BNL-113440-2017-JA

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Submitted to Chemistry of Materials

November 2016

Energy and Photon Sciences Directorate

Brookhaven National Laboratory

U.S. Department of Energy

USDOE Office of Science (SC),

Basic Energy Sciences (BES) (SC-22)

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Battery relevant electrochemistry of $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$: contrasting contributions from the redox chemistries of Ag^+ and Fe^{3+}

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ABSTRACT: $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ is an example of an electrochemical displacement material which contains two different electrochemically active metal cations, where one cation (Ag^+) forms metallic silver nanoparticles external to the crystals of $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ via an electrochemical reduction displacement reaction, while the other cation (Fe^{3+}) is electrochemically reduced with retention of iron cations within the anion structural framework concomitant with lithium insertion. These contrasting redox chemistries within one pure cathode material enable high rate capability and reversibility when $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ is employed as cathode material in a lithium ion battery (LIB). Further, pyrophosphate materials are thermally and electrically stable, desirable attributes for cathode materials in LIBs. In this paper, a bimetallic pyrophosphate material $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ is synthesized and confirmed to be a single phase by Rietveld refinement. Electrochemistry of $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ is reported for the first time in the context of lithium based batteries using cyclic voltammetry and galvanostatic discharge-charge cycling. The reduction displacement reaction and the lithium (de)insertion processes are investigated using ex-situ x-ray absorption spectroscopy and x-ray diffraction of electrochemically reduced and oxidized $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$. $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ exhibits good reversibility at the iron centers indicated by ~80% capacity retention over 100 cycles following the initial formation cycle and excellent rate capability exhibited by ~70% capacity retention upon four-fold increase in current.

Introduction

Lithium ion batteries play an important role in the current state of energy storage, but improvements on the capacity, power, cost, and safety of the materials must continue to be made in the search for new battery materials. Materials with polyanionic frameworks (such as materials with the NASICON structure and LiFePO_4) offer improvements in thermal and electrical stability while also allowing for increases in voltage and reversibility relative to their oxide counterparts.¹ Pyrophosphate cathode materials could be particularly appealing due to their exceptional thermal stability.^{2,3} While previous theory, supported by empirical data from the charged olivine structure LiMPO_4 materials ($M = \text{Fe}, \text{Mn}, \text{Co}, \text{Ni}$),⁴⁻⁷ states that voltage and partial pressure of oxygen constitute a linear relation, where a higher voltage implies a less stable cathode,^{8,9} a recent study verified that the high voltages of pyrophosphates do not diminish their stabilities, instead they are substantially more stable than phosphates.³ An early electrochemical study on one such polyanionic material was conducted by Goodenough's group

in which the $\text{Fe}^{3+} / \text{Fe}^{2+}$ redox couple of LiFeP_2O_7 was shown to occur at 2.9 V.¹⁰ Research on other LiMP_2O_7 ($M = \text{Cr}, \text{V}, \text{Mn}, \text{Co}, \text{Ni}$) cathodes has yielded improvements to the material, achieving potentials as high as 4.9 V and reversible capacities above 100 mAh/g.¹¹⁻¹⁹

Several groups investigated the electrochemistry of $\text{Na}_2\text{FeP}_2\text{O}_7$,^{20,21} which provides high voltage and good reversibility in secondary Na batteries (NIBs). Mixed-metal binary pyrophosphate phases, $\text{Na}_2(\text{Fe}_{1-y}\text{Mn}_y)\text{P}_2\text{O}_7$ [$y = 0 - 1$], were also investigated in NIBs where the $\text{Na}_2\text{FeP}_2\text{O}_7$ material delivered the highest capacity among a series of mixed metal phases.^{22,23} Continuing work established that this is a safe cathode material with high thermal stability tied to the stable pyrophosphate $(\text{P}_2\text{O}_7)^{4-}$ anion.² These materials are currently being studied as cathodes in sodium ion batteries and can be used with ionic liquid or aqueous electrolytes to further improve the safety of the materials.²⁴⁻²⁷ The Islam group predicted this material to have a favorable 3D framework for the Na^+ ion diffusion, resulting in high ion mobility.²⁸ This material was further developed to an iron redox

center based ($\text{Fe}_3\text{O}_4/\text{Na}_2\text{FeP}_2\text{O}_7$) sodium ion full cell with a capacity of 93 mAh/g and 93% capacity retention over 100 cycles.²⁹ In addition to the pyrophosphates, several other promising mixed $\text{P}_2\text{O}_7/\text{PO}_4$ framework materials have been recently reported for application as high energy density electrodes in both LIB³⁰⁻³³ and NIBs.³⁴⁻³⁹

