

Synthesis and characterization of a new trimetallic cathode material for lithium batteries

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Abstract

A new cathode material ($\text{Cu,Ag,V}_2\text{O}_5$) was investigated as a candidate for lithium batteries. Silver and copper-containing starting materials were examined in this study, using silver oxide, copper oxide, silver metal and copper metal, in addition to silver and copper nitrate. The Ag:Cu:V metal ion ratios were systematically varied to study the effect of this parameter on the electrochemical properties of the material. For $\text{Cu,Ag,V}_2\text{O}_5$ the metal ion ratios were in the range: $0.1 \leq x \leq 0.6$ and $0.2 \leq y \leq 0.8$, with $5.2 \leq z \leq 5.9$ for oxygen. The samples were characterized by differential scanning calorimetry, scanning electron microscopy, X-ray powder diffraction, and constant resistance discharge of test cells. The experimental capacity of $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{V}_2\text{O}_{5.75}$ (initial open-circuit voltage = +3.8 V versus Li/Li^+) discharged to +1.5 V versus Li/Li^+ was 332 mAh/g, resulting in the formation of $\text{Li}_{3.4}\text{Cu}_{0.5}\text{Ag}_{0.5}\text{V}_2\text{O}_{5.75}$. © 1997 Elsevier Science S.A.

Keywords Lithium batteries, Lithium, Cathodes; Silver; Copper, Vanadium

1. Introduction

Solid-state metal oxides have been used successfully as the cathode materials for both primary lithium and secondary lithium-ion batteries [1,2]. Materials such as silver vanadium oxide (AgV_2O_5) have been particularly useful in power sources for implantable biomedical devices, where high current pulses must be supplied by the battery [3,4]. Our research in this area has led to the synthesis and characterization of a new family of trimetallic cathode materials, $\text{Cu,Ag,V}_2\text{O}_5$ (CSV), as candidates for lithium batteries [5,6]. The details of the synthesis as well as the physical and electrochemical characterization of these new solid-state cathode materials are given in this report along with a comparison to existing data for AgV_2O_5 materials. The Cu:Ag:V ratio was systematically varied in the CSV materials, and the effect of the type of starting salts and metals on the final product was studied. Lastly, a comparison of the electrochemical performance of $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{V}_2\text{O}_{5.75}$ is made to the electrochemical performance of simple mixtures of metal oxides in the same Cu:Ag:V ratio of 1:1:4.

2. Experimental

A typical synthesis of CSV is illustrated for $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{V}_2\text{O}_{5.75}$. Silver nitrate, AgNO_3 (16.63 g, 0.098

mol) and copper(II) nitrate hydrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (23.66 g, 0.098 mol) were dissolved in 30 ml of deionized/distilled water. The aqueous salt solution was added to solid vanadium pentoxide, V_2O_5 (35.62 g, 0.196 mol), and the resulting slurry heated at 100 °C to evaporate the water. During this procedure a gel did not form. The resulting dry powder was ground to thoroughly mix the components. The solid was heated at 230 °C under an air atmosphere for 30 min, and mixed again. The temperature of the oven was increased to 260 °C for 2 h, followed by heating at 300 °C for 16 h. The material was then ground again, and heated at 375 °C for 48 h. Upon cooling, the material was used without further preparation. (Caution! The decomposition of nitrate during CSV synthesis liberates NO , gas, which is highly toxic. This synthesis should be performed only in a well-ventilated fume hood.) The oxide-based synthesis of $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{V}_2\text{O}_{5.75}$ utilized Ag_2O and CuO in a 1:2 ratio with 4 equivalents of V_2O_5 , while the metal-based synthesis utilized Ag^0 and Cu^0 powders in a 1:1 ratio mixed in the solid state with 2 equivalents of V_2O_5 . Identical heating times and temperatures (as indicated above) were used for these syntheses, as well as for the preparation of CSV materials using different metal ion ratios.

Differential scanning calorimetry (DSC) analyses of the CSV samples were obtained using a Du Pont Instruments TA 2000 DSC/DTA under a purge of argon (120 ml/min) in hermetically sealed Al pans at a heating rate of 5 °C/min.

