Solid-State Cathode Materials for Lithium Batteries: Effect of Synthesis Temperature on the Physical and Electrochemical Properties of Silver Vanadium Oxide

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Silver vanadium oxide (SVO, $AgV_2O_{5.5}$) was synthesized for use as a cathode material in lithium/SVO batteries. The material was prepared via a solid-state thermal reaction of silver nitrate and vanadium pentoxide in the presence of air. The surface morphology of the final product was found to be dependent on the temperature of synthesis of the material, as evidenced by SEM analysis of the samples. SVO synthesized at 320 and 375 °C displayed irregularly shaped particles, while material prepared at 450 °C was needlelike. SVO synthesized at 540 °C appeared to be a mixture of large crystalline plates and irregular particles. All of the samples were analyzed by DSC, chemical analysis, X-ray powder diffraction, resistivity measurements, and constant-resistance discharge of Li/SVO test cells. The experimental capacities of the lower temperature materials (320, 375 °C) were similar to that found for SVO prepared at 450 °C. A significant decrease in delivered capacity was noted when the SVO prepared at 540 °C was used as a cathode material.

Introduction

The semiconductive properties and tunnellike structure of silver vanadium oxide ($AgV_2O_{5.5}$, SVO) led to the investigation of this material for use in lithium power sources.[1,2] Successful application of SVO in these systems developed into the commercial production of Li/SVO batteries suitable for use as power sources for implantable biomedical devices.[3–5] Several recent studies have explored the reaction of lithium with SVO, focusing on the electrochemical properties of this system.[6–9] The synthesis of silver vanadium oxide is typically performed via the solid-state reaction of silver or a silver salt with vanadium oxide at high temperature (from 400 to 750 °C).[10–18] Recent interest in low-temperature sol–gel preparations of vanadium oxides[19] and vanadium bronzes[20,21] for the formation of kinetically stabilized solids has led us to examine the effect of synthesis temperature on solid-state SVO preparation. We have found that a solid-state synthesis of SVO at a slightly lower temperature provides a cathode material which possesses comparable or enhanced properties for lithium cells. This report details the synthesis of SVO at a series of temperatures, followed by the solid-state physical characterization of the materials. These results are compared with an electrochemical characterization of the samples in a Li/SVO battery system, to determine the application of these materials to lithium battery technology.

Experimental Section

Silver vanadium oxide was synthesized from a mixture of vanadium pentoxide with an aqueous solution of silver nitrate, using a ratio of silver to vanadium of 1:2. The mixture was brought to dryness and heated at incremental temperatures of 230, 260, and 300 °C. The final heating step was set to either 320, 375, 450, or 540 °C. All of the samples were heated under an air atmosphere, and ground at regular intervals throughout the synthesis to ensure adequate mixing of components.

Caution! The decomposition of NO_3^- during SVO synthesis liberates NO_x gas, which is highly toxic. This synthesis should only be performed in a well-ventilated fume hood.

X-ray powder diffraction spectra of silver vanadium oxide were recorded on a Siemens Diffrac 500 instrument using Cu Kα radiation. Spectra were recorded from 10 to 80° (2θ). Si powder (99.999%, Aldrich Chemical) was used as an internal standard for the samples. SEM micrographs of solid SVO samples were recorded at 1000 magnification using an ISI ABT-55 instrument. Differential scanning calorimetry (DSC) analyses of the SVO samples were obtained using a du Pont Instruments TA 2000 DSC/DTA. The samples were analyzed under a purge of argon (120 mL/min) in hermetically sealed Al plans pans to 600 °C at a heating rate of 20 °C/min. Multiple SVO samples were prepared

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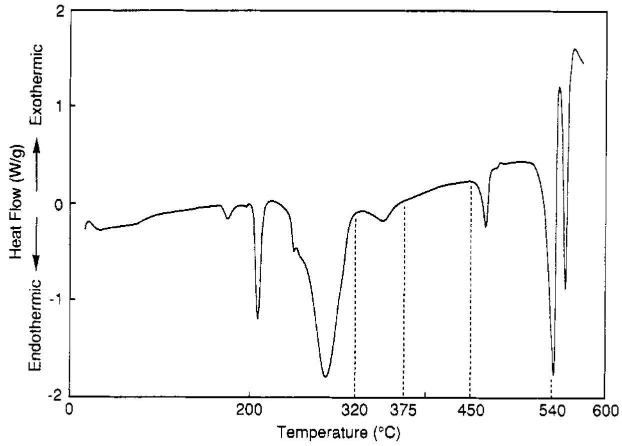

