

LITHIUM/SILVER VANADIUM OXIDE BATTERIES WITH VARIOUS SILVER TO VANADIUM RATIOS

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Summary

Silver vanadium oxides with silver to vanadium ratios of 0.01 to 1.0 were prepared by heat treatment of silver nitrate and vanadium pentoxide. The samples were analyzed by atomic absorption spectroscopy and X-ray powder diffraction. The reaction of silver vanadium oxide with n-butyl-lithium indicated that the material with a composition of $\text{AgV}_2\text{O}_{5.5}$ had the highest volumetric capacity. This finding was supported by the discharge of lithium/silver vanadium oxide batteries under constant resistance loads of 1, 2, and 5 $\text{k}\Omega$. The cells with $\text{AgV}_2\text{O}_{5.5}$ as the cathode material delivered the highest capacities and showed the least voltage drop under applied constant current pulses. The theoretical energy density of the $3\text{Li}/\text{AgV}_2\text{O}_{5.5}$ couple is 1.5 W h g^{-1} or 0.20 W h cm^{-3} .

1. Introduction

Nonstoichiometric compounds such as $\text{M}_x\text{V}_2\text{O}_y$ ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Ag}, \text{Cu}$) are commonly called vanadium bronzes. These bronzes have been considered for use as cathode materials due to their semiconductive properties and their tunnel-like structures which provide diffusion paths for metal ions. Silver vanadium oxide (SVO) is a vanadium bronze whose phases, conductivity, and density depend on its silver content [1, 2]. SVO was investigated as a cathode material in solid state cells consisting of silver/silver- β -alumina/silver vanadium oxide [3], but the cell system was deemed unsuitable due to the slow rate limiting step of silver diffusion into the silver vanadium oxide cathode.

Primary lithium/organic electrolyte/vanadium oxide batteries have been developed in both active and reserve configuration [4]. Vanadium oxides have also been found useful as cathode materials in secondary lithium batteries [5]. Primary lithium/organic electrolyte/silver vanadium oxide

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batteries were developed in 1979 [6]. Subsequently, lithium/organic electrolyte/silver vanadium oxide batteries for low rate applications were reported [7]. Recently, the use of lithium/silver vanadium oxide batteries for moderate to high rate applications has also been reported [8]. The batteries display a characteristic discharge where voltage decreases with depth of discharge, with the voltage acting as a state of charge indicator.

The correlation that has only been briefly reported is that between the silver content and the lithium battery performance [9]. This paper discusses the effect of silver content on the composition and structure of silver vanadium oxide and how this relates to energy density and performance of primary lithium/organic electrolyte/silver vanadium oxide batteries.

Experimental

Synthesis of silver vanadium oxide. Vanadium pentoxide was prepared by thermal decomposition of ammonium vanadate (Cerac) [10]. Vanadium pentoxide was mixed with an aqueous solution of silver nitrate (Engelhard Mineral) and the resultant slurry was brought to dryness. The dry solid was ground and heated with incremental increases in temperature to a maximum temperature of 380 °C. Silver vanadium oxides were prepared by this method with silver to vanadium ratios ranging from 0.01 to 1.0. The resultant silver vanadium oxides ranged in color from orange to black with the color dependent on the silver content.

Analysis of silver vanadium oxide. The silver vanadium oxide samples were analyzed by atomic absorption spectroscopy using a Perkin-Elmer Model 3030 spectrophotometer. The samples were prepared by dissolution in nitric acid with added potassium nitrate. Silver and vanadium were determined directly while the amount of oxygen in the sample was calculated by difference, assuming only the presence of silver, oxygen, and vanadium. The error in the silver and vanadium determinations was estimated at $\pm 2.5\%$. Because the oxygen was determined by difference the error is $\pm 5.0\%$.

X-ray powder diffraction. Data were obtained with the use of a water-cooled X-ray generator equipped with a wide range goniometer and strip chart recorder. Ni-filtered Cu K α X-rays were used.

Reaction of silver vanadium oxide with n-butyllithium. The potential of butyllithium has been reported as 1.0 - 1.4 V versus lithium [11]. All manipulations for this experiment were carried out in a Vacuum/Atmospheres glove box filled with argon. Samples of silver vanadium oxide were dried and weighed. An excess of freshly titrated n-butyllithium (Aldrich, n-butyllithium in hexane) was allowed to react with each sample for 4 days with agitation of the samples twice each day. The resultant slurries were

allowed to settle and the liquid was removed by pipet. The solid was rinsed repeatedly with dry hexane. The hexane washings were combined with the withdrawn solution and were titrated for n-butyllithium content with 2-butanol in xylene using 2,2'-dipyridyl as an indicator.

