Electrochemical reaction of lithium with nanosized vanadium antimonate

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Abstract

Nanometric vanadium antimonate, $\text{VSbO}_4$, was prepared by mechanical milling from $\text{Sb}_2\text{O}_3$ and $\text{V}_2\text{O}_5$ and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Mossbauer spectroscopy (MS) and X-ray photoelectron spectroscopy (XPS) techniques. Its reactivity towards lithium was examined by testing Li/VSbO$_4$ cells under galvanostatic and potentiostatic regimes. The amount of Li inserted was found to be consistent with a two-step process involving the reactions (i) $\text{VSbO}_4 + 8 \ \text{Li}^{-} \rightarrow \text{Sb} + \text{V} + 4 \ \text{Li}_2\text{O}$ and (ii) $\text{Sb} + 3 \ \text{Li}^{-} \rightarrow \text{Li}_3\text{Sb}$, the former being virtually irreversible and the latter reversible as suggested by the shape of the anodic and cathodic curves. Ex situ XPS measurements of the discharged and charged electrode provided direct evidence of the formation of alloyed Sb and confirmed the results of the potentiostatic curves regarding the irreversible or reversible character of the previous reactions. The Li/VSbO$_4$ cell exhibited acceptable electrochemical performance, which surpassed that of other Sb-based compounds as the likely result of the formation of V and its associated enhanced electrode conductivity.

Keywords: Vanadium antimonate; Electrode; Lithium batteries

1. Introduction

Although carbon-based materials are the most common choice for anodes in commercial lithium (Li)-ion batteries at present, there is an ongoing search for alternative materials to replace them. In the last decade, such a search has focussed primarily on systems such as Li-alloys and transition metal compounds (oxides, phosphides and nitrides). Li-alloys have attracted much attention by virtue of their high capacity and low reactive potentials [1]. The high theoretical capacity of antimony (Sb) upon reaction with Li (660 A h/kg) has proposed comprehensive studies of some Sb-based intermetallic compounds (viz $\text{MSb}_x$, with $1 < x < 3$ and $M = \text{Ti, Mn, Fe, Co, Ni, Cu, Zn, In, Sn}$ [2–11]) as potential anode materials for Li-ion batteries. These alloys exhibit an improved cycling behavior relative to pure Sb. The transition metal, which acts as inert matrix in the electrochemical process, accommodates the volumes changes in Li$_x$Sb active species during the lithiation and delithiation processes. However, cycling results in pulverization of active particles and hence in rapid capacity fading by effect of the drastic volume changes undergone by these intermetallic systems. This results in inadequate long-term cycling capabilities and rules out practical application.

There have been several attempts at alleviating the mechanical stress. Thus, reversibility in these intermetallic electrodes can be markedly improved by using (i) selected compounds with special structures such as Cu$_2$Sb [12] or Mn$_2$Sb [3], and (ii) thin-films [13] or nanosized materials [7,14]. In the former case, the lithiated product (Li$_2$Cu$_2$Sb) bears a strong structural relationship with its parent compound (Cu$_3$Sb). In the latter, the diffusion path for Li-ions and volume changes in active particles are reduced.

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Sb-based oxides have been underexplored as an alternative to improving the electrochemical performance of Sb. Tin compounds (SnO [15], SnO2 [16], CaSnO3 [17]) have proved especially efficient, even though they exhibit largely irreversible capacity during the first charge–discharge process. Li et al. [18] were the first to study the electrochemical reaction of Sb2O3 with Li. The poor reversibility found was subsequently mitigated by using Sb-based oxides as thin films electrodes [19]. Recently, we found a cell made from SbPO4 to perform acceptably [20]. Although Li3PO4 is a poorly conductive matrix, it exhibits good cycling properties. This paper reports the electrochemical properties of nanometric vanadium antimonite (VSbO4) in Li cells. The compound was obtained in the form of nanosized particles by prolonged grinding, and was characterized by X-ray diffraction, Mossbauer spectroscopy (MS) and X-ray photoelectron spectroscopy (XPS). Also, its reactivity towards Li was examined in Li cells of the types Li/EC–DEC 1 M LiPF6/VSbO4 under both potentiostatic and galvanostatic regimes.

2. Experimental

VSbO4 was prepared from stoichiometric mixtures of commercial grade V2O5 and Sb2O3. The mixtures were dry milled in the air in a Retch PM400 planetary ball mill, using stainless steel vials (250 mL) and balls (20 mm) at 200 rpm for 70 h. The powder to ball weight ratio was 1:20. X-ray powder diffraction (XRD) patterns were recorded on a Siemens D5000 X-ray diffractometer, using Cu Kα radiation and a graphite monochromator, in steps of 0.02° and 0.6 s. Transmission electron microscopy (TEM) images were obtained with a JEOL 2000fx microscope.