Figure 1. Differential scanning calorimetry curve for a 1:1 mixture of $AgNO_3$ and V_2O_5 measured under a purge of Ar gas. A heating rate of 20 °C/min and an argon purge rate of 120 mL/min was employed for the analysis. The dashed lines indicate the temperature of synthesis for the different SVO materials examined in this study.

independently at 375 °C, and all consistently displayed the same DSC curves. Chemical analysis of the SVO samples dissolved in sulfuric acid was performed via a combination of potassium permanganate titrations and sulfur dioxide reduction of the vanadium components of the materials.[8] Resistivity of silver vanadium oxide was measured via the linear four-point method,[22] on pellets sintered in air for 18 h. The pellets contained 1.2 g of SVO and were pressed under a pressure of 0.54 kg/m^2. One set of pellets was sintered at 300 °C, while the sinter temperature was varied for the second group to correspond to the maximum temperature used in the synthesis of the particular sample. The electrochemical test cell consisted of a single cathode sandwiched between two anodes. The cathode contained 94% silver vanadium oxide, 1% carbon, 2% graphite, and 3% Teflon. The cathode was formed by compressing the mix on a titanium current collector at a pressure of 0.54 kg/m^2. Anodes consisted of lithium metal pressed onto a nickel current collector. All assemblies were performed under a dry-air atmosphere. Two layers of polypropylene separator were placed between the cathode and each anode, and the electrodes were held in position by glass plates. The electrode assembly was placed in a glass jar, filled with 1 M lithium hexafluoroarsenate in 50/50 by volume propylene carbonate/dimethoxyethane electrolyte. The cell was capped and tested under a constant resistance load of 200 Ω at 25 °C.

Results and Discussion

Silver vanadium oxide samples were prepared by the thermal decomposition of silver nitrate and vanadium pentoxide under an air atmosphere. The synthesis of SVO in air and from an aqueous solution may favor dissociation and result in mixed valence states for the vanadium compound. However, the synthetic conditions in this study were chosen to mimic actual conditions which can be scaled up for an industrial process. The final temperature of the solid state synthesis was set at either 320, 375, 450, or 540 °C. These temperatures were specifically chosen following analysis of the DSC curve for a 1:1 mixture of $AgNO_3$ and V_2O_5, which is illustrated in Figure 1. The DSC curve for this mixture displays a major endothermic peak centered at 285 °C related to the decomposition of nitrate. All of the synthetic temperatures were chosen to be above this decomposition temperature. The 320 °C temperature preceded a broad but weak endotherm centered at 350 °C, while the synthesis temperature of 450 °C occurred directly before the onset of a sharp endotherm at 463 °C. The 540 °C temperature was set just prior to a very sharp endothermic peak centered at 541 °C. The final temperature of 375 °C followed a weak endotherm in the curve and was chosen based on the use of this temperature in the synthesis of SVO in previous studies.[7,8] All of the samples liberated NO_x gas during the reactions, indicating that the thermal decomposition of nitrate had taken place in each case. The DSC curve for the mixture of V_2O_5 and $AgNO_3$ presented in Figure 1 also displays endothermic peaks at 176 and 212 °C. These endotherms are present in the DSC curve measured for $AgNO_3$ alone, and appear to be related to the melting of the silver salt (lit. mp 212 °C).[23]

The surface morphology of the SVO materials synthesized at these temperatures was examined by SEM analysis of the samples, with the micrographs displayed in Figure 2. The samples synthesized at 320 and 375 °C possess similar conglomerations of smaller (~5–10 μm) irregularly shaped particles. In contrast, the sample synthesized at 450 °C displays thin needlelike particles, which are <1 μm in diameter and on the order of 10–20 μm in length. The appearance of these needles is quite distinct from that of the materials synthesized at lower temperature. Finally, the material heated to 540 °C displays a completely different surface morphology, with larger rectangular plates (e.g., 10 × 40 μm in dimension) mixed with irregular particles.