Construction of test cells. Cells were constructed to evaluate the discharge performance of the various silver vanadium oxides. Depolarizer mixtures were prepared by combining 95% silver vanadium oxide, 2% graphite, and 3% Teflon. Cathodes were formed by compressing the mixes on stainless steel current collectors. Due to changes in the silver vanadium oxide density with silver content the cathodes were not held at constant weight, but rather at a constant volume of 2.6 cm³ each. One cathode was welded on each side of a prismatic cell case made of 304L stainless steel. Anodes were formed by pressing two lithium sheets onto a nickel current collector which was welded to the pin of a header equipped with a glass-to-metal seal. The anodes were heat sealed in polypropylene separators prior to insertion into battery cases. After lid to case welding, the cells were vacuum filled with electrolyte consisting of 1 M LiBF₄ (Footo Mineral, vacuum dried) in propylene carbonate (Burdick and Jackson, dried over molecular sieves and alumina). A final close weld provided a case positive, prismatic, hermetically sealed cell. All the cells were cathode limited and had limiting surface areas of 14 cm².

Results and discussion

Silver vanadium oxide samples with silver to vanadium ratios of 0.01 - 1.0 were prepared by thermal decomposition of silver nitrate and vanadium pentoxide mixtures. Analysis of the silver vanadium oxide samples by atomic absorption spectroscopy allowed assignment of empirical formulae which are shown in Table 1. The empirical formulae are based on Ag_xV₂O_y, where values of *x* and *y* were assigned according to the analysis. The silver to vanadium ratios reflect the weighed amounts of silver and vanadium used in the preparation of each silver vanadium oxide, and as in the original mixtures range from 0.01 to 1.0. It is clear from the empirical formulae that some of the materials are nonstoichiometric. If all the vanadium was present as V(V) and all the silver as Ag(I) then *y* would be equal to (10 + *x*)/2. Since this is not always the case, vanadium and silver must be present in other oxidation states as well.

X-ray powder diffraction patterns were obtained for the silver vanadium oxide samples. The patterns were compared with those previously reported and phase assignments were made as shown in Table 2 [1]. Figure 1 shows the pattern obtained for the sample with the composition AgV₂O_{5.5} with the known pattern of Ag₂V₄O₁₁ superimposed. The figure reveals that the material with the assigned empirical formula of AgV₂O_{5.5} is structurally the same as Ag₂V₄O₁₁. All calculations in the rest of the paper will use

TABLE 1

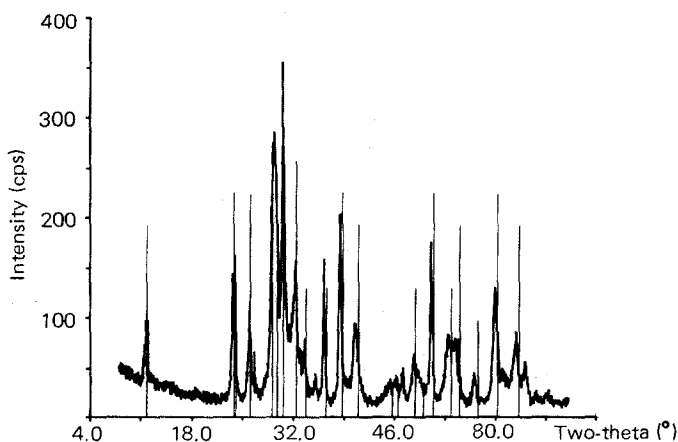
Empirical formulae assigned from analyses by atomic absorption spectroscopy

$\text{Ag}_x\text{V}_2\text{O}_y$	
X	Y
0.021	5.25
0.29	5.08
0.76	5.49
0.83	5.33
1.0	5.50
1.06	5.31
1.19	5.57
2.0	6.0

TABLE 2

Phases of silver vanadium oxide assigned by X-ray powder diffraction

x in $\text{Ag}_x\text{V}_2\text{O}_y$	Phase
0.021	V_2O_5
0.29	$\text{V}_2\text{O}_5 + \text{Ag}_{0.35}\text{V}_2\text{O}_5$
0.76	$\text{Ag}_2\text{V}_4\text{O}_{11} + \text{unidentified phase}$
1.0	$\text{Ag}_2\text{V}_4\text{O}_{11}$
2.0	AgVO_3

Fig. 1. X-ray powder diffraction pattern of $\text{AgV}_2\text{O}_{5.5}$ (continuous line) with the pattern of $\text{Ag}_2\text{V}_4\text{O}_{11}$ (bar representation) overlaid.

