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Constituents on Electrochemistry**

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Li/Ag₂VO₂PO₄ Batteries: The Roles of Composite Electrode Constituents on Electrochemistry

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In this study, we utilize silver vanadium phosphorous oxide, Ag₂VO₂PO₄, as a model system to systematically study the impact of the constituents of a composite electrode, including polymeric and conductive additives, on electrochemistry. Notably, although highly resistive³⁰, this bimetallic cathode can be discharged as a pure electroactive material in the absence of a conductive additive as it generates an *in-situ* conductive matrix via a reduction displacement reaction resulting in the formation of silver metal nanoparticles. Three different electrode compositions were investigated: Ag₂VO₂PO₄ only, Ag₂VO₂PO₄ with binder, and Ag₂VO₂PO₄ with binder and carbon. Constant current discharge, pulse testing and impedance spectroscopy measurements were used to characterize the electrochemical properties of the electrodes as a function of depth of discharge. *In-situ* EDXRD was used to spatially resolve the discharge progression within the cathode by following the formation of Ag⁰. *Ex-situ* XRD and EXAFS modeling were used to quantify the amount of Ag⁰ formed. Results indicate that the metal center reduced (V⁵⁺ or Ag⁺) was highly dependent on composite composition (presence of PTFE, carbon), depth of discharge (Ag⁰ nanoparticle formation), and spatial location within the cathode. The addition of a binder was found to increase cell polarization, and the percolation network provided by the carbon in the presence of PTFE was further increased with reduction and formation of Ag⁰. This study provides insight into the factors controlling the electrochemistry of resistive active materials in composite electrodes.

Introduction

The next generation of battery systems will require the full utilization of electroactive material capacity in order to improve energy density. To achieve this objective, the fast transport of both ions and electrons to all regions of the electrode is critical.¹ While strategies including dimension reduction, morphology control, and synthesis of layered and tunneled structures can be used to facilitate ion diffusion, the electron access must also be considered. Low electrical conductivity can limit active material utilization, especially at high discharge or charge rates, and may be a cause of capacity fade with extended cycling. Electron access is particularly problematic in polyanion type cathode materials which provide a path toward high voltage cathode materials yet have low conductivity, including olivine LiFePO₄ and LiMnPO₄.²

To overcome the issue of low electrical conductivity in cathode materials, battery systems utilize composite electrodes that contain conductive media, most often carbon. While widely employed, this strategy is imperfect, as inhomogeneous dispersion of the active

material in the conductive additive results in incomplete electrical contact to all particles in the electrode.^{3,4} Another general approach is to encapsulate individual active material particles with a carbon coating.^{2,5} While more effective for providing electrical contact to each particle, these methods have the disadvantages of additional synthesis steps and increased production cost. An alternative strategy for approximating an ideal electrode in which each active material particle is electrically connected is to generate a conductive network *in-situ*. Bimetallic cathode materials offer the opportunity for *in-situ* conductive matrix formation via reduction displacement reactions that result in the formation of metal nanoparticles. These materials include Ag₂V₄O₁₁,⁶⁻⁸ Ag₄V₂O₆F₂,⁹ AgFeO₂,^{10,11} Cu_{2.33}V₄O₁₁,¹² and CuFe₂O₄.¹³

In this study, we utilize silver vanadium phosphorous oxide, Ag₂VO₂PO₄, as a model bimetallic cathode system to study the impact of composite electrode composition on electrochemical polarization and the bimetallic discharge progression. Ag₂VO₂PO₄ has been developed as a cathode material intended for use in batteries that power implantable cardiac defibrillators (ICDs). This application demands primary battery systems that are reliable over long periods of implantation and are able to deliver high current pulses to charge the capacitors of the device.¹⁴ With these requirements in mind, primary Li/Ag₂VO₂PO₄ batteries are particularly promising because of their high capacity (~270 mAh/g), excellent rate capability with pulses > 30 mA/sq. cm¹⁵⁻¹⁷, and lower

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cathode dissolution compared to the commercially used Li/Ag₂VO₄O₁₁ system.^{15, 18-20}

Ag₂VO₂PO₄ is especially well suited for studies of discharge progression in bimetallic cathode systems. While Ag₂VO₂PO₄ is resistive, it can be discharged as a pure material due to the change in conductivity upon initial reduction.¹⁵⁻¹⁷ Further, the conductivity change occurs concurrently with the *in situ* formation of Ag⁰ nanoparticles, which are detectable by diffraction based techniques, allowing discharge pathways in the material to be spatially resolved. The electrochemical discharge of Ag⁺ and V⁵⁺ in Ag₂VO₂PO₄ has previously been determined to take place sequentially at low rates, with reduction of Ag⁺ to Ag⁰ occurring first but with low levels of V⁵⁺ reduction occurring concurrently.¹⁶ (Reaction Scheme 1)

REACTION SCHEME 1:

where $x < 2$ and $y > 2$

In addition to the active material and conductive additive in a composite electrode, an inert polymeric binder (PTFE, PVDF, etc.) is also typically added to provide mechanical integrity and to integrate the other components.²¹ The polymeric binder typically comprises only 2-5% of the total electrode mass in commercial electrodes.²² It is a critical component as it provides adhesion strength and can improve contact between active material particles with the conductive additive.²³ At the same time, because of its insulating nature and electrochemical inactivity, the amount of binder in the electrode needs to be carefully considered for the specific system under study.²⁴ While the modification of binder type and loading have been shown to affect battery performance for a range of cathode materials,²² the influence of binder on the electrochemistry of bimetallic, reduction displacement materials has not been previously reported. To provide insight, in this study Ag₂VO₂PO₄ electrodes are investigated with three compositions: active material only, active material with 5% PTFE binder, and active material with 5% PTFE binder and 5% carbon black additive.

In order to spatially resolve the progression of discharge in the electrodes with varying composite compositions, we utilize synchrotron based Energy dispersive X-ray Diffraction (EDXRD). This technique provides unique insight into the state of the electrode by enabling evaluation of discharged phases as a function of spatial location. Furthermore, the white beam energy of the synchrotron light source can penetrate the steel casing of the battery, providing *in-situ* measurements of coin type cells without the need for specially designed X-ray windows. Past studies using EDXRD have observed heterogeneous discharge with a variety of materials as a function of spatial distribution in the bulk electrode by observing the emergence of new phases and significant peak shifting.²⁵⁻³⁰ Liang et. al³¹ showed that EDXRD could successfully profile the state of charge of a LiMnO₂-based coin cell by monitoring the emergence of the (400) peak of a compressed lattice phase of the parent material both by the peak area and the peak intensity.