Previously $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ was reported to be a fast-ion conducting system^{40,41}; however it is a poor electronic conductor which can limit its performance as a cathode material. Electrical conductivity can be enhanced by integration with carbon. For example, a $\text{Na}_2\text{FeP}_2\text{O}_7$ -carbon nanotube (CNT) motif delivered 68 mAh/g capacity at a 10C rate.⁴² $\text{Na}_{3.12}\text{Fe}_{2.44}(\text{P}_2\text{O}_7)_4$ / multi-walled CNT composites and graphene encapsulated $\text{Na}_{3.12}\text{Fe}_{2.44}(\text{P}_2\text{O}_7)_4$ materials exhibited higher capacity and better rate performance than the pristine $\text{Na}_{3.12}\text{Fe}_{2.44}(\text{P}_2\text{O}_7)_4$ material.^{43,44} However, introducing carbon decreases the battery volumetric capacity and requires additional processing of the cathode. An alternate approach is to create materials which will improve the conductivity by forming their own conductive network *in-situ* upon electrochemical reduction.⁴⁵⁻⁴⁷ In particular, this strategy works well with the silver vanadium phosphate, $\text{Ag}_x\text{V}_y(\text{PO}_4)_z$, family of materials.⁴⁸⁻⁵² In $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$, it is possible to replace some or all of the sodium ions with silver ions.^{53,54}

In this study, our hypothesis was that the silver ions from the structure would be reduced to form a conductive silver metal network external to the crystals of $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ on discharge providing a highly electrically conductive matrix for the discharge of the iron pyrophosphate based material. Towards this end, herein we provide the first report of the LIB-relevant electrochemistry of $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$. Using cyclic voltammetry (CV), quasi-reversibility of the material was demonstrated. Galvanostatic discharge-charge data over 100 cycles was collected. The multi-mechanism electrochemical behavior associated with the lithium (de)insertion and conversion processes was investigated using *ex-situ* x-ray absorption spectroscopy of electrochemically reduced and oxidized materials, including x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) analysis. Fe K-edge X-ray absorption spectroscopy analysis shows the specific CV feature which is associated with Fe^{3+} reduction. Also, with galvanostatic charge-discharge measurements we show that the Fe center of the material cycles well and can be discharged at a high current. Lastly, prospects for future studies of $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ are discussed.

Experimental Methods

Synthesis and characterization

Synthesis. $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ material was synthesized via a solid state reaction using a modification of a previously reported method.^{40,41} A mixture of $\text{Na}_4\text{P}_2\text{O}_7$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and P_2O_5 was mixed at room temperature and heated to 550°C. After cooling to room temperature, the sample was washed with purified water and dried in vacuo.

$\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ powder was prepared by ion exchange from $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$, using excess AgNO_3 and heating at 250°C in muffle furnace. After cooling to room temperature, excess nitrate salts were eliminated by extensive rinsing with water.

The exchange procedure was repeated twice to favor total ion exchange.

Materials Characterization. Quantitative elemental analysis of silver, sodium, phosphorus and iron was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) performed using a ThermoScientific iCap 6000 ICP spectrometer. All calculations are based on the assumption that the oxidation state of iron corresponds to 3+ (Fe^{3+} ions), the theoretical number indicated by the formula.

Room temperature x-ray diffraction data for the $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ products were collected on a Rigaku SmartLab diffractometer utilizing $\text{Cu-K}\alpha$ radiation with a 1D position-sensitive scintillation detector with 128 channels equipped with a graphite monochromator. X-ray diffraction patterns were fit using Rietveld analysis, which was conducted using the EXPGUI package of GSAS.⁵⁵ *Ex-situ* x-ray diffraction data on partially discharged electrodes were collected on the same Rigaku Smartlab diffractometer utilizing a D/tex detector and $\text{K}\beta$ filter with 2θ range of 20-60° and 0.04° step size.

