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# Electrochemical reaction of lithium with nanosized vanadium antimonate

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## Abstract

Nanometric vanadium antimonate, $VSbO_4$, was prepared by mechanical milling from $Sb_2O_3$ and $V_2O_5$ and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Mossbaüer 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) $VSbO_4 + 8\ Li \rightarrow Sb + V + 4\ Li_2O$ and (ii) $Sb + 3\ Li \rightarrow Li_3Sb$, 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 $MSb_x$ with $1<x<3$ and $M =$ 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 $Li_xSb$ 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 $Cu_2Sb$ [12] or $Mn_2Sb$ [3], and (ii) thin-films [13] or nanosized materials [7,14]. In the former case, the lithiated product ($Li_2Cu_2Sb$) bears a strong structural relationship with its parent compound ($Cu_2Sb$). 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], $SnO_2$ [16], $CaSnO_3$ [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 $Sb_2O_3$ 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 $SbPO_4$ to perform acceptably [20]. Although $Li_3PO_4$ is a poorly conductive matrix, it exhibits good cycling properties. This paper reports the electrochemical properties of nanometric vanadium antimonite ($VSbO_4$) in Li cells. The compound was obtained in the form of nanosized particles by prolonged grinding, and was characterized by X-ray diffraction, Mossbaüer 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 $LiPF_6/VSbO_4$ under both potentiostatic and galvanostatic regimes.

## 2. Experimental

$VSbO_4$ was prepared from stoichiometric mixtures of commercial grade $V_2O_5$ and $Sb_2O_3$. The mixtures were dry milled in the air in a Restch 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 $K\alpha$ 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 $^{121}Sb$ Mossbaüer spectrum was recorded from powdered samples, using a constant acceleration spectrometer and a $Ca^{121}SbO_3$ source at 77 K. X-ray photoelectron spectra were recorded on a Physical Electronics PHI 5700 spectrometer, using non-monochromated $MgK\alpha$ 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. The energy scale of the spectrometer was calibrated by using the Cu $2p3/2$, Ag $3d5/2$ and Au $4f7/2$ photoelectron lines at 932.7, 368.3 and 84.0 eV, respectively. The vacuum in the analysis chamber was better than $10^{-9}$ Torr. Binding energies were corrected against that for C $1s$ of adventitious carbon (and the methyl group) fixed at 284.8 eV together with the F $1s$ at 685.5 eV. Samples were mounted on a holder without adhesive tape and kept under high vacuum in the preparation chamber overnight prior to transfer to the analysis chamber of the spectrometer. Survey spectra over the range 0–1100 eV were recorded at a 187.85 pass energy, each region being scanned several times to ensure an adequate signal-to-noise ratio. A $4\times4$ mm sample area was sputtered with 4 keV $Ar^+$; the sputter rate was assumed to be $\sim$2.1 nm min$^{-1}$ as determined for $Ta_2O_5$ under identical sputtering conditions. Spectra were processed by using PHI-Access V.6 and Multipak software, both from Physical Electronics. High-resolution spectra were fitted after Shirley background correction. Satellite subtraction was carried out for the V $2p$ region before fitting. Surface atomic concentrations were determined from peak areas, using Shirley background subtraction and sensitivity factors provided by the spectrometer manufacturer (Physical Electronics, Eden Prairie, MN). In order to avoid reduction of higher metallic oxidation states by X-rays, spectra were collected with short acquisition times. Ex situ XPS measurements were performed on the acetonitrile-washed pellet from the dismantled cell. All manipulations were done under an argon atmosphere; also, a special glove-box connected to the spectrometer antechamber allowed samples to be transferred to the spectrometer without direct contact with air.

Electrochemical measurements were performed in two electrode cells, using Li as a counter-electrode. The electrolyte was Merck battery electrolyte LP 40 (EC:DEC = 1:1 w/w, 1 M $LiPF_6$). Electrode pellets were prepared by pressing, in an stainless-steel grid, ca. 4 mg of active material with polytetrafluoroethylene (PTFE) (5 wt%) and acetylene black (10 wt%) at 4 ton. Galvanostatic tests were conducted at a rate of $C/12$ ($C$ being defined as 1 $Li^+$ ion exchanged in 1 h). Step potential curves were recorded at 2.5 mV/0.22 h per step. All electrochemical measurements were controlled via a MacPile II potentiostat–galvanostat.

## 3. Results and discussion

Fig. 1 shows the X-ray powder diffraction pattern for the $VSbO_4$ 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. The TEM image (Fig. 2) showed agglomerates of rounded nanoparticles, ca. 25 nm

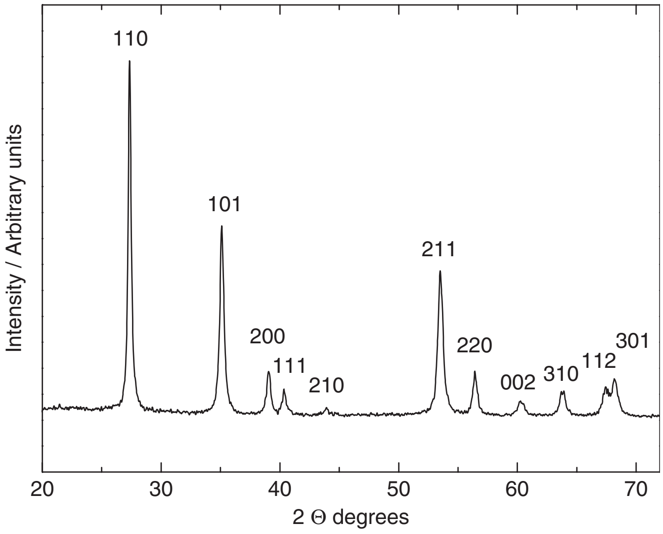

Fig. 1. XRD pattern for the $VSbO_4$ sample.