EDXRD has also been used extensively to investigate the discharge characteristics of Ag₂VP₂O₈, another member of the

Ag_wV_xP_yO_z family.^{25, 32, 33} The studies indicated that the spatial distribution of the Ag⁰ network formed is dependent on discharge rate.³³ In cathodes without conductive additive, low rate initial discharge provided a more even distribution of Ag⁰ and thus a more effective conductive network compared to a faster discharge rate. In contrast, in cathodes containing carbon, higher initial discharge rate more effectively decreased cell impedance as a result of the formation of a greater number of smaller Ag⁰ crystallites. A preliminary EDXRD study of the Li/Ag₂VO₂PO₄ cells was also performed with cathodes discharged to 2 discharge levels, indicating that reaction progress in the system could be effectively tracked.

In contrast to previous EDXRD based studies on the Ag_wV_xP_yO_z family of materials, the current work focuses on investigating the component parts of a composite electrode and the how they influence electrochemical polarization and the bimetallic discharge mechanism. Several aspects of this work distinguish it from our prior publications: 1) For the first time, the role of polymeric binder on the formation of the Ag⁰ conductive network is considered. 2) Pulse discharge of the test cells was performed in order to quantify subtle differences in polarization among the electrode compositions. 3) The low rate discharge voltage profiles of the cells are evaluated with respect to the bimetallic discharge mechanism (reduction of Ag⁺ vs. V⁵⁺). 4) Ex-situ extended X-ray absorption fine structure (EXAFS) at the Ag K-edge of the discharged cathodes was modelled to quantify the amount of Ag⁰ metal formed. In conjunction with these analyses, electrochemical impedance spectroscopy and ex-situ X-ray diffraction measurements were also used to characterize Ag⁰ percolation network as a function of electrode composition. Results indicate a composition-dependent discharge progression in the cathodes and provide insight into the factors controlling electrochemical performance in composite cathodes containing bimetallic, reduction displacement type active materials.

Experimental Methods

Materials Synthesis and Characterization

Silver vanadium phosphorous oxide (Ag₂VO₂PO₄) was synthesized by a previously reported hydrothermal method.³⁴ Briefly, the material was prepared by heating silver (I) oxide (Ag₂O), vanadium (V) oxide (V₂O₅) and phosphoric acid (H₃PO₄, 85%) for 96 h at 230° C. Differential scanning calorimetry (DSC) analysis was performed using a TA instruments Q20 with a temperature range of 40-580° C. Powder X-ray diffraction (XRD) measurements were recorded with a Rigaku Ultima IV X-ray diffractometer using Cu Kα radiation and Bragg-Brentano focusing geometry. Samples matched the reference pattern (PDF # 97-007-3580) with no impurity phases detected.

Cell Assembly and Testing

Three types of cathode formulations were prepared for electrochemical testing: 100% Ag₂VO₂PO₄, 95% Ag₂VO₂PO₄ + 5% polytetrafluoroethylene (PTFE) binder, and 90% Ag₂VO₂PO₄ + 5% PTFE + 5% carbon black. Cathode pellets were pressed at 4500 psi and were 13 mm in diameter with a thickness of ~0.4 mm.

Stainless steel coin cells were constructed using the cathodes, lithium metal anodes, polypropylene membrane separators, and electrolyte consisting of 1 M LiPF₆ in 30:70 ethylene carbonate: dimethyl carbonate.

Coin cells from each of the three cathode formulation groups were discharged to 0.08, 0.2, and 0.5 electron equivalents at a C/500 rate (full discharge in 500 hours). An additional cell from each group was kept in the non-discharged state. Before and after discharge, Electrochemical Impedance Spectroscopy (EIS) measurements were collected using a Biologic VSP multichannel potentiostat with a 5 mV sinus amplitude and frequency range of 10 mHz to 1 MHz. Electrochemical measurements were taken at 30°C, consistent with previous EDXRD investigations of Li/Ag_wV_xO_yP_z batteries.^{25, 32, 33} While the operating temperature is 37° C for the intended application (implanted biomedical batteries), 30° C was chosen because it is similar to the ambient temperature of the EDXRD measurement. The small temperature difference is expected to have negligible effect on the discharge characteristics on the batteries and the spatial distribution of Ag⁰ formation. Equivalent circuit analysis was performed using Zview software. For undischarged cells, the charge transfer impedance was too high for the diffusional tail to be accurately quantified in the measured frequency range. When modeling impedance in these cases, the Warburg element values ($Z_{W,R}$ (Ω), $Z_{W,T}$ (Ω), $Z_{W,P}$) were fixed to values of 4000, 2000, and 0.35.

In-Situ EDXRD

Energy dispersive X-ray diffraction (EDXRD) measurements were performed on intact, coin cells at beamline 6-BM, B at the Advanced Photon Light Source at Argonne National Laboratory. A LaB₆ standard was used to calibrate the detector. The incident white beam impinged upon the sample was 20 μ m in height and parallel to the sample stage, while the germanium detector used to measure the diffracted radiation was set at $2\theta = 3.0^\circ$. The slit size for the detector was set such that the length of the z-direction from which diffracted X-rays were collected was ~ 3.6 mm. In the x-direction, the width of the incident beam was 1.0 mm, making the dimensions of the gauge volume approximately 3.6 x 1.0 x 0.02 mm. The coin cell was placed on an automated stage such that the gauge volume was centered radially on the cell. The stage was moved upwards in the y direction through the incident beam. Thus, diffraction patterns were collected as a function of y, and a spatial profile for the cell was collected. The entire profile of the cell was measured, with measurements collected every 0.04 mm. A description of the experimental EDXRD setup including figures has been published previously.^{25, 35} Analysis of the data was performed using MATLAB software.