The 121Sb Mossbauer spectrum was recorded from powdered samples, using a constant acceleration spectrometer and a Ca121SbO3 source at 77 K. X-ray photoelectron spectra were recorded on a Physical Electronics PHI 5700 spectrometer, using non-monochromated MgKα radiation (\(h\nu = 1253.6\) eV) and a hemispherical analyzer operating at a constant pass energy of 29.35 eV. Spectra were recorded with the X-ray generator operating at 15 kV and 20 mA.

3. Results and discussion

Fig. 1 shows the X-ray powder diffraction pattern for the VSbO4 sample. The characteristic peaks of vanadium antimonate [21] were observed after 70 h of milling and the crystallite size as determined using the Scherrer equation [22] was ca. 23 nm.

**Fig. 1.** XRD pattern for the VSbO4 sample.
in size, consistent with the crystal size value calculated from the XRD pattern. The $^{121}$Sb Mossbauer spectrum, Fig. 3, exhibited a single-peak typical of Sb$^{5+}$. A VSbO$_4$ stochiometry was thus confirmed from the combination of XRD and Mossbauer data. The small absorption signal observed at $-12$ mm/s can be ascribed to the presence of Sb$^{3+}$ species. The calculated content was ca. 3% and probably came from un-reacted Sb$_2$O$_3$ remaining after milling. The XPS spectra confirmed these results. Fig. 4a shows the Sb 4$d$ spectrum—the strongest peak for this element, 3$d$, and, particularly, the component 3$d_{5/2}$, could no be analyzed because its binding energy is coincident with that of O 1$s$ peak—was fitted to two components the binding energies (BE) of which are listed in Table 1. The higher BE was assigned to Sb$^{5+}$ and the lower one to Sb$^{3+}$ [23] the minor component. The V 2$p$ spectrum, Fig. 4b, was more complex and fitted to four chemical environments (V$^{5+}$, V$^{4+}$, V$^{3+}$ and V$^{2+}$, in decreasing order of binding energy). The first three peaks had a similar contribution and accounted for more than 90% of the overall spectrum. The presence of V in high valence states is consistent with the strong reducing power of V$^{3+}$ and its oxidation in contact with air. This can explain why part of V$^{3+}$ was oxidized to a mixture of V$^{4+}$ and V$^{5+}$ at the surface level. In any case, these results show that grinding is an effective method for preparing highly pure VSbO$_4$ in nanometric particle size.
The reactivity of the compound towards Li was initially monitored by step potential electrochemical spectroscopy (SPES). Fig. 5 shows the SPES curves for Li/VSbO₄ cells as obtained in different potential ranges. The first cathodic curve for VSbO₄ recorded between 3.7 and 0.0 V, Fig. 5a, exhibited two broad, strong peaks at 1.35 and 0.75 plus an unresolved peak below 0.3 V. As expected, the discharge profile for this curve, Fig. 5b, exhibited two extended plateaux at ca. 1.3 and 0.7 V responsible for the previous peaks. The Li amount inserted at the end of the latter plateau was about 11.5 atoms per mole of compound, which is somewhat greater than that consumed in the following reactions:

VSbO₄ + 8 Li → Sb + V + 4 Li₂O,  
(1)

Sb + 3 Li → Li₃Sb.  
(2)

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ar⁺ sputtering time/min</th>
<th>Antimony valence state</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>−x</td>
</tr>
<tr>
<td>VSbO₄</td>
<td>0.5</td>
<td>—</td>
</tr>
<tr>
<td>VSbO₄ electrode discharged at 0.5 V</td>
<td>16</td>
<td>31.2 (26)</td>
</tr>
<tr>
<td>VSbO₄ electrode charged at 2.0 V</td>
<td>4</td>
<td>—</td>
</tr>
</tbody>
</table>

Values in brackets are the atomic percentages.

Fig. 5. Step potential curves (a, c) for the first, third and fifth cycle of the Li/VSbO₄ cell as recorded in different potential windows. (b, d) Potential vs. capacity plot corresponding to SPES curves (a) and (c), respectively.
The shape of the SPES curve is quite similar to that reported for the electrochemical reaction of other based Sb compounds such as Sb₂O₃ and SbPO₄ with Li, which also exhibit two peaks of which that appearing at the higher voltage is ascribed to the formation of Sb particles according to

\[ \text{Sb}_2\text{O}_3 + 6 \text{Li} \rightarrow 2 \text{Sb} + 3 \text{Li}_2\text{O} \]  

and that observed at the lower to the formation of Li–Sb alloys of composition Li₃Sb or Li₄Sb in our case, the asymmetry of both peaks might reflect a multistep mechanism for reactions (1) and (2) due to the presence of V and the formation of Li₃Sb as an intermediate species, respectively. The additional capacity observed below 0.3 V can be ascribed to partial electrolyte decomposition catalysed by metallic particles forming a solid electrochemical interface (SEI) film.

