. Alternating current impedance spectroscopy measurements show a 34% decrease in charge transfer resistance upon one electron equivalent (ee) of reduction, which is coincident with the formation of a Ag metal conductive network evidenced by both *ex-situ* and *operando* x-ray diffraction. Quantitative assessment of Ag metal formation derived from *operando* XRD shows that only Ag^+ ions are reduced during the first 3ee, followed by simultaneous reduction of Ag^+ and Fe^{3+} reduction for the next 5ee (3ee to 8ee), culminating in reduction of the remaining Ag^+ . Scanning electron microscopy images show smaller Ag metal crystallite size and shorter nearest neighbor distance between and among Ag particles with higher depth of discharge. A high rate intermittent pulsatile discharge test is conducted where the cell delivered 12 total pulses during full discharge to probe the effect of Ag metal formation on the $\text{Li}/\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ cell electrochemistry. The Ohmic resistance is derived from the voltage drop of each pulse. The resistance is 65 Ohm initially, reaches its minimum 26 Ohm at 4.5 ee discharge and levels off at 35 Ohm after 7.0 ee reduction. The initial Ag reduction is more significant for the conductive network formation indicated by the decrease of both R_{ct} and ohmic resistance, which facilitates the high power output of the cell.

Introduction

Compared to oxide cathode materials, polyanion cathodes can offer improved stability and avoid oxygen evolution during cycling.¹ Among the polyanion framework materials, (e.g. PO_4^{2-} , $\text{P}_2\text{O}_7^{3-}$, XO_4 (X= Fe, Mo and W)⁸, SiO_4 ⁹, PO_4F^{10}), the phosphates have been a material class of particular interest since the commercialization of LiFePO_4 ^{2, 11}. However, the inherently low electrical conductivity of the LiFePO_4 material² has been a barrier to full realization of its theoretical capacity at high rate. Significant work has been done to modify the LiFePO_4 material to improve its electrical conductivity, including size reduction and intimately mixing the material with carbon. Nanocomposites of LiFePO_4 and conductive carbon were prepared by using carbon xerogel from formaldehyde and surface-oxidized carbon. Both synthetic methods resulted in LiFePO_4/C composite which achieved 90% theoretical capacity at C/2 and 70% capacity at 5C.¹² Nanoscale LiFePO_4 powder with high crystallinity synthesized in a Polyol medium delivered 50 mAh/g capacity at 60°C.¹³ While such approaches have markedly improved the functional capacity of the material, they complicate the synthesis which can prohibit scale up and commercialization.

Pyrophosphate materials often exhibit similar low electrical conductivity with that of phosphate materials since their metal (M) polyhedrons are bridged by phosphate groups (PO_4^{3-}) with no direct M-O-M bond.^{11, 14} However, the open framework provides the opportunity for relatively high ionic diffusion in the solid which can enhance the rate capability for ion transport. An illustrative example in this regard is the $\text{A}_2\text{MP}_2\text{O}_7$ (A = Li, Na and M = Fe, Mn, Co) family of materials. $\text{Na}_2\text{FeP}_2\text{O}_7$ delivered two thirds of its theoretical capacity in a sodium ion battery at 1C without nanosizing or carbon coating.¹⁵ The antisite defect structure in $\text{Na}_2\text{MP}_2\text{O}_7$ (M = Fe, Mn) results in low activation energy for long-range three-dimensional Na-ion diffusion,

contributing favorably to its high rate capability.^{3, 16-18} $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ has also been reported to be a fast ionic conductor on the order of 10^{-6} S/cm at 100 °C with two dimensional diffusion pathways in the π_2 plane formed by the phosphate group.¹⁹ Thus, the identification of materials with structures analogous to the $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ framework could potentially result in battery electrodes with high rate capability.

