

Advanced lithium batteries for implantable medical devices: mechanistic study of SVO cathode synthesis

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Abstract

Silver vanadium oxide (SVO, $\text{Ag}_2\text{V}_4\text{O}_{11}$) was synthesized in solid-state reactions from silver carbonate and silver metal powder starting materials with vanadium oxide (V_2O_5) as the vanadium source. These powders were prepared as primary cathode materials for lithium batteries. Thermal analyses of stoichiometric mixtures of V_2O_5 and silver sources were used to elucidate the mechanism of $\text{Ag}_2\text{V}_4\text{O}_{11}$ formation. V_2O_5 reacts with Ag_2CO_3 in a two step decomposition/combination (DC) reaction. Weight gain measured by TGA during the reaction of $\text{Ag}(0) + \text{V}_2\text{O}_5$ in O_2 indicated the formation of $\text{Ag}_2\text{V}_4\text{O}_{11}$. XRD analysis of the synthesis products of the $\text{Ag}(0) + \text{V}_2\text{O}_5$ reaction indicated the formation of AgV_2O_5 under inert atmosphere and $\text{Ag}_2\text{V}_4\text{O}_{11}$ under oxidizing (air or O_2) conditions. The surface area and morphology of the materials were strongly influenced by the synthesis method, linked to the parameters of time, temperature, and reaction atmosphere. The electrochemical performance of the SVO cathode material also depended on the synthesis method, where SVO prepared from the DC reaction mechanism yielded improved long-term performance.

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1. Introduction

Silver vanadium oxide (SVO, $\text{Ag}_2\text{V}_4\text{O}_{11}$) has demonstrated commercial success as a solid-state cathode material in primary (non-rechargeable) lithium power sources for implantable biomedical devices [1]. The structure of SVO provides paths for diffusion of lithium ions, and the formation of silver metal during the discharge reaction enhances the conductivity of the cathode. These factors contribute to the advantages displayed by SVO as a cathode material in high-rate discharge pulse applications (20 mA/cm² current density or greater) such as the implantable cardiac defibrillator. Other factors critical for the use of SVO in this application include high reliability, a sloping discharge voltage curve for state-of-charge indication, low self-discharge, and long-term stability, since cells must remain implanted for several years. The preparation of SVO [2,3] powder for this application typically involves the thermal decomposition of AgNO_3 in a mixture with V_2O_5 under an air atmosphere to form the ϵ -phase of SVO with a stoichiometry of 2Ag:4V:11O. The preparation of SVO from silver

oxide and vanadium oxide starting materials has also been reported [4]. The effect of the silver precursor on the resulting SVO material was explored previously, where silver nitrate, silver nitrite, silver vanadate, silver oxide, silver carbonate, and silver metal powder have all been used to prepare SVO cathode materials [5]. Characterization of these SVO materials included SEM, XRD, DSC, resistivity, and wet chemical analysis. However, the mechanism of the reaction to form SVO was not investigated in these previous reports. This report details a systematic study of the mechanisms of the reactions of silver carbonate and vanadium oxide and silver powder plus vanadium oxide to give SVO.

2. Experimental

A typical synthesis of $\text{Ag}_2\text{V}_4\text{O}_{11}$ from a mixture of Ag_2CO_3 and V_2O_5 was conducted at 500 °C under an air atmosphere. Preparation of silver vanadium oxides from V_2O_5 and $\text{Ag}(0)$ powder was conducted under argon to give the bronze AgV_2O_5 and air or oxygen atmosphere to give $\text{Ag}_2\text{V}_4\text{O}_{11}$. Simultaneous Differential Thermal Analysis and Thermal Gravimetric Analysis measurements of SVO samples and mixtures of starting materials were conducted on

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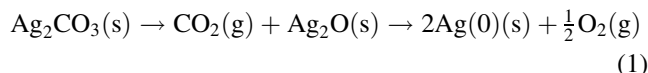
E-mail address: rleising@greatbatch.com (K.J. Takeuchi).