Ex-Situ Analysis

Post EDXRD and electrochemical measurements, the coin cells were disassembled and the cathodes and anodes were recovered for further analyses after rinsing with dimethyl carbonate and drying. Cathodes were ground and measured by angle-resolved x-ray diffraction (XRD) using a Rigaku Miniflex XRD system (Cu K α radiation). Peaks in the diffraction patterns were fit using PeakFit

software and Pearson VII lineshape. The crystallite sizes of Ag⁰ component in the powders was calculated by applying the Scherrer equation^{36, 37} to the FWHM of the Ag⁰ (111) peak. An instrumental broadening correction was applied using a LaB₆ standard. Lithium anodes were dissolved in a nitric acid solution which was then measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using a Thermofisher ICAP 6000.

Ex-Situ XAS

Full XAS spectra were collected at the Ag K-edge (25.51 keV) at sector 10-BM of the Advanced Photon Source at Argonne National Laboratory. Ground cathodes were sealed between Kapton tape and stored in an inert atmosphere environment until XAS measurements were collected. Each sample was measured in transmission mode with incident and transmission ion chambers filled with 100% Ar. The Si (111) double crystal monochromator was detuned to 50% for harmonic rejection. A silver metal foil was used for initial X-ray beam energy calibration and was also measured simultaneously with each sample to ensure proper energy alignment of multiple XAS scans during analysis. XAS spectra were aligned, merged and normalized using Athena.^{38, 39} Spectra were fit using Artemis with theoretical models created by FEFF6^{40, 41} of Ag₂VO₂PO₄ and metallic Ag crystal structures. Fits were made using a k-range of 2 – 9 $\text{\AA}^{-1}$ with a Hanning window in k² and k³ weighting. An R-range of 1.0 – 3.8 $\text{\AA}$ was used to fully encompass the $|\chi(R)|$ coordination shells of Ag atoms in Ag₂VO₂PO₄ and Ag⁰ phases.

Results

Materials Synthesis and Characterization

Synthesized Ag₂VO₂PO₄ (SVPO) samples were characterized using X-ray powder diffraction, and the experimental XRD patterns compared well with previously reported reference data (PDF # 97-007-3580). SVPO crystallized in the monoclinic space group C2/m. As shown in Figure S1, the comprised of layers of distorted vanadium octahedra and PO₄³⁻ tetrahedra sheets, with Ag⁺ ions located between the layers in a distorted octahedral coordination with oxygen. Differential scanning calorimetry was used to further assess the purity of the synthesized material (Figure S2). A single endothermic transition was observed, indicating the presence of a single phase material.

Electrochemistry

Three types of Ag₂VO₂PO₄ cathode formulations were electrochemically tested: 100% Ag₂VO₂PO₄ (SVPO), 95% Ag₂VO₂PO₄ + 5% polytetrafluoroethylene (PTFE) binder (Ag₂VO₂PO₄ + PTFE), and 90% Ag₂VO₂PO₄ + 5% PTFE + 5% carbon black (Ag₂VO₂PO₄ + PTFE +C). In the ICD batteries for which the Ag₂VO₂PO₄ cathode material is intended, the percentage of active material in the cathode composite is typically greater than 90% in order to maximize volumetric energy density.⁴² Thus, the selected weight ratio of active material, binder, and conductive additive is relevant for the anticipated application of the Li / Ag₂VO₂PO₄ battery demanding high volumetric energy density.

Figure 1. Discharge profiles cells with cathodes $\text{Ag}_2\text{VO}_2\text{PO}_4$ – only, $\text{Ag}_2\text{VO}_2\text{PO}_4$ + PTFE, and $\text{Ag}_2\text{VO}_2\text{PO}_4$ + PTFE + C.

PTFE was selected instead of PVDF as the polymeric binder because it provides good adhesion to the $\text{Ag}_2\text{VO}_2\text{PO}_4$ cathode material in a pressed pellet electrode form, permitting a low percentage of binder in the electrode. PTFE is commonly used as the binder in electrodes of silver vanadium oxide, the current state of the art cathode material for the ICD's, both in literature investigations^{7, 43-47} and commercial application^{42, 48} of the material.

$\text{Li}/\text{Ag}_2\text{VO}_2\text{PO}_4$ cells were galvanostatically discharged at a C/500 rate to 0.08, 0.2, and 0.5 electron equivalents, corresponding to 5.4 mAh/g, 13.6 mAh/g and 34 mAh/g, respectively (Figure 1). These discharge levels were selected based on prior reports which indicated significant conductivity changes in $\text{Ag}_2\text{VO}_2\text{PO}_4$ in the early stages of discharge.^{17, 49, 50} The C/500 rate permitted cells without conductive additive to be discharged while maintaining a loaded voltage above 2.0 V. The full discharge profile of a

$\text{Li}/\text{Ag}_2\text{VO}_2\text{PO}_4$ cell to theoretical capacity (4 electron equivalents, 272 mAh/g) is presented in Figure S3. Despite the relatively low rate, $\text{Ag}_2\text{VO}_2\text{PO}_4$ and $\text{Ag}_2\text{VO}_2\text{PO}_4$ + PTFE cells display significant polarization, with voltage dropping to between 2.3 – 2.5 V initially and recovering as the discharge progressed. The voltage recovery behavior is consistent with the formation of Ag^0 upon discharge, which enhances electronic conduction and thus allows electron access to undischarged regions of the cathode.⁵¹ It is notable that addition of the PTFE binder resulted in a lower loaded voltage (~2.76 V for $\text{Ag}_2\text{VO}_2\text{PO}_4$ + PTFE, ~2.87 V for SVPO), suggesting that the presence of PTFE is not benign. In contrast, $\text{Ag}_2\text{VO}_2\text{PO}_4$ + PTFE + C cells maintained a significantly higher loaded voltage of approximately 2.9 V throughout discharge, indicating that the addition of 5% carbon to the $\text{Ag}_2\text{VO}_2\text{PO}_4$ + PTFE mixture significantly improved electron access to the $\text{Ag}_2\text{VO}_2\text{PO}_4$ particles.

