EVALUATION OF SILVER VANADIUM PHOSPHOROUS OXIDE AS A CATHODE MATERIAL IN LITHIUM PRIMARY CELLS

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Introduction

Silver vanadium oxide (SVO, $Ag_2V_4O_{11}$) has drawn significant attention as the cathode material of choice in batteries used for implantable cardiac defibrillators.[1, 2] The application requires years of microampere current delivery with intermittent pulses in the ampere range. Lithium/SVO batteries successfully meet these demanding requirements. The discharge process of silver vanadium oxide in a lithium primary cell has been studied and begins with the reduction of Ag^+ to Ag^o followed by reduction of the vanadium centers from V(V) to V(IV) and V(III).[3] The reduced silver ions form silver metal particles and nanowires in the cathode matrix.[4] Consistent with the formation of the silver metal matrix, the conductivity of the cathode increases by several orders of magnitude. Similarly, copper vanadium oxides have also been investigated for their use as cathode materials in lithium based batteries, but in rechargeable systems.[5] The mechanism of reduction has been studied and also shown to progress with the formation of very small copper fibers or nano-wires on the surface of the electrode particles.[6]

Lithium iron phosphate, $LiFePO_4$ specifically,[7-53] and other phosphate based materials generally, have considered desirable for lithium battery cathode applications due to their to their high thermal and chemical stabilities.[54] However, a significant challenge to their practical implementation is overcoming their typically low electronic conductivity. Various methods to improve conductivity have been exploited including using carbon coatings,[13, 19, 55-73] doping agents,[12, 14, 18, 74-80] conductive current collectors,[52] the addition of conducting polymers.[81]

In order to obtain high stability and high conductivity characteristics, we have deliberately selected a silver vanadium phosphorous oxide cathode material. The layered phosphate based structure should possess an inherently low solubility and high stability in the battery cathode matrix. Similar to the silver vanadium oxide and copper vanadium oxide systems, the silver(I) ions in $Ag_2VO_2PO_4$ should be reduced to the metallic state via reduction elimination reactions as the batteries discharge, resulting in a significant increase in cathode pellet conductivity as a result of the reduction process. We propose therefore that silver vanadium phosphorous oxide will be an excellent cathode material for high power lithium battery applications.

Experimental

Silver vanadium phosphorous oxide ($Ag_2VO_2PO_4$) was prepared using a previously reported hydrothermal synthesis method.[82] $Ag_2VO_2PO_4$ was produced on a 0.5 g scale, by heating Ag_2O, V_2O_5, and H_3PO_4 in aqueous solution at 230°C in a Teflon-lined autoclave for 96 hours. The material was characterized by several methods including scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and x-ray powder diffraction (XRD). A Micromeritics Tristar II 3020 was used for BET surface area and porosity analysis, with N_2 as the adsorbate. Samples were degassed under flowing $N_{2(g)}$ for 2 hours at 50°C prior to surface area analysis. A Micromeritics Accupyc II 1340 pycnometer was used for true density analysis made via helium gas displacement. A TA instruments Q600 was used for differential scanning calorimetry (DSC). A Rigaku Ultima IV x-ray powder diffractometer was used for XRD analysis. Cu Kα radiation was utilized at 40 kV, 44 mA, with Bragg-Brentano focusing geometry. MDI JADE version 8.5.3 software with ICDD and NIST databases was used for search-match analysis. Scanning electron microscopy (SEM) data was collected using a Hitachi SU-70 field emitting scanning electron microscope equipped with an Oxford Inca energy dispersive x-ray spectroscopy (EDS) system. Secondary electron images were acquired at 5 kV. Backscatter electron images were observed and EDS data was collected at

20 kV.