samples using a TA Instruments Model 2960 DTA/TGA Instrument. BET surface area measurements were recorded using a Micromeritics Gemini Instrument. Scanning electron microscopy (SEM) micrographs of solid SVO samples were recorded using an ISI ABT-55 instrument. X-ray powder diffraction (XRD) plots were collected using a Shimadzu XRD-6000 with Cu K α radiation. Prismatic, hermetically sealed cells were constructed using SVO materials pressed into pellets as cathodes and lithium anodes. The cell dimensions were 26.9 mm high \times 42.9 mm wide \times 8.9 mm thick. The cathodes consisted of 94 wt.% SVO along with 3 wt.% polytetrafluoroethylene, 2 wt.% graphite and 1 wt.% carbon black. The cell capacity was \sim 2.3 Ah. The cells used polypropylene separator and 1 M LiAsF₆ (PC)/DME (1:1) electrolyte. The cells were pulse tested at 37 °C with a 17 k Ω constant resistance load applied throughout the test. Pulse trains were applied every two months. Pulse trains consisted of four 10 s constant current pulses of 2.0 A magnitude, with 15 s of rest in-between pulses. Only discharge pulses were applied, the cells were not charged during this test.

3. Results and discussion

Simultaneous DTA/TGA measurements were made on silver carbonate starting material to determine the tempera-

ture of decomposition. Ag₂CO₃ thermally decomposes stepwise according to Eq. (1):



where the decomposition of silver carbonate to silver oxide and carbon dioxide occurs at \sim 250 °C in the DTA/TGA experiment, and the formation of silver metal with liberation of oxygen occurs at \sim 420 °C. Mixtures of silver carbonate and vanadium oxide were also analyzed by DTA/TGA. V₂O₅ catalyzes the decomposition of Ag₂CO₃; weight loss occurs at a lower temperature (\sim 200 °C) in the presence of V₂O₅, as illustrated in Fig. 1. The synthesis of ϵ -phase Ag₂V₄O₁₁ from silver carbonate and vanadium oxide occurs via a two step decomposition/combination reaction [7]. Eq. (2) represents the decomposition step in this mechanism, where Ag₂CO₃ thermally decomposes:



The combination step is represented in Eq. (3), where the in situ-formed silver oxide combines with vanadium oxide:



The reaction of silver powder with vanadium oxide was carried out in the presence of air, oxygen and argon gas to elucidate the role of the atmosphere in the formation of different phases of SVO. From thermal analysis (DTA/TGA)