Post discharge, the cells rested at open circuit potential for 24 hours followed by measurement of the electrochemical impedance spectroscopy (EIS) response. Cells of each composition in the non-discharged state were also measured. Results are presented as Nyquist plots in Figure 2, where 2A, 2C, and 2E show the full frequency range and 2B, 2D, 2F focus on features in the high frequency region. Significant differences in the impedance spectra are observed dependent on both the discharge state of the $\text{Ag}_2\text{VO}_2\text{PO}_4$ and the presence of PTFE and carbon in the composite. In cells without carbon, either with or without PTFE, the most prominent feature in the impedance spectra is a large semicircle in the nondischarged state which dramatically decreases in magnitude upon reduction. For the nondischarged cell with carbon, the initial magnitude of the middle/low frequency semicircle is lower such that it overlaps with an observable diffusional tail. Analogous to cells without carbon, the size of the semicircle markedly decreases even at low depths of discharge. EIS response was also measured after the EDXRD experiment to ensure that the X-ray exposure did not affect the properties of the cells; there were insignificant changes in the

Figure 2. Electrochemical Impedance Spectroscopy Results for cells with (a, b) $\text{Ag}_2\text{VO}_2\text{PO}_4$ – only, (c, d) $\text{Ag}_2\text{VO}_2\text{PO}_4$ + PTFE, and (e, f) $\text{Ag}_2\text{VO}_2\text{PO}_4$ + PTFE + C cathodes.

Figure 3. Equivalent circuit used to fit impedance spectroscopy data.

Figure 4. Equivalent Circuit Fit Results as a function of depth of discharge for R_1 , R_2 and R_3 .

EIS response post EDXRD measurements.

All impedance spectra were fit to the equivalent circuit model in Figure 3 to allow quantitative comparison of the impedance data.^{52, 53} The selected equivalent circuit used to fit the data is a modified version of the Randles circuit⁵⁴ consisting of a resistor in series with two RC elements and a Warburg element. The first resistor, R_1 , represents DC electrolyte resistance and ohmic resistances of the cell components and fits the intercept of the Nyquist plot in the high frequency region. R_2 and CPE_1 in the first parallel resistor-constant phase element component fits the high frequency semicircular features in the Nyquist plot and correspond to the ionic resistance and capacitance, respectively, of the surface film on the lithium. The third resistor (R_3) and Warburg element (W_o) in parallel with constant phase element (CPE_2) are used to fit the middle to low frequency spectra and approximate the charge transfer resistance, double layer capacitance and solid state diffusion of Li^+ in the cathode. Assignments of these equivalent circuit elements to EIS features are consistent with previous literature.^{25, 55-61}

Equivalent circuit fit results are tabulated in Table S4, and the magnitude of R_1 , R_2 , and R_3 are plotted as a function of depth of discharge in Figure 4. While R_1 (electrolyte, electrical contacts resistance) and R_2 (anode film resistance) have low magnitude ($< 7 \Omega$ for R_1 , $< 50 \Omega$ for R_2) under all conditions, the charge transfer resistance R_3 is highly dependent on both the cathode composition and depth of discharge. In $Ag_2VO_2PO_4$ only cathodes, upon initiation of discharge, the value of R_3 decreases from 535 k Ω to ca. 155 Ω at only 0.08 electron equivalents of discharge. R_3 further decreases to

ca. 23 Ω and ca. 8 Ω by 0.2 and 0.5 electron equivalents, respectively. A similar trend is observed for $Ag_2VO_2PO_4 + PTFE$ cells, however, it is notable that at each depth of discharge the $Ag_2VO_2PO_4 + PTFE$ cell has a higher charge transfer resistance than its corresponding $Ag_2VO_2PO_4$ only cell. At 0.5 electron equivalents, the charge transfer resistance of the $Ag_2VO_2PO_4 + PTFE$ cell is ca. 3x higher than the $Ag_2VO_2PO_4$ only cell, indicating that the addition of PTFE to the cathode pellet hinders interparticle contact and limits the Ag^0 percolation network. The addition of carbon to the cathode pellet greatly reduces the charge transfer resistance in the non-discharge state by a factor of ca. 70x. This observation was expected based on a previous study reporting that 5% carbon loading is sufficient in forming a foundational percolation network in composites with similarly sized active material particles.⁶² Upon reduction the charge transfer resistance in cells with carbon further reduces, suggesting that the silver reduction process still provides a conductivity benefit.

Post EDXRD measurement, the pulse discharge capability of the cells was tested to further probe the changes in conductivity observed by EIS. The pulse tests simulate intermittent therapy delivery of an implantable cardioverter defibrillator (ICD), which is the primary application for which $Li/Ag_2VO_2PO_4$ batteries are intended. One cell at each condition was pulse tested with a single 10s, 20 mA/cm² pulse and lower voltage cutoff of 0.1 V. The voltage versus time response is shown in Figure 5. The voltage profile of each pulse consists of 3 main parts.^{58, 63} The initial voltage drop is due to the internal ohmic resistance of the cell and is proportional to the pulse current. The second drop occurs due to

Figure 5. Pulse discharge tests for (a) $Ag_2VO_2PO_4$ only, (b) $Ag_2VO_2PO_4 + PTFE$, and (c) $Ag_2VO_2PO_4 + PTFE + C$. Pulsing parameters were 10 mA/cm² for 10 s, with a voltage cutoff of 0.1 V.

Composition	DOD	Total DC Resistance (Ω)	Ohmic Resistance (Ω)	Energy Delivered (J)
$\text{Ag}_2\text{VO}_2\text{PO}_4$	0	259	259	0.001
$\text{Ag}_2\text{VO}_2\text{PO}_4$	0.08	225	177	0.078
$\text{Ag}_2\text{VO}_2\text{PO}_4$	0.2	96	67	0.293
$\text{Ag}_2\text{VO}_2\text{PO}_4$	0.5	56	33	0.356
$\text{Ag}_2\text{VO}_2\text{PO}_4 + \text{PTFE}$	0	259	259	0.001
$\text{Ag}_2\text{VO}_2\text{PO}_4 + \text{PTFE}$	0.08	245	203	0.005
$\text{Ag}_2\text{VO}_2\text{PO}_4 + \text{PTFE}$	0.2	120	90	0.249
$\text{Ag}_2\text{VO}_2\text{PO}_4 + \text{PTFE}$	0.5	77	58	0.306
$\text{Ag}_2\text{VO}_2\text{PO}_4 + \text{PTFE} + \text{C}$	0	100	51	0.279
$\text{Ag}_2\text{VO}_2\text{PO}_4 + \text{PTFE} + \text{C}$	0.08	90	38	0.306
$\text{Ag}_2\text{VO}_2\text{PO}_4 + \text{PTFE} + \text{C}$	0.2	77	29	0.335
$\text{Ag}_2\text{VO}_2\text{PO}_4 + \text{PTFE} + \text{C}$	0.5	67	29	0.343

Table 1. Calculated DC resistance, ohmic resistance, and delivered energy for pulse discharge tests.

lithium intercalation in the electrode. The third component of the pulse response corresponds to the current interruption, during which the ohmic drop is regained and the cell subsequently undergoes slow relaxation to an equilibrium voltage.