Thermal analysis of the SVO materials was conducted, and the DSC curves obtained for the samples are displayed in Figure 3. As found with SEM, the samples synthesized at 320 and 375 °C give nearly identical results, consistent with compositionally similar species. The appearance of a small, sharp endothermic transition at 463 °C in the DSC of these materials suggests that some $AgVO_3$ impurity may exist in the samples, since $AgV_2O_{5.5}$ is known to form a eutectic with $AgVO_3$ which melts at 463 °C.[24] On the basis of transitions assigned to the composition of $AgV_2O_{5.5}$ in a phase diagram for the mixture of $AgVO_3$ and V_2O_5 reported by Volkov et al.[24] (Table I), the remaining endotherms of 537 and 552 °C in the DSC curve are most likely due to a peritectic transformation (527 °C) and eutectic point (545 °C). The melting point of $AgV_2O_{5.5}$ is ~640 °C, which is beyond the 600 °C limit of the experiment. In comparison to the samples synthesized at lower temperatures, the 450 °C sample gives a simpler DSC curve. The endotherm at 463 °C is now absent, with an increase in the transition at 537 °C. This result suggests that the 450 °C SVO material is more homogeneous than the samples prepared at 320 and 375 °C. With this in mind, it is not surprising that the SEM micrographs of the 450 °C sample are so different from the low-temperature materials. The sample prepared at 540 °C again displays quite different results, where the DSC curve (Figure 3) shows the reappearance and increase in the transition at 463 °C, along with a broad transition centered at 516 °C and a new sharp endotherm at 564 °C. Since the 540 °C temperature of synthesis is above the peritectic temperature of 527 °C and close to the phase-transition temperature of 545 °C, it is likely that a new phase of SVO was formed. At the composition of the ε- phase

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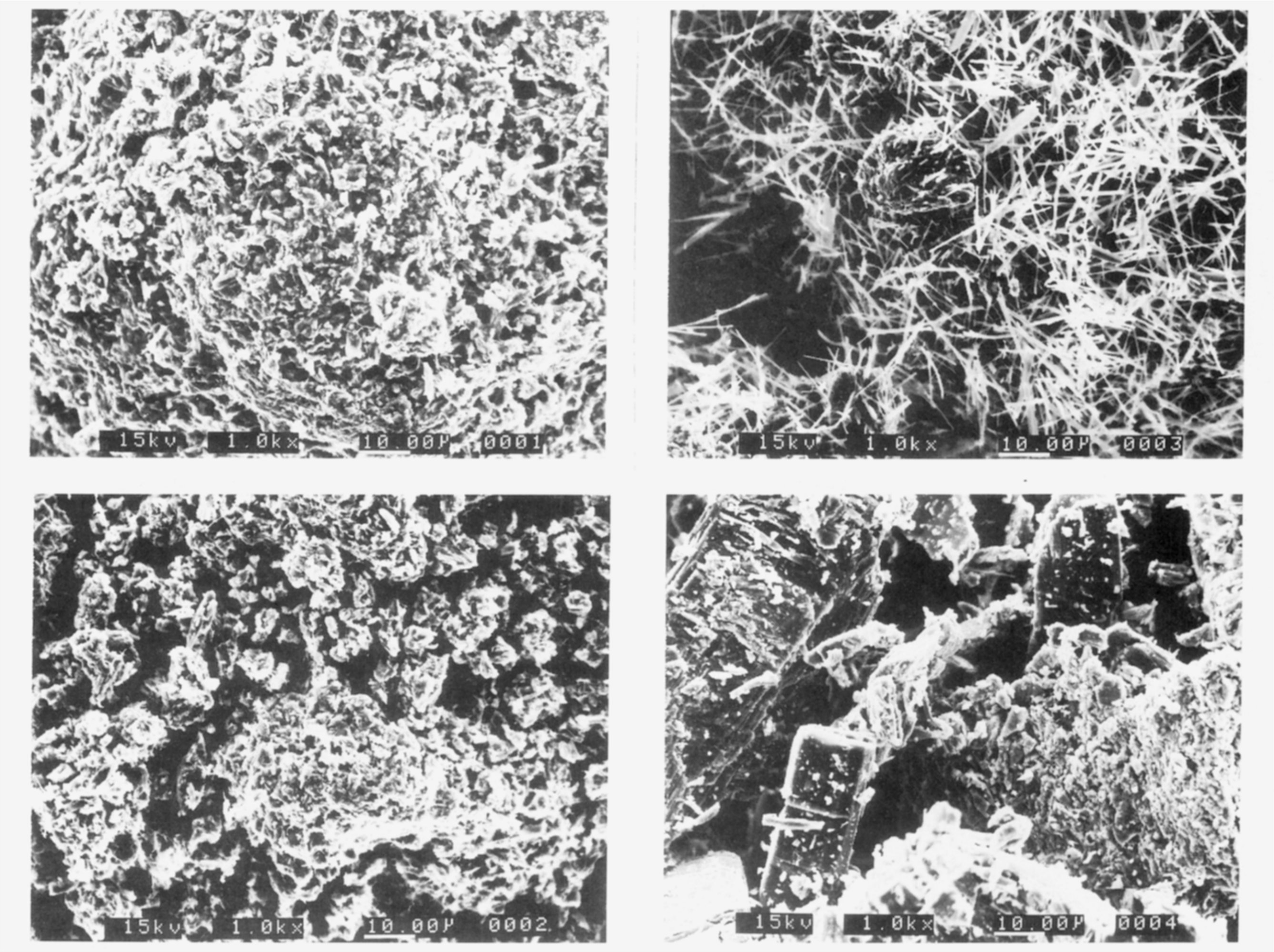