Electrochemical Testing. $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ material was combined with conductive carbon and binder (85:10:5 wt%) and cast onto aluminum foil to form a uniform coating which was used as the electrode. The electrolyte used in this study was 1 M LiBF_4 in ethylene carbonate and dimethylcarbonate solution with a volume ratio of 1:1. Three electrode cells were used for cyclic voltammetry with lithium metal as the reference and counter electrodes. Cyclic voltammetry (CV) measurements were performed at 5×10^{-5} V/s over the voltage range from 3.7 V to 2.0 V. Galvanostatic charge-discharge tests were conducted using coin cells with lithium anodes and voltage limits of 2.0 to 3.6 V. Cycling performance was tested at C/10 rate (16 mA/g), while the rate capability was tested under a series of discharge rates ranging from C/2.5 (64 mA/g) to 3.2 C (516 mA/g). Electrochemistry of a mixture of Ag metal with $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ at molar ratio of 7:1 and $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ discharged at C/5 rate in a Li based coin cell was also collected. For the AC impedance spectroscopy measurement, pure $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ powder was pressed into a pellet with 13mm diameter and 0.5 mm thickness which was used as the cathode in a Li based coin cell. AC impedance spectroscopy of the pellet coin cell before and after discharge was collected within a frequency range from 1 MHz to 1 mHz with voltage variation of 10 mV.

X-ray absorption spectroscopy (XAS)

X-ray absorption spectroscopy (XAS) data at Fe K-edge were collected at beamline X-19A of the National Synchrotron Light Source (NSLS-I) at Brookhaven National Laboratory. Electrodes were discharged under constant voltage using the 3-electrode cell as described above and recovered in an inert atmosphere before being sealed between layers of polyimide tape prior to measurement. Samples were placed in the beam in transmission mode between ionization chambers used as detectors. In addition to the $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ samples, data for Fe_2O_3 and FeO reference samples were acquired. A Fe metal foil was measured simultaneously and used as the reference for energy calibration. X-ray absorption near edge structure (XANES) data was processed using the ATHENA software package.^{56,57} Absorption spectra were calibrated using the Fe metal foil and the pre- and post-edges were normalized to compare results across samples.

Results and discussion

Material characterization results

Figure 1 (a) The XRD spectrum and Rietveld analysis of $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ ($R_p = 7.76\%$, $R_{wp} = 9.81\%$, $\chi^2 = 3.654$), Red markers are the experimental diffraction pattern from lab Cu $K\alpha$ X-ray, black line represents the calculated intensities, blue line is the difference curve and the green bar represents the Bragg diffraction peaks; (b) Projection of the structure of $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ along $[010]$ direction. Blue: Na(1), dark red: Na(2), pink: Na(3) and green: Na(4) site

Figure 2 (a) The XRD spectrum and Rietveld analysis of $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ ($R_p = 7.53\%$, $R_{wp} = 10.14\%$, $\chi^2 = 5.510$), Red markers are the experimental diffraction pattern from lab Cu $K\alpha$ X-ray, black line stands for the calculated intensities, blue line is the difference curve and the green bar stands for the Bragg diffraction peaks; (b) Projection of the structure of $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ along $[010]$ direction showing alternating A and B layers while π_1 and π_2 diffusion planes are located in the A layer, Blue: Ag(1), dark red: Ag(2), pink: Ag(3) and green: Ag(4) site; (c) 2D diffusion path with i and j indicated in π_1 plane in $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$

The elemental compositions of the $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ parent material and the $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ product material were both verified by inductively coupled plasma-optical emission spectroscopy. Measurement of thirty samples gave the Na and P elemental contents of 7.55 ± 0.51 and 8.12 ± 0.13 respectively, with an average composition of $\text{Na}_{7.55}\text{Fe}_3(\text{P}_{2.03}\text{O}_7)_4$. 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 1(a) and Figure 2(a) present Rietveld refinement results for the as-synthesized $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ and $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ materials, respectively. Both

materials are in the space group $C2/c$. While an α - $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ modulated phase, with $a_\alpha = 3a_\beta$, $b_\alpha = b_\beta$, $c_\alpha = -a_\beta + c_\beta$ has been identified,^[20] our material did not show the superlattice peak in the diffraction pattern. Therefore, we choose the β - $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ as the model for the refinement. The atomic coordinates and thermal parameters for $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ and $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ are shown in Table S1 and Table S3, respectively. Table 1 gives the multiplicity and occupancy of Na ions for different sites in the structure. For the convenience of discussing the reduction peaks in the cyclic voltammetry section, the multiplicity and occupancy of the redox active centers: Ag^+ ion and Fe^{3+} ion are listed in Table 2. Important bond distances and angles (Tables S2, S4) are also provided in the Supporting Information.