Calculated total DC resistance, ohmic resistance and delivered energy of the pulse discharge tests are tabulated in Table 1. In cells without carbon (both with and without PTFE), before any discharge the ohmic resistance is too high to deliver useful power. As a result, significant polarization occurs and the voltage drops to 0.1 V (cutoff voltage). At 0.08 electron equivalents initialization of Ag^0 reduction has occurred and the ohmic resistance of the $\text{Ag}_2\text{VO}_2\text{PO}_4$ cell is ca. 200 Ω , such that the duration of the pulse is maintained albeit at 0.5 V. In contrast, the $\text{Ag}_2\text{VO}_2\text{PO}_4 + \text{PTFE}$ displays significantly higher polarization, with the voltage reaching the cutoff when the load is applied. By 0.2 e and 0.5 e DOD both $\text{Ag}_2\text{VO}_2\text{PO}_4$ and $\text{Ag}_2\text{VO}_2\text{PO}_4 + \text{PTFE}$ cells are able to deliver useful power, consistent with the formation of a conductive Ag^0 network that significantly decreases interparticle contact resistance. However, in agreement with the impedance data, the resistance of cells with PTFE is higher than those without at each depth of discharge, suggesting that the addition of PTFE impedes formation of an ideal Ag^0 network where all individual particles are electrically connected.

In contrast to the $\text{Ag}_2\text{VO}_2\text{PO}_4$ only and $\text{Ag}_2\text{VO}_2\text{PO}_4 + \text{PTFE}$ groups, cells with the carbon additive are able to deliver a pulse voltage above 2.0 V even at the 0 DOD level, thus the carbon additive is effective in creating a primary percolation network even in the presence of the insulating PTFE binder. However, the magnitude of the ohmic drop still decreases upon discharge, from 51 Ω in the non-discharged cell to 29 Ω in the 0.5 e DOD cell. Thus, the initial percolation network in the $\text{Ag}_2\text{VO}_2\text{PO}_4 + \text{PTFE} + \text{C}$ electrode is not entirely sufficient for electrically connecting all particles in the cathode, and the Ag^0 formation still provides significant benefit. Interestingly, at 0.5 electron DOD, the ohmic resistance of the SVPO only cell is similar to that of the $\text{Ag}_2\text{VO}_2\text{PO}_4 + \text{PTFE} + \text{C}$ cell (33 Ω and 29 Ω for SVPO only and SVPO + PTFE + C cells respectively), demonstrating that the carbon additive is not necessary to achieve optimum interparticle conductivity at higher depths of discharge.

In Situ Energy Dispersive X-ray Diffraction (EDXRD)

The homogeneity of the electrode discharge can be monitored by energy dispersive X-ray diffraction (EDXRD) by spatially identifying where the Ag^0 is being formed within the cathode. The diffraction pattern of each cell discharged to 0.5 e⁻ equivalents is shown in Figure 6 where the Ag (111) peak is clearly visible in each cell. In the $\text{Ag}_2\text{VO}_2\text{PO}_4$ only cell, the Ag (111) peak appears primarily at the Li anode and steel can interfaces, indicating a heterogeneous discharge. In $\text{Ag}_2\text{VO}_2\text{PO}_4 + \text{PTFE}$ cathodes, a similar condition was observed where the Ag (111) peaks were observed at both interfaces rather than throughout the electrode. Adding conductive carbon caused a dramatic difference in the EDXRD results with the Ag (111) peak clearly visible at both interfaces and in the interior of the electrode.

The formation of Ag^0 was evaluated as a function of discharge at 0 e⁻ equiv., 0.08 e⁻ equiv., 0.2 e⁻ equiv., and 0.5 e⁻ equiv. To analyze the formation of Ag^0 compared to the distribution of $\text{Ag}_2\text{VO}_2\text{PO}_4$, the peak intensity of the Ag (111) diffraction plane was compared to the peak intensity of the $\text{Ag}_2\text{VO}_2\text{PO}_4$ (222) diffraction plane in individual cells. This method compensates for differences in attenuation from cells that are constructed with different electrode compositions. Figure 7 shows the Ag (111) / $\text{Ag}_2\text{VO}_2\text{PO}_4$ (222) ratio as a function of y axis position where the zero position is the center of the $\text{Ag}_2\text{VO}_2\text{PO}_4$ containing electrode. The positive values in the y axis position are towards the steel can interface and the negative values are towards the Li anode interface. Each electrode was approximately 400 - 450 microns thick, and additional scans

Figure 6: The collected EDXRD patterns from 0.35-0.55 inverse d-spacing. The arrow indicates beam position increasing away from the Li anode. The blue dashed line shows the Ag(111) peak and the red dashed line at $1/d = 0.430$ is $\text{Ag}_2\text{VO}_2\text{PO}_4$ (312) which is shown to distinguish it from the Ag (111) peak. The red dashed line at $1/d = 0.478$ is the $\text{Ag}_2\text{VO}_2\text{PO}_4$ (222) and the black dashed line shows the Fe^0 (110) peak which indicates the steel can.

were taken up to 100 microns along each interface to observe Ag^0 formation at the current collector and Li anode. The position of the current collector interface differs by up to 50 microns due to slight differences in cathode thickness among the individual cells. The intensity ratio is plotted on a logarithmic scale to highlight subtle changes in the Ag^0 formation within the cathodes. A ratio of $\text{Ag}(111)/\text{Ag}_2\text{VO}_2\text{PO}_4(222)$ equal to 1 indicates an area with very little presence of either phase, while a $\text{Ag}(111)/\text{Ag}_2\text{VO}_2\text{PO}_4(222)$ ratio > 1 indicates a Ag^0 rich region and < 1 indicates a SVPO rich region. The raw $\text{Ag}(111)$ and $\text{Ag}_2\text{VO}_2\text{PO}_4(222)$ intensities can be found in the supplemental figures S5 – S7.