Figure 2. SEM micrographs (1000× magnification) of (A) 320 °C SVO, (B) 375 °C SVO, (C) 450 °C SVO, and (D) 540 °C SVO.

($Ag_2V_4O_{10.85}$) in the phase diagram for $AgVO_3$ and V_2O_5, a mixture of $Ag_{1.2}V_3O_8$ (γ-phase) and liquid SVO develops above 545 °C.[24] The γ-phase is a low-silver form of SVO, and the formation of this material would be consistent with the simultaneous appearance of high-silver $AgVO_3$ in the material.

Chemical analysis of the samples provided information on the oxidation states of the vanadium components of the materials. The respective percentages of vanadium(IV) and vanadium(V) present in the samples are listed in Table II along with the empirical formulas calculated for these species. The SVO samples synthesized from 320 to 450 °C contained primarily vanadium(V), with only a small amount (1–2%) of vanadium(IV). However, the sample prepared at 540 °C contained slightly more vanadium(IV), at 10% of the entire vanadium content. The increased amount of vanadium(IV) in this sample most likely results from a chemical reaction taking place at 540 °C, since the phase-transition temperature of 545 °C produces a mixture of liquid and γ-phase material (Table I). SVO is known to undergo disproportionation with melting.[10]

X-ray powder diffraction was also used to characterize the materials, and the powder patterns are presented in Figure 4. Despite the apparent differences in surface morphology for the 320/375 and 450 °C samples from the SEM photos, the X-ray data are quite similar for these species. In particular, the overall peak intensities for the samples are very close, suggesting that these materials possess similar degrees of crystallinity. The results of the experiments are summarized in Table III, and all three of these samples display spectra corresponding to that reported for $Ag_2V_4O_{11}$.[25,26] In contrast, the 540 °C sample displays a new crystalline material, as well as peaks corresponding to $Ag_2V_4O_{11}$. The new phase in this sample displays intense peaks at 3.54, 3.03, 3.00, and 2.36 Å, which is a good match for the powder pattern corresponding to $Ag_{1.2}V_3O_8$ (γ-phase) reported by Casalot and Pouchard.[27] In addition, low-intensity signals corresponding to α-$AgVO_3$[25] are also found in the pattern. The X-ray diffraction result is in agreement with the findings from the thermal analysis of the 540 °C SVO sample, where a mixture of the γ-phase and $AgVO_3$ was detected. It should be noted that the X-ray powder pattern for the γ-phase is distinct from that found for the δ-phase of SVO ($Ag_xV_2O_5$, $0.67 > x > 0.86$).[27] The formation of γ-phase SVO at 540 °C in this study is consistent with the presence of oxygen during the synthesis of the material.