Designing materials that generate conductive Ag^0 metal *in-situ* upon electrochemical discharge through reduction-displacement of Ag^+ from the parent polyanion framework structure is a strategy to enhance the electrical conductivity via formation of a conducting network which promotes full active material utilization.²⁰⁻²¹ This concept has been successfully applied to several members of the silver vanadium phosphorous oxide ($\text{Ag}_w\text{V}_x\text{P}_y\text{O}_z$) family of cathode materials in Li based batteries,²²⁻²⁵ and is relevant to structurally related materials such as $\text{Ag}_2\text{V}_4\text{O}_{11}$ and other silver vanadium oxides,²⁶⁻²⁸ $\text{Ag}_4\text{V}_2\text{O}_6\text{F}_2$,²⁹ and $\beta\text{-Ag}_{0.33}\text{V}_2\text{O}_5$.³⁰ In the phosphate based $\text{Ag}_2\text{VO}_2\text{PO}_4$ material, the formation of silver nanoparticles upon initial electrochemical reduction results in a 15,000 fold decreases.²¹ More recent work discharging $\text{Ag}_2\text{VO}_2\text{PO}_4$ single particles illustrated that Ag metal formation upon initial discharge could affect both inter-and intra-particle conductivities.³¹ The silver vanadium diphosphate, $\text{Ag}_2\text{VP}_2\text{O}_8$ also demonstrated a significant increase in conductivity via in-situ formation of silver metal nanoparticles²⁵.

$\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$, a material analogous in structure to $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$, but with Ag^+ substituted, was hypothesized to have both excellent electrical and ionic conductivity. We verified that $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ functions well as the cathode material in Li based batteries with high rate capability, delivering six electrons at the rate of C/2.5 in the first discharge.³² In addition, the

$\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple shows good reversibility and excellent rate capability with 66% capacity retention when current density increased from 64 mA/g to 256 mA/g.

Operando synchrotron based XRD techniques have been intensively applied in a variety of battery related research, including investigations related to the Li-S^{33-35} , Li/Na-O_2^{36} , $\text{LiFePO}_4/\text{FePO}_4$ systems³⁷⁻⁴⁰, AB_2O_4 (A, B = transition metal, e.g. A = Co, B = Fe, Mn) spinel anode material⁴¹⁻⁴³ or anatase⁴⁴⁻⁴⁵ in Li ion battery, and Zn-Ni aqueous secondary battery⁴⁶. Notably, transmission synchrotron XRD geometry is widely employed due to convenient set up.^{35, 47-48} Compared to *ex-situ* measurements, *in-situ* and *operando* techniques can provide direct information on the system in a non-equilibrium state, allowing a truer visualization of what is happening during the electrochemical reduction and oxidation processes. For example, the metastable phase of Li_xFePO_4 under electrochemical phase transition has been directly observed with this technique.³⁸ Our prior studies on the $\text{Ag}_w\text{V}_x\text{P}_y\text{O}_z$ family materials via *in-situ* energy dispersive X-ray diffraction (EDXRD) method have demonstrated the ability to follow the reduction-displacement process through Ag metal network formation in the electrode and provides opportunity to study the effect of the conductive network structure on the electrochemistry of the electrode.⁴⁹⁻⁵¹

In this paper, we monitor the formation of conductive Ag metal as a function of discharge in an $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ electrode using a combination of *ex-situ* and *operando* measurements. In contrast to the prior energy dispersive XRD method used to understand the silver reduction-displacement process, a monochromatic angle dispersed XRD measurement is used here. The first *operando* transmission synchrotron XRD measurements tracking Ag^0 formation *operando* during a reduction-displacement and insertion reactions is conducted. The resulting two dimensional Ag metal formations are visualized using *ex-situ* scanning electron microscopy (SEM). AC

impedance spectroscopy is applied to determine the change in charge transfer resistance (R_{ct}) during the early stage of electrochemical reduction for lithium/silver iron pyrophosphate, Li/Ag₇Fe₃(P₂O₇)₄ electrochemical cells. An intermittent 10 mA/cm² current pulse test is used to study the impact of Ag metal formation on the ohmic resistance of Li/ Ag₇Fe₃(P₂O₇)₄ cells under conditions demanding high power output.

