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Microwave-Assisted Synthesis of Silver Vanadium Phosphorous Oxide, $\text{Ag}_2\text{VO}_2\text{PO}_4$: Crystallite Size Control and Impact on Electrochemistry

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ABSTRACT: Silver vanadium phosphorous oxide, $\text{Ag}_2\text{VO}_2\text{PO}_4$, is a promising cathode material for Li batteries due in part to its large capacity and high current capability. Herein, a new synthesis of $\text{Ag}_2\text{VO}_2\text{PO}_4$ based on microwave heating is presented, where the reaction time is reduced by approximately 100x relative to other reported methods, and the crystallite size is controlled via synthesis temperature, showing a linear correlation of crystallite size with temperature. Notably, under galvanostatic reduction, the $\text{Ag}_2\text{VO}_2\text{PO}_4$ sample with the smallest crystallite size delivers the highest capacity and shows the highest loaded voltage. Further, pulse discharge tests show a significant resistance decrease during the initial discharge coincident with the formation of Ag metal. Thus, the magnitude of the resistance decrease observed during pulse tests depends on the $\text{Ag}_2\text{VO}_2\text{PO}_4$ crystallite size, with the largest resistance decrease observed for the smallest crystallite size. Additional electrochemical measurements indicate a quasi-reversible redox reaction involving Li^+ insertion / de-insertion, with capacity fade due to structural changes associated with the discharge / charge process. In summary, this work demonstrates a faster synthetic approach for bimetallic polyanionic materials which also provides the opportunity for tuning of electrochemical properties through control of material physical properties such as crystallite size.

1. Introduction

Key issues associated with the development of cathode materials for secondary Li-ion battery applications continue to be high voltage, large discharge capacity, high power output, and long term cycle stability.¹⁻⁴ Further, lithium transition metal phosphates, generally described as LiMPO_4 (M equals Fe, Mn, Co, etc.), are appealing due to their high chemical and thermal stability.⁵⁻⁹ By introducing the PO_4^{3-} polyanion into the crystal structure, an enhanced stabilization is observed.^{8,9} Additionally, due to a stronger polarizing effect of P^{5+} on O^{2-} relative to the polarizing effect of M^{2+} on O^{2-} , the potential of the $\text{M}^{3+}/\text{M}^{2+}$ redox couple is reduced with phosphates relative to oxides, resulting in an increase in the open circuit voltage as well as the operating voltage.⁵ Based on this “inductive effect”, the voltages for $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{Mn}^{3+}/\text{Mn}^{2+}$ and $\text{Co}^{3+}/\text{Co}^{2+}$ couples in the LiMPO_4 compounds are 3.4, 4.1, and 4.8 V (versus Li), respectively.¹⁰ However, the poor electrical conductivities and low volumetric capacities associated with phosphate materials mitigate the possible advantages in Li-ion batteries.¹⁰ Specifically, to overcome the inherently low electrical conductivity of LiMPO_4 , several strategies have been proposed in recent years, such as controlling the particle size, carbon coating and metal doping.¹¹⁻¹⁶

We have established a paradigm for increasing the conductivity of polyanionic cathode materials through the use of bimetallic materials where one of the metal centers can be reduced *in situ* through a reduction-displacement reaction to form a conductive metallic network.^{17,18} A family of materials described as $\text{Ag}_w\text{V}_x\text{O}_y\text{PO}_z$ have been explored, including

$\text{Ag}_2\text{VO}_2\text{PO}_4$,¹⁸⁻²⁰ $\text{Ag}_{0.48}\text{VOPO}_4 \cdot 1.9\text{H}_2\text{O}$,^{21,22} $\text{Ag}_2\text{VP}_2\text{O}_8$,^{23,24} and $\text{Ag}_{3.2}\text{VP}_{1.5}\text{O}_{7.8}$.²⁵ Several other oxide and polyanion framework materials present the opportunity for enhanced conductivity due to *in situ* metal formation on electrochemical reduction, including $\text{Ag}_2\text{V}_4\text{O}_{11}$,²⁶⁻²⁸ $\text{Ag}_4\text{V}_2\text{O}_6\text{F}_2$,²⁹ $\text{Ag}_6\text{Mo}_2\text{O}_7\text{F}_3\text{Cl}$,³⁰ AgFeO_2 ,³¹ $\text{Cu}_{2.33}\text{V}_4\text{O}_{11}$,³² and $\text{Cu}_{0.5}\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$.³³ This strategy should continue to lead to a variety of future battery materials, especially for high power applications.