$\text{AgV}_2\text{O}_{5.5}$ as the empirical formula for the material with a silver to vanadium ratio of 1 to 2.

As a preliminary screening vehicle, the silver vanadium oxide samples were treated with n-butyllithium [11]. The results of the experiments are

summarized in Table 3. The number of mmoles of butyllithium that reacted per gram of SVO decreased with increasing silver content ranging from 22 mmol butyllithium per gram of SVO at $x = 0.021$ to 13 mmol butyllithium per gram SVO at $x = 2.0$. The sample with the lowest silver content reacted with more n-butyllithium than did the others on a weight basis. The amount of butyllithium that reacted per cm^3 of compressed silver vanadium oxide was determined. The compressed density of silver vanadium oxide was obtained by compression of each sample into a pellet at 60 000 psi and measurement of the pellet thickness. The reactivity of butyllithium per cm^3 of silver vanadium oxide was calculated and found to be highest for the silver vanadium oxides with $x = 1.0 - 1.06$. As the silver content increased or decreased from $x = 1.0 - 1.06$, the reactivity per cm^3 of compressed powder decreased.

The number of moles of butyllithium that reacted per mole of silver vanadium oxide was calculated based on the empirical formula assignments in Table 1. The reaction per mole ranged from a low of 2.75 mol BuLi/mol SVO at $x = 2.0$ to a high of 4.96 mol BuLi/mol SVO at $x = 1.06$. The mol of butyllithium that reacted per equivalent of metal was calculated based on 2 equivalents per vanadium site and one equivalent per silver site which is consistent with reduction of vanadium (V) to vanadium (III) and reduction of silver (I) to silver (0). As mentioned previously, some of the samples are nonstoichiometric and contain vanadium or silver other than vanadium (V) and silver (I). The theoretical capacity calculations were, however, based on the assumption that vanadium (V) and silver (I) were the only species initially present. When $0.021 \leq x \leq 1.19$, approximately one equivalent of butyllithium reacted per metal equivalent. When $x = 2.0$, 0.46 equivalents of BuLi reacted per metal equivalent. The preliminary indication from the reaction of the silver vanadium oxide samples with n-butyllithium is that the sample with the lowest silver content has the highest gravimetric capacity, while the material with a silver to vanadium ratio of one to two has the highest volumetric capacity.

TABLE 3

Reaction of silver vanadium oxide, $\text{Ag}_x\text{V}_2\text{O}_y$, with n-butyllithium

x	BuLi/g SVO (mmol)	BuLi/ cm^3 SVO (mmol)	BuLi/mol SVO (mol)	BuLi/mol M (mol)
0.021	22	260	4.05	1.00
0.29	18	277	3.90	0.90
0.76	17	286	4.15	0.87
0.83	17	322	4.76	0.98
1.0	16	353	4.77	0.95
1.06	16	353	4.96	0.98
1.19	15	290	4.80	0.93
2.00	13	308	2.75	0.46

$$M = 2 (\text{mol V}) + \text{mol Ag}.$$

Cells were assembled using the silver vanadium oxide samples and were discharged under 1, 2, and 5 k Ω loads (average current densities of 0.18, 0.09, and 0.036 mA cm⁻²). Testing lasted 6 months at the highest load. Additionally, two groups of cells were subjected to pulse testing which consisted of five, one-second, 5 or 10 mA pulses, with one second of open circuit voltage rest after each pulse, applied once per week with the remainder of the discharge under 1 or 2 k Ω loads.

The delivered capacity of a cell was assigned at the point in discharge where the load voltage fell below 2.0 V. It should be noted that this is less reducing than butyllithium. Theoretical capacities to 2.0 V were based on a reaction of 2 equivalents per mole of vanadium and one equivalent per mole of silver. The delivered capacities for cells containing silver vanadium oxide cathodes with various levels of silver are summarized in Table 4. The theoretical capacity and the percentage of theoretical capacity delivered are also shown.