Charging the cell to 4 V produced a broad asymmetric peak at 0.7–1.75 V that might correspond to the reverse process for the reduction peak observed at 0.7 V (viz. the de-alloying of Li₃Sb). Identifying a peak associated with the reverse reaction defined by Eq. (1) proved more difficult. In fact, the potential vs. de-inserted Li plot (Fig. 5b) exhibited a single plateau above 1 V, followed by continuous polarization up to 4 V. The amount of Li removed, around 9 Li atoms per mole of compound, suggests that reaction (1) is somewhat reversible. However, the following cycles resulted in a pronounced decrease in the intensity of the peaks in both the cathodic and anodic scans (Fig. 5a); this suggests that reactions (1) and (2) are irreversible in this voltage window. The formation of an SEI film of significant thickness as a consequence of the electrolyte decomposition might reduce the mobility of the charge carriers and decrease the rates of reactions (1) and (2) as a result. This was further confirmed by modifying the potential window to 1.8–0.5 V. Under these conditions, the step associated to the electrolyte decomposition and its polarization—the origin of which is unclear—was suppressed. The corresponding SPES curves, Fig. 5c, exhibit the main characteristics of the curves of Fig. 5a, but are consistent with the reversibility in reaction (2) on cycling (the calculated capacity, 4 Li atoms per mole of compound, Fig. 5d, was somewhat higher than that predicted from the reaction) and limited reversibility in reaction (1) as revealed by the low intensity of the high-voltage peak in the anodic scan, which gradually vanished with cycling.

The exact role played by V is unclear. In fact, there is some controversy concerning the ability of vanadium compounds to act as negative electrodes in Li batteries. According to Denis et al., orthorhombic InVO₄ can react reversibly with up to 7 Li atoms per mole of compound, whereas CrVO₄ reacts irreversibly with Li. Other compounds such as MnV₂O₆ also react reversibly with Li. In all these compounds, the vanadium is formally as V⁵⁺. In our compound, V³⁺ must be the main oxidation state; also, from the above described electrochemical results, it can hardly react reversibly with Li.

The structural and electronic changes undergone by V₃SbO₄ upon reaction with Li were examined from ex situ XRD patterns and XPS measurements. Fig. 6 shows the XRD patterns for the compound at three different discharge depths (1.5, 1.0 and 0.5 V). At 1.5 V, where the Faradaic yield was 0.5 Li per V₃SbO₄ mole, the XRD pattern was similar to that for the pristine sample (Fig. 1). The system retained its tetragonal structure, with a slight expansion (0.17 Å) of the unit cell volume. The low signal-to-noise ratio observed in the XRD patterns for the sample discharged at 1.0 and 0.5 V (Fig. 5a) precluded the identification of crystalline phases. This is indicative of drastic amorphization of the compound upon Li insertion and, unfortunately, prevents the identification of the products suggested for reactions (1) and (2). This is also a common occurrence in other Sb-based systems such as SbPO₄.

The ex situ XPS measurements of the discharged and charged electrode were affected by the presence of electrolyte impurities on the electrode surface, even though it was washed carefully with acetonitrile. This impurity layer decreased the intensity of the photoemission peaks for the active material, thus concealing the electronic changes that occurred during the electrochemical process. In order to remove the electrolyte impurities, the electrode was sputtered with argon over short periods. Because the instability of the low oxidation states of V precluded obtaining information about the electronic changes in this element, the discussion will focus on Sb. Fig. 7a shows the Sb 4d spectrum for the electrode discharged up to 0.5 V and cleaned for 4 min. Based on Fig. 5, all Sb should be alloyed with Li and V in metallic form at this discharge depth. Compared with the spectrum of the original sample, a shoulder is observed in the low BE region that can be assigned to the F 2s photoemission peak and ascribed to LiF traces adsorbed on the electrode surface. This peak tended to disappear as the sputtering time (Fig. 7b) was...
Fig. 7. Sb 4d XPS spectra for VSbO₄. (a, b) Electrode discharged at 0.5 V, and sputtered for 4 and 16 min, respectively. (d) Electrode charged at 2.0 V and sputtered for 4 min. (c, e) Atomic percentages for the different antimony valence states as a function of sputtering the time for the discharged and charged electrode, respectively.
increased. The best fit for this latter spectrum was obtained with three components for the Sb signal the BE of which are listed in Table 1. The two higher BE components are consistent with oxidized Sb (Sb$^{3+}$). The peak at 32.5 eV can be assigned to Sb$^0$ and the lowest energy peak at 31.2 to the element bound to Li in the Li-Sb alloy. Sb in a chemical environment alloyed to Li has not been reported in the literature previously. The depth profile of this electrode is shown in Fig. 7c as the variation of the concentration of the three Sb species as a function of the sputtering time. The main observation is an increase in alloyed Sb content and a decrease in those of the other three species (particularly the oxidized species Sb$^{3+}$, the origin of which could be contact with oxygen traces). The origin of the high Sb$^0$ content is unclear. An oxidation process such as that proposed for the presence of Sb$^{3+}$ is unlikely as its content changed little with the sputtering time. A conversion of alloyed Sb to elemental Sb caused by either the X-ray beam and/or Ar$^+$ bombardment cannot be excluded but requires confirmation. In fact, the interconversion of the Sb oxidation states upon Ar$^+$ bombardment has recently been suggested [27].

