BNL-112481-2016-JA

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Submitted to Chemistry of Materials

July 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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Electrode Reaction Mechanism of $\text{Ag}_2\text{VO}_2\text{PO}_4$ Cathode

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Supporting Information

ABSTRACT: The high capacity of primary lithium-ion cathode $\text{Ag}_2\text{VO}_2\text{PO}_4$ is facilitated by both displacement and insertion reaction mechanisms. Whether the Ag extrusion (specifically, Ag reduction with Ag metal displaced from the host crystal) and V reduction are sequential or concurrent remains unclear. A microscopic description of the reaction mechanism is required for developing design rules for new multimechanism cathodes, combining both displacement and insertion reactions. However, the amorphization of $\text{Ag}_2\text{VO}_2\text{PO}_4$ during lithiation makes the investigation of the electrode reaction mechanism difficult with conventional characterization tools. For addressing this issue, a combination of local probes of pair-distribution function and X-ray spectroscopy were used to obtain a description of the discharge reaction. We determine that the initial reaction is dominated by silver extrusion with vanadium playing a supporting role. Once sufficient Ag has been displaced, the residual Ag^+ in the host can no longer stabilize the host structure and V–O environment (i.e., onset of amorphization). After amorphization, silver extrusion continues but the vanadium reduction dominates the reaction. As a result, the crossover from primarily silver reduction displacement to vanadium reduction is facilitated by the amorphization that makes vanadium reduction increasingly more favorable.

INTRODUCTION

Silver vanadate phosphate, $\text{Ag}_2\text{VO}_2\text{PO}_4$, is a high energy primary lithium-ion battery cathode with capacities of ~ 205 mAh/g (discharged to 2.0 V) or ~ 270 mAh/g (discharged to 1.5 V).¹ It has recently gained interest for medical Li-ion batteries to power implantable cardiac defibrillators (ICDs),^{1,2} exhibiting improved stability relative to a state of the art oxide-based ICD cathode material.^{3–5} The high capacity of $\text{Ag}_2\text{VO}_2\text{PO}_4$ (and structurally related materials) is attributed to its multimechanism character in which both a displacement and a multielectron insertion reaction occur during the discharge.² As a result, $\text{Ag}_2\text{VO}_2\text{PO}_4$ presents an interesting material to examine various design principles that include: (1) the use of chemically stable PO_4^{3-} anions to improve the thermodynamic stability, (2) utilizing the operando formation of Ag conductive networks to overcome the low electrical conductivity of the electrode, and (3) combining both displacement and insertion reactions to increase the capacity, i.e., multimechanism electrodes. Of these, the latter is least

understood. Various studies have been devoted to determining whether the Ag extrusion and V reduction are sequential or concurrent.^{2,6–9} These studies have shown that neither description is completely adequate with both reactions participating in a complicated, rate-dependent fashion.^{8,10,11} Recent studies of the $\text{Ag}_w\text{V}_x\text{P}_y\text{O}_z$ material family have determined that the Ag^+ ions are reduced and displaced from the crystal structure facilitating the formation of silver crystallites preferably at the cathode surface, which we refer to as a reduction-displacement reaction to distinguish from typical extrusion.⁸ A microscopic description of the discharge reaction of $\text{Li}/\text{Ag}_2\text{VO}_2\text{PO}_4$ is still sought to determine design principles that can be used to develop the next generation of high capacity multimechanism cathodes. The major difficulty in developing a microscopic description of the lithiation of

$\text{Ag}_2\text{VO}_2\text{PO}_4$ is the pronounced loss of long-range order (i.e., amorphization).^{1,2} Conventional characterization tools are found to be incapable of probing in-depth structural evolution and chemical reactions of this material during lithiation.

Here, we have employed cross-cutting experimental techniques that are especially powerful to probe amorphous materials, i.e., pair-distribution function (PDF) and soft X-ray absorption spectroscopy (XAS). We conclude that both Ag and V reduction occur during the discharge reaction. Initially, Ag^+ ion reduction dominates the electrode reaction (i.e., the formation of Ag metal) with vanadium playing a supporting role. With the discharge progressing beyond 2 electron equivalents, vanadium reduction becomes dominant. However, the formation of Ag metal does not stop at the stage of 2 electron equivalents of reduction and continues throughout. As a result, a straightforward sequential reaction is not occurring. We are able to resolve this issue in terms of the amorphization. The crossover from primarily silver reduction-displacement to vanadium reduction corresponds to a critical point at which the majority of Ag^+ in $\text{Ag}_2\text{VO}_2\text{PO}_4$ has been consumed. The loss of the long-range order and resulting morphological changes are likely responsible for hindering the participation of the remaining Ag^+ ions, thereby making vanadium reduction more favorable.