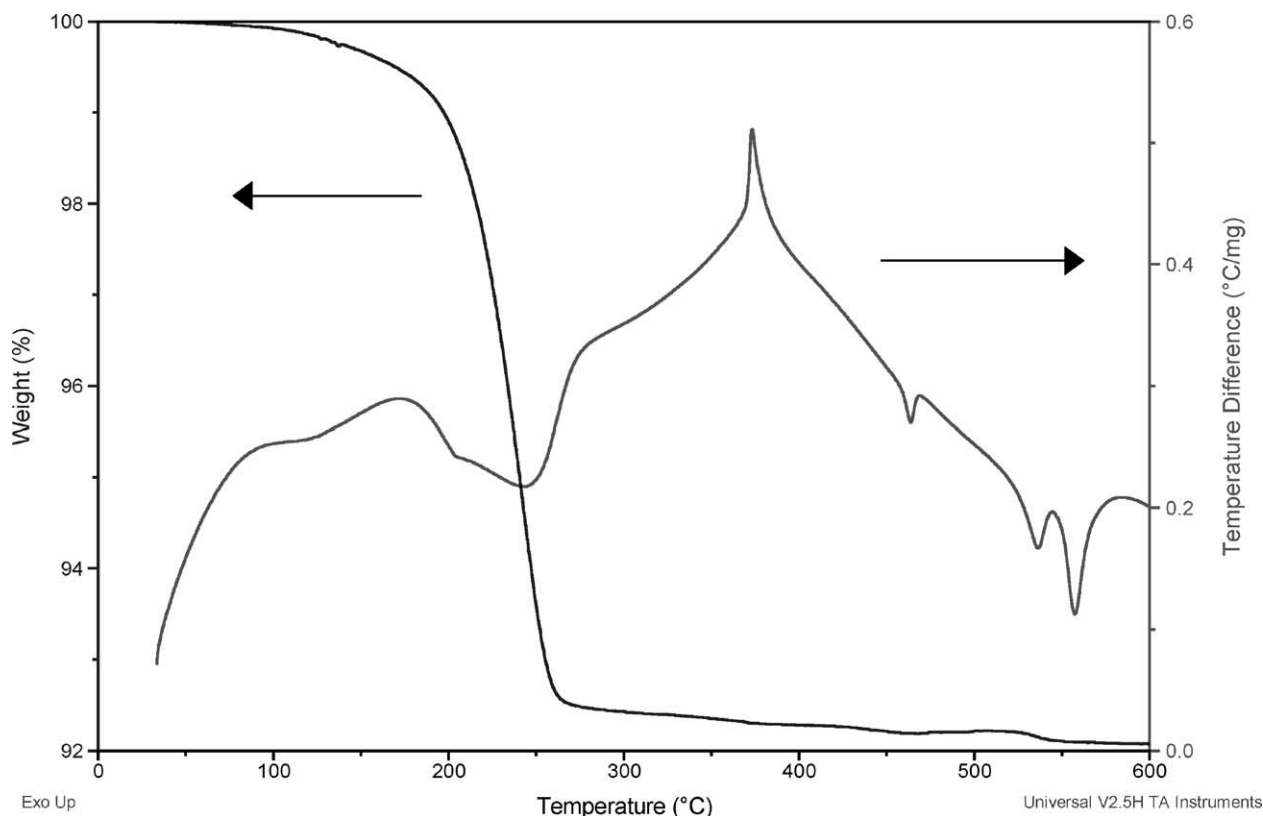


Fig. 1. Thermal analysis (simultaneous DTA/TGA) of a 1:2 mixture of Ag₂CO₃ and V₂O₅ conducted at 20 °C/min and a 120 ml/min purge of argon.