The conductivity of the samples was analyzed via resistivity measurements of pressed plates of SVO, and the results are given in Table IV. The plates sintered at 300 °C containing 320 and 375 °C SVO produced comparable results, while the 450 °C sample displayed significantly lower resistivity. This may be another indication of the difference in particle shape and size between the 320/375 and 450 °C samples, as first deter-

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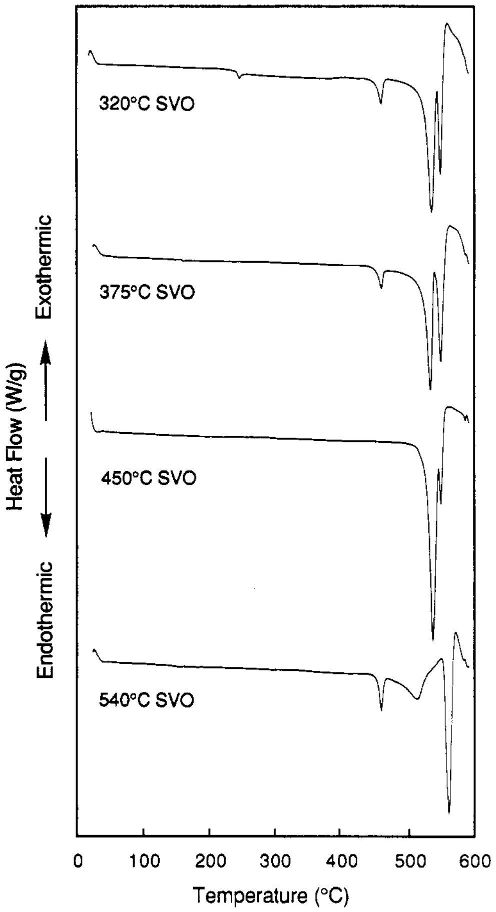

Figure 3. Differential scanning calorimetry curves for SVO samples measured under a purge of Ar gas. A heating rate of 20 °C/min and an argon purge rate of 120 mL/min was employed for the analysis.

Table I. Phase Transitions for the V_2O_5–$AgVO_3$ System[a]

composition	temp (°C)	phase
V_2O_5	<675	V_2O_5
	>675	liquid
$Ag_{0.17}V_2O_x$	<670	V_2O_5 + β phase
	670–716	liquid + β phase
	>716	liquid
$Ag_{0.48}V_2O_x$	<730	β phase
	>730	liquid
$Ag_{0.58}V_2O_x$	<545	β phase + γ phase
	545–721	liquid + β phase
	>721	liquid
$Ag_{0.74}V_2O_x$	<545	γ phase
	545–700	liquid + β phase
	>700	liquid
$Ag_{0.86}V_2O_x$	<525	γ phase + ϵ phase
	545–675	liquid + γ phase
	>675	liquid
$Ag_{1.0}V_2O_x$	<527	ϵ phase
	545–641	liquid + γ phase
	>641	liquid
$Ag_{1.5}V_2O_x$	<463	ϵ phase + $AgVO_3$
	463–513	liquid + ϵ phase
	>513	liquid
$Ag_2V_2O_6$	<463	$AgVO_3$
	>476	liquid

[a] Reference 24.

mined by SEM. The 540 °C sample displayed the lowest resistivity of any of the samples. It should be noted that resistivity measurements of this type are highly sensitive to grain boundaries in the pressed powder plates,[22] which may depend on the surface morphology of the sample. Interpretation of these results have thus been limited to determining trends in the conductivity of the pressed plates. However, similar values have been reported for other silver vanadium bronzes. Electrical conductivity measurements were reported for polycrystalline pellets of β-$Ag_xV_2O_5$ ($0.29 < x < 0.41$) sintered at 450 °C, giving resistivity values of 3–25 Ω cm at room temperature.[28] SVO of the δ-phase also provided comparable results, giving 1 Ω cm at 25 °C.[29,30] When pressed plates of the different samples from this study were sintered at the temperatures used for the original synthesis of the materials, the resistivities followed the same trend, but with significantly lower resistance. This result highlights the substantial effect of sinter temperature on the measurements.