■ EXPERIMENTAL PROCEDURES

$\text{Ag}_2\text{VO}_2\text{PO}_4$ was prepared by following the previously reported hydrothermal method,^{12,13} using Ag_2O , V_2O_5 , and H_3PO_4 precursors. The as-made and lithiated $\text{Ag}_2\text{VO}_2\text{PO}_4$ samples were characterized by powder X-ray diffraction (XRD) on a Rigaku Smartlab diffractometer using Cu K_α radiation ($\lambda = 1.54 \text{ \AA}$) and parallel-beam geometry. XRD data were collected from 5 to 90° (2θ) through continuous measurement mode with a step size of 0.05° and a scan speed of $0.1^\circ/\text{min}$. The Rietveld refinement was done using the GSAS/EXPGUI package¹⁴ in a 2θ range of 25 – 75° to minimize the background interference. The morphology of $\text{Ag}_2\text{VO}_2\text{PO}_4$ powder was characterized using a LEO 1550 Scanning electron microscope (SEM) with an accelerating voltage of 4 keV . The elemental composition was also studied through energy-dispersive X-ray spectrometry (EDS). Cathodes were prepared by pressing pristine $\text{Ag}_2\text{VO}_2\text{PO}_4$ powder into pellets. The dried electrodes with each area of 1.33 cm^2 were placed in 2325-type coin cells. The cells were assembled in an Ar-filled glovebox with pure lithium foils as the counter and reference electrodes. One molar lithium tetrafluoroborate (LiBF_4) dissolved in a solution of propylene carbonate and dimethyl carbonate (1:1 by volume) was used as the electrolyte. The cells were discharged on a Maccor Series 4000 battery tester under a constant current of 0.45 mA (2 mA/g) to different depths of discharge (DOD). After electrochemical discharge, the cathode pellets were recovered and washed prior to further characterization.

X-ray photoemission spectroscopy (XPS) was performed using a Phi VersaProbe 5000 system with a monochromated Al K_α source and hemispherical analyzer at the Analytical and Diagnostics Laboratory (ADL) at SUNY Binghamton. The samples were mounted using Ta foil to improve conductivity (and in contact with a Au foil). The core-levels (O 1s, V 2p, Ag 3d, P 2p, Li 1s, C 1s) and the valence band (VB) region were measured with a pass energy of 23.5 eV , corresponding to an instrumental resolution of 0.5 eV from analyzing both the Au $4f_{7/2}$ and Fermi edge of the Au foil. Charge compensation was initially required for the pristine powder and electrodes with the lowest depth of discharge. Meanwhile, the electrodes at the highest depth of discharge showed evidence of surface lithium oxide and carbonate species. For accounting for artificial shifts due to charging and issues aligning to the C 1s and O 1s core-levels, the energy alignment here was calibrated to the P 2p core-level of the pristine electrode. Soft XAS measurements were carried out at beamline 6.3.1.2 at Advanced Light Source (ALS), Lawrence Berkeley National

Laboratory. The XAS spectra were recorded in the total electron yield (TEY) mode with an effective beamline resolution of 0.2 eV . The absorption spectra were normalized to the current from a reference Au-coated mesh in the incident photon beam. The energy scale was calibrated using first- and second-order diffraction Ti $L_{3,2}$ edge absorption features of rutile TiO_2 .

