

MW-assisted synthesis of SVO for ICD primary batteries

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Abstract

An $\text{Ag}_2\text{V}_4\text{O}_{11}$ (SVO) cathode material prepared by microwave (MW)-assisted solid-state synthesis (MW-SVO) was developed for lithium primary batteries for implantable cardioverter/defibrillators (ICDs). This paper presents the results of physical–chemical and electrochemical characterizations of MW-SVO as well as those of SVO prepared by conventional thermal route (T-SVO). A specific effect of MWs which accelerates the synthesis reaction and contributes to yield a material of different morphology and degree of crystallinity compared with those of T-SVO was observed. The results of pulsed electrochemical tests carried out at 37 °C in operative conditions of ICDs on Li/MW-SVO batteries with cathode mass loading sized for practical use are also reported. These tests demonstrated that MW-SVO can be used for high performing lithium primary battery delivering in few seconds the specific energy values required by ICD application.

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1. Introduction

Primary lithium batteries, for their high energy density, longevity and high reliability are playing a crucial role for miniaturization and multifunctionality of implantable biomedical devices [1]. Particularly, Li/ $\text{Ag}_2\text{V}_4\text{O}_{11}$ batteries meet the power requirements of implantable cardioverter/defibrillators (ICDs) which administer 30–35 J in a few seconds for the high-voltage shocks to the right ventricle, when ventricular fibrillation is detected [2].

Several studies have been focused on the $\text{Ag}_2\text{V}_4\text{O}_{11}$ (SVO) preparation which typically consists in a solid-state reaction at high temperature of vanadium oxide and silver-based precursors which lasts several hours. At $T = 500$ °C the reaction yields acicular or tabular products with 100–200 μm particle dimensions and specific surface area lower of the 3–20% than that of the V_2O_5 precursor [3,4]. More recently efforts are devoting to novel synthesis procedures, such as sol–gel synthesis eventually assisted by ultrasonic irradiation, which can bring about nanostructured, high surface area and high-rate capacity SVO [5,6].

Microwave (MW)-assisted solid-state synthesis of inorganic materials is gaining even more importance for its peculiar characteristic of rapidity which contributes to lowering cost production. Furthermore, some authors observed genuine non-thermal effects of microwaves which result in chemical–physical and morphological properties of the materials different from that displayed when prepared by conventional routes [7].

MW-assisted solid-state reactions have been proved to be powerful methods for grain size control of materials for lithium rechargeable batteries [8,9] and we pursued the strategy of using MW for the synthesis of SVO for ICD primary Li batteries. In this paper we describe a novel MW-assisted method for the preparation of SVO (MW-SVO) starting from AgNO_3 and V_2O_5 and we present the results of its physical–chemical and electrochemical characterizations as well as those of SVO prepared by “conventional” solid-state reaction at 500 °C (T-SVO) starting from the same precursors. Also the results of the electrochemical tests carried out in operative conditions of ICDs on Li/MW-SVO batteries with cathode mass loading sized for practical use are reported and compared to those of Li/T-SVOs.

2. Experimental

The precursors for the MW-assisted and conventional synthesis of a few grams of $\text{Ag}_2\text{V}_4\text{O}_{11}$ were AgNO_3 (Fluka, $\geq 99.8\%$)

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and V_2O_5 (Fluka, $\geq 99\%$) in 1:1 molar ratio. MW-SVO was prepared with a domestic microwave oven operating at 2.45 GHz with maximum output power of 600 W. The precursor powders were ground for homogeneity in a silica crucible and MW irradiated at 600 W for about 5 min with intermittent grinding. The temperature was monitored by a PC-interfaced Impac-Mikron infrared Pyrometer with a spot size of ca. 3 cm diameter, covering almost the entire sample surface, and setting the emissivity value of the materials $\varepsilon = 1.0$.

T-SVO was prepared by heating the precursors at 500 °C for 48 h in air with a Metalchim S.p.A. thermostatic oven, and grinding the powders every 12 h as in Ref. [10].