Silver vanadium phosphorus oxide ($\text{Ag}_2\text{VO}_2\text{PO}_4$, SVOP) can provide 270 mAh/g from the reduction of Ag^+ to Ag metal and V^{5+} to V^{4+} or V^{3+} . Notably, *in situ* formation of conductive silver nanoparticles during the initial reduction process decreases the impedance of $\text{Li}/\text{Ag}_2\text{VO}_2\text{PO}_4$ batteries by 15,000 fold, resulting in high current capability throughout the cell lifetime.¹⁸ The silver formation in $\text{Ag}_2\text{VO}_2\text{PO}_4$ is highly rate dependent, where the use of lower current densities early in the discharge of a multifunctional bimetallic cathode-containing cell results in metallic silver formation that is more evenly distributed, resulting in the opportunity for more complete cathode use and higher functional capacity.²³

Compared to silver vanadium oxide ($\text{Ag}_2\text{V}_4\text{O}_{11}$, SVO), which has been successfully deployed for Li/SVO batteries used to power implantable cardioverter defibrillators (ICD),^{27,34,35} silver vanadium phosphorus oxide (SVOP) exhibits reduced cathode solubility in Li/SVOP cells, likely due to PO_4^{3-} .^{36,37} Additionally, nanocrystalline SVO is reported to show new electrochemical features relative to microcrystalline SVO.³⁸ For example, nanocrystalline SVO exhibits a qua-

si-reversible silver displacement reaction, where the reduction potential of silver ion is higher than that of microcrystalline SVO. Reversible capacity (~ 100 mAh/g) can be maintained for over 30 cycles at a 2C rate when the cell is cycled between 3.8 and 2.3 V. In larger voltage windows, more than 300 mAh/g is delivered with gradual capacity decline, attributed to a lack of reversibility of V^{5+}/V^{3+} redox couple by the authors. After 30 cycles, the materials are still able to provide a capacity exceeding 120 mAh/g. By analogy, we anticipate reversibility and cycle stability for SVOP by controlling crystallite size.

In general, material crystallite size has been reported to play an important role in affecting physical, chemical, and functional properties, such as catalytic activity, photocatalytic properties and electrochemical performance.³⁹⁻⁴⁶ For Li ion batteries, the effect of material crystallite size on Li ion insertion/extraction in host materials continues to be an important research and design strategy.⁴¹⁻⁴⁶ Due to shorter Li ion diffusion pathways and larger surface area based on small crystallite size, electrode materials are able to achieve better rate capability, longer cycle life and higher operating voltage. We recently reported the electrochemical investigation of silver hollandite ($Ag_xMn_8O_{16}$) as a potential cathode material in rechargeable Li battery.^{41,42} The crystallite size is tuned by controlling Ag content per formula unit, where low Ag content material with small crystallite size shows elevated discharge voltage and high capacity. Furthermore, small DC resistance, good current capability and fast Li ion kinetics are associated with small crystallite size materials, presenting the promise of improving electrochemical performance of materials by tuning the crystallite size.^{44,46} For example, a synthetic control of crystallite size for the anode material $Li_4Ti_5O_{12}$ based on a pulsed supercritical reactor was recently reported.⁴⁵ It is observed that $Li_4Ti_5O_{12}$ nanoparticles with small crystallite size and high crystallinity exhibit the best rate capability and cycle stability because of small charge transfer and low Li^+ diffusion impedance.

For the preparation of $Ag_2VO_2PO_4$, previously reported syntheses, including both hydrothermal and reflux-based synthesis methods,⁴⁷ required three to four days. Fundamentally different from conventional heating methods, microwave-based reactions can provide the possibility of dramatically shortening reaction time, due to very localized increases in energy and temperature.^{48,49,50} Thus, microwave-based synthetic procedures have been developed for a number of inorganic materials in the liquid phase^{49,51} as well as in the solid state⁴⁸. Specifically, there are a variety of microwave-based syntheses for battery electrode materials, mainly microwave hydrothermal/solvothermal synthesis and microwave solid-state synthesis.⁵²⁻⁵⁷ For example, $LiFePO_4$ was synthesized using microwave processing where pure phase $LiFePO_4$ is obtained within 10 min and shows high electrochemical capacity and good cycle stability.⁵³ A microwave solvothermal approach is also employed to synthesize $LiFePO_4$ with uniform nanorod morphology in 5 min.⁵⁴ The size of such nanorods could be controlled by changing reactant concentration.