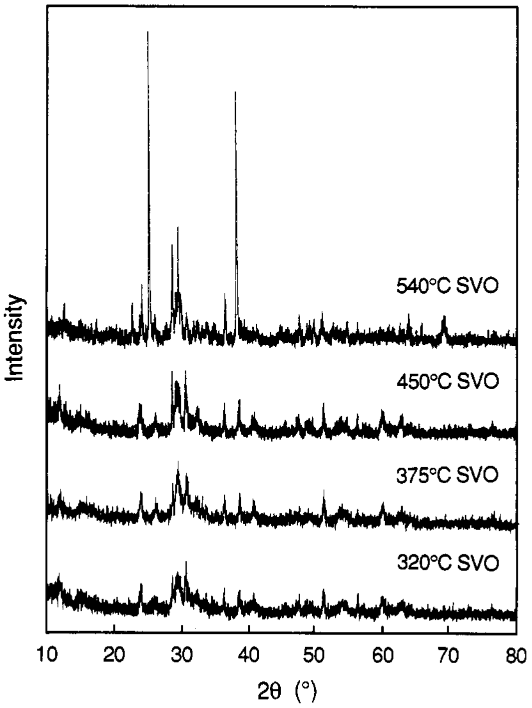

Figure 4. X-ray powder diffraction patterns of SVO samples recorded using Cu Kα radiation.

Table II. Chemical Analyses of Silver Vanadium Oxide Materials

synth temp (°C)	% V^{4+}	% V^{5+}	empirical formula
320	2	98	$AgV_2O_{5.48}$
375	2	98	$AgV_2O_{5.48}$
450	1	99	$AgV_2O_{5.49}$
540	10	90	$AgV_2O_{5.40}$

Since the ultimate goal of this work was to investigate the properties of SVO as a cathode material, test batteries were assembled using the SVO samples, with lithium anodes and organic electrolyte. These cells were discharged under constant resistance loads at room temperature, and the capacities of the SVO samples were calculated on a per weight basis. Excess lithium and electrolyte were used in the cells, so that capacity was limited by the cathode material. The experimental capacity results are listed in Table V. From these results it is apparent that SVO synthesized at 320 and 375 °C delivers as much capacity as material prepared at 450 °C.

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Table III. X-ray Powder Diffraction Peaks (*d* Spacings, Intensities) for SVO Samples

320 °C SVO		375 °C SVO		450 °C SVO		540 °C SVO		$Ag_2V_4O_{11}$[a]		$Ag_2V_4O_{11}$[b]	
d (Å)	int	d (Å)	int	d (Å)	int	d (Å)	int	d (Å)	int	d (Å)	int
7.62	60	7.56	40	7.41	50	7.05	10	7.46	60	7.50	60
5.94	30	5.94	30	5.94	30	5.94	5	3.74	30	3.75	70
3.71	40	3.82	50	3.75	50	5.13	10	3.69	30	3.71	30
3.70	60	3.75	40	3.71	50	3.93	15	3.41	60	3.43	70
3.45	40	3.45	30	3.44	30	3.75	10	3.06	80	3.08	70
3.03	80	3.06	100	3.03	80	3.70	20	2.99	80	3.00	60
3.01	70	3.01	70	3.00	70	3.54	100	2.90	100	2.92	100
2.92	100	2.93	80	2.93	100	3.43	10	2.76	80	2.77	80
2.79	40	2.79	40	2.77	40	3.07	15	2.65	30	2.66	40
2.48	50	2.49	40	2.48	50	3.03	40	2.46	30	2.46	40
2.35	40	2.34	50	2.34	50	3.00	40	2.32	60	2.32	70
2.22	40	2.23	40	2.22	30	2.92	10	1.86	10	2.20	60
2.00	20	1.97	20	2.00	20	2.83	5	1.78	60	1.99	10
1.98	10	1.92	20	1.92	30	2.77	5	1.71	10	1.96	10
1.92	40	1.87	20	1.88	20	2.66	5	1.67	30	1.86	40
1.79	50	1.79	50	1.70	50	2.58	5	1.60	10	1.83	10
1.70	30	1.71	30	1.72	30	2.47	20	1.53	30	1.78	70
1.69	20	1.69	20	1.68	30	2.36	80	1.47	10	1.70	40
1.63	40	1.63	20	1.64	30	2.20	5			1.67	60
1.54	30	1.54	30	1.54	40	2.03	5			1.60	30
1.48	20	1.48	30	1.48	30	1.91	10			1.54	70
						1.84	5			1.47	60
						1.78	10				
						1.66	5				
						1.62	5				
						1.45	10				
						1.36	10				

[a] Reference 25. [b] Reference 26.