X-ray diffraction (XRD) analysis of the powders was performed with a Philips PW1050/81 diffractometer, a Cu $K\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation source and Ni filter, with continuous acquisition in 5–80° 2θ range, 0.05° $2\theta \text{ s}^{-1}$ scan rate.

Scanning electron micrographs (SEM) were acquired with a Philips 515 SEM.

The electronic resistivity of MW-SVO and T-SVO was measured in pellets (2 cm diameter, obtained by pressing the powders at 7 t for 3 min) via four-point technique (FPT) with contacts made by a Jandel Multiheight Probe and using an AMEL Model 2053 potentiostat/galvanostat for current supply and a Hewlett Packard 3478A multimeter for voltage reading.

Electrochemical characterization was performed on SVO composite electrodes prepared by mixing 94% SVO, 3% carbon conducting additive (SuperP, MMM Carbon Co.) and 3% polytetrafluoroethylene binder to yield a paste which was then laminated on carbon coated aluminum grid (Lamart) and dried at 80 °C under vacuum over night. The electrode mass loading was in the range 45–60 mg cm^{-2} of geometric area i.e. of the same order than that used in commercial batteries for ICDs. The electrochemical cell was “T-type” with Li in excess as the counterelectrode and Li as reference electrode; a dried and degassed glass separator (Whatman GF/D 400 μm thick) was used after soaking in the cell electrolyte, ethylene carbonate (EC):dimethylcarbonate (DMC) 2:1–1 M LiPF_6 (Merck LP31); the electrode geometric area was of ca. 0.77 cm^2 . Cell assembly and sealing were performed in argon atmosphere (MBraun Labmaster 130 dry box, H_2O and $\text{O}_2 < 1 \text{ ppm}$) and the cells were tested at 37 °C using a thermostatic oven (Thermoblock). All the electrochemical tests were carried out with a Perkin-Elmer VMP multichannel potentiostat.

3. Results and discussion

3.1. Synthesis of MW-SVO

It is well known that the materials can be classified on the basis of their capability to absorb MW, i.e. to take up energy from MW field and very rapidly heat [7]. The curves (a) and (b) in Fig. 1 represent the temperature trend (recorded by pyrometer, $\varepsilon = 1.0$) during MW irradiation at 600 W of the single precursors AgNO_3 and V_2O_5 and show that the first compound is almost transparent to the radiation (it takes 10 min to reach 80 °C), whereas the latter reaches temperatures as high as 350 °C in 120 s, so that the V_2O_5 precursor is a good “MW-susceptor”

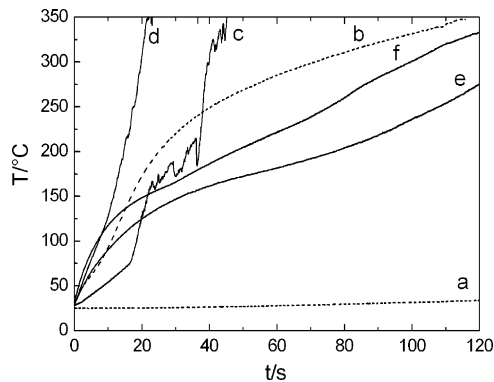


Fig. 1. Temperature recorded by pyrometer during MW irradiation at 600 W of AgNO_3 (a) and V_2O_5 (b) and during the first (c), second (d), third (e) and fourth (f) step of the MW-SVO synthesis.

[11] for synthesis of SVO by the following reaction:



The synthesis of MW-SVO consisted of four irradiation steps at 600 W (full power) manually interrupted when the temperature, monitored with the pyrometer, reached 350 °C or at the appearance of electric discharge, followed by grinding, and the reaction was complete after a total irradiation time of ca. 5 min. The curves (c)–(f) in Fig. 1 are the temperature trends during each step. During the first, after ca. 16 s the AgNO_3 decomposition took place and red vapours of N_xO_y were observed (they are the cause of the noise in curve (c)). After the second step the powder was still not homogeneous and precursors were still present; only after the third step the powder looked like a single phase. During the third and fourth steps the curves (e) and (f) in Fig. 1 indicate a similar microwave coupling of the materials, thus suggesting that their chemical composition is not very different.