In the $\text{Ag}_2\text{VO}_2\text{PO}_4$ only undischarged cell, intensity for $\text{Ag}(111)$ is observed on the Li anode, but no additional Ag^0 is observed throughout the cell or at the current collector interface. Previous studies of $\text{Ag}_2\text{VO}_2\text{PO}_4$ have shown that silver ions dissolved (through ion exchange) can deposit as a silver metal layer on the lithium anode.^{15, 19, 20} This possibility was investigated further by ex-situ analyses of the lithium anodes, as will be described subsequently. At higher depths of discharge, $\text{Ag}_2\text{VO}_2\text{PO}_4$ cells show increased Ag^0 formation primarily at the current collector interface. However, by 0.5 e⁻, low levels of Ag^0 formation are observed to spread from the current collector interface towards the center of the cathode. In $\text{Ag}_2\text{VO}_2\text{PO}_4 + \text{PTFE}$ cells, a similar trend is observed where Ag^0 formation is observed on the Li interface even in the non-discharged cell, and additional Ag^0 formation occurs primarily at the current collector interface. By 0.5 e⁻ the Ag^0 is also observed deeper

into the cathode spreading from the current collector, but at lower amounts compared to the 0.5 e⁻ $\text{Ag}_2\text{VO}_2\text{PO}_4$ only cell. The Ag^0 distribution is strikingly different in the $\text{Ag}_2\text{VO}_2\text{PO}_4 + \text{PTFE} + \text{C}$ cells compared to the two other groups. Ag^0 is visible at the Li interface in the non-discharged cell, indicating some Ag^0 formation at the anode prior to discharge. However, additional Ag^0 formation occurs throughout the electrode, compared to the cells without carbon where Ag^0 formation occurs primarily at the cathode interface.

Ex situ Analyses

Post EDXRD and electrochemical analyses, the coin cells were disassembled, and both the $\text{Ag}_2\text{VO}_2\text{PO}_4$ cathodes and Li anodes were recovered for further study. The cathodes were measured by X-ray diffraction after grinding the pellet type electrodes into a fine powder where the emergence of the silver phase was apparent at higher depths of discharge, Figure S8. The $\text{Ag}^0(111)$ peak area and Scherrer crystallite size determined from the measurements are plotted as a function of discharge level in Figure 8. Electrodes containing carbon had higher levels of Ag^0 present at each DOD, consistent with the EDXRD data. The discrepancy in the amount of silver metal formed originates at 0.08 electron equivalents, does not increase at higher levels of discharge, and thus is likely related to the conductivity of the cathode which is dependent on both depth of discharge and the presence of PTFE and/or binder.

Ex-situ X-ray absorption spectroscopy (XAS) measurements were performed on the ground pellets to further investigate the formation of Ag^0 at different depths of discharge. While XRD can evaluate phase fractions of crystalline materials, XAS gives insight into the local environment of the Ag^0 and $\text{Ag}_2\text{VO}_2\text{PO}_4$ phases in the discharged cathodes. Unlike X-ray diffraction which relies on long range periodic structure to obtain spectra, XAS is dependent only on the local atomic structure, providing accurate evaluation of the state of Ag atoms in the electrode.⁶⁴⁻⁶⁶ X-ray absorption fine structure (EXAFS) k^2 weighted-R-space spectra are shown in Figure 9, and are overlaid with the spectra for Ag^0 metal. In the undischarged state at each composition, the EXAFS spectra primarily consist of a major peak at ca. 1.6 Å originating from neighboring oxygen atoms and at ca. 3 Å correlated to Ag-P, Ag-V, as well as additional Ag-O

Figure 7: A comparison of the $\text{Ag}^0(111)/\text{Ag}_2\text{VO}_2\text{PO}_4(222)$ peak intensities on a log scale from EDXRD cells as a function of spatial position where 0 is the center of the cathode. Negative spatial values are towards the Li anode and positive values are towards the steel can. The three different cell conditions ($\text{Ag}_2\text{VO}_2\text{PO}_4$ only, $\text{Ag}_2\text{VO}_2\text{PO}_4 + \text{PTFE}$, and $\text{Ag}_2\text{VO}_2\text{PO}_4 + \text{PTFE} + \text{C}$) are shown in four different depths of discharge (0, 0.08, 0.2, and 0.5 e⁻ equivalence).

Figure 8: Ex-situ X-ray diffraction results including $\text{Ag}^0(111)$ peak area.

contributions. Qualitatively it is evident that as the discharge proceeds, two new peaks form at ca. 2.25 Å and 2.75 Å which are consistent with Ag-Ag distances of fcc Ag⁰. For the Ag₂VO₂PO₄ + PTFE + C composition, the peaks associated with Ag⁰ begin developing at lower DOD compared with the compositions which did not contain carbon. However, by 0.5 electron equivalents the magnitude of the Ag⁰ peaks appears more similar for all three compositions.

The EXAFS spectra were fit using Artemis to quantify the relative amount of Ag⁰ metal and Ag₂VO₂PO₄ in the discharged electrodes using theoretical models based on Ag₂VO₂PO₄ and Ag⁰ crystal structures. For electrodes in the non-discharged state, the theoretical model of Ag₂VO₂PO₄ consisted of 4 distinct Ag-O paths, 2 Ag-Ag paths, 1 Ag-V path, and 1 Ag-P path. Discharged electrodes were fit with an additional Ag-Ag path corresponding to the Ag-Ag interatomic distance in fcc Ag metal. Full EXAFS fitting results are tabulated in Tables S9 - S12 and example EXAFS fits in $k^2 \chi(k)$ and $|\chi(R)|$ are shown in Figures S13 - S16. Results showing the relative amplitude of the Ag₂VO₂PO₄ and Ag⁰ phases at each depth of discharge are shown in Figure 10. At 0.08 electron equivalents, the relative amplitude of the Ag⁰ formed in Ag₂VO₂PO₄ + PTFE + C electrodes is ca. 0.5 ± 0.2, while the amplitude in Ag₂VO₂PO₄ and Ag₂VO₂PO₄ + PTFE cathodes is 0. At higher electron equivalents, while the total amount of Ag⁰ formed increases in all electrode types, the difference in amplitude between cells with and without carbon remains between 0.4 - 0.7. Thus, the data are in agreement with the ex situ XRD result, and indicate that at 0.08 e- the amount of Ag⁰ formed in cells without carbon is significantly lower than cells with carbon, but that the amount of Ag⁰ formed is similar for all three groups at higher DOD. The amplitude of Ag₂VO₂PO₄ phase consistently decreases for all electrode types by 0.5 e-, also indicating loss of Ag⁺ from the structure. Notably, the