Experimental details

Synthesis and characterization

Ag₇Fe₃(P₂O₇)₄ was synthesized by ion exchange from Na₇Fe₃(P₂O₇)₄ and AgNO₃ at 250°C. Na₇Fe₃(P₂O₇)₄ material was synthesized via a solid state reaction using a modification of a previously reported method.⁵²⁻⁵³ Briefly, Na₄P₂O₇, Fe(NO₃)₃·9H₂O, and P₂O₅ were mixed at room temperature and heated to 550°C. After cooling, the sample was washed with deionized water and dried in a vacuum oven. Room temperature x-ray diffraction data for the Ag₇Fe₃(P₂O₇)₄ products were collected using a Rigaku SmartLab diffractometer with Cu-Kα radiation in Bragg Brentano geometry with a D/tex detector and a K_β filter. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed using a ThermoScientific iCap 6000 ICP spectrometer. Scanning electron microscopy (SEM) images were obtained using a JSM-6010Plus instrument at 10kV voltage with low vacuum mode. Analysis of the SEM images was conducted using ImageJ software⁵⁴.

Electrochemical testing

Ag₇Fe₃(P₂O₇)₄ electrodes were made from Ag₇Fe₃(P₂O₇)₄ active material, carbon and polyvinylidene fluoride binder with the weight ratio of 85:10:5, which was mixed with N-

methyl-2-pyrrolidone solvent and tape cast on Al foil. Polymeric separator and 1M LiBF₄ in 50/50 ethylene carbonate/ dimethyl carbonate electrolyte were used for all cells.

Three electrode cells were assembled in an Ar-filled glovebox with lithium foil as reference and counter electrodes. Three electrode cells were tested using a Biologic potentiostat using linear sweep voltammetry at 0.05 mV/s to a series of voltages: (1) OCV-3.434V, (2) OCV-3.096V, (3) OCV-2.332V, (4) OCV-2.0V. The electrodes were recovered in an Argon-filled glovebox and sealed between polyimide tape prior to *ex-situ* XRD measurements. The cell design for the synchrotron based measurements was a pouch type design (**Figure 1(a)**).

Two electrode coin type cells were tested using lithium metal as anode with a Maccor test station or Biologic potentiostat. Electrochemical impedance spectroscopy (EIS) measurements were collected as a function of discharge. The frequency range for impedance measurement was 1MHz to 5 mHz with a 10 mV amplitude. EIS data were fitted to equivalent circuits using Z-view software.⁵⁵ Galvanostatic discharge curved is obtained at C/15 rate with 1.0 V as discharge voltage limit. In pulse test, the same C/15 rate is used as the background discharge current and applied the 10 mA/cm² current density for 2s pulse every 1 hour with 4 hours rest time after each pulse.

Operando x-ray diffraction measurements were performed at beamline 6-ID-D at the Advanced Photon Source at Argonne National Laboratory. Using a monochromatic x-ray beam (wavelength $\lambda = 0.123584 \pm 0.000025$ Å, cross-sectional area 0.5 x 0.5 mm²), the diffracted signal was measured using a Perkin Elmer area detector placed approximately 800 mm behind the cell (see **Figure 1(b)**). A similar setup geometry has been used in studies of *in-situ* lead zirconate titanate thin film growth⁵⁶ and *operando* Li₂O₂ grain growth in Li-O₂ batteries.⁵⁷ In

this study, the cell was discharged using a Maccor model 4300 battery tester using a constant current of 0.093 mA, approximately C/15 discharge rate, for 15 hours. Diffraction patterns were obtained by measuring the bright-field images on the detector for 2 minutes. A diffraction pattern was collected every 10 minutes over a 15 hour period. 2D diffraction rings were integrated into 1D diffraction patterns using Fit2D V12.077 software (A.P. Hammersley, ESRF98HA01T).⁵⁸ At the time of the measurement, APS was running in top-off mode and so changes to the beam intensity over time were minimal. The Ag(113) and Al(113) peak for each scan were fit using to a Voigt line shape with a linear background using PeakFit.⁵⁹

Figure 1. (a) Pouch cell components from left to right: plastic coated aluminum foil, Li metal anode on Cu foil (current collector), polypropylene separator, $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ electrode (with Al foil as current collector), another layer of plastic coated aluminum foil; (b) *Operando* XRD transmission experimental setup

Results and discussion

Material characterization results

Figure 2 presents the XRD pattern from a laboratory diffractometer for the synthesized $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ material with the reference pattern (PDF no. 01-078-2996). No extra peaks were observed indicating a pure phase for the as-synthesized material. The structure details from the refinement have been discussed in our previous study.³² The elemental composition of the $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ material was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Measurement of thirty samples gave the Na, Ag, and P elemental contents of 0.04 ± 0.0071 , 7.50 ± 0.48 , and 8.02 ± 0.29 respectively, with an average composition of $\text{Na}_{0.04}\text{Ag}_{7.50}\text{Fe}_3(\text{P}_{2.00}\text{O}_7)_4$.