The structural modification during MW-assisted synthesis was monitored by XRD after each irradiation step. This analysis indicated that after the fourth step the AgNO_3 and V_2O_5 precursors were absent and the reaction was complete; further irradiation did not change the crystallographic composition of the MW-SVO. Fig. 2 reports the XRD patterns normalized to the amount of analyzed powder of the final product MW-SVO (curve (a)) and of T-SVO prepared by conventional thermal method at 500 °C (curve (b)), for a comparison; the two materials display almost the same crystalline phase $\varepsilon\text{-Ag}_2\text{V}_4\text{O}_{11}$ [12]. In the XRD spectrum of MW-SVO are present additional peaks (evidenced by a star) not related to $\varepsilon\text{-Ag}_2\text{V}_4\text{O}_{11}$ and which correspond to $\gamma\text{-SVO}$ ($\text{Ag}_{1.2}\text{V}_3\text{O}_8$). The latter crystalline phase is the reaction product when thermal syntheses are performed at T higher than 500 °C or in oxygen defect [13,10]. Presumably, during MW-SVO synthesis the temperature detected by the pyrometer represents a mean value, and it is reasonable that a portion of the sample reaches temperatures higher than 350 °C (maximum temperature set for irradiation steps). However, given that the intensity of the $\gamma\text{-SVO}$ pattern is significantly lower than that of the $\varepsilon\text{-SVO}$ pattern we can infer that the main part of material is $\varepsilon\text{-SVO}$ which experiences temperatures lower than

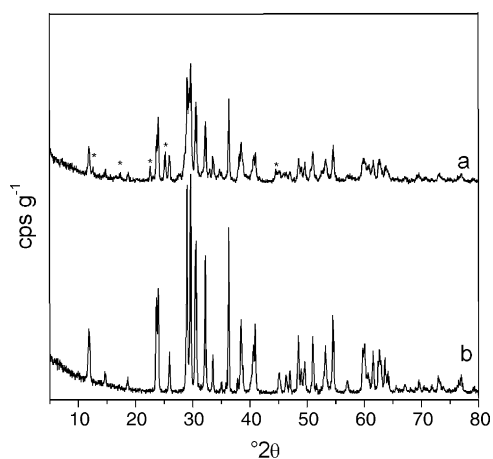


Fig. 2. XRD patterns normalized to the amount of analyzed powder of MW-SVO (a) and of T-SVO (b).

500 °C. The comparison of the specific intensities (in cps g^{-1}) of the diffraction peaks of MW-SVO and T-SVO indicates that in the first material the amount of crystalline phase ϵ -SVO is ca. 40% lower than in the T-SVO. The lower crystallinity of MW-SVO compared to T-SVO is evidenced also by the SEM micrographs reported in Fig. 3. The T-SVO displays only acicular crystals some microns long in agreement with literature for SVO prepared in air at 500 °C [10], whereas the MW-SVO shows grains of different size with a high percentage of submicrometric particles which may be the amorphous phase not detected by XRD analysis. The difference in grain size and crystallinity

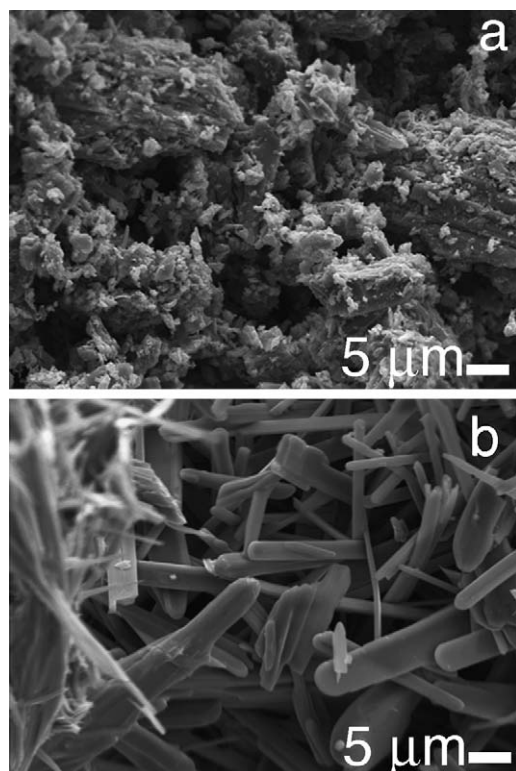


Fig. 3. SEM images of MW-SVO (a) and T-SVO (b).