Site	Type	Multiplicity	Occupancy
Fe1	Fe^{+3}	4	1
Fe2	Fe^{+3}	8	1
Na1	Na^{+1}	8	1
Na2	Na^{+1}	8	0.3696
Na2'	Na^{+1}	8	0.6304
Na3	Na^{+1}	4	0.3600
Na3'	Na^{+1}	8	0.4700
Na3''	Na^{+1}	8	0.1700
Na4	Na^{+1}	8	0.5709
Na4'	Na^{+1}	8	0.4291

Table 1: Multiplicity and occupancy of each Na^+ and Fe^{3+} site in as-synthesized $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ material

Site	Type	Multiplicity	Occupancy
Fe1	Fe^{+3}	4	1
Fe2	Fe^{+3}	8	1
Ag1	Ag^{+1}	8	0.72
Ag1'	Ag^{+1}	8	0.28
Ag2	Ag^{+1}	8	0.8859
Ag3	Ag^{+1}	8	0.1467
Ag3'	Ag^{+1}	8	0.5152
Ag3''	Ag^{+1}	8	0.3255
Ag4	Ag^{+1}	8	0.3498
Ag4'	Ag^{+1}	8	0.3205

Table 2: Multiplicity and occupancy of each Ag^+ and Fe^{3+} sites in as-synthesized $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ material

Structures projected along the $[010]$ axis for $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ or $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ are shown in Figure 1 (b) and Figure 2(b) respectively. The FeO_6 octahedra are corner sharing with P_2O_7 groups forming a three-dimensional framework $[\text{Fe}_3(\text{P}_2\text{O}_7)]_\infty$ within which the Na^+ ions or Ag^+ ions are located. The framework could be described as a succession of two alternating layers, with $[\text{Fe}_2(\text{P}_2\text{O}_7)_4]^{5-}$ as the A layer and $[\text{Fe}_4(\text{P}_2\text{O}_7)_4]^{2-}$ as the B layer (Figure 2(b)). Both Na^+ ions and

Ag^+ ions are distributed in 8 different sites within the iron pyrophosphate frameworks, however many of these sites are too close to be simultaneously occupied. Most of the reported silver sites are split into groups of two or three sites, and the distances between the sites within a doublet or triplet are generally less than 1 Å. There are two differences in terms of ion distribution for the two materials. In the Ag compound, the Ag(1) site is split into two sites with occupancies of 0.72 and 0.28 while Na(1) is fully occupied at that site. The Ag(2) has one site with an occupancy of 0.8859 while the Na(2) is split into two sites with occupancies of 0.3696 and 0.6304. Another difference lies in the Na3 and Ag3 sites. In $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$, the distances among the Na3 sites are 1.81 Å ($\text{Na3-Na3}'$), 2.37 Å ($\text{Na3-Na3}''$) and 0.64 Å ($\text{Na3}'-\text{Na3}''$), which are larger than those distances among the Ag3 sites in $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$: 0.8489 Å ($\text{Ag3-Ag3}'$), 0.5302 Å ($\text{Ag3-Ag3}''$), 0.7128 Å ($\text{Ag3}'-\text{Ag3}''$). The Fe and P clusters in $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ and $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ are indicated in Figure S1 and Figure S2 respectively. Even though distortions are observed in Fe1 and P1 in both materials, they still maintain octahedral and tetrahedral geometries respectively. These results match the previously reported diffraction patterns very closely and show that both as-prepared materials had the desired target structures.^{40,54}

Material	a [Å]	b [Å]	c [Å]	β [°]	ref.
$\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ Single Crystal	9.506 (3)	8.332 (2)	27.732 (5)	93.33 (3)	[22]
$\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ powder	9.5177 (3)	8.3483 (3)	27.782 9(7)	93.35 0(3)	This work
$\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ Single Crystal	9.5561 (5)	8.4417 (4)	28.226 (1)	93.4 65(2)	[57]
$\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ Powder	9.547 9(4)	8.4343 (4)	28.187 (1)	93.4 87(4)	This work

Table 3. Lattice parameters for $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ and $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$

For $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$, most Ag^+ ions are located in the A layer form a 2D ion diffusion path (Figure 2(c)) while the Ag(1) site is in the B layer and is not in this diffusion path. This character explains multiple reduction potentials observed during initial discharge, which will be described in the section below.

A comparison of the lattice parameters between the previously reported single crystal data and the powder data for both materials in this study are provided in Table 3. There is no substantial difference between the structures of the single crystals and the powders. As expected based on the difference in the ionic radii of Na^+ and Ag^+ (1.16 Å and 1.29 Å respectively)⁵⁸ the $\text{Fe}_3(\text{P}_2\text{O}_7)_4$ lattice slightly expanded after ion exchange which is consistent with larger Ag^+ radius.