Figure 2. X-ray powder diffraction of as synthesized $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$

Electrochemical characterization

Discharge curves (**Figure 3(a)**) were obtained from the $\text{Li}/\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ electrochemical cell using a galvanostatic test at a C/15 rate. The high voltage plateau at 3.1 V is ~ 1.0 electron equivalent (ee), followed by the long plateau to 6.6ee with operating voltage of 2.7 V. The final 1.5 V plateau occurred from 6.8ee to 8ee, followed by a tail which reached 10ee. In order to identify the plateaus more clearly, the differential of charge over potential as a function of discharge potential was plotted (**Figure 3(b)**). Five resultant peaks in the differential charge plot were identified at voltage positions of 3.02 V, 2.87 V, 2.75 V, 2.46 V and 1.64 V.

Figure 3. (a) Discharge curve and (b) Differential capacity plot of $\text{Li}/\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ electrochemical cell discharged at C/15 rate.

In order to interpret the peaks in a quantitative way, the differential curve was fitted using Peak Fit software and the results are presented in **Table 1**. Based on the electron equivalents number of each peak, an electrochemical reaction mechanism was derived, which will be discussed in the *operando* section below.

Peak ID	Peak Position (V)	Peak Area/Capacity (mAh/g)	Electron Equivalents (ee)
(1)	3.02	4.2	0.25
(2)	2.87	55.5	3.34
(3)	2.75	67.8	4.08
(4)	2.46	0.4	0.03
(5)	1.64	23.1	1.40
Total		151	9.1

Table 1. Peak positions, peak areas (capacities) and their corresponding electron equivalents from the Peakfit results.

Alternating current impedance studies

Figure 4(a) shows the discharge profile for the initial 1.0ee. The arrows on the discharge curve indicate depths of discharge to 0, 0.1, 0.25, 0.5 and 1.0ee which are also the points where the impedance data was acquired. There is a steady decrease in the internal resistance of the cell as a function of discharge indicated by the AC impedance (ACI) data. The Nyquist plot (**Figure 4(b)**) shows a decrease in the diameter of the semi-circles at higher depths of discharge. The Bode plot (**Figure 4(c)**), impedance as a function of frequency is shown, demonstrating a decrease in impedance most notably in the low frequency range. The equivalent circuit used for the fits is

shown in **Figure 4(d)**, where R_s is the solution resistance, R_m is the resistance at the Li interface and R_{ct} refers to the charge-transfer resistance of the cathode.^{51, 60} **Table 2** lists R_s , R_m and R_{ct} derived from the equivalent circuit fits. The initial R_{ct} is 41 Ohm with an absolute resistance of 300 Ohm at 0.01Hz.

Based on the fitting results of the ACI data, the charge transfer resistance decreases as a function of DOD, which is consistent with the formation of metallic silver. Percolation theory can be used to predict the minimum amount of conductor needed to provide a consistent conductive path and an associated increase in conductivity of a bulk electrode.⁴⁹ For the $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ electrode composition used in this study, the threshold for electrode percolation has already been surpassed, due to the presence of 10% conductive carbon additive. However, it is important to note that intraparticle conductivity can also be a barrier,³¹ where a percolation network may be necessary but not sufficient to achieve full utilization of an electroactive material.⁶¹ The fitting results of the impedance spectroscopy data showed a rapid decrease (19%) of R_{ct} at 0.1 ee, coincident with formation of Ag^0 as discussed below. The change in R_{ct} becomes less significant after 0.5 ee discharge where the R_{ct} remains at ~25 Ohm at 1ee and 2ee discharge.

Figure 4. (a) Discharge profile for low depth of discharge (DOD), the arrows indicate the electron equivalent (ee) values with corresponding AC impedance measurements; (b) Nyquist plot of the AC impedance response of $Ag_7Fe_3(P_2O_7)_4/Li$ cell at undischarged, 0.15 ee, 0.25ee, 0.5ee and 1ee DOD; (c) Absolute value of the AC impedance as a function of frequency at different DOD and (d) Equivalent circuit model used for fit.