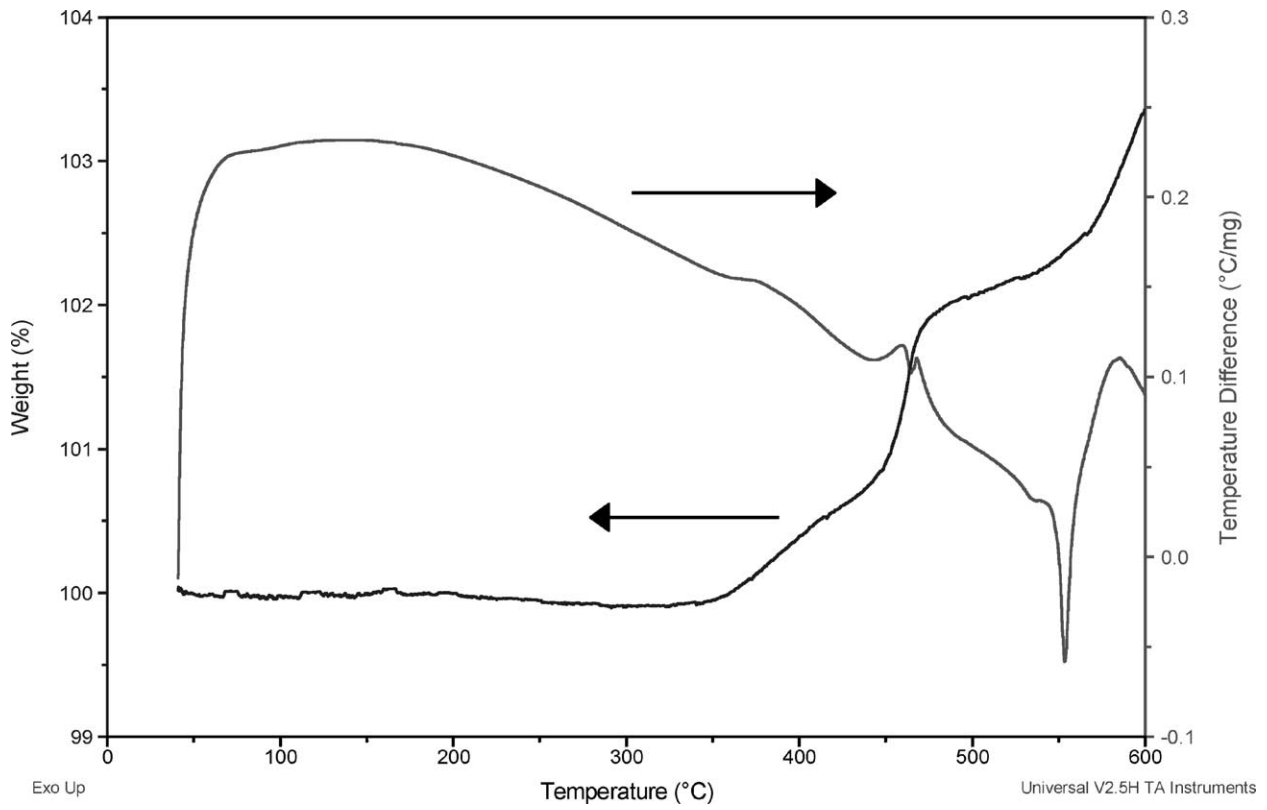


Fig. 2. Thermal analysis (simultaneous DTA/TGA) of a 1:1 mixture of Ag(0) powder and V₂O₅ conducted at 10 °C/min and a 120 ml/min purge of oxygen.