Cyclic Voltammetry

Figure 3 shows the cyclic voltammetry curves for the $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ electrode at a scan rate of 0.05 mV s^{-1} between 2.0 and 3.7 V. In segment 1, there are multiple cathodic peaks with the initial peak around 3.4 V and the main peak at 2.7 V. An anodic peak at 3.1 V is shown in the oxidation process. On subsequent reduction cycles, only one cathodic peak is shown up at 3.0 V, and the area under the curve is reduced.

Figure 3. Cyclic voltammetry curves of $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ from three electrode cell

These results indicate that there are significant changes to the material that occur during the first reduction that are not reversible upon oxidation. The large change in capacity between the first and second cycle on CV may be the result of the irreversible formation of silver metal. The small ΔE_{peak} , cathodic peak (2.99 V) and anodic peak (3.12 V) after the initial discharge, is indicative of reasonably fast kinetics for these processes. Similar behavior is observed from CV at a scan rate of 0.1 mV s^{-1} , Figure S3.

Each cathodic peak in the CV scan was fit as a Gaussian peak with a linear background, Figure 4.⁵⁹ The first cycle was fit to five peaks, while cycles 2 and 3 were fit to two peaks. The results of this fit, including peak position, corresponding capacity and electron equivalents and their corresponding probable redox reactions, are presented in Table 4. It is noteworthy that peak c at 2.8 V (the green peak in Cycle 1 of Figure 4) indicates 48.1 mAh g^{-1} capacity (2.9 electron equivalents). Note that while peak c has been assigned to the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox process, and peak d has been assigned to the Ag^+/Ag redox process due to good correspondence with the expected electron equivalents of the respective peaks, there is significant overlap between peaks c and d. Therefore, some $\text{Fe}^{3+}/\text{Fe}^{2+}$ and Ag^+/Ag reduction occurs concurrently. The four dots on the figure labeled (1) through (4) represent the voltages of cells used in *ex-situ* x-ray absorption measurements and *ex-situ* x-ray diffraction patterns for some of these electrode are also provided (see Figure 6 below). We will show that the edge shift occurs between points (2) and (3) after the peak corresponding to the Fe^{3+} reduction, affirming that the peak is related to the reduction of iron.

In cycles 2 and 3, there is only one cathodic peak at 3.0 V. In these cycles, the area of this peak decreases from 2.9 electron e.q. in cycle 1 to 2.8 and 2.5 electron equivalents in cycles 2 and 3, respectively. The measured anodic peak current (20.2, 19.4 and 17.4 mA/g for cycles 1, 2, and 3, respectively) and the cathodic peak current for cycle 2 (-23.2 mA/g) and 3 (-21.2 mA/g) show 91.4% current retention, indicating reversibility of this couple. Fitting results for the anodic peak are shown in Figure S4 and Table S5. Notably, only 1.8 equivalents of Li^+ ions were extracted from the structure in the CV experiment. A difference in reduction potential was noted between Cycle 1 and Cycle 2. Since the Ag^+ ions are replaced by Li^+ ions in the Fe-P-O framework upon discharge, the Fe local structure

may be different in the undischarged and the charge material, resulting in the observed difference in reduction potential.

Figure 4. The reduction stage of the first three cycles in CV measurements of $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ electrode fit to Gaussian lineshapes.

Cathodic Peak in Cycle 1	Peak (V)	Capacity (mAh/g)	Capacity (mAh/cc)	Elect. E.q.	Redox Couple
a	3.50	3	16	0.2	Ag^+/Ag
b	3.29	38	181	2.3	Ag^+/Ag
c	2.82	48	228	2.9	$\text{Fe}^{3+}/\text{Fe}^{2+}$
d	2.68	70	330	4.2	Ag^+/Ag
e	2.44	2	8	0.1	Ag^+/Ag
Total		161	761	9.7	9.7
Cathodic Peak in Cycle 2	Peak (V)	Capacity (mAh/g)	Capacity (mAh/cc)	Elect. E.q.	Redox Couple
a'	3.46	1	7	0.1	Ag^+/Ag
c'	2.99	47	222	2.8	$\text{Fe}^{3+}/\text{Fe}^{2+}$
Total		48	229	2.9	
Cathodic Peak in Cycle 3	Peak (V)	Capacity (mAh/g)	Capacity (mAh/cc)	Elect. E.q.	Redox Couple
a''	3.46	0.2	1	0.0	0.0
c''	2.98	42	198	2.5	$\text{Fe}^{3+}/\text{Fe}^{2+}$
Total		42	199	2.5	2.5

Table 4: Peak fitting numeric results for cathodic peaks in first three CV cycles from $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ electrode