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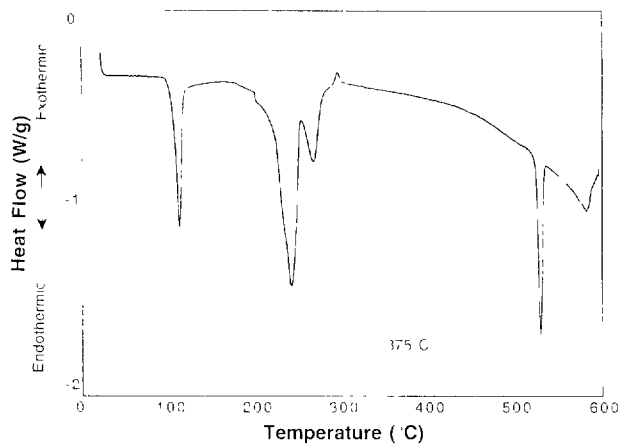


Fig. 1. DSC for a 1:1:2 mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, AgNO_3 , and V_2O_5 , measured under a purge of argon gas (120 ml/min). A heating rate of $5^\circ\text{C}/\text{min}$ was used for the analysis.

Scanning electron microscopy (SEM) graphs of solid CSV samples were recorded using an ISI ABT-55 instrument. X-ray powder diffraction spectra were recorded with a Siemens Diffractometer 500 instrument using $\text{Cu K}\alpha$ radiation.

The CSV cathode materials were incorporated into pressed pellet cathodes and used in test cells with lithium metal anodes and 1 M LiAsF_6 /propylene carbonate (PC)–dimethoxyethane (DME) electrolyte. The cathodes consisted of 94 wt.% CSV along with 3 wt.% polytetrafluoroethylene, 2 wt.% graphite, and 1 wt.% carbon black. The cells were discharged at room temperature under constant resistance loads to a voltage of +1.5 V versus Li/Li^+ [7]. Multiple measurements were recorded under these conditions, with capacity values varying by less than 2% between tests on the same cathode materials. Hermetically sealed, prismatic cells contained $\text{Cu}_{0.16}\text{Ag}_{0.67}\text{V}_2\text{O}_{5.5}$ cathodes, lithium anodes, and 1 M LiAsF_6 /PC–DME electrolyte. These cells were discharged via constant current pulse testing at 37°C to mimic temperature conditions experienced in an implantable medical device. Pulse trains consisted of four 10 s pulses, with 15 s rest between pulses. The pulse trains were applied every 30 min and pulse current density was $18 \text{ mA}/\text{cm}^2$ [8].

3. Results and discussion

3.1. Synthesis

$\text{Cu}_x\text{Ag}_y\text{V}_2\text{O}_z$ (CSV) materials were synthesized via the solid-state reaction of copper and silver starting materials with vanadium pentoxide under air at a maximum temperature of 375°C . Fig. 1 displays the DSC curve for the mixture: $\text{AgNO}_3 + \text{Cu}(\text{NO}_3)_2 + \text{V}_2\text{O}_5$. The copper and silver nitrate salts melt near 120 and 243°C , respectively, and the nitrates decompose below the synthesis temperature of 375°C as indicated by the endotherms displayed in Fig. 1. The ratio of metal ions in the CSV materials was systematically varied to produce materials in the range of $0.1 \leq x \leq 0.6$ and $0.2 \leq y \leq 0.8$ for $\text{Cu}_x\text{Ag}_y\text{V}_2\text{O}_z$, as listed in Table 1. All of the samples were synthesized using the appropriate ratios of AgNO_3 , $\text{Cu}(\text{NO}_3)_2$, and V_2O_5 with the same heating steps described for $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{V}_2\text{O}_{5.75}$. An air atmosphere was used in the synthesis of the CSV materials based on the results of studies of the synthesis of $\text{AgV}_2\text{O}_{5.5}$ (SVO) materials under air and argon atmospheres [9]. The SVO materials prepared under air delivered significantly higher capacity than the SVO samples prepared under an inert atmosphere.