DOD (ee)	0	0.1	0.15	0.2	0.25	0.5	1
R_s (Ohm)	13.9(2)	5.7(1)	5.6(1)	5.7(1)	5.5(0.1)	5.5(1)	5.6(1)
R_m (Ohm)	30.7(2)	35.8(1)	36.9(1)	37.2(2)	37.5(1)	39.5(3)	39.4(5)
R_{ct} (Ohm)	40.7(5)	33.1(3)	31.4(2)	30.6(4)	27.8(3)	26.7(6)	26.9(1)

Table 2. Fitting results of AC impedance data to resistance elements of equivalent circuit model

***Ex-situ* x-ray diffraction**

The *ex-situ* samples were prepared by cyclic voltammetry sweep at 0.05 mV/s rate, and the end potential for each sample are indicated with grey dots in **Figure 5(a)**. *Ex-situ* X-ray diffraction from Cu K_α radiation reveals the formation of Ag metal in discharged $Ag_7Fe_3(P_2O_7)_4$ electrodes.

Figure 5(b) shows the XRD pattern for discharged electrodes along with the undischarged $Ag_7Fe_3(P_2O_7)_4$ electrode. The Ag metal diffraction peak is observed for the lowest depth of discharge electrode (reduced to 3.43 V), indicating Ag^+ ions are preferentially reduced. The Ag(111) peak was fitted to quantify the Ag metal based on the peak area and derive the crystallite size from the Scherrer equation. The fits are shown in the inset graph in **Figure 5(b)**. The experimental data are indicated in different colors for each electrode while the fitted lines are expressed in grey. The amount of metallic silver increases as the electrodes are discharged to greater depth (low voltage), as shown by the increase in peak intensity and area.

The area of the Ag(111) peak is plotted as a function of discharge voltage (**Figure 5(c)**). The peak area increases with reduction indicating that Ag^+ ions are reduced to form Ag metal. The increase in peak area is nonlinear and the largest change in the amount of Ag metal formation occurs between 3.10 V and 2.33 V, with a small change between 2.33 V and 2.0 V. These results indicate that a significant amount of Ag metal formation takes place during the early stage of discharge. In the later stages of discharge, the amount of Ag continues to increase, but to a lesser extent. The average Ag metal crystallite size (as determined by the peak width) is plotted as a function of depth of discharge in red in **Figure 5(c)**, where no significant change in size is observed. As more Ag metal accumulates during the reduction process, more heterogeneous nuclei of Ag metal form due to the multiple locations of Ag^+ ions sites in the $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ structure. Therefore, although the amount of Ag^0 increases significantly, the average Ag^0 crystallite size remains unchanged throughout discharge.

Figure 5. (a) Cyclic voltammetry sweep for the first reduction segment, grey dots indicate the samples for ex-situ XRD ; (b) XRD pattern of Ag₇Fe₃(P₂O₇)₄ electrodes discharged to different voltages, Ag(111) peak fit detail shown in inset graph; (c) Fitted area as a function of depth of discharge (black) and Ag metal crystallite size for each electrode (red).

Scanning electron microscope images

The SEM images for undischarged, discharged to 2.76 V (3.6 ee) and discharged to 2.50 V (7.7 ee) electrodes are shown in **Figure 6**. In the undischarged electrode, $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ material shows a plate-like shape with maximum dimensions of $2\text{ }\mu\text{m} \times 4\text{ }\mu\text{m}$. The plates lay flat due to the pressure applied during electrode preparation. In the discharged electrode, shown in (b₁), the white contrast indicated the presence of Ag metal formed from the reduction-displacement reaction. Energy dispersive spectroscopy (EDS) analysis on Ag metal content in three locations of interest is shown in the embedded table. Compared with the Ag content of the undischarged electrode, the Ag concentration is higher in the white region (red mark) and decreased in the dark area (orange mark) for the discharged electrode. This result illustrates that Ag^+ ions are mobile during discharge, which confirms our assumption in the previous report.³²