Herein, we report a microwave hydrothermal method to synthesize $Ag_2VO_2PO_4$ within 1 h, about 100 times shorter than previous methods. Notably, the crystallite size is successfully controlled, showing a linear trend with reaction temperature. Cyclic voltammetry and galvanostatic meas-

urements are used to characterize the Li^+ insertion / extraction processes. Under galvanostatic reduction, the $Ag_2VO_2PO_4$ sample with the smallest crystallite size delivers the highest capacity and shows the highest loaded voltage. Pulse discharge tests show a significant resistance decrease during the initial discharge coincident with the formation of Ag metal where the magnitude of the resistance decrease observed during pulse tests depends on the $Ag_2VO_2PO_4$ crystallite size, with the largest resistance decrease observed for the smallest crystallite size. Partial reversibility of the $Li/Ag_2VO_2PO_4$ electrochemical reaction is observed after the replacement of Ag^+ with Li^+ , but the original V-O-P-O layered structure cannot be fully recovered. Thus, these results demonstrate the ability to control crystallite size via microwave synthesis, and a relationship between material crystallite size and resulting electrochemistry.

2. Experimental

2.1. Material synthesis

Vanadium oxide (V_2O_5), silver oxide (Ag_2O) and phosphoric acid (H_3PO_4 , 85%) were mixed with deionized water analogous to the previously reported hydrothermal method.^{17,58} The mixture was then transferred to a CEM Discover SP for microwave heating. The dynamic control option (**maximum power: 200 W**) was selected as the heating program, in which the temperature ramped to a given temperature **at heating rates of 50-60 °C/min** and then held at that temperature for 1 h. In order to obtain $Ag_2VO_2PO_4$ with different crystallite sizes, six reaction temperatures (50, 75, 100, 125, 150 and 180 °C) were used while the same reaction time was maintained. The as prepared samples were washed with deionized water and dried in a vacuum oven.

2.2. Material characterization

Powder X-ray diffraction (XRD) was employed to characterize the crystal structure and estimate crystallite sizes. The XRD patterns were measured by a Rigaku SmartLab X-ray diffractometer with Cu $K\alpha$ radiation and Bragg-Brentano focusing geometry. PDXL2 software was used for search-match analysis, and PeakFit version 4.12 was used to fit peaks for crystallite size calculation via the Sherrer equation.⁵⁹ A TA instruments Q600 was used to perform differential scanning calorimetry (DSC). Raman spectra were recorded using the Xplora Raman spectrometer (Horiba Scientific, laser at 532 nm). Surface area of the samples was determined by a Quantachrome NOVA 4200 E using the Brunauer-Emmett-Teller (BET) method. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was utilized to analyze the elemental composition by a Thermofisher iCAP 6300 series instrument. Particle size of as prepared samples was investigated by a Horiba La-950V2 laser scattering particle size analyzer.

2.3. Electrochemical measurements

For all electrochemical tests, the electrolyte was $LiPF_6$ (1 M) in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). Electrode preparation was through a slurry of as synthesized $Ag_2VO_2PO_4$ materials, graphite, acetylene black carbon and polyvinylidene fluoride (PVDF) cast onto aluminum foil. A three electrode assembly with lithium reference and auxiliary electrodes was utilized to collect cyclic voltammetry data. A scan rate of 5.00×10^{-5} V/s was applied to the cell with voltage limits of 2.0 V and 3.8 V (vs.

Li/Li⁺). Coin cells were fabricated with lithium metal electrodes to conduct galvanostatic measurements under a current density of 30 mA/g. AC impedance measurements were carried out using a BioLogic VSP impedance analyzer with a 10 mV amplitude and a frequency range of 100 kHz to 0.1 Hz, and the Nyquist plots were normalized assuming a zero intercept at the high frequency x-axis intercept. For the pulse discharge tests, cells were discharged at a background current 1.4 mA/g (0.0045 mA/cm²) with 5 second intermittent pulses at a current density of 36 mA/g (0.12 mA/cm²).