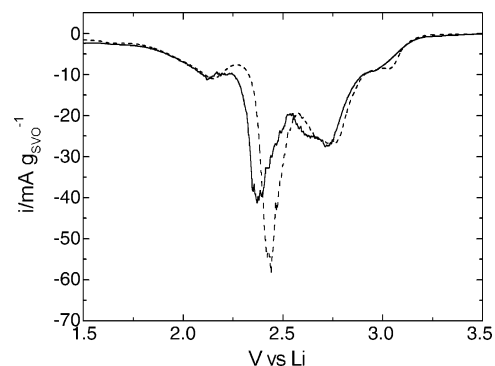


Fig. 4. Specific currents from LSVs at $20 \mu\text{V s}^{-1}$ and 37°C in EC: 2:1–1 M LiPF_6 of the composite electrodes with MW-SVO (solid line, 47.9 mg cm^{-2} SVO) and T-SVO (dashed line, 46.7 mg cm^{-2} SVO).

between MW-SVO and T-SVO are reflected in their resistivities of 1.7×10^3 and $1.1 \times 10^3 \Omega \text{ cm}$, respectively. The morphology and resistivity of MW-SVO are in agreement with those of SVO prepared by thermal route at temperature lower than 500 °C [13,14], further confirming that the main part of MW-SVO experienced $T < 500^\circ\text{C}$. Given that MW-SVO was obtained in a few minutes at low temperatures we can claim a MW specific effect which accelerates the SVO synthesis and provides a material of different degree of crystallinity and morphology. The MWs may interact with solid-state materials inducing ionic currents which accelerate diffusion processes [11,15] and this may be the case for the MW-SVO synthesis with silver diffusion into the vanadium oxide framework.

3.2. Electrochemical characterization of MW-SVO

Fig. 4 compares the specific currents from linear sweep voltammeteries (LSVs) at $20 \mu\text{V s}^{-1}$ and 37°C in EC:DMC 2:1–1 M LiPF_6 of composite electrodes based on MW-SVO and T-SVO having almost the same mass in the order of 50 mg cm^{-2} . The voltammetric responses of the two composites are comparable and the integrated charge is the same for the two materials, i.e. 295 mAh g^{-1} of SVO which on the basis of the following SVO lithium intercalation reaction corresponds to $x = 6.56$



The two materials display the voltammetric peaks for the reduction steps $\text{V}^{5+} \rightarrow \text{V}^{4+}$; $\text{Ag}^+ \rightarrow \text{Ag}^0$; $\text{V}^{5+} \rightarrow \text{V}^{4+}, \text{V}^{3+}$ and $\text{V}^{4+} \rightarrow \text{V}^{3+}$ [3] at almost the same potentials of 3.0, 2.7, 2.4 and 2.1 V versus Li, respectively, and such peaks are broader for the MW-SVO than for T-SVO, presumably for the lower crystallinity of the former.

Fig. 5 reports the discharge profiles of MW-SVO and T-SVO at different C-rates in order to compare the capacity response of the two electrode materials under different galvanostatic discharge conditions. At C/180, C/80 and C/10 the MW-SVO delivers the 93.4%, 91.4% and 86.6% of the theoretical specific capacity of 315 mAh g^{-1} (as evaluated for $x = 7$ in $\text{Li}_x\text{Ag}_2\text{V}_4\text{O}_{11}$), which correspond to $x = 6.49$, 6.39 and 6.06