Cathode pellets were prepared by mixing Ketjenblack carbon, Fisher 38 graphite, powdered poly(tetrafluoroethane) (PTFE) binder and $Ag_2VO_2PO_4$, containing 79% $Ag_2VO_2PO_4$ by weight. Cathode pellets were pressed at 10 tons/cm^2. Type 2325 coin cells were fabricated within an Argon filled glove box. Electrolyte was 1 M $LiAsF_6$ in 50/50 (v/v) propylene carbonate/ dimethoxyethane. For the differential capacity test, coin cells were discharged at 37^{o}C using a Maccor Series 4000 Battery Testing Unit. Cells were discharged under a constant current until the voltage dropped below 1.5 V. A 0.04 mA/cm^2 current was selected which allowed the cells to discharge completely within 12 days. For the pulse capability test, coin cells were discharged at room temperature and tested using a Bitrode SCN Cycle Life Tester battery testing unit. Four 10 second pulses at current densities of 20, 30, 40 and 50 mA/cm^2 were applied, separated by 15 second rests at open circuit potential. Between pulse trains, the cells were rested at open circuit potential for 30 minutes. This process was repeated until the pulse voltage dropped below 0.5 V.

Results and Discussion

Material characterization

The XRD pattern was recorded of the silver vanadium phosphorous oxide ($Ag_2VO_2PO_4$) sample prepared in our laboratories and showed a good match to that reported in the literature, confirming the successful preparation of the material.[83] It should be noted that silver vanadium phosphorous oxide ($Ag_2VO_2PO_4$) crystals have been reported to be in the monoclinic space group C2/m. The structure itself consists of layers of dimers of edge-sharing VO octahedra and PO tetrahedra, extending parallel to the (001) crystallographic plane with silver ions between the layers as illustrated in Figure 1.[83]

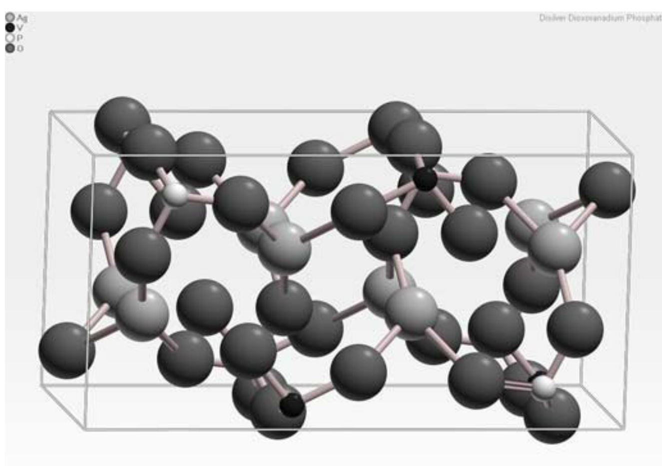
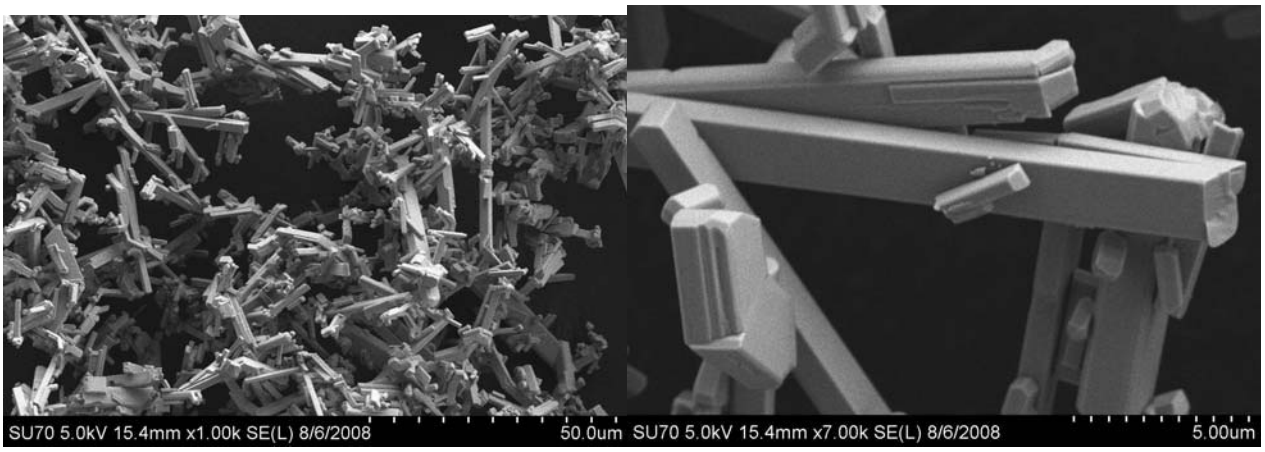