CSV materials were also prepared from silver(I) oxide and copper(II) oxide mixed as dry powders with V_2O_5 and thermally treated as described above. Likewise, silver metal and copper metal were reacted with V_2O_5 at 375°C to produce CSV samples. The bimetallic materials, $\text{Ag}_{0.5}\text{V}_2\text{O}_{5.25}$ and $\text{Cu}_{0.5}\text{V}_2\text{O}_{5.5}$, were prepared from the appropriate mixtures of Ag_2O and CuO with V_2O_5 heated at 375°C under air for 72 h.

3.2. Physical characterization

The thermal properties of the CSV samples were analyzed using differential scanning calorimetry (DSC) between 25 and 600°C . The material $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{V}_2\text{O}_{5.75}$ displayed a single endothermic transition at 535°C , while $\text{Cu}_{0.16}\text{Ag}_{0.67}\text{V}_2\text{O}_{5.5}$ displayed three endothermic transitions at 523, 537 and 592°C . Similar to the thermal properties of $\text{AgV}_2\text{O}_{5.5}$ [7], the

Table 1
Experimental capacities for Li/CSV cells with 1 M LiAsF_6 /PC–DME electrolyte

Cathode	Starting material	Delivered capacity (mAh/g)		Theoretical capacity (mAh/g)
		to +2.0 V	to +1.5 V	
$\text{Cu}_{0.1}\text{Ag}_{0.8}\text{V}_2\text{O}_{5.5}$	Nitrate	258	301	332
$\text{Cu}_{0.16}\text{Ag}_{0.67}\text{V}_2\text{O}_{5.5}$	Nitrate	270	307	344
$\text{Cu}_{0.33}\text{Ag}_{0.55}\text{V}_2\text{O}_{5.6}$	Nitrate	267	316	366
$\text{Cu}_{0.5}\text{Ag}_{0.5}\text{V}_2\text{O}_{5.75}$	Nitrate	285	332	383
$\text{Cu}_{0.4}\text{Ag}_{0.2}\text{V}_2\text{O}_{5.5}$	Nitrate	214	292	396
$\text{Cu}_{0.5}\text{Ag}_{0.5}\text{V}_2\text{O}_{5.75}$	Oxide	245	309	
$\text{Cu}_{0.5}\text{Ag}_{0.5}\text{V}_2\text{O}_{5.75}$	Metal	192	237	
$\text{Ag}_{0.5}\text{V}_2\text{O}_{5.25} + 0.5\text{CuO}$		180	240	
$\text{Cu}_{0.5}\text{V}_2\text{O}_{5.5} + 0.25\text{Ag}_2\text{O}$		143	287	

melting points for the CSV materials are above the 600 °C limit of the DSC experiment.

SEM analysis of the samples was utilized to examine the surface morphology of the CSV materials. The materials synthesized from nitrate-based starting materials displayed agglomerations of small ($\sim 5\text{--}10\ \mu\text{m}$), irregularly shaped particles. These particles were very similar in shape and size to those observed for AgV_2O_5 synthesized at 375 °C from silver nitrate and vanadium pentoxide [7]. CSV prepared from oxide-based starting materials displayed similar agglomerations of irregular particles, but contained significantly smaller particles ($\sim 2\text{--}10\ \mu\text{m}$). The trend to smaller particle size in using Ag_2O precursor was also seen in the synthesis of AgV_2O_5 [9]. The 500°C preparation of SVO from silver oxide and vanadium pentoxide led to the formation of rodlike particles in the order of 1–3 μm in diameter, while use of silver nitrate and vanadium pentoxide starting materials under the same conditions gave rodlike particles in the order of 2–5 μm in diameter.

X-ray powder diffraction was used to characterize $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{V}_2\text{O}_5$, giving d spacings (\AA) of 6.86, 5.34, 3.60, 3.44, 3.09, 3.06, and 1.92. A sample of $\text{Cu}_{0.16}\text{Ag}_{0.67}\text{V}_2\text{O}_5$ displayed d spacings (\AA) of 6.81, 4.36, 3.75, 3.59, 3.45, 3.08, 3.03, 2.97, 2.34, 1.79, and 1.55. Both samples displayed relatively broad peaks of low intensity, indicating that these samples are of low crystallinity, similar to the nearly amorphous samples of AgV_2O_5 [7] produced at 375 °C.