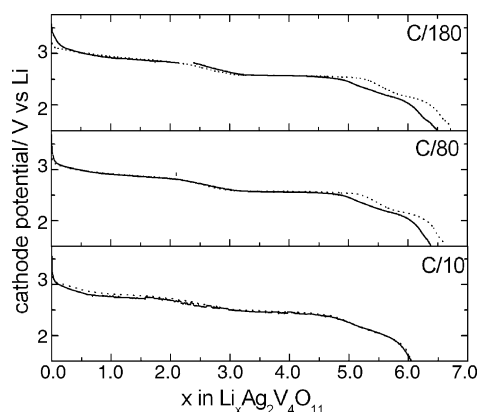


Fig. 5. Discharge profiles at different C-rates at 37 °C in EC:DMC 2:1–1 M LiPF₆ of MW-SVO (solid lines, SVO mass loadings: 54.2, 49.3, 43.8 mg cm⁻² for C/180, C/80, and C/10 tests, respectively) and T-SVO (dotted lines, SVO mass loadings: 62.0, 55.2, 53.0 mg cm⁻² for C/180, C/80, and C/10 tests, respectively).

in Li_xAg₂V₄O₁₁ after reaction (2), respectively. At the highest C-rate C/10, which corresponds to 31.5 mA g⁻¹, MW-SVO and T-SVO deliver the same specific capacity of 272 mAh g⁻¹, whereas at the low C-rates C/80 and C/180 T-SVO performs slightly better than MW-SVO. However, taking into account that the reproducibility of the discharge tests (mainly carried out on MW-SVO, also from different synthesis) was within 1.5%, such differences are not relevant.

In order to evaluate the performance of MW-SVO in ICD operative conditions Li/MW-SVO batteries with cathode mass loading sized for practical use were tested at 37 °C following the protocol in Fig. 6, i.e. the cells were discharged with pulse trains applied every 30 min until the cell voltage under pulsed current was 1.5 V and every train consisted of four 10 s pulses at C/1, corresponding to ca 18 mA cm⁻², followed by a 15 s rest time. Fig. 7a reports the cell potential at the end of the first and fourth pulse and at the rest time versus *x* in Li_xAg₂V₄O₁₁ of a Li/MW-SVO battery with 55.1 mg cm⁻² SVO mass loading. Taking into account the charge released by all the pulses the delivered specific capacity was ca. 70% of the theoretical value. The same tests were also performed on Li/T-SVO batteries, and the result for a battery with 54.2 mg cm⁻² SVO mass loading is in Fig. 7b. The comparison of Fig. 7a and b demonstrates that also under high pulsed currents the MW-SVO performs like the T-SVO, particularly up to *x* = 3.0 in Li_xAg₂V₄O₁₁ which corresponds to the suggested intercalation limit to ensure a sufficiently low

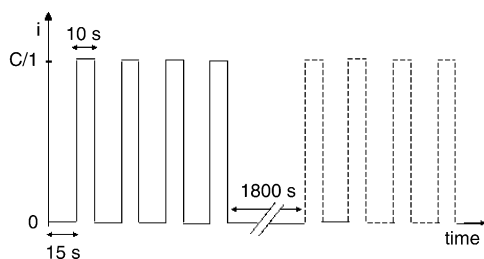


Fig. 6. Scheme of the pulse sequence for Li/SVO battery test.

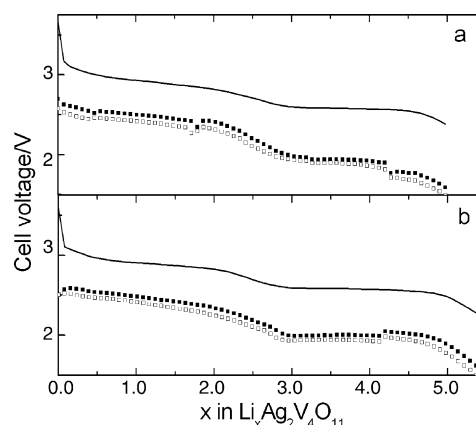


Fig. 7. Cell potential at the end of the first (■) and the fourth pulse (□) and at rest time (straight line) of the Li/MW-SVO (a) SVO mass loading = 55.1 mg cm⁻² and Li/T-SVO (b) SVO mass loading = 54.2 mg cm⁻² batteries, discharged by the protocol in Fig. 6.