For in situ PDF measurements, the $\text{Ag}_2\text{VO}_2\text{PO}_4$ electrode was prepared by mixing $\text{Ag}_2\text{VO}_2\text{PO}_4$ powder with carbon (“super P”, Alfa Aesar), carbon black, and polytetrafluoroethylene (PTFE) binder (Sigma-Aldrich) in the mass ratio 6:1:1:2 and formed into a pellet (10 mm diameter, $\sim 130 \text{ }\mu\text{m}$ thick). The electrode pellet was assembled into an electrochemical cell (i.e., the AMPIX cell)¹⁵ with a glass fiber separator, Li metal foil, and liquid electrolyte (1 M LiPF_6 in ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of 1:1). The cell (with a loading mass of 15.96 mg for the active material) was discharged galvanostatically from OCV (3.55 V) to 1.4 V against lithium at constant current density of 0.034 mA/cm^2 at room temperature. While real time electrochemistry progressed, X-ray total scattering data suitable for PDF analysis were collected using 6 min exposures at 30 min intervals at the dedicated PDF beamline 11-ID-B at the Advanced Photon Source (APS), Argonne National Laboratory.

Ex situ PDF measurements (on powder samples with different states of discharge, i.e., $\text{Li}_x\text{Ag}_2\text{VO}_2\text{PO}_4$, $x = 2.25, 2.5, 2.75$, and 3) were carried out at XPD beamline 28-ID at the National Synchrotron Light Source II (NSLS II), Brookhaven National Laboratory. For both in situ and ex situ PDF measurements, high-energy X-rays (86.7 keV , $\lambda = 0.143 \text{ \AA}$ for APS 11-ID-B; 65.6 keV , $\lambda = 0.189 \text{ \AA}$ for NSLS II 28-ID) were used in combination with a large, amorphous, silicon-based area detector to collect total scattering data to high values of momentum transfer. The collected data were corrected for background scattering, Compton scattering, and detector effects within PDFgetX2 and Fourier transformed to get $G(r)$, the PDF.¹⁶

The density functional theory (DFT) calculations were performed using the Quantum Espresso package¹⁷ within the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE).¹⁸ Electron–ion interactions were described by ultrasoft pseudopotentials.¹⁹ A relatively large supercell structure containing 160 atoms (16 units of $\text{Ag}_2\text{VO}_2\text{PO}_4$) was used.

■ RESULTS AND DISCUSSION

1. $\text{Ag}_2\text{VO}_2\text{PO}_4$. Before addressing the discharged electrodes, we focus on the as-made $\text{Ag}_2\text{VO}_2\text{PO}_4$ material. The chemical composition was determined using a combination of XPS and SEM-EDS mapping. Figure S1a shows SEM images and EDS mapping results of as-made $\text{Ag}_2\text{VO}_2\text{PO}_4$. SEM shows that many grains of $\text{Ag}_2\text{VO}_2\text{PO}_4$ appear between 300 and 700 nm , whereas large grains are on the order of a couple micrometers (typically buried under smaller grains). EDS results (Table S1) indicate the atomic ratios of as-made $\text{Ag}_2\text{VO}_2\text{PO}_4$ are consistent with the expected $2:1:1:6$ of Ag/V/P/O. Moreover, the surface composition of $\text{Ag}_2\text{VO}_2\text{PO}_4$ obtained from XPS is also similar to the expected bulk ratio (Figure S1b), revealing a uniform bulk and surface composition of as-made $\text{Ag}_2\text{VO}_2\text{PO}_4$.

Rietveld refinement verified the phase purity (i.e., single phase) of the as-made $\text{Ag}_2\text{VO}_2\text{PO}_4$. The XRD pattern and refinement analysis are shown in Figure 1. The refined cell parameters of $a = 12.453(4) \text{ \AA}$, $b = 6.302(3) \text{ \AA}$, $c = 6.312(4) \text{ \AA}$, $\beta = 90.37(6)^\circ$, $V = 495.36(4) \text{ \AA}^3$ are very close to the previously reported single crystal XRD data (i.e., $a = 12.431(3) \text{ \AA}$, $b = 6.298(1) \text{ \AA}$, $c = 6.300(2) \text{ \AA}$, $\beta = 90.38(2)^\circ$, $V = 493.2 \text{ \AA}^3$);¹² the R_p and R_{wp} values of the refinement are 0.0282 and 0.0360 , respectively.