3.3. Electrochemical characterization

The electrochemical properties of the CSV samples were examined to determine the ability of these materials to act as cathodes in lithium batteries. The cathode materials were discharged at room temperature against lithium metal anodes using organic electrolyte, and the capacities of the CSV samples were calculated on a per weight of active material basis. Excess lithium and electrolyte were used in the test cells, so that the capacity was limited by the cathode. The experimental capacities for these materials are summarized in Table 1. For CSV samples synthesized from nitrate-based starting materials containing different metal ion ratios, $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{V}_2\text{O}_5$ delivered the highest capacity to both the +2.0 and +1.5 V cutoffs. Also, comparing the experimental capacities of samples of $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{V}_2\text{O}_5$ synthesized from nitrate, oxide and metal-based starting materials (Table 1), shows that the nitrate-based material delivers the highest capacity. Similar electrochemical studies carried out with AgV_2O_5 cathode materials displayed lower capacity for SVO prepared from silver metal when compared with materials prepared from silver nitrate and silver oxide [9].

Theoretical capacities for the CSV samples prepared with different metal ion ratios were calculated based on the amount of lithium needed to electrochemically reduce all of the Ag^+ to Ag^0 , Cu^{2+} to Cu^+ and Cu^+ to Cu^0 , V^{5+} to V^{4+} and finally, 25% of the V^{4+} to V^{3+} . The amount of lithium was converted to capacity using the conversion factor of 3.86 Ah/g for

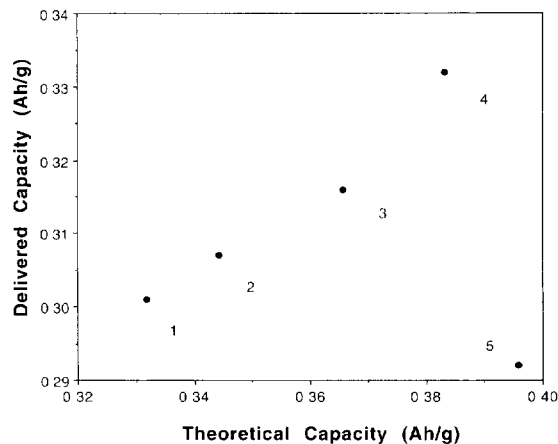


Fig. 2. Plot of delivered capacity (to a +1.5 V cutoff) vs. theoretical capacity for CSV cathode materials: (1) $\text{Cu}_{0.1}\text{Ag}_{0.8}\text{V}_2\text{O}_5$; (2) $\text{Cu}_{0.16}\text{Ag}_{0.67}\text{V}_2\text{O}_5$; (3) $\text{Cu}_{0.33}\text{Ag}_{0.55}\text{V}_2\text{O}_5$; (4) $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{V}_2\text{O}_5$; and (5) $\text{Cu}_{0.4}\text{Ag}_{0.2}\text{V}_2\text{O}_5$. The Li/CSV cells were discharged under a constant resistance (200 Ω) load using 1 M $\text{LiAsF}_6/\text{PC-DME}$ 50/50 by volume at 25 °C.

lithium. This calculation is similar to that used to determine the theoretical capacity of 315 mAh/g (3.5 equiv of Li) for AgV_2O_5 [10]. These calculated capacity values are given in Table 1, and plotted against the delivered capacity values for the Li/CSV cells discharged to +1.5 V versus Li/Li^+ in Fig. 2. Close examination of this plot shows that the delivered capacity from four of the samples: $\text{Cu}_{0.1}\text{Ag}_{0.8}\text{V}_2\text{O}_5$, $\text{Cu}_{0.16}\text{Ag}_{0.67}\text{V}_2\text{O}_5$, $\text{Cu}_{0.33}\text{Ag}_{0.55}\text{V}_2\text{O}_5$, and $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{V}_2\text{O}_5$, closely resembles the theoretical capacity for these materials, giving a linear relationship ($R^2 = 0.966$) between these data points. However, the material $\text{Cu}_{0.4}\text{Ag}_{0.2}\text{V}_2\text{O}_5$ does not deliver the capacity expected based on the calculated theoretical capacity. Interestingly, silver vanadium oxide samples utilizing a low amount of silver ($x = 0.29$ and 0.021 in $\text{Ag}_x\text{V}_2\text{O}_5$) also delivered very low capacities when compared with SVO samples with higher concentrations of silver [11]. The low delivered capacity for the silver deficient SVO materials was attributed to a low conductivity for the materials when partially lithiated, which did not allow the materials to discharge effectively [11]. Applied to the CSV samples tested here, this demonstrates that a certain percentage of silver (between $y = 0.2$ and 0.5 in $\text{Cu}_y\text{Ag}_{1-y}\text{V}_2\text{O}_5$) is critical to maintaining the discharge performance of the CSV materials. Furthermore, the amount of copper(II) in the sample apparently provides oxidizing equivalents to the cathode material which can be readily predicted based on theoretical capacity calculations.