A thresholding and inverse image analysis was done to quantify the size and relative position of the silver deposits. Specifically, **Figure 6 (b₂)** and **(c₂)** clearly shows the Ag metal particles in black for 3.6 ee and 7.7 ee reduction respectively in order to obtain the size and nearest neighbor distributions (NND) analysis results (**Figure 7**). The NND method was used to quantify the spatial location of Ag metal formed with discharge in which the distance r is defined as the distance between the centroid of a particle and that of its nearest neighbor.⁶² Notably, although the silver crystallite size does not change as a function of depth of reduction as evidenced from the *ex-situ* XRD data discussed above, the average Ag^0 deposit size and distribution of the Ag^0 deposits changes, as seen by SEM. In the 7.7ee reduction electrode ($0.04\text{ }\mu\text{m}^2$) the Ag^0 deposits are seven times smaller than that in the 3.6 ee reduction sample ($0.3\text{ }\mu\text{m}^2$). Both samples have the highest population at the smallest size region of 0- $0.05\text{ }\mu\text{m}^2$. However, the 7.7ee reduction sample show higher incidence (52%) than the 3.6ee electrodes (38%) at this range and lower

incidence at other regions above $0.05 \mu\text{m}^2$. Therefore, the 7.7ee reduction sample showed a smaller Ag^0 deposit size than the 3.6ee reduction sample. In addition, the 7.7ee reduction electrode had shorter NND than the 3.6ee electrode, indicated by higher NND frequency below $0.6 \mu\text{m}$ and lower frequency above $0.8 \mu\text{m}$ distance (**Figure 7(b)**). Thus, in the 7.7ee reduction sample, we are closer to the goal of wiring every electroactive particle.

Figure 6. SEM images from undischarged coating (**(a)**), discharged to 2.76 V (3.6 ee) (**(b₁)**) and discharged to 2.50 V (7.7 ee) (**(c₁)**). The table shows the mass percentage of P and Ag element from EDS mapping of the green, orange and red locations and also the normalized Ag content. (**(b₂)**) and (**(c₂)**) show the clear location of Ag metal particles in black for corresponding (**(b₁)**) and (**(c₁)**), respectively.

Figure 7. Ag metal crystallite size distributions (a) and nearest neighbor distance (b) analysis for 3.6 ee and 7.7 ee reduction samples

***Operando* x-ray diffraction**

Using a high energy (~ 100 keV) synchrotron x-ray beam, we studied the formation of silver metal and evolution of the $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ cathode material upon electrochemical reduction *operando* by measuring the diffraction pattern as a function of discharge. Due to the geometry of the experiment (**Figure 1**), the measured diffraction pattern contains peaks from the aluminum pouch material, aluminum foil cathode, and copper foil anode current collectors in addition to the active cathode material $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ and silver metal. Silver and aluminum have similar

crystal structures: both are face-centered cubic with comparable lattice constants (Ag: 4.0862 Å from AMCSD #0011135, Al: 4.04958 Å from AMCSD #0011136). Because of this, at low angles the presence of silver is obscured by the aluminum foil and pouch material. Nonetheless, due to the high intensity of the synchrotron based XRD and the high precision of the data, we are able to differentiate the Ag metal peak from the Al peak and resolve Ag metal peak at high diffraction angles.

Cu, Al, Ag metal and $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ electrode peaks are indicated in the stack plots of the diffraction patterns (**Figure 8(a)**). The associated discharge curve is shown on the right.

Ag(113) and Al(113) peaks, indicated in the red box (2θ region of .45 – 7.6 degrees), are used for the analysis. $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ peak evolution in the 2θ region of 2 to 3.5 deg are shown in **Figure 8(b)**. With lithiation to 2.5e (scan 9, shown in red), peak (11-9) shifted to higher diffraction angle, indicating the decrease of cell parameters due to the displacement of Ag^+ ions with substitution of smaller radii of Li^+ cation. However, (22-5) peak position (2.625 deg) does not change during the discharge except a shoulder peak at 2.70 deg appears at 2.5e (scan 9, red) and distinguishes at 7.0e (scan 24, blue). Area from peak (22-5) from each scan is derived to track the change of $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ electrode.