Figure 1. Structure of $Ag_2VO_2PO_4$

Differential scanning calorimetry (DSC) was used to evaluate the silver vanadium phosphorous oxide material purity. One major endotherm was noted at 535^o with no other isotherms observed. The $Ag_2VO_2PO_4$ powder had a BET surface area of 0.98 ± 0.02 m^2/g, with an average pore width ~70 Angstroms. In order to determine the particle morphology and particle size, scanning electron microscopy (SEM) was recorded for samples of the hydrothermally prepared material and revealed our $Ag_2VO_2PO_4$ to have a structure consisting of micron sized bladed particles, as shown in Figure 2. The particles were acicular in appearance with an aspect ratio greater than twenty for many of the particles.

The samples were also imaged by SEM in backscatter electron mode, in order to obtain visual confirmation of sample homogeneity . No differences in contrast were observed in backscatter mode, indicating that the samples were uniform in terms of atomic number composition. Localized energy dispersive x-ray spectroscopy (EDS) was also utilized on two particles of differing morphology, shown in Figure 3. Both particles had Ag:V:P ratios of approximately 2:1:1, as shown in Table 1. This indicates that the composition of our $Ag_2VO_2PO_4$ material was uniform, irrespective of particle morphology. In addition to the silver, vanadium, phosphorous, and oxygen observed, carbon was also detected during EDS, likely from the double sided carbon tape used to support the $Ag_2VO_2PO_4$ powder during SEM and EDS analysis.



a) 1000x magnification b) 7000x magnification

Figure 2. Scanning electron microscopy of $Ag_2VO_2PO_4$

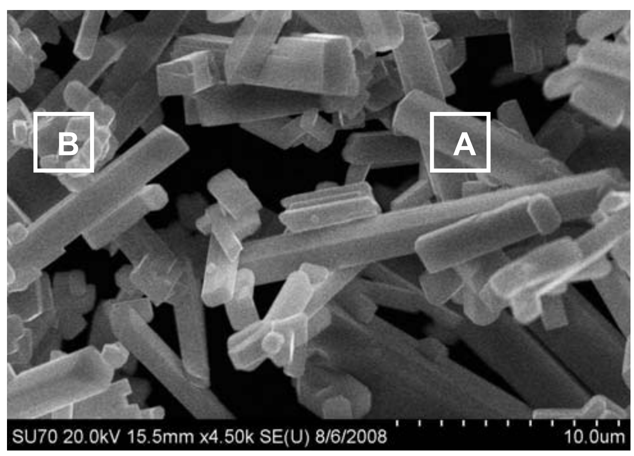


Figure 3. Scanning electron microscopy of $Ag_2VO_2PO_4$

Element	Atomic Composition (%)	
	Region A	Region B
Ag	13.8	9.4
V	7.0	4.3
P	8.4	4.9
C	31.4	33.6
O	39.4	47.8

Table 1. Energy dispersive x-ray spectroscopy analysis of $Ag_2VO_2PO_4$

Electrochemical evaluation

$Ag_2VO_2PO_4$ cathodes were prepared and placed in coin type cells containing lithium anodes. To our knowledge, this is the first use of $Ag_2VO_2PO_4$ as a cathode material. The voltage shows a gradual decrease from an initial potential of 3.3 V to an end of test potential of 1.5 V, as shown in Figure 4. Several plateaus or inflection points are present in the discharge curve.