We also compared the measured electronic structure of $\text{Ag}_2\text{VO}_2\text{PO}_4$ from X-ray spectroscopy measurements with our DFT calculations. The valence band (VB) states of $\text{Ag}_2\text{VO}_2\text{PO}_4$ were determined from XPS (topmost occupied), and the

Figure 1. Rietveld refinement of XRD for the as-made $\text{Ag}_2\text{VO}_2\text{PO}_4$: the experimental pattern, refined pattern, and difference curve are indicated as black, red, and blue, respectively.

conduction band states were determined from the O K-edge XAS (bottommost unoccupied). The VB-XPS in Figure 2a

Figure 2. (a) XPS valence band region, (b) GGA-calculated weighted partial density of states (PDOS), and (c) GGA-calculated partial density of states (PDOS).

shows the occupied O 2p valence states hybridized with the Ag 4d states centered at ~ 5 eV, typical of silver vanadate.²⁰ The two smaller weaker peaks at higher binding energies below the main valence band are typical of phosphates and reflect P 2s and P 2p strong sigma bonds formed with O 2p.^{21–25} The GGA-calculated partial densities of states (PDOS) of $\text{Ag}_2\text{VO}_2\text{PO}_4$ are also plotted in Figure 2c. For fairer comparison with experimental data, the PDOS have been weighted by their orbital cross sections,²⁶ summed, and convoluted to match the experimental broadening. We note that all the main features of the valence band region are reproduced once a rigid shift of 3.4 eV is used to align with XPS. This shift accounts for the relative line-up of the Fermi level and the well-known band gap error from DFT calculations. The GGA calculations also reproduce 2.2 eV crystal splitting in the e_g and t_{2g} unoccupied states in agreement with the observed splitting of the O K-edge XAS of $\text{Ag}_2\text{VO}_2\text{PO}_4$,⁷ as shown in Figure S2. Meanwhile, the corresponding V L-edge is consistent with a V^{5+} line shape and is discussed further below.

2. $\text{Li}/\text{Ag}_2\text{VO}_2\text{PO}_4$ Electrodes. The discharge curve of $\text{Li}/\text{Ag}_2\text{VO}_2\text{PO}_4$ electrodes is shown in Figure 3 and displays

Figure 3. A representative discharge curve of $\text{Li}/\text{Ag}_2\text{VO}_2\text{PO}_4$.

evidence of two staged reactions. The first reaction has been considered as a two-phase displacement reaction that would allow up to 2 electron equivalents attributed to Ag reduction displacement, resulting in a conductive metallic Ag network. After 2 electron equivalents of discharge, the second reaction is considered to be initiated, that is, vanadium reduction along with Li insertion. Therefore, the reduction of $\text{Ag}_2\text{VO}_2\text{PO}_4$ cathode would follow the reaction scheme²

When lithium ions are inserted into $\text{Ag}_2\text{VO}_2\text{PO}_4$ electrodes during the discharge, Ag metal phase is clearly identified through XRD, as shown in Figure 4. The Bragg peaks of

Figure 4. XRD patterns of the as-made and lithiated $\text{Ag}_2\text{VO}_2\text{PO}_4$ ($\text{Li}_x\text{Ag}_x\text{VO}_2\text{PO}_4$ ($x = 0, 1.5, 2.4, 3.2, 4.0$)). Red bar: Ag; blue bar: $\text{Ag}_2\text{VO}_2\text{PO}_4$.

$\text{Ag}_2\text{VO}_2\text{PO}_4$ can still be observed at 1.5 electron equivalents but with a significantly decreased intensity. Further lithiation results in a total loss of diffraction signals of $\text{Ag}_2\text{VO}_2\text{PO}_4$, indicating a complete amorphization of this material. For instance, only the Ag metal phase is observed from XRD when $\text{Ag}_2\text{VO}_2\text{PO}_4$ is discharged to 2.4 electron equivalents. This finding initially supports the aforementioned proposed reaction mechanism, i.e., Ag reduction dominates the initial reaction. However, the amorphization makes it difficult to say more beyond this.

Figure 5. (a) V 2p and O 1s XPS core level and (b) Ag 3d XPS core level regions.