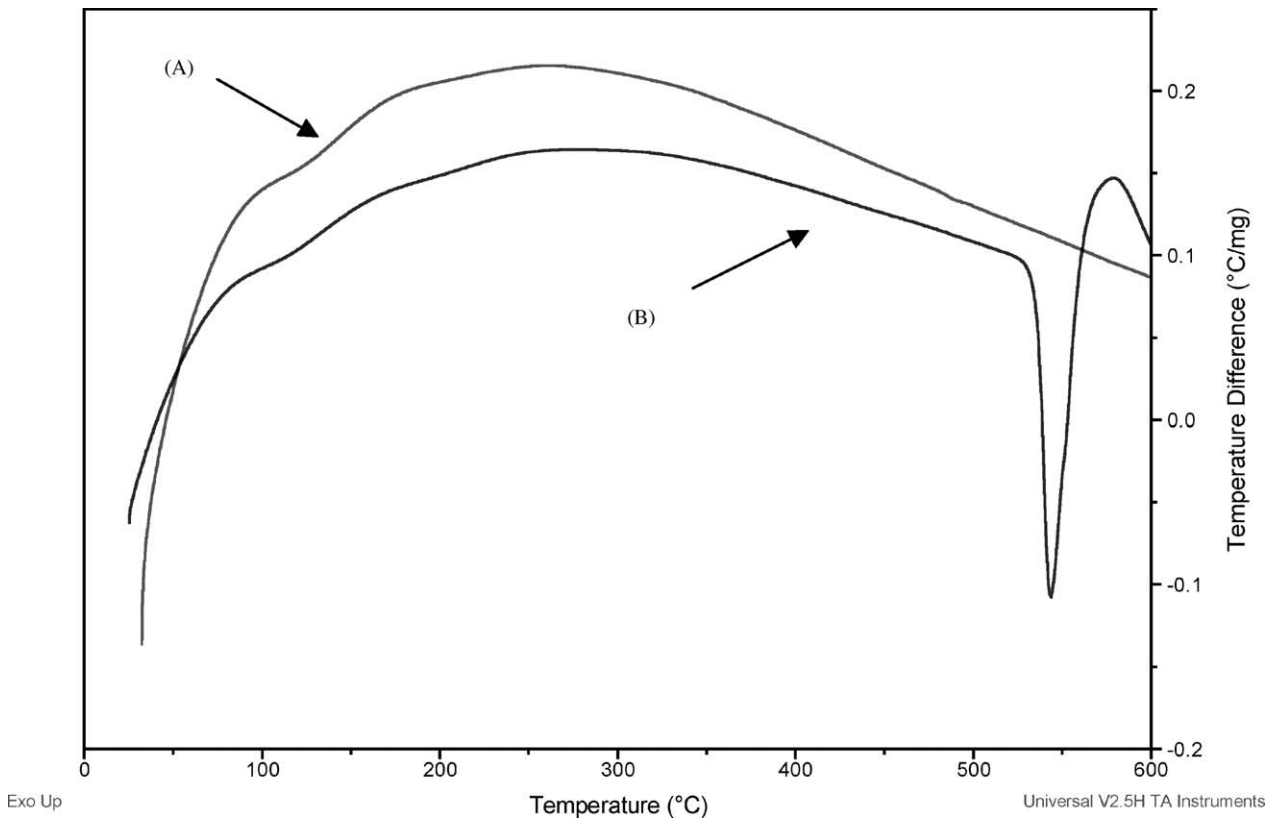


Fig. 3. Thermal analysis (DTA) of SVO prepared from Ag(0) + V₂O₅ at 500 °C under (A) argon and (B) oxygen. Both DTA scans conducted at 20 °C/min and a 120 ml/min purge of argon.

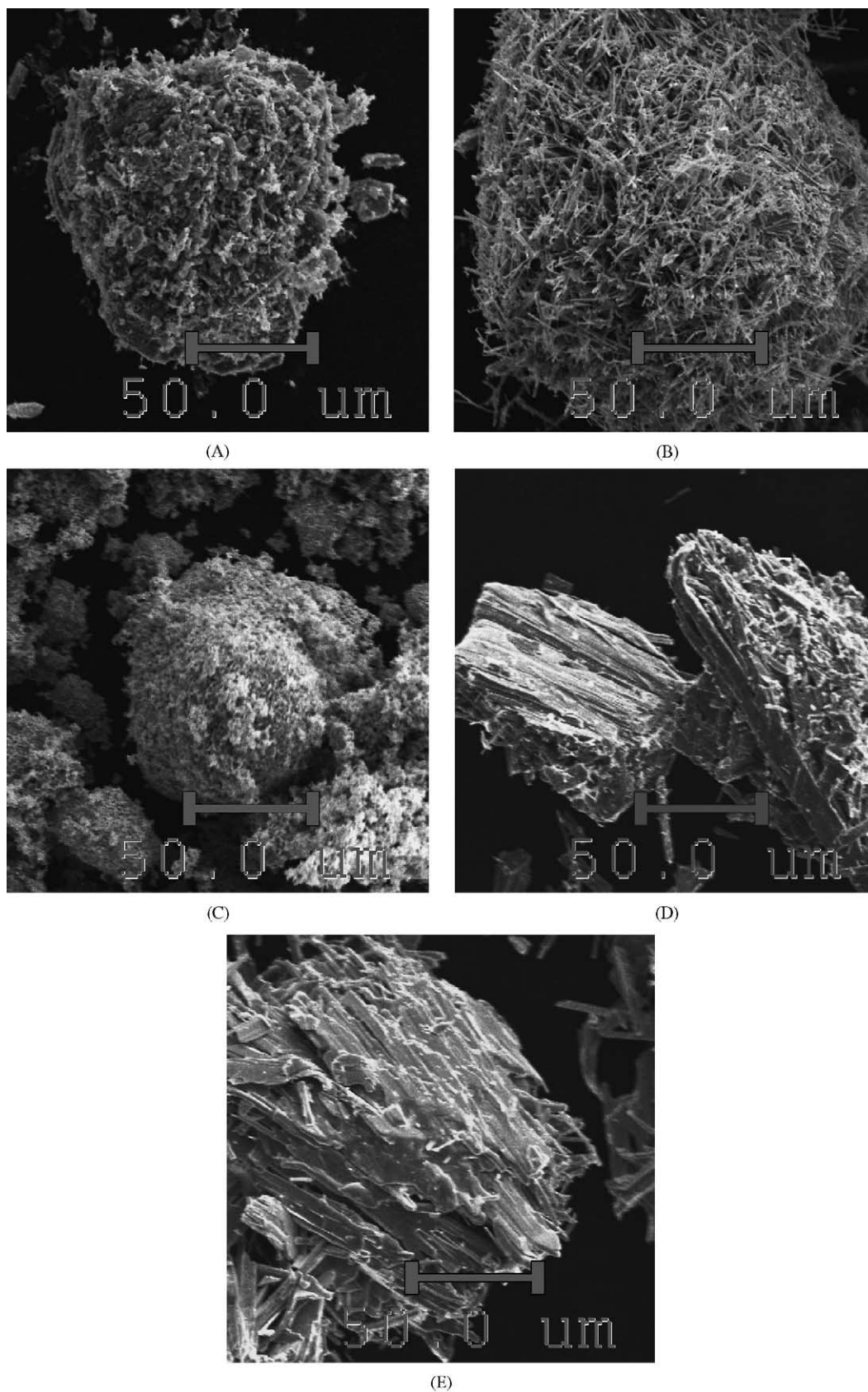
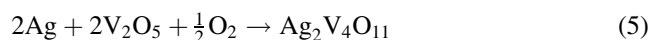