Figure 8. Stack plot of 32 scans of *operando* synchrotron XRD from undischarged to fully discharged ($\lambda = 0.123584 \text{ \AA}$). In (a), the high intensity peaks from Cu and Al are labeled, Ag(113) and Al(113) peaks used for Ag metal analysis are indicated in the red box; (b) Peak evolution of $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ electrode upon discharge. Solid and dotted red lines are provided every 0.125 degree for visual reference.

The Ag(113) and Al(113) peaks are separated by ~ 0.1 degree which is sufficient in the resolution of our experiment to resolve the peaks clearly, as indicated in **Figure 9**. Before discharge there is a small amount of metallic silver present (**Figure 9(a)**) probably due to the ion exchange behavior of $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ material and some reduction at the lithium anode surface. With

relatively high mobility of Ag^+ ions in the structure, ion exchange between Li^+ from the electrolyte and Ag^+ in $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ framework is likely to be kinetically favorable. This phenomenon has also observed in previous studies of materials containing mobile Ag^+ ions, such as $\text{Ag}_2\text{VP}_2\text{O}_8$ and $\text{Ag}_2\text{VO}_2\text{PO}_4$ where Ag metal peaks were identified on the surface of the Li anode with energy dispersive X-ray diffraction (EDXRD) technique.⁴⁹⁻⁵⁰

Figure 9. Results of fitting Ag(331) and Al(331) peaks before discharge (a) and after fully discharge (b)

To quantify the amount of silver metal present and the corresponding decrease of the parent $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ material, the Ag(113) and $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4(22-5)$ peak areas as a function of discharge are shown in **Figure 10**. To account for small changes in the beam intensity as a function of time, the Ag(113) and $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4(22-5)$ peak areas were normalized to the area of

the Al(113) peak. The Ag(113) peak area evolution could be divided into three regions based on the change in its slope and the plateaus in the Li/ $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ discharge curve. These three regions were assigned to their corresponding electrochemical reactions indicated in **Scheme 1**. The rapid increase in the amount of silver metal in region 1, is associated with peaks (1) and (2) in **Figure 3(b)** and the R1, R2 reactions in **Scheme 1**. This region corresponds to the first plateau and the beginning of the second plateau (below 50 mAh/g, 3.0 electron equivalent), indicating that the onset of Ag^+ ions reduction occurred before the onset of Fe^{3+} reduction. Notably, AC impedance spectroscopy shows a significant decrease in cell resistance after only the initial 0.1 ee discharge. Correspondingly, the $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4(22-5)$ peak area decreases dramatically in this region indicating the displacement of Ag^+ ions significantly affects the crystallinity of the parent structure.

Next, the amount of silver increases more slowly during the second plateau (3.0ee to 8.0ee), which is due to the involvement of Fe^{3+} reduction, indicated by the peak (3) in **Figure 3(b)** and the R3 reaction in **Scheme 1**. In concert, the $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4(22-5)$ peak area continues to decrease, albeit more slowly than in Region 1. Above 8.0ee (133 mAh/g), silver metal increases more rapidly than in the second plateau, indicating that mostly Ag^+ ions reduction occurs here, as illustrated in the R4, R5 reactions. The $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4(22-5)$ peak area reaches its minimum at the end of discharge.

Figure 10. (a) Analysis on Ag(113) peak area (red) and Ag₇Fe₃(P₂O₇)₄(22-5) peak area (black) evolution along with the discharge curve (blue). The corresponding reactions (R1, R2, R3, R4 and R5) from **Scheme 1** listed below are also shown. Error bars come from uncertainty in PeakFit fit to peaks. Intensities of Ag(113) and Ag₇Fe₃(P₂O₇)₄(22-5) peaks are normalized to the

intensity of the Al(113) peak to adjust for small variations in beam intensity over time; **(b)** Two dimensional diffusion path showing the locations of Ag(2), Ag(3) and Ag(4). The Ag(4) sites are at intersections while the and Ag(2) and Ag(3) sites are on the path with directions of $(a + b)$ and $(a - b)$, respectively; **(c)** Ag(1) site plane, where the mobility is hindered by the surrounding FeO₆ octahedra (green) and PO₄ tetrahedra (grey).