The evolution of the vanadium and silver oxidation states was monitored by core-level XPS of the electrodes as a function of inserted lithium. **Figure 5** (a) displays the V 2p XPS core level of lithiated $\text{Ag}_2\text{VO}_2\text{PO}_4$ electrodes. The vanadium oxidation state is not significantly changed until discharging to 3.2 electron equivalents of Li^+ . The initial vanadium oxidation state was assigned as primarily V^{5+} (up to 2.4 equiv of Li^+) and then a mixed $\text{V}^{4+}/\text{V}^{3+}$ by 3.2 electron equivalents. To confirm our oxidation assignments, we intentionally Ar ion irradiated $\text{Ag}_2\text{VO}_2\text{PO}_4$ pristine electrodes to reduce the vanadium. The sputter-induced V reduction displayed an evolution from V^{5+} to V^{3+} with increasing irradiation, as shown in **Figure S3**. The corresponding Ag 3d core level is displayed in **Figure 5** (b), which shows that Ag^+ in $\text{Ag}_2\text{VO}_2\text{PO}_4$ is reduced to metallic Ag upon lithiation.^{27,28} However, some Ag^+ ions still remain up to 2.4 Li insertion, that is, the Ag^+ ions are not entirely reduced up to 2 equiv of Li^+ .

Vanadium L-edge XAS of the electrodes was performed to further investigate the vanadium oxidation state during discharge. The vanadium line shape reflects allowed dipole transitions between the V 2p and V 3d states. The line shape is very sensitive to the d orbital occupation, i.e., vanadium oxidation state. **Figure 6** displays the V L-edge XAS of the

Figure 6. V L-edge XAS spectra of pristine and lithiated $\text{Ag}_2\text{VO}_2\text{PO}_4$.

electrodes and is in agreement with the previous studies.⁷ We note that these data are most importantly in agreement with our V 2p XPS results, i.e., the most pronounced change in the XAS occurs by 3.2 electron equivalents of Li^+ . As discussed previously, the pristine $\text{Ag}_2\text{VO}_2\text{PO}_4$ is considered to be primarily in the V^{5+} oxidation state. We note that more multiplet features for V^{5+} are expected from direct comparison of high-quality V_2O_5 nanowires.²⁹ However, these features are

typically lost by reducing crystalline quality and/or the inclusion of small amounts of V^{4+} . We cannot rule out a small V^{4+} contribution (<5%) from the complementary XPS (**Figure 5** a), but we note that this would still suggest the occurrence of very limited V reduction. Instead, our XRD clearly shows that the host crystal structure is being degraded with lithiation (**Figure 4**). As a result, we consider our V L-edge XAS to represent a primarily V^{5+} line shape up to 2.4 Li. We also note that electrodes displayed a more reduced V L-edge line shape whenever the electrodes were in the fully amorphous phase (>2.4 Li).

Our ex situ XAS and XPS studies suggest that the reduction of Ag^+ dominates the electrode reaction with the formation of Ag metal up to ~2.4 electron equivalents. Some vanadium reduction is likely occurring initially because Ag reduction is not entirely reduced by 2 equiv of Li^+ . We note that previous ex situ magnetic studies of $\text{Ag}_2\text{VO}_2\text{PO}_4$ showed some small reduction of V^{5+} occurring in parallel with Ag^+ reduction (on initial reduction from 0 to 2.5 electron equivalents).⁶ Upon discharging beyond 2.4 electron equivalents of Li^+ , an abrupt change in the vanadium environment occurs, suggesting that vanadium participates more once the material is entirely amorphous. However, such a concurrent V^{5+} reduction was not clearly observed under our ex situ XPS and XAS experiments.

To better understand our XPS and XAS data, which present the surface properties of ex situ samples under equilibrium, we also performed in situ bulk-sensitive characterization for the $\text{Ag}_2\text{VO}_2\text{PO}_4$ cathode. A major feature of this material is its amorphization during lithiation, which results in the loss of long-range order so that routine X-ray diffraction analysis is inapplicable of monitoring the detailed structure information. Therefore, we applied in situ hard X-ray PDF analysis on $\text{Ag}_2\text{VO}_2\text{PO}_4$ to comprehensively characterize the chemical phase transition along with probing the structural evolution during the electrode reaction.