3. Results and discussion

3.1. Materials synthesis and characterization

Ag₂VO₂PO₄ was previously synthesized by a hydrothermal method or a reflux-based method which both required a long reaction times of up to 4 days.^{18,47} Thus, the use of microwave assisted synthesis was pursued to decrease total synthesis time and explore possibility opportunity for crystallite size control. Samples of Ag₂VO₂PO₄ were prepared over a range of temperatures, specifically at 50, 75, 100, 125, 150 and 180 °C and identified as SVOP-50, SVOP-75, SVOP-100, SVOP-125, SVOP-150 and SVOP-180. XRD patterns were recorded for the samples, **Figure 1**. All of the XRD peaks can be assigned to Ag₂VO₂PO₄ (JCPDS #07-3580) with no apparent impurities. As the reaction temperature decreases, peak broadening is apparent at 2θ = 27 - 30° and 52 - 56°, indicating a decrease in crystallite size. Similarly, the relative intensity of the peak at 2θ = 28° gradually increases when reaction temperature becomes higher consistent with more crystalline materials.

Figure 1. XRD patterns for Ag₂VO₂PO₄ synthesized by microwave heating at different temperatures.

Differential scanning calorimetry (DSC) analysis of as prepared Ag₂VO₂PO₄ shows only one single endothermic peak at ~540 °C, **Figure S1**, consistent with previous reports.^{17,47} Raman spectra of as synthesized materials are compared with V₂O₅ (a starting material in the reaction) and hydrothermally synthesized Ag₂VO₂PO₄ (SVOP-HT), **Figure 2**. Raman spectrum of V₂O₅ powder displays a significant peak at 144 cm⁻¹ which is ascribed to signals of B_{1g} and B_{3g}.⁶⁰⁻⁶² For SVOP-HT, two intense peaks at 790 cm⁻¹ and 903 cm⁻¹ are observed, and there is no indication of such two bands in V₂O₅ spectrum. All the as synthesized materials show the same Raman spectra as SVOP-HT without peak shift. Additionally, no V₂O₅ Raman peak is detected from the spectra of hydrothermally

synthesized and microwave synthesized materials, indicating phase purity of the as prepared samples.

Figure 2. Raman spectra for V₂O₅, microwave synthesized Ag₂VO₂PO₄ and hydrothermally synthesized Ag₂VO₂PO₄.

Figure 3. The relationship between crystallite size (black dots: (001) plane), red triangles: (400) plane) and reaction temperature. (Inset: Crystal structure of Ag₂VO₂PO₄ viewed along b-axis direction. Yellow and blue polyhedra represent VO₆ and PO₄ respectively, and silver is shown as grey.)

The crystallite size was calculated from the XRD patterns using the Scherrer equation.⁵⁹ Two diffraction peaks at 2θ = 14.05° and 2θ = 28.70°, indexed as (001) and (400) plane respectively, were selected for size analysis. The (001) plane is located in the position of the layers, which consist of dimers of edge-sharing VO octahedra and PO tetrahedra, **Figure 3 inset**. The as prepared samples have smaller crystallite size than previously reported materials. Based on (001) peak, the crystallite size varies from 42 nm to 60 nm and shows a linear relationship with reaction temperature, **Figure 3**, indicating that temperature is an important factor influencing the formation of layers. **Synthesis under room temperature for 72 h were conducted, but there are some small peaks in the range of 400-500 °C in the DSC data, showing incomplete formation of Ag₂VO₂PO₄ phase.** Although there is no similar correlation for crystallite size along a-axis, an increase in size is observed when the temperature is above 100 °C. SEM showed all samples have similar particle size and granular morphology, with dimensions ranging from 0.2 μm to 0.8 μm, **Figure S2**. **The inconsistency of crystallite size and particle size indicates SVOP crystallites tend to aggregate into large particles. In order to verify the observed particle sizes from**

SEM, particle size distribution of as prepared materials was measured by particle size analyzer, Figure S3. All the samples showed mean particle sizes ranging from 0.4 to 0.7 μm , consistent with observed particle sizes in SEM images. BET surface area measurements showed little difference in the surface areas with a range of 5.7 to 7.5 m^2/g for the as prepared samples. In order to better understand the synthesis temperature effects on crystallite size and elemental composition, ICP-OES was used to analyze the Ag/V ratio of $\text{Ag}_2\text{VO}_2\text{PO}_4$ materials with different crystallite sizes, **Figure 4**. It is shown that the Ag/V ratio for SVOP-50 is 1.96, which is lower than the other samples. Such silver deficiency might be due to the surface defects of $\text{Ag}_2\text{VO}_2\text{PO}_4$ particles which are formed under low temperature. When the reaction temperature becomes higher, the Ag/V ratio reaches 2.00 to 2.04, indicating a slight elemental compositional change based on temperature.