Fig. 4. SEM micrographs ($\sim 500\times$) of (A) V_2O_5 starting material; (B) $Ag_2V_4O_{11}$ synthesized from $Ag_2CO_3 + 2V_2O_5$ at $500^\circ C$ under air; (C) AgV_2O_5 synthesized from $Ag(0) + V_2O_5$ at $500^\circ C$ under argon; (D) $Ag_2V_4O_{11}$ synthesized from $Ag(0) + V_2O_5$ at $500^\circ C$ under air; (E) $Ag_2V_4O_{11}$ synthesized from $Ag(0) + V_2O_5$ at $500^\circ C$ under oxygen.

of mixtures of Ag(0) powder and V₂O₅ using varied purge gases the following equations were derived. Eq. (4) describes the reaction of silver powder with vanadium oxide under an inert atmosphere:



and Eq. (5) describes the same reaction conducted under an air or oxygen atmosphere:



The reaction of oxygen with silver powder and vanadium oxide as illustrated in Eq. (5) is consistent with the observation of the DTA/TGA of a mixture of Ag(0) + V₂O₅ under an oxygen purge, as displayed in Fig. 2. The weight gain observed in this TGA curve starting at ~350 °C is attributed to the uptake of oxygen in the reaction. The silver vanadium oxide products of Eqs. (4) and (5) were also analyzed by DTA/TGA, and the DTA curves are illustrated in Fig. 3. Note that the curve for SVO prepared from Ag(0) + V₂O₅ in the presence of O₂ gives an endotherm centered at ~540 °C, consistent with the DTA curve typically found for Ag₂V₄O₁₁, while the curve for the product of the Ag(0) + V₂O₅ reaction in the presence of an argon atmosphere is featureless up to the 600 °C limit of the experiment. XRD of the samples were collected between 10 and 80 2θ, and the powder patterns for the samples of SVO prepared from Ag₂CO₃ + V₂O₅ and Ag(0) + V₂O₅ in air or O₂ indicate the formation of ε-phase Ag₂V₄O₁₁. However, the XRD of SVO prepared from Ag(0) + V₂O₅ under argon is consistent with XRD pattern for the bronze AgV₂O₅ [6].

BET surface area of SVO samples and starting materials was measured by nitrogen absorption, with the results listed in Table 1. As illustrated in the table, SVO products displayed a significantly lower specific surface area than the V₂O₅ starting material. The surface area of AgV₂O₅ was found to be comparable to that for Ag₂V₄O₁₁ prepared from Ag₂CO₃. However, Ag₂V₄O₁₁ prepared from Ag(0) displayed a much lower surface area. Furthermore, heating AgV₂O₅ in the presence of air or oxygen produced ε-phase

Table 1
BET surface area of cathode powders and related materials

Material	Synthesis	BET surface area (m ² /g)
V ₂ O ₅	–	4.62
AgV ₂ O ₅	Ag(0) powder + V ₂ O ₅ under argon at 500 °C	0.81
Ag ₂ V ₄ O ₁₁	2Ag(0) powder + 2V ₂ O ₅ under air at 500 °C	0.23
Ag ₂ V ₄ O ₁₁	Ag ₂ CO ₃ + 2V ₂ O ₅ under air at 500 °C	0.68
Ag ₂ V ₄ O ₁₁	2AgV ₂ O ₅ under air for 3 h at 500 °C	0.34
Ag ₂ V ₄ O ₁₁	2AgV ₂ O ₅ under air for 72 h at 500 °C	0.26
Ag ₂ V ₄ O ₁₁	2AgV ₂ O ₅ under oxygen for 48 h at 500 °C	0.17
Ag ₂ V ₄ O ₁₁	2AgV ₂ O ₅ under oxygen for 72 h at 500 °C	0.17

Ag₂V₄O₁₁ with a lower surface area, comparable to material produced from Ag(0) directly under air or oxygen.