Figure 9. Relative amplitude of Ag₂VO₂PO₄ and Ag⁰ phases determined from EXAFS fitting.

fitted interatomic distances for all paths within the Ag₂VO₂PO₄ structure (Tables S9 - S12) do not shift significantly at any DOD. These data suggest that the reduction of Ag⁺ ions results in Ag ions exiting the lattice to form Ag⁰, which is consistent with previous literature showing Ag⁰ nanoparticle formation on the surface of Ag₂VO₂PO₄ crystals.¹⁶

Ex-situ quantitative analysis of the lithium anodes was also conducted to investigate the source of silver metal detected at the cathode/anode interface by EDXRD. Previous studies of Ag₂VO₂PO₄ have indicated that silver ions can dissolve into the electrolyte due to an ion exchange mechanism and subsequently deposit as Ag⁰ metal on the lithium surface.^{15, 19, 20} Results are shown in Figure S17. Significant levels of Ag on the lithium surface were detected by ICP-OES for all 12 lithium anodes analyzed, suggesting Ag⁰ detected by EDXRD near the anode interface likely originates from silver metal deposited on the lithium subsequent to dissolution in the electrolyte. The level of vanadium on deposited on the anode was low (below 0.8 μg/cm²) for all samples, which is also consistent with previous reports that report significantly higher levels of Ag⁺ dissolution relative to Vⁿ⁺.^{15, 19, 20}

Discussion

The experimental data provide a comprehensive understanding of the components of the composite electrode and the how they impact the electrochemistry of a bimetallic phosphate active material. Results show that the discharge reaction in these cathodes is primarily limited by the kinetics of interparticle electron transfer, and as a result the addition of insulating polymeric binder and conductive carbon have a large impact on the electrode polarization both at low rate and high rates of discharge. In Ag₂VO₂PO₄ only

Figure 9. Ag K-edge k^2 weighted $|\chi(R)|$ comparison of Ag₂VO₂PO₄, Ag₂VO₂PO₄ + PTFE, and Ag₂VO₂PO₄ + PTFE + C cathodes at various charge/discharge levels. The spectra for Ag⁰ metal is included as a reference.

electrodes, significant polarization upon initial discharge at C/500 is observed, as evidenced by a drop in voltage from an OCV of ca. 3.5 V to a loaded voltage of ca. 2.3 V consistent with limited electron access among insulating $\text{Ag}_2\text{VO}_2\text{PO}_4$ particles. Once a low level of Ag^0 is formed via the reduction displacement mechanism in Reaction Scheme 1, electron conduction improves, allowing electron access to undischarged regions of the cathode and causing the voltage to recover to ca. 2.8 V by 0.5 electron equivalents of reduction. The Ag^0 percolation network which forms dramatically decreases the charge transfer resistance of the cell, with R_{CT} decreasing from ca. 540,000 Ω in the non-discharged state to 150 Ω after 0.08 electron equivalents of discharge. The change in polarization is also observed in the pulse discharge results. The nondischarged cell is unable to deliver useful power, but after only 0.2 electron equivalents of reduction, 290 mJ of energy are delivered for a 10s, 10 mA/cm² pulse. Energy dispersive X-ray diffraction results show that the formation of Ag^0 in $\text{Ag}_2\text{VO}_2\text{PO}_4$ only cells occurs primarily at the current collector interface, and spreads further towards the center of the electrode at higher levels of discharge. Despite the spatial inhomogeneity of the reduced Ag^0 , the conduction network is adequate for functional operation at the pulse current tested.

The addition of PTFE polymeric binder to the active material has a notable effect on the polarization of the electrode. While the EDXRD results are similar to $\text{Ag}_2\text{VO}_2\text{PO}_4$ only cells, with Ag^0 formation occurring primarily at the current collector and extending into the cathode as the discharge progresses, electrochemical analysis reveals significant differences between the electrodes with and without binder. Addition of the PTFE resulted in consistently lower loaded voltages under a C/500 discharge rate when compared to the $\text{Ag}_2\text{VO}_2\text{PO}_4$ only cells. Even at 0.5 electron equivalents, when

ca. 12.5% of the Ag atoms in $\text{Ag}_2\text{VO}_2\text{PO}_4$ are theoretically reduced, the loaded voltage is still ~ 0.1 V lower in cells containing the PTFE additive. Furthermore, the charge transfer resistance, as determined via EIS, of $\text{Ag}_2\text{VO}_2\text{PO}_4$ + PTFE cathodes is higher relative to $\text{Ag}_2\text{VO}_2\text{PO}_4$ -only cathodes at each depth of discharge. The increased polarization caused by the addition of PTFE is also manifested in the pulse discharge, with PTFE cells showing higher ohmic resistance (33 Ω and 58 Ω for $\text{Ag}_2\text{VO}_2\text{PO}_4$ and $\text{Ag}_2\text{VO}_2\text{PO}_4$ + PTFE cells, respectively, at 0.5 electron equivalents discharge) and lower delivered energy per pulse. These results suggest that the addition of insulating PTFE to the active material interferes with the conduction network among $\text{Ag}_2\text{VO}_2\text{PO}_4$ particles.

The addition of carbon conductive additive considerably improves the electrochemical properties of the cathodes. Polarization upon initial discharge under C/500 current is minimized, with <0.1 V difference between OCV and the loaded voltage. In contrast to the other two electrode types, EDXRD shows that formation of Ag^0 occurs uniformly throughout the cathode. However, the EIS and pulse discharge results suggest that the percolation network provided by the carbon in the presence of PTFE is not sufficient for optimum conductivity in the electrode. Upon reduction the charge transfer resistance of $\text{Ag}_2\text{VO}_2\text{PO}_4$ + PTFE + C cells significantly decreases. Furthermore, delivered pulse power improved at each depth of discharge, indicating that formation of the Ag^0 conductive network is necessary for ideal electrical connections between non-conductive active material particles in the composite.