Figure 4. The relationship between Ag/V ratio and crystallite size along c-axis. Inset: chemical formula of as-prepared materials based on ICP results.

Figure 5. Cyclic voltammetry of (a) SVOP-50 C and (b) SVOP-180 C.

3.2. Electrochemical performance

Cyclic voltammetry (CV) of $\text{Ag}_2\text{VO}_2\text{PO}_4$ was previously reported using a slow scan rate 2.00×10^{-5} V/s, and a major reduction peak was observed at 2.6 V with a minor peak at 2.9 V.¹⁸ Notably, there was no oxidation peak during oxidation. The reversibility of Li insertion into $\text{Ag}_2\text{VO}_2\text{PO}_4$ prepared via microwave assisted synthesis was conducted. The voltammetry for SVOP-50 and SVOP-180 are shown as examples where both show major reduction peaks at ~2.7 V with a minor peak at 2.8 V and 2.6 V respectively, **Figure 5**. On the reverse scan, oxidation peaks at ~3.5 are seen for both samples. During the second scan, a reduction peak of lower current is apparent for both samples at 3.1 V, a significantly higher voltage than seen for the reduction peak during the first scan seen at 2.6 – 2.7 V. The redox peaks for the third scan are similar to those of the second scan located at 3.1 V and 3.6 V. The voltammetric peak voltages for as prepared materials are summarized in **Table S2** as well as their associated discharge capacities. The results for the second cycle are summarized in **Table S3** where some level of reversibility is noted for all samples.

The first discharge curves under galvanostatic control of as prepared samples at a current density of 30 mA/g are used to illustrate the discharge characteristics, **Figure 6**. All cells delivered capacities ranging from 200 – 215 mAh/g when discharged to 2.0 V. SVOP-50 shows the highest capacity, 214 mAh/g, while SVOP-150 and SVOP-180 deliver 201 mAh/g and 205 mAh/g, respectively. Thus, a trend of decreasing capacity as crystallite size increases is observed. The discharge curves display relatively flat voltage plateaus above 2.5 V, where the samples prepared at lower temperatures show higher operating voltage during discharge. The discharge

voltage at 100 mAh/g is plotted vs. crystallite size along c-axis. Operating voltage increases as crystallite size decreases when the size is smaller than 50 nm but remains constant as the crystallite size becomes larger. In addition, a higher voltage plateau in the initial discharge process of SVOP-50 is observed, which corresponds to a minor peak in the CV plot. It was reported that $\text{Ag}_{0.48}\text{VOPO}_4 \cdot 1.9\text{H}_2\text{O}$ showed two voltage plateaus where the reduction of vanadium dominated during the higher voltage plateau, while the reductions of silver and vanadium occurred concurrently for $\text{Ag}_2\text{VO}_2\text{PO}_4$.^{18,21} These differences have been previously rationalized by the Ag/V ratio and the accompanying difference in average electronegativity per atom.²¹ Thus, it is likely that the surface silver deficiency of SVOP-50 could induce a predominant reduction of vanadium during the initial discharge process, resulting in a higher discharge voltage. Compared to the samples synthesized by microwave-assisted method, SVOP-HT delivers a capacity of 205 mAh/g showing a similar discharge profile as SVOP-150 and SVOP-180.

Figure 6. The first discharge curves of as prepared materials in Li/ $\text{Ag}_2\text{VO}_2\text{PO}_4$ cells. Inset: The relationship between discharge voltage at 100 mAh/g and crystallite size along c-axis.

To probe the mechanism of Li insertion/extraction, the discharge-charge curves for the samples were collected where SVOP-50 and SVOP-180 are shown, **Figure 7**. For SVOP-50, 3.14 electron equivalents per formula unit are transferred during the first discharge cycle. Based on previous research,¹⁸ full discharge of 4 electron equivalents is the reduction of V^{5+} . In this case, the reduction by 3.14 electron equivalents would represent less than the full theoretical capacity. When the cell is charged to 3.8 V, 1.94 electron equivalents are realized where the oxidation of the vanadium site is expected. The voltage plateau of the second cycle is similar to the third cycle, but is significantly different from the first cycle, which is in good agreement with results of the CV measurements. As cycling test proceeds, the second and third discharge cycles deliver 2.09 and 1.84 electron equivalents, respectively. Comparison of the discharge-charge curves of samples with SVOP-50 and SVOP-180, the SVOP-50 sample with small crystallite size shows higher discharge capacity in each cycle. Notably, SVOP-50 maintains reduction of about 1 electron equivalents in the 10th cycle while only 0.57 electron equivalents are realized for SVOP-180. This demonstrates that small crystallite size is conducive to maintaining capacity during the discharge/charge process. For the 20th through 50th cycles, the SVOP-50 containing