In situ PDF measurements can provide detailed and real-time insights into the local structure and chemical information independent of long-range order. Because the high energy focused beam and fast data-acquisition detectors are essentially required for in situ PDF analysis, synchrotron X-ray diffraction facilities are prerequisite for this study. Our in situ PDF measurements were performed on beamline 11-ID-B, a dedicated PDF instrument at APS, Argonne National Lab. It can offer high-speed data collection (using a fast data-acquisition 2D detector) and a high energy focused beam (affording much higher Q space measurements) and is optimized for in situ and high throughput measurements. More importantly, Chupas et al. have developed a specific

Figure 7. (a) In situ PDF of $\text{Ag}_2\text{VO}_2\text{PO}_4$, where the blue arrows indicate the main Ag–Ag atomic pairs of fcc Ag, and (b) the crystal structure of $\text{Ag}_2\text{VO}_2\text{PO}_4$.

Figure 8. (a) In situ PDF in the local range and (b) Ag–O, (c) Ag–Ag, (d) Ag–V, Ag–P, and (e) V–O atomic distances of $\text{Ag}_2\text{VO}_2\text{PO}_4$.

Figure 9. Comparison between (a) ex situ and (b) in situ PDF patterns from 2.0 to 3.0 electron equivalents of discharge.

electrochemical cell suitable for in situ PDF measurements of battery electrodes (i.e., the “AMPIX” electrochemical cell),¹⁵ which has been utilized in our in situ PDF experiments. Total scattering data were taken at constant time intervals while the real time electrochemistry progressed from 0 to 4 electron equivalents per $\text{Ag}_2\text{VO}_2\text{PO}_4$ (Figure S4). The PDFs ($G(r)$), depicted as peaks corresponding to the atom–atom distances within the sample (weighted by the scattering power of the atoms involved), are shown in Figure 7a at different states of discharge.

Figure 7a shows that Ag–Ag atomic pairs of the metallic silver (fcc silver) do increase upon lithiation (as depicted by blue arrows). These Ag–Ag atomic pairs obtained from in situ

PDF are quite consistent with crystal structural Ag–Ag atomic distances of fcc silver (i.e., Ag–Ag = 2.889, 4.086, 5.005, 5.779, 6.461, 7.078, 7.645 Å, etc.).³⁰ The increase of Ag is most pronounced initially but does continue beyond 2 electron equivalents of reduction. This observation confirms that the reduction of Ag^+ does not stop at 2 electron equivalents of reduction. It also shows that the insertion of 2 Li^+ per $\text{Ag}_2\text{VO}_2\text{PO}_4$ is insufficient for the full reduction of residual Ag^+ in $\text{Ag}_2\text{VO}_2\text{PO}_4$.

The reduction-displacement mechanism of Ag from $\text{Ag}_2\text{VO}_2\text{PO}_4$ is examined from the local range in situ PDF patterns (Figure 8a). We note a broad PDF peak can be observed for pristine $\text{Ag}_2\text{VO}_2\text{PO}_4$ (the black color pattern in

Figure 8a) within the range of $r = 2.8\text{--}4.0\text{ \AA}$. This broad peak is contributed from a combination of Ag–O (Figure 8b), Ag–Ag (Figure 8c), Ag–V (Figure 8d), and Ag–P (Figure 8d) atomic pairs of $\text{Ag}_2\text{VO}_2\text{PO}_4$. A full list of these atomic pairs is provided in Table S2. As shown in Figure 8a, this broad peak starts disappearing once lithiation begins, verifying the decrease of the Ag component in $\text{Ag}_2\text{VO}_2\text{PO}_4$ (i.e., displacement occurring with the aforementioned reduction of Ag). In addition, in situ PDF also shows the nearest V–O atomic pairs (Figure 8e) change little upon lithiation, suggesting averaged V–O pairs in VO_6 units (with octahedral coordination geometry) exhibit only subtle changes when Ag^+ is removed from the $\text{Ag}_2\text{VO}_2\text{PO}_4$ structure (i.e., no evidence of pronounced vanadium reduction).