equivalent series resistance to Li/SVO batteries for ICD application [2]. The pulsed specific energy (*E*) of the Li/MW-SVO battery, which was calculated by the equation $E = (V_i + V_f)jt_{on}/2$, where *V_i* and *V_f* are the cell potentials at the beginning and at the end of the pulse and *j* the specific current applied for *t_{on}* seconds, satisfies the requirements for ICD application. During the first pulse of the second train the energy was 8.5 J g⁻¹ of SVO and 0.47 J cm⁻² at *V_f* = 2.63 V, so that in order to obtain 30 J delivered in 10 s the battery electrode area should be of 65 cm², a value which fits very well with that of commercial batteries for ICDs [14]. At the fourth pulse of the 39th train at *V_f* = 1.94 V, after insertion of *x* = 3.0 in Li_xAg₂V₄O₁₁, the specific energy was still of 6.2 J g⁻¹. It is worth noting that, as evidenced by Fig. 8, which reports the cell and the positive and negative electrode voltage profiles upon the third pulse train of the Li/MW-SVO battery, the anode significantly contributes with ca. 70% to the battery voltage loss. The high loss due to the Li electrode has already been evidenced for Li/SVO batteries [16] and by lowering such term to a half the battery would deliver up to 8% higher specific energy values. Furthermore, the performance of the cells we assembled is affected by the use of not-optimized separator (two sheets of fiber-glass, 400 μm and 80% porosity each) which could be substitute by a 25 μm-thick separator of the same type of that used in commercial Li/SVO batteries,

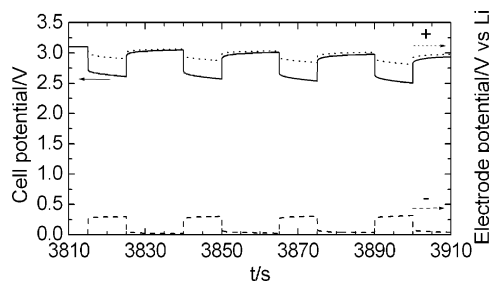


Fig. 8. Cell (solid line) and positive (dotted line) and negative (dashed line) electrode voltage profiles upon the third pulse train of a Li/MW-SVO battery (SVO mass loading = 55.1 mg cm⁻²) at 18 mA cm⁻².

allowing to decrease the voltage loss by 110 mV (on the basis of electrolyte conductivity of 15 mS cm^{-1} at 37°C) and to increase the specific energy by 5%.

4. Conclusions

For the first time at our knowledge, it is here demonstrated that MW-assisted solid-state reaction is a powerful method to synthesize high performing cathode materials for primary lithium batteries, and particularly SVO for ICDs. The MW-method provides very short preparation time of SVO in the order of a few minutes instead of several hours and materials with different morphology from that displayed by T-SVO prepared by thermal synthesis at 500°C . Given that the rapidity of the MW-assisted synthesis is not due to enhanced heating of reactants, a specific effect of MW may be claimed. This effect could be a MW induction of ionic currents which accelerate silver insertion in the vanadium oxide structure to yield $\epsilon\text{-Ag}_2\text{V}_4\text{O}_{11}$. The MW-SVO displays very high performance delivering 272 mAh g^{-1} when discharged to 1.5 V at fast discharge rate of 31.5 mA g^{-1} as T-SVO prepared in optimized thermal conditions does. We also demonstrate that Li/MW-SVO cells, assembled with heavy cathode mass loading such as that required for ICD batteries, delivered in few seconds at 37°C with pulsed currents of 315 mA g^{-1} (18 mA cm^{-2}) up to 8.5 J g^{-1} , i.e. the high specific energy values required for powering implantable cardioverter/defibrillators.

The fact that MW-SVO synthesized in 5 min well performs as T-SVO thermally prepared in 2 days is a relevant result also in view of the development of MW-assisted synthesis of other cathode materials for lithium primary batteries. A drastic reduction of synthesis time without any penalty in materials performance is a great advantage in terms of costs, and this is particularly appealing for lithium batteries for electronics.

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