cells still deliver higher electron equivalents, but the profile of discharge-charge curves for both samples becomes similar.

The long term cycling performance for six SVOP materials was compared under cycling from 3.8 – 2.0 V, **Figure 8**. Dramatic capacity fading before cycle 10 is observed for all the samples. However, SVOP-50 and SVOP-75 deliver more electron equivalents at cycle 10 and show slower capacity fading than the other samples. After cycle 10, electron equivalents are maintained at the range of 0.2 to 0.5 for samples with large crystallite size, while SVOP-50 is still able to utilize over 0.5 electron equivalents until cycle 30.

Figure 7. Discharge-charge curves of (a) SVOP-50 C and (b) SVOP-180 C.

In order to assess the fade under lower depth of discharge cycling, a narrower voltage window (2.65 – 3.80 V) was utilized for a second discharge/charge test. The magnitude of fade was similar under this test to the cycling under a wider voltage window. The discharge capacity in the first cycle was about 2.3 electron equivalents while it decreased to 1.2 electron equivalents in the second cycle, implying the partial reversibility of this material is from the vanadium site.

Figure 8. Cycle performance of as prepared materials.

3.3. Analysis of Charged $\text{Ag}_2\text{VO}_2\text{PO}_4$

The cathodes recovered from charged cells were characterized by XRD. The XRD patterns of re-charged SVOP-50 cathode are compared with SVOP-50 powder and SVOP-50 cath-

ode before electrochemical measurement, **Figure 9**. SVOP-50 C cathode maintains all the peaks of the powder sample with little change in the peak position and intensity. In the charged sample, it is found that the peaks of metallic Ag can still be observed after oxidation, indicating that not all Ag is reversibly re-inserted into the host material. In addition, the charged sample indicates that the materials after oxidation become amorphous without showing most of major peaks of $\text{Ag}_2\text{VO}_2\text{PO}_4$. This indicates that small Li^+ is not able to support layered structure of SVOP after the replacement of Ag^+ with Li^+ , therefore, resulting in the collapse of layers and low crystallinity.

Figure 9. XRD patterns of SVOP-50 C powder, SVOP-50 C cathode before electrochemical measurements and SVOP-50 C cathode after charging.

3.4. Resistance change in $\text{Ag}_2\text{VO}_2\text{PO}_4$ as a function of discharge

AC impedance was measured for cells with SVOP materials before the discharge/charge test was conducted. A simple equivalent circuit consisting of a resistor (R_s), a parallel combination of a resistor (R_{ct}) and a constant phase element (CPE), and a Warburg element (open, W_o) was used to fit the impedance data, **Figure 10(a) inset**. All the Nyquist plots of as prepared materials showed a similar characteristic with a semicircle followed by a straight line, **Figure 10(a)**. Different diameters of semicircles can be observed, suggesting a correlation between crystallite size and resistance. Therefore, resistance of semicircle vs. crystallite size along c-axis is plotted to investigate the effect of crystallite size on cell resistance, **Figure 10(b)**. The sample with the lowest crystallite size shows a charge transfer resistance value of 39.9 Ω , and resistance increases with crystallite size following a linear trend. This result demonstrates small crystallite size facilitates charge transfer and the movement of guest ions.

Figure 10. (a) Nyquist plots of as prepared materials before battery test and (b) relationship between resistance and crystallite size along c-axis.