Fig. 7d shows the Sb 4$d$ spectrum obtained after charging the cell at 2.0 V. The main difference from the discharged electrode was the weakness of the F 2$s$ peak, which suggests lower impurity content in this electrode. Moreover, only two Sb chemical environments were required to fit the profile. Their BE, listed in Table 1, are consistent with Sb$^0$ and Sb$^{3+}$. The predominant species was Sb$^0$. Its concentration increased with increasing bombardment time, Fig. 7c, and reached nearly 80% of the total Sb content after 16 min. The absence of the low-energy peak and the presence of Sb$^0$ as the main component is consistent with the model of electrochemical reactivity towards Li derived from the SPES curve, namely: the reversibility of reaction (2) and the difficulty of oxidizing the Sb formed after the de-alloying process.

The cycling properties of the cells made from VSbO$_4$ were examined from galvanostatic measurements, a more usual regime for analyzing this cell parameter. Based on the above considerations, two voltage windows were selected (viz. 2.5–0.5 and 1.5–0.5 V). Fig. 8 shows the variation of the discharge capacity as a function of the cycle number. The initial capacities for the wide and narrow window (650 and 450 A h/kg, respectively) markedly exceed that calculated from Eq. (2) (339 A h/kg). However, the delivered capacity faded with cycling in both cells, especially in the wider voltage range—possibly as a result of the increased polarization observed in the charge curve above 1.5 V, Fig. 6. Thus, although increasing the voltage window the delivered capacity increased, both cells delivered a similar capacity (around 250 A h/kg) in the 30th cycle. As noted earlier, the beneficial effect of V on cell performance is arguable if one also consider the difficulty of directly comparing our results with those reported for other Sb-based compounds (viz. Sb$_2$O$_3$ [19], Sb$_2$O$_5$ [18], Sb alloys [2–11]) as a consequence of the different conditions used (particle size, electrode preparation, voltage window, charge/discharge rate). Nevertheless, the electrochemical properties of VSbO$_4$ are better than those of SbPO$_4$ [20], a closely related compound. The formation of metal V in the first discharge process against Li$_3$PO$_4$, a poor electronic conductor, could explain the improved cell performance obtained by replacing P with V.

4. Conclusions

Nanosized VSbO$_4$ obtained by grinding a stoichiometric mixture of the respective oxides has the ability to react reversibly with Li at a low potential vs. the Li electrode and is a potential candidate to act as anode in a Li battery. The galvanostatic and SPES curves obtained for the Li/VSbO$_4$ cell were interpreted by assuming two reactions, namely: (i) complete, irreversible reduction of V and Sb over the 3.7–1.1 V range; and (ii) formation of Li$_2$Sb alloys at lower potentials. The latter reaction is reversible, but reversibility is reduced by the formation of an SEI film at discharge depths up to 0.0 V.

The reaction with Li completely destroyed the rutile-like framework and precluded identification of the resulting phases by X-ray diffraction. This difficulty was overcome by using the XPS technique, which exposed the electronic changes undergone by VSbO$_4$ upon reaction with Li. Fitting the Sb 4$d$ peak of the electrode discharged at 0.0 V exposed a low energy component at 31.2 eV consistent with a chemical environment for Sb other than Sb$^0$ or Sb$^{3+}$. This component, ascribed to alloyed Sb, disappeared on charging the cell at 2.0 V. Under these conditions, Sb$^0$ was the main species found. All these results are consistent with a reversible alloying/de-alloying reaction, Sb$^0$ + $n$Li $\rightleftharpoons$ Li$_n$Sb ($n = 2, 3$), and confirm the difficulty of oxidizing the Sb once formed during the discharge process.

The capacity delivered by the Li/VSbO$_4$ cell as measured in the voltage windows 2.5–0.5 and 1.5–0.5 V faded on cycling—more markedly in the broader window—and
levelled at around 250 A h/kg, a value somewhat lower than that estimated from reaction (2), 339 A h/kg—after 30 cycles. However, the capacity was higher than that for SbPO$_4$, which is isostoichiometric with the V compound. The formation of V as an inert metallic matrix countering the insulating properties of Li$_3$PO$_4$ could be the origin of the improved capacity delivered by the cell.

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