X-ray absorption near edge structure and X-ray diffraction analysis

Ex-situ X-ray absorption spectroscopy was used to study the behavior of Fe^{3+} during the first discharge and also the following two cycles. To investigate the mechanism during initial discharge, four electrodes were prepared with different end voltages: (1) OCV-3.43 V; (2) OCV-3.10 V; (3) OCV-2.33 V; and (4) OCV-2.00 V. Another three electrodes were prepared and subjected to lithiation and delithiation using CV: (5) OCV-2.00 V in cycle 2, (6) OCV-3.60 V with 1 full cycle and (7) OCV-3.60 V with 2 full cycles (dots in Figure 4). Cyclic voltammetry graph for each electrode are indicated in Figure S5. Figure 5 presents the XANES and EXAFS results at the Fe K-edge for these seven electrodes along with as prepared $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ electrode, FeO and Fe_2O_3 standards.

Figure 5 *Ex-situ* Fe K-edge XAFS spectrum of $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ electrode at different voltage: (a) XANES spectrum of electrodes in first discharge along with Fe_2O_3 and FeO standard; (b) XANES spectrum of fully discharged electrodes in cycle 1 (C1) and cycle 2 (C2); (c) $|\chi(R)|$ plot for electrode in first discharge EXAFS spectrum (d) $|\chi(R)|$ plot for cycled electrodes EXAFS spectrum.

Compared to the as prepared $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ electrode, the Fe K-edge position does not change for electrodes (1) and (2) and is comparable to that seen in the Fe_2O_3 standard, indicating that the oxidation state of Fe in both electrodes is close to 3^+ even after partial discharge. From this we can conclude that the high voltage peaks (at 3.3 and 3.5 V) are likely associated with Ag^+ ion reduction. Similarly, the Fe K-edge position is the same in electrodes (3) and (4) and is close to the position of the FeO standard indicating a 2^+ oxidation state. Thus we conclude that Fe^{3+} is reduced to Fe^{2+} between electrodes (2) and (3). This can also be examined in the EXAFS spectrum in $|\chi(R)|$ plots: electrodes (1) and (2) are consistent with the as prepared $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ electrode, illustrating no change in Fe coordination environment between 3.43 V and 3.10 V. Compared with these two electrodes, the main peaks for electrodes (3) and (4) shift 0.04 Å to the right indicating a significant change in the Fe coordination environment between 3.10 V and 2.33 V (Figure 5(c)). Based on the peak list in Table 2, we deduce that it is the higher voltage peak (peak c) that is associated with the iron

reduction based on the area (capacity) associated with the peak.

Figure 5(b) shows XANES for cycled electrodes along with FeO and Fe_2O_3 standards. Two fully reduced electrodes, (4) (from Cycle 1) and (5) (from Cycle 2), overlay with each other and align with the FeO standard. Similarly, the oxidized electrodes (6) (from Cycle 1) and (7) (from Cycle 2) are consistent with the Fe_2O_3 standard. Both phenomena indicate reversible electrochemistry of $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple in the $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ electrode. The EXAFS spectrum in $|\chi(R)|$ plots for these cycled electrode can be seen in Figure 5(d). Electrode (5) corresponded very well with electrode (4), while electrodes (6) and (7) corresponded well with each other, further indicating the good reversibility of the Fe electrochemistry.

The XRD patterns of two partially discharged $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ electrodes along with non-discharged $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ electrode are shown in Figure 6. Ag metal peaks: Ag(111) and Ag(002) are present in electrode (1) which was partially discharged to 3.434V. This is consistent with the results from XANES data that indicate peak a (in Figure 4, Cycle 1) is attributable to Ag^+ reduction. With increasing depth of discharge, we observed that the intensity of Ag(111) and Ag(002) peaks are growing and peaks corresponding to the $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ parent phase decreased in intensity, indicating amorphization upon electrochemical reduction.

Figure 6 *Ex-situ* XRD pattern for undischarged $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ coating, electrode (1) and electrode (3).

In XRD patterns of cycled $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ electrodes (Figure S6), only Ag metal peaks are observed in the charged electrode at both cycle 1 and cycle 2. The structure of the $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ parent material is not maintained in the cycled electrodes likely due to the displacement of Ag^+ ions and replacement with smaller Li^+ ions.

