

Silver Vanadium Phosphates $Ag_wV_xP_yO_z$: Electrochemistry and Characterization of Reduced Material providing Mechanistic Insights

Esther S. Takeuchi^{a,b,c},
Amy C. Marschilok^{a,b}, Kenneth J. Takeuchi^b

a. Department of Materials Science and Engineering

b. Department of Chemistry
Stony Brook University (SUNY)
Stony Brook, NY 11794

c. Brookhaven National Laboratory
Upton, NY 11973

Introduction

Energy storage materials have taken on expanded significance due to the needed ability to store electricity for many applications including aerospace, transportation, portable electronics, and biomedical devices. Recently, phosphate based materials have been implemented for energy storage, the most notable example being lithium iron phosphate, $LiFePO_4$. While the voltage and energy density of phosphate based materials may be lower than oxide materials when used for lithium based systems, the chemical and electrochemical stability of the phosphate based materials are viewed as significant assets. In order to achieve practical deployment of phosphate based materials, their inherently low electrical conductivity must be addressed.

Bimetallic cathode materials are desirable for energy storage because they can provide multiple electron reductions per formula unit. We have embarked on the rational study of a new family of cathode materials for lithium batteries, namely silver vanadium phosphorous oxides ($Ag_wV_xP_yO_z$), with the goal of combining the stability of lithium iron phosphate with the enhanced electrical conductivity of partially reduced silver vanadium oxide.

We recently introduced the first member of the silver vanadium phosphorous oxide family for electrochemical study, $Ag_2VO_2PO_4$ (Figure 1).

When used as a cathode in a lithium based battery, $Ag_2VO_2PO_4$ displayed high discharge capacity and high current pulse capability, both promising attributes toward future use in high power biomedical applications.

Results and Discussion

Here we present two additional compositions and structures of the family of cathode materials described by $Ag_wV_xP_yO_z$. We examined a silver vanadium phosphorous oxide $Ag_{0.48}VOPO_4 \cdot 1.9H_2O$. Lithium based electrochemical cells displayed a multi-plateau voltage profile and analysis of electrochemically reduced cathodes indicated significant formation of silver metal by reduction of Ag^+ to Ag^0 after ~ 0.37 electron equivalents were

added. Thus, in this case, the in-situ formation of silver metal on electrochemical reduction was delayed compared to $Ag_2VO_2PO_4$ where formation of silver metal is the predominant process upon initial reduction.

While interest in phosphate based materials continues, there have been fewer reports of metal ion vanadyl diphosphate, $M_xVP_2O_8$, materials examined for lithium based batteries. Diphosphate materials are chemically related to phosphate materials, but due to the P-O-P bond found in the diphosphate anion, we anticipate that the structural rigidity of diphosphate relative to phosphate might affect properties such as discharge profiles and rechargeability, especially in terms of usable depth of discharge and current capability. Thus, we report here the first electrochemical study of a diphosphate SVPO type material, $Ag_2VP_2O_8$ (Figure 2).

Summary

Silver vanadium phosphorous oxides ($Ag_wV_xP_yO_z$) are presented as a material family of interest for next generation batteries. Specifically, these materials show capability as cathodes for high power lithium batteries. The battery performance characteristics will be rationalized with respect to the changes in material composition and structure upon electrochemical reduction.

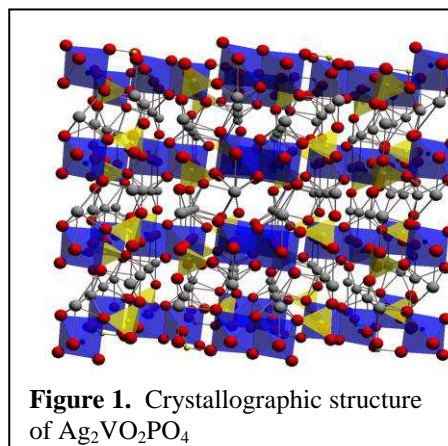


Figure 1. Crystallographic structure of $Ag_2VO_2PO_4$

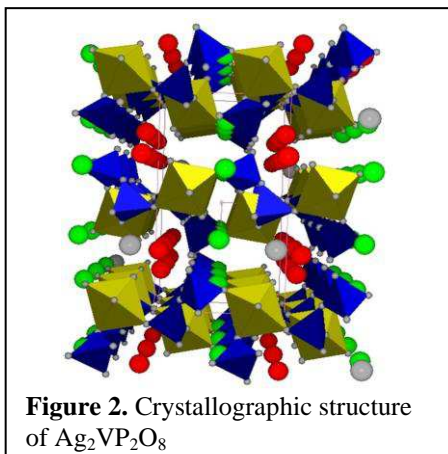


Figure 2. Crystallographic structure of $Ag_2VP_2O_8$