Table IV. Resistivity Values for SVO Plates Pressed at 0.54 kg/m^2 and Sintered under Air

synth temp (°C)	sinter temp (°C)	resistivity (Ω cm)	synth temp (°C)	sinter temp (°C)	resistivity (Ω cm)
320	300	2120	320	320	1060
375	300	1790	375	375	540
450	300	710	450	450	195
540	300	90	540	540	8

Table V. Experimental Capacities for Li/SVO Cells Containing 1 M $LiAsF_6$ PC/DME Electrolyte

synth temp (°C)	exptl capacity			
	to +2.0 V cutoff		to +1.5 V cutoff	
320	256 Ah/kg	633 Wh/kg	299 Ah/kg	702 Wh/kg
375	262 Ah/kg	650 Wh/kg	296 Ah/kg	705 Wh/kg
450	257 Ah/kg	630 Wh/kg	294 Ah/kg	690 Wh/kg
540	216 Ah/kg	523 Wh/kg	238 Ah/kg	558 Wh/kg

Furthermore, little difference was found in the shape of the voltage vs time curves for the samples synthesized from 320 to 450 °C. However, use of the highest temperature (540 °C) material did result in a significant decrease in delivered capacity. A comparison of the voltage versus time discharge curves for Li/SVO cells containing 375 and 540 °C material is displayed in Figure 5.

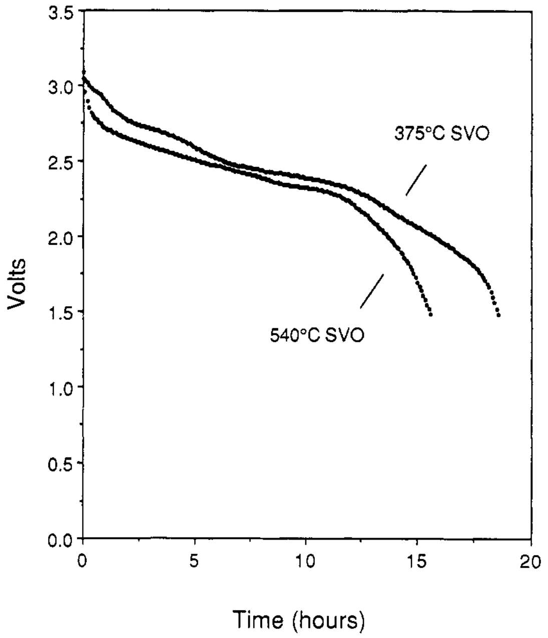

Figure 5. Constant resistance (200 Ω) discharge of lithium/SVO in 1 M $LiAsF_6$ 50/50 by volume propylene carbonate/dimethoxyethane electrolyte at 25 °C.

Conclusions

The synthesis of silver vanadium oxide at temperatures of 320 and 375 °C produced irregularly shaped particles, quite different in appearance from the needlelike particles found for SVO prepared at 450 °C. Thermal analysis of the samples displayed identical constituents for the 320 and 375 °C samples, while the 450 °C SVO appeared to be more homogeneous. The difference in particle morphology between these samples was reflected in resistivity measurements of pressed plates of the materials, where the needles of the 450 °C sample provided lower resistance. In contrast to these differences, the X-ray powder diffraction patterns for the 320–450 °C samples were found to be very similar, and the resulting discharge of Li/SVO test cells also provided similar experimental capacity values for all three samples. The synthesis of SVO at 540 °C, near the phase transition temperature, resulted in a very different material. SEM, DSC, chemical analysis, X-ray powder diffraction, and resistivity values were all very different from results for the samples prepared at lower temperatures and pointed to a complex composition for the 540 °C material. In addition, the delivered capacity of a Li/SVO cell containing this material was found to be significantly lower than that for the other samples.