Scheme 1. Lithiation and reduction-displacement processes upon cycle 1 reduction of Ag₇Fe₃(P₂O₇)₄ from galvanostatic discharge.

From the *operando* XRD and galvanostatic discharge curve studies, we conclude that the first plateau and the beginning of the second plateau (to 3.0 ee) are both associated with the formation of Ag⁰. This is consistent with the AC impedance results where the significant decrease in R_{ct} occurs at as early as 0.1 ee discharge due to the formation of conductive Ag⁰ network. The *ex-situ* XRD showed the same result where the Ag⁰ diffraction peak present after the first CV peak at 3.43 V. The rest of the second plateau (from 3.0ee to 8.0ee) is associated with both Ag⁺ and Fe³⁺ reduction. At the end of discharge (8.0ee to 9.4ee), the reaction is Ag⁺ ion reduction-displacement. The electrochemical reactions indicated from *operando* XRD match very well

with the electron equivalents assignment from the galvanostatic study. These results are consistent with the assignment of each peak from the prior slow scan cyclic voltammetry of $\text{Li/Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$.³² The Ag^+ ions in Ag(4) site are reduced first, due to its location in the diffusion path, followed by the Ag(3) and Ag(2) sites (**Figure 10(b)**). Notably, the Ag(1) site is reduced last since it is off the 2D diffusion plane has the lowest Ag^+ ion mobility among the various sites (**Figure 10(c)**).

Effect of Ag metal formation on the cathode Ohmic resistance

To investigate the effect of the Ag metal formation on the cell performance, the intermittent pulse during discharge of $\text{Li/Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ cell is conducted at 10 mA/cm^2 current density for two seconds of each pulse. **Figure 11(a)** shows the discharge curve including 12 intermittent pulses and the inset graph shows the shape of pulse 6 to illustrate the voltages that were used in the calculation of Ohmic resistance.

The changes in Ohmic resistance are shown in **Figure 11(b)** along with the discharge curve and Ag metal formation from *operando* study. In early discharge (before 2.5ee), a rapid decrease in Ohmic resistance is observed, consistent with the rapid Ag metal formation. At 4.8ee reduction, the resistance decreased by 62% (from 65 Ohm to 25 Ohm) and reached its minimum value. The resistance stays the same at 34 Ohm after 7ee reduction, indicating that additional Ag metal formation later in the discharge process does not result in a further decrease in cell resistance.

Figure 11. (a) Intermittent pulse discharge curve, voltage response at pulse 6 shown in inset; (b) Overall Ohmic contributions from the pulse test in Li/Ag₇Fe₃(P₂O₇)₄ cell.

CONCLUSIONS

We studied the Ag metal formation upon the discharge of an Li/Ag₇Fe₃(P₂O₇)₄ cell using several techniques, including AC impedance spectroscopy, *ex-situ* XRD, *ex-situ* SEM, and *operando* XRD from a synchrotron source. The charge transfer resistance (R_{ct}) decreased from 41 to 33 Ohm (19% reduction) as early as 0.1ee discharge and remained low at ~25 Ohm at 1ee and 2ee discharge. *Ex-situ* XRD showed the presence of Ag metal after the first CV reduction peak with continued formation of additional Ag⁰ until the end of discharge. SEM images of electrodes

reduced by 7.7 ee showed smaller size features of Ag metal and shorter nearest neighbor distances compared with those of an electrode reduced by 3.6 ee. Specifically, all these results were consistent with the *operando* study which showed the onset of Ag^+ ion reduction preferentially occurred upon the initial discharge up to 3 ee, followed by a majority of Fe^{3+} reduction concurrent with the Ag^+ ions reduction in the later stages of reduction. The remainder of the Ag^+ ions reduction occurred in the final stages of discharge beyond 7 ee. The initial Ag^+ ion reductions are proposed to be from Ag(4) structural sites which intersect locations along the ion diffusion path. Finally, a pulse test was conducted to investigate the effect of Ag^0 formation on electrochemical performance. The Ohmic resistance decreased by 62% and reached a minimum of 26 Ohm at 4.8 ee reduction. It remained at 34 Ohm after 7 ee reduction illustrating that the formation of additional silver nanoparticles did not further decrease the cell resistance once a sufficient conductive network was established.

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