The data show that with increasing silver content the delivered capacity and percent theoretical capacity increase and reach a maximum when the silver to vanadium ratio is 0.50 to 0.55. The cells containing silver vanadium oxide, where $x = 0.21, 0.29$, failed early in life. It has been reported that the conductivity of silver vanadium oxide increases with silver content [2] and that the conductivity of vanadium oxide decreases with increasing lithiation [12]. Apparently the silver vanadium oxide cathodes with low silver content were not sufficiently conductive when partially lithiated to discharge effectively. The addition of higher levels of conductive material such as graphite or carbon increased discharge efficiency but further reduced the theoretical capacities of these cells, which were already lower than those with higher silver content. The highest delivered capacity for any group of cells was obtained when the silver vanadium oxide used for the cathodes had the formulation AgV₂O_{5.5}.

The batteries would not effectively discharge below 1.6 V. Thus, a direct comparison of battery discharge data with the n-butyllithium titration is not

TABLE 4

Discharge of Li/silver vanadium oxide cells, capacity to 2.0 V

x in Ag _{x} V ₂ O _{y}	Average (mA h)	1 k Ω load (mA h)	2 k Ω load (mA h)	5 k Ω load (mA h)	Theoretical capacity (mA h)	% Theoretical delivered
0.021	250	230	210	310	2726	9
0.29	337	340	290	380	3047	11
0.76	1648	1525	1600	1820	3112	53
0.83	1961	1851	1973	2060	3378	58
1.0	2090	2050	2100	2120	3417	61
1.06	2112	2023	2116	2196	3417	62
1.19	1997	1924	2007	2060	3213	62
2.0	1708	1725	1660	1740	2950	58

possible as it has been reported that butyllithium has a potential of 1.0 - 1.4 V *versus* lithium [11]. However, in a relative sense, both the chemical tests and battery discharge data show that the silver vanadium oxide formulation with the maximum volumetric energy density is $\text{AgV}_2\text{O}_{5.5}$.

The shape of the discharge curve was affected by the silver vanadium oxide. Figure 2 shows the voltage profiles under 2 k Ω loads for cells constructed with cathodes made from silver vanadium oxides with $x = 0.76$, 1.0, and 2.0. When the silver content was 0.76 the discharge curve sloped sharply from an initial voltage of 3.6 V with short plateaux at 2.9, 2.4, and 2.0 V. The total number of electrons per mole to 2.0 V was 2.5 as calculated from the empirical formula shown in Table 1. When the silver content was 1.0 the voltage decreased with discharge, with short plateaux at 2.8 and 2.1 and a long plateau at 2.5 V. The number of electrons per mole delivered to 2.0 V was 3.0 yielding $\text{Li}_3\text{AgV}_2\text{O}_{5.5}$. When the silver content was 2.0 the discharge curve consisted of two long plateaux at 3.1 V and 2.3 V with a sharply decreasing voltage region joining them. The number of electrons per mole was 1.73 - 2.0 V. The silver vanadium oxide sample where $x = 1.0$ delivered the highest number of equivalents per mole.

Along with low rate behaviour, the ability of the cells to deliver one second 5 or 10 mA constant current pulses was evaluated. Once per week a train of five, one-second pulses, with one second of open circuit rest after each pulse, was applied. The voltage response of each cell was monitored with a recording oscilloscope. Several characteristics were common to all

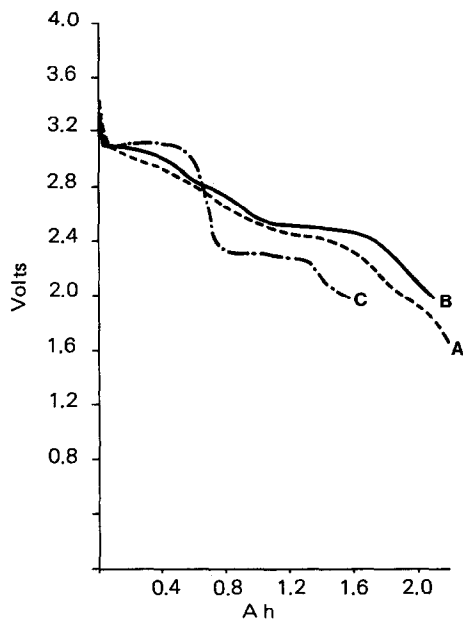


Fig. 2. Constant resistance, 2 k Ω , discharge of lithium/silver vanadium oxide, $\text{Ag}_x\text{V}_2\text{O}_y$, batteries where A, $x = 0.76$; B, $x = 1.0$; C, $x = 2.0$.