Discharge characteristics

The performance of a $\text{Li}/\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ cell during galvanostatic discharge and charge is shown in Figure 7 (a-c). Since the as-synthesized $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ material has both Ag^+ and Fe^{3+} in their oxidized states (with OCV ~ 3.6 V), the cell is discharged first to intercalate Li^+ ions into the structure. Cells were cycled at a C/10 rate for 100 cycles. As shown in

Figure 7 Electrochemical performance of Li/Ag₇Fe₃(P₂O₇)₄ cells. (a) Discharge and charge profiles at C/10 at cycles 1, 2, 5, 15, 50 and 100; (b) Capacity retention and charge efficiency at C/10 rate; (c) Rate capability performance from C/2.5 to 3.2C rates; (d) Bode plot from AC impedance spectroscopy Li/Ag₇Fe₃(P₂O₇)₄ cell before (black) and after 0.25 electron equivalents (red) of discharge.

Figure 7 (a), 7.6 electron equivalents (126 mAh/g) are achieved in the initial discharge process at C/10 rate. Two plateaus at average potentials of 3.2 V and 2.9 V indicate both Ag⁺ and Fe³⁺ could be reduced during the first cycle discharge. In comparison with cycle 8 where the capacity stabilized and the theoretical 3 electron equivalents expected for Fe³⁺ reduction to Fe²⁺ were achieved, Figure 7 (b), 2.3 electron equivalents (38 mAh/g) were obtained at cycle 100. Thus, in comparison to cycle 8, a 77% capacity retention was observed at cycle 100, with 90% retention at cycle 15 and 80% retention at cycle 50. Notably, a 90% charge efficiency was observed at 100 cycle.

Rate capability of the Ag₇Fe₃(P₂O₇)₄ material was investigated at various current densities from 64 mA/g (C/2.5) to 516 mA/g (3.2C) (Figure 7(c)). Even at a high current density of 516 mA/g, the Ag₇Fe₃(P₂O₇)₄ material delivered 1.3 electron equivalents (21.6 mAh/g) after 15 cycles. We deduce that Ag metal formation is crucial for the rate capability performance of the Ag₇Fe₃(P₂O₇)₄ material as illustrated by the decrease in cell impedance from 10⁵ to 10³ Ohm at 0.01 Hz after just 0.25 electron equivalents of discharge (Figure 7(d)).

The benefit of *in-situ* formation of Ag metal could be seen by comparison of the discharge behavior of Ag₇Fe₃(P₂O₇)₄ (Figure S7(a)) with that of a physical mixture of Ag metal with Na₇Fe₃(P₂O₇)₄ (7:1 molar ratio) and pure Na₇Fe₃(P₂O₇)₄ (Figure S7(b)). The physical mixture of Na₇Fe₃(P₂O₇)₄ + Ag metal delivered 1.3 electron equivalents (36 mAh/g) and 0.7 electron equivalents (28 mAh/g) on Cycles 1 and 2, respectively. The pure Na₇Fe₃(P₂O₇)₄ delivered 0.9 electron equivalents (39 mAh/g) and 0.5 electron equivalents (31 mAh/g) on Cycles 1 and 2, respectively. In contrast, the Ag₇Fe₃(P₂O₇)₄ material delivered 6.2 electron equivalents (103 mAh/g) and 3.4 electron equivalents (56 mAh/g) on Cycles 1 and 2, respectively, although tested at 2 times the rate of the pure Na₇Fe₃(P₂O₇)₄ and the physical mixture of Na₇Fe₃(P₂O₇)₄ + Ag metal.

Based on the peak fit results from CV scan and *ex-situ* XAS and XRD measurement, multiple electron transfer process

could be conceptualized as shown below (Scheme 1). Equations (1) through (5) show the lithiation process in which Ag⁺ ions are reduced indicated by (1), (2), (4) and (5) while Fe³⁺ reduction is shown in equation (3). In detail, Ag⁺ ions are reduced in the initial 2.5 electron equivalents, followed by 2.9 equivalents of Fe³⁺ reduction (which is very close to theoretical transfer). At the end, another 4.3 equivalents of Ag⁺ ions are reduced.

Equation (6), Scheme 2, shows the reversible lithiation and delithiation processes associated with Fe³⁺/Fe²⁺ redox following cycle 1. The amount of Ag metal stays same in reversible process (6) indicating the irreversibility of the silver reduction-displacement process.