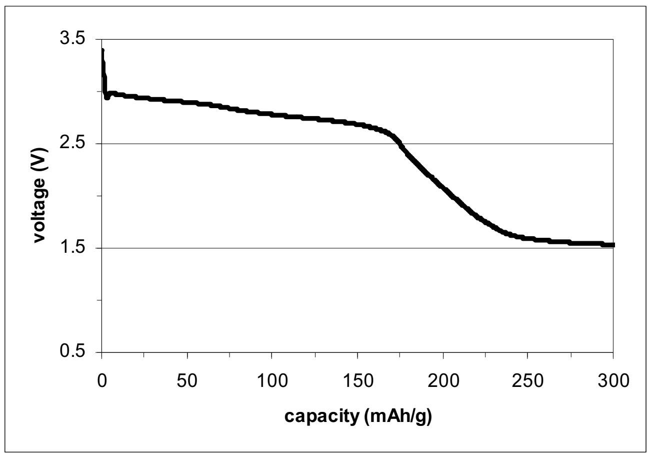


Figure 4. Voltage versus capacity for Li/$Ag_2VO_2PO_4$ batteries: constant current discharge test

The batteries delivered 270 mAh/g of $Ag_2VO_2PO_4$ cathode material above 1.5 V, as shown in Figure 4. Assuming complete reduction of Ag^+ to Ag^o and V^{+5} to V^{+3}, the $Ag_2VO_2PO_4$ would transfer 4 electrons per formula unit, translating to a 272 mAh/g theoretical gravimetric capacity. Notably, nearly 100% of the theoretical capacity of this material has been accessed. The measured true density of our $Ag_2VO_2PO_4$ was 5.32 g/cc. This translates to a high volumetric energy density of 1440 mAh/cc for $Ag_2VO_2PO_4$.

A second electrochemical test was conducted to assess the pulse power capability of the coin cells. Pulse trains consisting of four 10 second constant current pulses every 30 minutes. Each pulse of the train increased in current density and progressed as 20, 30, 40 and 50 mA/cm^2. The minimum voltage recorded under each pulse was recorded and is summarized in Figure 5. Even with a low surface area material and relatively large particle size, the cells demonstrated pulse capability of 50 mA/cm^2 above 1.5 V at the beginning of life. The pulse current under 30 mA/cm^2 remained above 1.5 volts through about 150 mAh/g of cathode material.

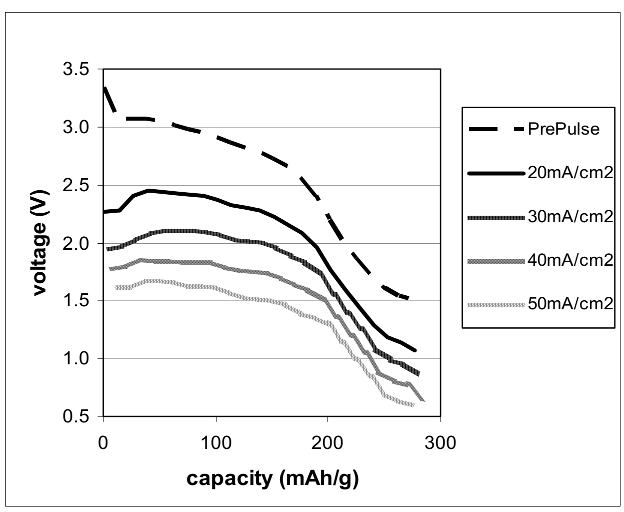


Figure 5. Voltage versus capacity of Li/$Ag_2VO_2PO_4$ batteries: pulse capability test

Summary

The silver vanadium phosphorous oxide $Ag_2VO_2PO_4$ has been established to be a viable cathode material for lithium primary cells. In addition, further research with this and additional members of the material family of mixed metal phosphorous oxides (*MM'*POs) holds promise for next generation high power battery applications.

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