For confirming that the reduction displacement of Ag^+ from $\text{Ag}_2\text{VO}_2\text{PO}_4$ beyond 2 electron equivalents is not due to beam damage during in situ PDF measurements, ex situ PDF data were also collected on powder samples with these states of discharge: $\text{Li}_x\text{Ag}_y\text{VO}_2\text{PO}_4$, where $x = 2.25, 2.5, 2.75$, and 3. These four ex situ samples were particularly selected to cover the transition range before and after the “knee” (crossover) point on the discharge curve of $\text{Ag}_2\text{VO}_2\text{PO}_4$ (Figure S4). As shown by ex situ PDF (Figure 9a), Ag reduction displacement is still progressing from the state of discharge of 2 to 3.0 electron equivalents. Although ex situ PDF data were taken from a different facility (NSLS II 28-ID) with a different wavelength compared to that of in situ, both ex situ and in situ results match very well with each other (Figure 9a and b), i.e., Ag reduction displacement does continue beyond 2 electron equivalents albeit at a slower rate. The consistency of ex situ and in situ PDF patterns, as well as the same increasing trend of the metallic Ag–Ag pair distribution, unambiguously confirms that the increase of metallic Ag signals during in situ PDF measurements is not due to beam damage.

CONCLUSIONS

In conclusion, using a combination of local probe X-ray techniques, we have obtained a microscopic description of the discharge mechanism of $\text{Ag}_2\text{VO}_2\text{PO}_4$. We made the following determinations: (1) First reaction (up to ~ 2 electron equivalents of Li^+): Ag reduction-displacement process dominates the initial reaction, with some small vanadium reduction also occurring. However, Ag reduction-displacement continues up to 4 electron equivalents ruling against straightforward sequential reactions. (2) Second reaction (after ~ 2 electron equivalents of Li^+): Vanadium reduction is more pronounced when the host material has lost its long-range order. This is consistent with the experimental observation of a primarily V^{5+} environment with some V reduction up to the crossover “knee” point, followed by a change to lower oxidation environment more typical of disordered systems at higher lithium concentrations. We explain the crossover from the first to the second reactions as mediated by the disordering of the host material. Full amorphization occurs after the majority of silver has been reduced and displaced. Prior to this point, the silver reduction-displacement dominates the reaction (with vanadium reduction playing a supporting role). After significant disordering, the vanadium must participate more in the reaction since most Ag^+ ions are reduced. The amorphization and resulted morphological change of $\text{Ag}_2\text{VO}_2\text{PO}_4$ (e.g., surface accumulation of Ag crystallites)^{2,8} may be considered responsible for hindering the remaining Ag reduction-displacement.

Our approach demonstrates the importance of local probe techniques to solve reaction mechanisms in cathode systems in which disorder is inherent to the system. We note that disordered materials have already shown surprising promise for Li-ion batteries applications.³¹ It also provides insight into how competing electrode reactions operate in multimechanism cathodes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.chemmater.6b00828](https://doi.org/10.1021/acs.chemmater.6b00828).

SEM-EDS analysis (including chemical mapping), additional XAS analysis, full DFT calculations, and atomic pair distances of $\text{Ag}_2\text{VO}_2\text{PO}_4$ (PDF)

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Author Contributions

L.F.J.P. conceived and organized the study. A.B.B., D.B., A.C.M., K.J.T., and E.S.T. performed the synthesis, structural, and electrochemistry studies of the cathodes at SBU. H.E. performed the SEM-EDS at CNSE. The Rietveld analysis of the XRD was performed by R.Z., along with all of the PDF experiments and analysis. T.A.A. and P.Z. performed and analyzed the DFT calculations. L.W.W. and N.F.Q. performed the XPS and XAS experiments and analysis. R.Z., T.A.A., N.F.Q., and L.F.J.P. prepared the manuscript. All authors read and approved the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Drs. Peter Chupas, Karena Chapman, Olaf Borkiewicz, and Kamila Wiaderek for their help at APS beamline 11-ID-B. We thank Drs. Eric Dooryhee, Sanjit Ghose, and Jianming Bai for their help at NSLS II beamline 28-ID. We also thank Drs. Jinghua Guo and Anders Glans for their help at ALS beamline 6.3.1.2 ISAAC. This research was funded by the SUNY Research Foundation as part of the Network of Excellence in Materials and Advanced Manufacturing. We acknowledge the computational support provided by the Center for Computational Research at the University at Buffalo, SUNY. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. This research used resources [beamline 28-ID] of the National Synchrotron Light Source II, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-SC0012704. The use of Advanced Light Source, Lawrence Berkeley National Laboratory, is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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