The voltage versus time plot for the discharge of the Li/ $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{V}_2\text{O}_5$ cell is displayed in Fig. 3. The discharge of this material to +1.5 V results in the formation of a material with a nominal composition of $\text{Li}_{3.4}\text{Cu}_{0.5}\text{Ag}_{0.5}\text{V}_2\text{O}_5$. However, at this potential the silver and copper ions will be reduced to Ag^0 and Cu^0 , as seen in the lithiation of AgV_2O_5 [12] and CuV_2O_6 [13], and these reduced metals likely deposit out of the lithiated product. X-ray powder diffraction of electrochemically lithiated AgV_2O_5 samples displayed

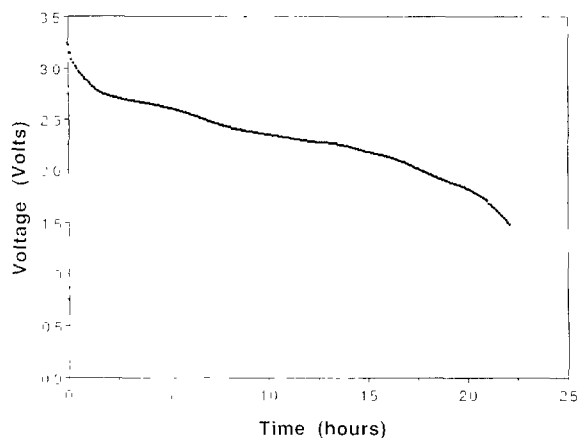


Fig. 3. Constant resistance (200 Ω) discharge of Li/Cu_{0.5}Ag_{0.5}V₂O_{5.75} in 1 M LiAsF₆/PC-DEM 50/50 by volume at 25 °C.

well-resolved peaks due to silver metal [12], suggesting that lithium replaces silver between the vanadium oxide layers of the material. The formation of elemental silver in this system took place at the beginning of the discharge reaction. In a similar manner, X-ray diffraction patterns of lithium/copper vanadate systems discharged beyond 20% depth-of-discharge showed the presence of elemental copper [13]. Based on these results it is likely that the reduction of Ag⁺ to Ag⁰, and Cu²⁺ to Cu⁺ and Cu⁰ take place near the start of the CSV discharge reaction. The reduction of V⁵⁺ to V⁴⁺ and partial reduction of V⁴⁺ to V³⁺ must also take place during the discharge of the CSV materials, given the high delivered capacity values measured for these samples (Table 1).

Hermetically sealed, prismatic cells were constructed to test the high-rate pulse discharge performance of the Li/CSV system. The pulse discharge test was employed to determine the ability of the cathode materials to withstand a heavy discharge load, an important function in batteries for implantable biomedical devices. These Li/Cu_{0.16}Ag_{0.67}V₂O_{5.5} cells were discharged via constant current pulse testing at 37 °C. The open-circuit voltage and minimum pulse voltage for each pulse train are plotted in Fig. 4. As can be seen in the plot, the CSV cathode material is able to deliver high capacity

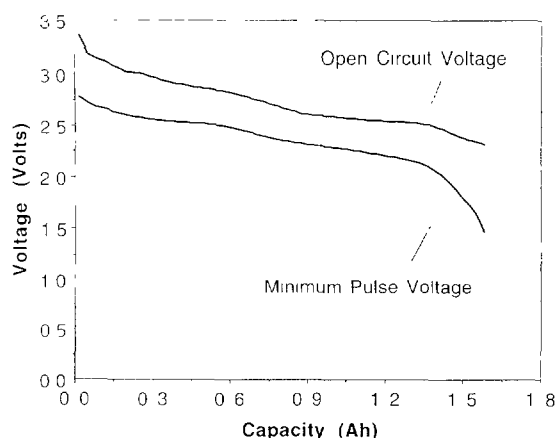


Fig. 4. Voltage vs. capacity curve for Li/Cu_{0.16}Ag_{0.67}V₂O_{5.5} cell pulse discharged at 37 °C with a current density of 18 mA/cm².