In order to further investigate the current capability of microwave synthesized materials, test cells were discharged with intermittent pulses at a current density of 36 mA/g, **Figure 11a**. The discharge profiles are similar to that of constant discharge test for these samples, and the capacity can be delivered to ~200 mAh/g when the voltage reaches to 2.0 V. During the discharge process, initial pulses show larger voltage drop than the middle and the end of pulses. Such difference should be due to the formation of Ag nanoparticle in the initial discharge stage. The in-situ formed conductive Ag metal could dramatically increase the conductivity and contribute to the power performance of $\text{Ag}_2\text{VO}_2\text{PO}_4$ cathode in lithium based batteries. However, the samples with small crystallite size have larger voltage drop than large crystallite size samples in the initial pulses, indicating larger resistance in those cells. Therefore, resistance as a function of electron equivalents is plotted to probe the difference of cell resistance and its change during discharge, **Figure 11b**. Re-

sistance at each pulse was calculated based on the point of maximum voltage drop and Ohm's law. SVOP-180 shows a rapid resistance drop after discharge and the resistance becomes stable when ~ 0.8 electron equivalents are transferred. In contrast, for SVOP-50, the resistance exhibits an apparent decrease in the initial state of discharge, keeps a slow decrease rate from 0.2 to 0.7 electron equivalents, and finally

Figure 11. (a) Pulse discharge curves of Li/Ag₂VO₂PO₄ electrochemical cells containing as prepared Ag₂VO₂PO₄ materials. (b) Cell resistances for Li/SVOP cells under 36 mA/g pulses. (c) Polarization contribution and (d) ohmic contribution to cell resistance from 36 mA/g pulse waveforms.

reaches to a stable value when ~ 1.45 electron equivalents are utilized. Moreover, it is interesting that the resistance decreases faster when crystallite size of cathode materials increases. More grain boundaries in small crystallite size materials might have an influence on the formation of conductive network because more metallic silver in the grain boundaries would be required to connect each crystallite.

In order to probe the phenomenon further, the ohmic and polarization contributions from the pulse waveforms were determined, **Figure 11c** and **Figure 11d**. **Ohmic resistance is calculated based on prominent initial voltage drop of a single pulse, and polarization resistance is calculated from the remaining voltage drop part.** The resistance contributions due to polarization were fairly consistent among all the sample cells, **Figure 11c**. In contrast, the ohmic contributions to resistance were highly dependent on the synthesis temperature of the SVOP where the SVOP-50 material shows higher resistance up to 1.0 electron equivalents of discharge, **Figure 11d**. The ohmic contribution to the overall resistance more

closely reflect the total resistance as shown in **Figure 11b**. This can be rationalized as follows. Prior to the discharge of the SVOP, the cell resistance is high and grain boundaries of the SVOP can be regarded as a contribution to the resistance. As the cell discharges, Ag metal starts to form on the surface of Ag₂VO₂PO₄ crystallites, with accompanying resistance drop due to the formation of conductive material. The material samples with small crystallites have a higher number of grain boundaries compared to the larger crystallite samples. Thus, the resistance values for the SVOP-50 containing cells may remain high over a larger range of electron equivalents until sufficient Ag forms in the grain boundaries to reduce the overall ohmic resistance. Once a conductive network is established, formation of more silver nanoparticles will have little effect on resistance decrease consistent with the low resistance for all samples beyond 1.45 electron equivalents.

4. Conclusion

Pure $\text{Ag}_2\text{VO}_2\text{PO}_4$ has been readily prepared by a new microwave synthesis method. Notably, the crystallite size of the samples was successfully controlled and showed a linear relationship with reaction temperature. Electrochemical measurements under galvanostatic discharge indicate that smaller crystallite size provided higher operating voltage and larger initial discharge capacity. In addition, the $\text{Ag}_2\text{VO}_2\text{PO}_4$ samples show some degree of reversibility for Li^+ insertion/extraction. The delivered capacity does show dramatic fade within the first 10 cycles until a limited reversibility at a level equal to ~ 0.3 electron equivalents is reached. Notably, the $\text{Ag}_2\text{VO}_2\text{PO}_4$ materials with small crystallite size did show better cycle stability. Investigation of the pulse behavior showed that under galvanostatic pulses, the ohmic contribution to the voltage drop was larger for the small crystallite size materials. This is consistent with higher numbers of grain boundaries for the smaller crystallite size samples, assuming the grain boundaries contribute to the ohmic resistance. Thus, this study illustrates that control and variation of the physical properties of materials can significantly impact electrochemical properties and can lend insight into the structure / function complexity associated with battery discharge / charge processes. Specifically, synthetic control of materials crystallite size presents the opportunity to directly study electrochemical properties of materials such as cycle life and voltage drop, and indirectly affect properties such as usable capacity and power.

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Notes

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