The experiments also provide insight into the discharge mechanism occurring in the cathode pellets, and how it is impacted by the addition of PTFE and carbon. Both ex-situ XRD and EXAFS indicate that at 0.08 electron equivalents DOD, the total amount of Ag^0 formed in $\text{Ag}_2\text{VO}_2\text{PO}_4$ + PTFE + C cells is higher than in the

Figure 11. Schematic diagram of the discharge progression in $\text{Ag}_2\text{VO}_2\text{PO}_4$, $\text{Ag}_2\text{VO}_2\text{PO}_4$ + PTFE, and $\text{Ag}_2\text{VO}_2\text{PO}_4$ + PTFE + C. The current collector is represented by the grey bar on the left of each figure.

other 2 cells groups. However, results show that further formation of Ag^0 proceeds at a similar rate for all cells regardless of conductive additive. The data suggest that whether Ag^+ or V^{5+} metal centers reduce in $\text{Ag}_2\text{VO}_2\text{PO}_4$ pellets is highly dependent on the cathode conductivity, which is determined by 1) the initial components of the composite electrode and 2) the formation of Ag^0 percolation networks as the cathode is reduced. The reduction of $\text{Ag}^+ \rightarrow \text{Ag}^0$ occurs at higher voltages and is preferred to $\text{V}^{5+} \rightarrow \text{V}^{4+}$ at low discharge rates based on previous reports on $\text{Ag}_2\text{VO}_2\text{PO}_4$.^{16, 49} The higher loaded voltage of $\text{Ag}_2\text{VO}_2\text{PO}_4 + \text{PTFE} + \text{C}$ cells and greater levels of Ag^0 formation by XAS and EXAFS all indicate that in the presence of carbon, the preferred $\text{Ag}^+ \rightarrow \text{Ag}^0$ reduction primarily occurs, likely due to the pre-formed percolation network afforded by the conductive additive. In comparison, in resistive $\text{Ag}_2\text{VO}_2\text{PO}_4$ only and $\text{Ag}_2\text{VO}_2\text{PO}_4 + \text{PTFE}$ cathodes, initially only a very limited amount of active material is accessed by electrons at the current collector interface. As a result, at low levels of discharge, $\text{V}^{5+} \rightarrow \text{V}^{4+}$ reduction must occur concurrent to $\text{Ag}^+ \rightarrow \text{Ag}^0$ reduction to satisfy the electron flux. Once a sufficient conductive network is formed by in-situ reduction of Ag^0 , a greater number of $\text{Ag}_2\text{VO}_2\text{PO}_4$ particles are able to be accessed by electrons and the rate of $\text{Ag}^+ \rightarrow \text{Ag}^0$ reduction occurs similarly to that in cathodes containing the carbon additive. In comparing $\text{Ag}_2\text{VO}_2\text{PO}_4$ only and $\text{Ag}_2\text{VO}_2\text{PO}_4 + \text{PTFE}$ cathodes, EIS and pulse discharge data indicate that the addition of PTFE without carbon is detrimental to the conductivity of the cathode. While XRD and EXAFS results do not detect significant differences in the amount of Ag^0 formed, the addition of PTFE does result in consistently lower loaded voltages. Thus, it is likely that cathodes with PTFE may have a higher level of vanadium reduction rather than silver ion reduction relative to the pure active material.

The conductivity-dependent discharge progression is summarized in Figure 11. Upon initial discharge in insulating $\text{Ag}_2\text{VO}_2\text{PO}_4$ cathodes, the preferred $\text{Ag}^+ \rightarrow \text{Ag}^0$ reduction occurs primarily at the current collector interface, with $\text{V}^{5+} \rightarrow \text{V}^{4+}$ occurring concurrently due to lack electron access. In $\text{Ag}_2\text{VO}_2\text{PO}_4 + \text{PTFE}$ cathodes, the insulating binder blocks some $\text{Ag}_2\text{VO}_2\text{PO}_4 - \text{Ag}^0 - \text{Ag}_2\text{VO}_2\text{PO}_4$ connections, further reducing interparticle conductivity. In cathodes with the carbon additive, $\text{Ag}^+ \rightarrow \text{Ag}^0$ reduction is the primary discharge mechanism and occurs uniformly throughout the electrode. As the discharge progresses, in cathodes w/out carbon, a greater number of $\text{Ag}_2\text{VO}_2\text{PO}_4$ particles are accessible to electrons due to the conductive silver network, and Ag^+ reduction occurs at rate similar to that in cells with carbon. The reduced Ag^0 is concentrated close to the current collector but spreads into the cathode as the discharge progresses. The presence of PTFE blocks some conductive pathways created by the Ag^0 network, resulting in a higher amount of vanadium reduction, lower loaded voltage, and poorer pulse performance. In $\text{Ag}_2\text{VO}_2\text{PO}_4 + \text{PTFE} + \text{C}$ cathodes, the discharge continues to progress uniformly with Ag reduction being the primary mechanism, with some amount of V reduction likely as well. The carbon alone does not yet provide ideal interparticle contact between SVPO particles, as indicated by the improved pulse capability as the material is reduced and Ag^0 is formed.

Conclusions

In batteries with composite cathodes containing the insulating bimetallic active material $\text{Ag}_2\text{VO}_2\text{PO}_4$, consideration of both insulating polymeric binder and conductive carbon additive incorporation is critical for understanding electrochemical polarization in the system. Results from a combination of measurement techniques including EIS, pulse testing, in situ EDXRD, ex situ XRD, and EXAFS modeling show that electrical conductivity can be the limiting factor for discharging the material, thus, the reduction mechanism (extent of $\text{V}^{5+} \rightarrow \text{V}^{4+}$ vs. $\text{Ag}^+ \rightarrow \text{Ag}^0$ reduction) is highly dependent on composite composition (presence of PTFE, carbon), depth of discharge (Ag^0 nanoparticle formation), and spatial location within the cathode. The findings suggest that the incorporation of PTFE without carbon limits the effectiveness of the Ag^0 conduction network formed on reduction. Furthermore, carbon in the presence of PTFE decreases impedance significantly. However, the impedance is further reduced on initiation of reduction concomitant with the formation of Ag^0 nanoparticles. The implications of these results can be extended to consider electrode constructs to reduce the impedance of other resistive electroactive materials which are utilized as composites.

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Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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