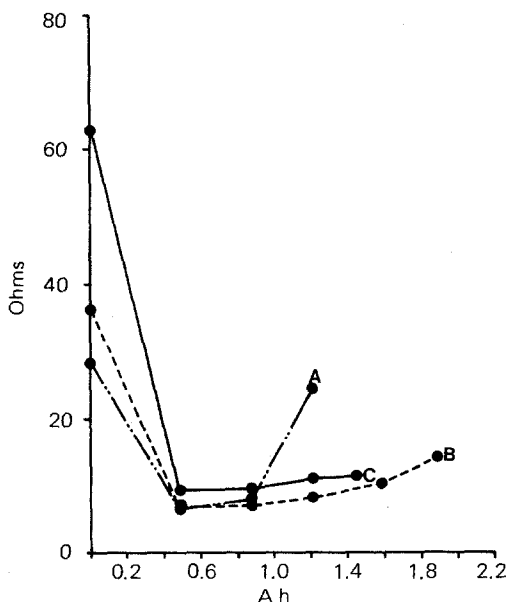


Fig. 3. Cell resistance calculated from voltage drop under pulse trains consisting of five, 5 mA one-second-pulses, with one second rest after each pulse, applied to lithium/silver vanadium oxide, $\text{Ag}_x\text{V}_2\text{O}_y$, batteries where A, $x = 0.76$; B, $x = 1.0$; C, $x = 2.0$ in $\text{Ag}_x\text{V}_2\text{O}_y$.

cells tested under the pulse schemes. The first pulse train for a fresh cell showed the largest voltage drop and ranged from 140 to 300 mV under 5 mA pulses. The voltage drop under pulse decreased with discharge to a minimum of 30 mV at 20 - 50% depth of discharge and then began to increase again. Cells were constructed with internal lithium reference electrodes to investigate this behavior further. Pulse testing of these cells revealed that the initial large voltage drop during the first pulse train in a fresh cell was due to anode passivation. After about 1% discharge the voltage drop at the anode remained at a constant low level. The voltage drop at the cathode paralleled that of the cell during the remaining life of the cell and showed the decreasing and then increasing voltage drop under pulse with discharge of the cell. This behavior is characteristic of the silver vanadium oxide system and occurred in all cells tested.

For comparative purposes a calculated cell resistance was determined for each pulse train by dividing the difference between the open circuit voltage and the lowest voltage under the third pulse of each train by the applied current. Figure 3 shows the calculated cell resistance for cells with cathodes with silver levels of $x = 0.76$, 1.0, and 2.0. The Figure graphically illustrates that the voltage drop was not constant throughout the discharge of the cell. The smallest voltage drop was consistently seen with the cells that had cathodes with silver contents of $x = 1.0$.

Conclusions

Silver vanadium oxide samples were prepared with silver to vanadium ratios that ranged from 0.01 to 1.0. The samples were analyzed by atomic absorption spectroscopy and empirical formulae were assigned. X-ray powder diffraction allowed determination of the materials' structures. Reaction of silver vanadium oxide with butyllithium indicated that the material with a composition of $\text{AgV}_2\text{O}_{5.5}$ had the highest volumetric energy density. This finding was supported by discharge results of lithium/silver vanadium oxide cells with cathodes made from $\text{AgV}_2\text{O}_{5.5}$. These cells also showed the smallest voltage drop under applied constant current pulses. Thus, of those tested, the silver vanadium oxide that is most suitable for use in high energy density lithium batteries has the formulation $\text{AgV}_2\text{O}_{5.5}$ and yields $\text{Li}_3\text{AgV}_2\text{O}_{5.5}$ on discharge. The $3\text{Li}/\text{AgV}_2\text{O}_{5.5}$ couple has a theoretical energy density of 1.5 Wh g^{-1} and delivers 0.28 Ah g^{-1} to 2.0 V.

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