As shown in Scheme 1, the first two peaks in the CV can be attributed to Ag⁺ reduction. These are followed by Fe³⁺ reduction in the third CV peak. The last two peaks in the CV can also be attributed to Ag⁺ reduction. As there are 4 non-equivalent Ag⁺ sites in the structure, it is interesting to consider which Ag⁺ sites would reduce first and play the critical role of decreasing the impedance of the cell through the formation of Ag⁰. Based on prior ion exchange experiments involving substitution of Na⁺ for Ag⁺ in Na_xAg_yFe₃(P₂O₇)₄, the Ag⁺ ions in the Ag(4) sites are most mobile, followed by Ag(3), Ag(2), and Ag(1) sites sequentially.[52] Further, as Ag(4) sites are at the intersection of the diffusion path (Figure 2(c)), one could postulate that the Ag(4) sites should be reduced most readily upon electrochemical lithiation. The total occupancy of the Ag (4) site is 0.6703 (Ag(4) + Ag(4')) = 0.3498 + 0.3205 = 0.6703, which is indicated in Table 2. Therefore, the electron equivalent fraction of this site would be 0.6703 * 8 * 100% / 40 = 13.4% (8 is the site multiplicity, 40 is the total electron equivalents for reducing all cations in one unit cell). However, the first two Ag⁺ reduction peaks account for 25.0% of the total which suggests that more silver sites participate than just the Ag(4) sites. If the silver ions in the Ag(4) site are reduced first as the structure would suggest, additional Ag⁺ ions may move toward the Ag(4) site during the process of discharge. Our results from fit of the CV scan indicate that each cathodic peak in cycle one must originate from a combination of multiple sites, consistent with the high mobility of Ag⁺ ions in the structure. AC impedance spectroscopy indicates reduction of the initial Ag⁺ ions plays a crucial role in decreasing overall cell impedance. The Ag⁺ ions that are reduced last have a high over potential and show no further benefit in decreasing impedance.

Scheme 1. Lithiation and reduction-displacement processes for cycle 1 reduction of $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$

Scheme 2. Reversible lithiation/delithiation process for $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$

Conclusion

Materials with an iron-based pyrophosphate framework $[\text{Fe}_3(\text{P}_2\text{O}_7)]_\infty$ in which sodium ions or silver ions are located to form $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ and $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ respectively were successfully synthesized, where x-ray diffraction and Rietveld analysis indicated single phase materials. The electrochemistry of the $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ electrode was studied by cyclic voltammetry for the first time. X-ray absorption spectroscopy (XAS) at the Fe K-edge was conducted on partially reduced and cycled electrodes recovered from lithium based three electrode cells. The initial process was attributed to the reduction of ~18% of the Ag^+ ions. The Fe^{3+} reduction to Fe^{2+} occurs between 3.43 and 3.10 V, which shows a capacity comparable to the theoretical 3 electron equivalents expected from Fe reduction. This peak persists in cycles 2 and 3 indicating good reversibility of the $\text{Fe}^{3+} / \text{Fe}^{2+}$ couple. The majority of the remaining Ag^+ is reduced concurrent with the Fe^{3+} , consistent with higher Ag^+ mobility in some sites and lower Ag^+ mobility in others.

Further electrochemical investigation using a galvanostatic charge-discharge method showed 77% capacity retention after 100 cycles for the 3 theoretical electron equivalents transfer (50 mAh/g) based on $\text{Fe}^{3+} / \text{Fe}^{2+}$ chemistry. The material demonstrated high rate capability with 68% capacity retention as the discharge rate was increased from a C/2.5 rate to a 1.6C rate. This manuscript presents an example of a bimetallic silver iron pyrophosphate demonstrating high rate capability and good reversibility of the iron redox center, illustrating that the concept of in-situ silver ion reduction-displacement can successfully be extended to the pyrophosphate family of materials.

ASSOCIATED CONTENT

Supporting Information. Detailed results of Rietveld refinement (atomic coordinates and thermal parameters, bond lengths and angles); additional views of structures; Ex-situ XRD data for the charged electrode at cycle 1 and cycle 2; cyclic voltammetry data; comparison of discharge behavior of $\text{Ag}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ with that of a physical mixture of Ag metal with $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ (7:1 molar ratio) and pure $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ACKNOWLEDGMENT

Funds for synthesis of the material were provided by the Department of Energy, Basic Energy Sciences, under grant DE-SC0008512. Characterization and electrochemical evaluation was supported by the Center for Mesoscale Transport Properties, an Energy Frontier Research Center supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under award #DE-SC0012673. Utilization of the National Synchrotron Light Source (NSLS) beamline X17B1 was supported by U.S. Department of Energy Contract DE-AC02-98CH10886. K. Kirshenbaum acknowledges postdoctoral support from Brookhaven National Laboratory and the Gertrude and Maurice Goldhaber Distinguished Fellowship.

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