The primary particle size and morphology of the SVO products were evaluated by SEM analysis. Fig. 4A–E display 500× magnification photos of the samples. For all of the materials, particles as large as 100–200 μm in diameter were found which consisted of aggregates of smaller primary particles. Ag₂V₄O₁₁ prepared from Ag₂CO₃ displayed collections of small needle-like (acicular) particles, while Ag₂V₄O₁₁ synthesized from Ag(0) displayed aggregates of slab-like (tabular) particles. In general, the samples prepared from silver powder displayed the largest primary particle size.

The electrochemical properties of the SVO cathode materials have been tested under long-term test conditions to mimic the operation of a battery in a medical device application. Hermetically sealed lithium anode batteries were constructed using these SVO cathode materials and filled with 1 M LiAsF₆ PC/DME (1:1) electrolyte. The pulse discharge of the cells was accomplished at 37 °C under conditions resulting in an 18 month total test time. Cells

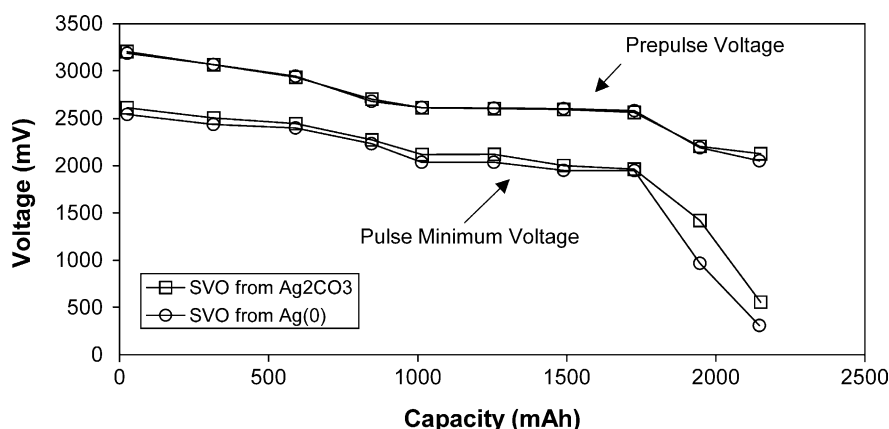


Fig. 5. Voltage vs. capacity curve for Li/Ag₂V₄O₁₁ cells pulse discharged at 37 °C with a 2.0 A pulse current.

containing SVO prepared from silver carbonate displayed slightly higher pulse voltages, and higher overall capacity when compared to cells containing SVO prepared from silver powder starting material, as illustrated in Fig. 5. The lower specific surface area of the SVO cathode material prepared from silver powder may be the cause for the higher internal resistance of the cells using these cathodes, other factors influencing impedance rise may also be electrolyte degradation and changes in the lithium anode during the test.

4. Conclusions

Thermal analyses of mixtures of V_2O_5 and Ag_2CO_3 or $Ag(0)$ powder were used to elucidate the mechanism of $Ag_2V_4O_{11}$ formation using these starting materials. V_2O_5 reacts with Ag_2CO_3 in a two step decomposition/combination (DC) reaction. The DC reaction occurs in the temperature range of 150–400 °C. A similar thermal analysis of silver powder plus vanadium oxide showed that the reaction of $Ag(0) + V_2O_5$ in O_2 to give SVO starts at ~ 350 °C. XRD analysis of the synthesis products of the $Ag(0) + V_2O_5$ reaction indicated the formation of AgV_2O_5 under inert

atmosphere and $Ag_2V_4O_{11}$ under oxidizing (air or O_2) conditions.

The surface area and morphology of the materials was strongly influenced by the synthesis method. Systematic control of these two material properties can be obtained through variation of time, temperature, and reaction atmosphere. The electrochemical performance of the SVO cathode material also depends on the method of synthesis. SVO prepared from the DC reaction mechanism yields improved long-term performance.

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