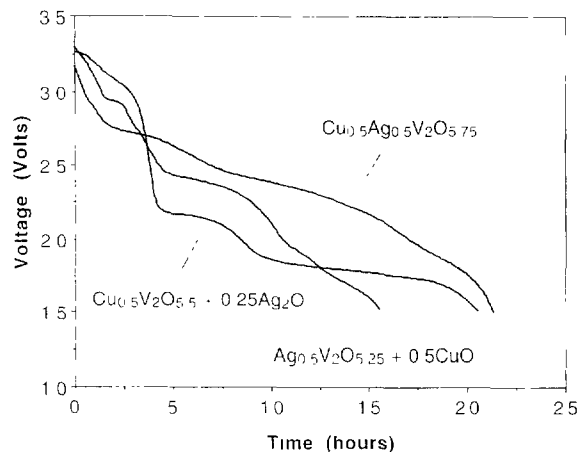


Fig. 5. Constant resistance (200 Ω) discharge of Li/Cu_{0.5}Ag_{0.5}V₂O_{5.75} and Li/mixed metal oxide cathodes in 1 M LiAsF₆/PC-DEM 50/50 by volume at 25 °C.

under high-rate discharge conditions, similar to the results of high-rate discharge of Li/SVO batteries [9].

The discharge performance of one of the new trimetallic CSV cathode materials, Cu_{0.5}Ag_{0.5}V₂O_{5.75}, was compared with the performance of a mixture of metal oxides containing the same ratios of copper, silver, and vanadium. In this way, the influence of the structure of the trimetallic CSV material on the discharge properties of the system could be measured in comparison with simple mixtures of metal oxides. To prepare the mixtures of metal oxides, silver vanadium oxide, Ag_{0.5}V₂O_{5.25}, was mixed with 0.5 equiv CuO at 25 °C. Likewise, copper vanadium oxide, Cu_{0.5}V₂O_{5.5}, was mixed with 0.25 equiv Ag₂O to give a metal oxide mixture. These materials were utilized as cathodes in lithium cells and discharged under constant resistance loads. The results are summarized in Table 1, and voltage versus time plots are displayed in Fig. 5. From the discharge capacities and voltage profiles, it is apparent that new trimetallic cathode materials provide significantly higher capacity than simple mixtures of metal oxides of the same elemental composition. Interestingly, the mixture of Cu_{0.5}V₂O_{5.5} and Ag₂O displays the highest initial voltage plateau at ~ +3.2 V in Fig. 5, due to the discharge of the silver oxide component of the cathode. The remaining low-voltage plateaus in the discharge curve for this cell match those reported for Li/Cu_xV₂O_y systems [14–16]. Likewise, the voltage plateaus observed at +2.9, +2.4, and +2.0 V in the discharge curve for the mixture of Ag_{0.5}V₂O_{5.25} and CuO (Fig. 5) match those reported for the discharge of a Li/Ag_{0.76}V₂O_{5.49} cell [11].

4. Conclusions

New trimetallic materials, Cu_xAg_yV₂O_z (CSV), display potential for use as solid-state cathode materials for high-rate lithium batteries. Synthesis of CSV with a Cu:Ag:V ratio of 1:1:4 provided the highest capacity of the materials tested, and incorporates 3.4 equiv of lithium when discharged to a

+1.5 V cutoff. The use of nitrate-based starting materials also resulted in significantly higher discharge capacity than samples prepared from oxide and metal-based starting materials. The synthesis of CSV at 375 °C under air produced a nearly amorphous solid with agglomerations of small, irregularly shaped particles. Finally, the CSV material gave a distinctively improved discharge capacity when compared with simple mixtures of metal oxides of the same elemental composition, illustrating the unique nature of the CSV material.

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