



Short communication

Electrochemical performances of BiSbO₄ as electrode material for lithium batteries

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ARTICLE INFO

Article history:

Received 8 January 2008
 Received in revised form 7 March 2008
 Accepted 17 March 2008
 Available online 28 March 2008

Keywords:

Electrode material
 Electrochemical performances
 Lithium batteries
 Primary batteries

ABSTRACT

We present an electrochemical study of BiSbO₄, an opened layered oxide having a structure related to Aurivillius phases. Li//BiSbO₄ cells show a large specific capacity as high as 1250 mAh g⁻¹ during reduction down to 0.5 V. This reaction involves 18Li atoms per formula unit, pointing it towards a very promising cathode material for primary lithium batteries, in particular for ICD devices. The characterization of the reduction products indicates that the reduction of BiSbO₄ with lithium presumably goes along firstly with the formation of metallic Sb and Bi to follow the formation of the alloys Li₃Bi and Li₃Sb dispersed in a lithium oxide matrix. *In situ* X-ray diffraction experiments proved the amorphous nature of both metals and final alloys. On the other hand when Li//BiSbO₄ cells are limited to discharge down to 1.2 V, BiSbO₄ reacts with 5Li atoms. After the first discharge, that develops a specific capacity of 350 mAh g⁻¹, high cyclability has been observed.

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1. Introduction

After the intense research activity during the middle and late 1970s on positive electrode materials for ambient temperature rechargeable lithium batteries (see for example Ref. [1]), the oxide LiCoO₂ [2] emerged as one of the most attractive materials and reached the market in the early 1990s.

On the other hand carbon-based materials have been widely used as the negative and still dominate the market [3]. After an intense research effort during the last decade new materials whose reactions with lithium are not topotactic (i.e. cannot be considered as intercalation reactions) have been proposed as possible electrodes: tin-based amorphous composite oxide (TCO) [4], simple MO oxides (M=Co, Ni, Cu, Fe) [5], Ag₂V₄O₁₁ [6] and Cu_{2.2}V₄O₁₁ [7]. In the case of TCO the reaction with lithium produces firstly Li₂O and Sn. Afterwards, the latter alloys reversibly with lithium.

A similar electrochemical behaviour regarding the presence of an alloying process at low voltage has been found in Bi₄V₂O₁₁ that crystallizes with the Aurivillius type structure [8,9]. We found that ca. 12lithium/formula unit reacted reversibly in the high voltage range (above 1 V) [10,11] making the oxide useful as positive electrode for rechargeable lithium batteries. However, we also pro-

posed it to be used as negative electrode for primary lithium batteries in as much as ca. 700 mAh g⁻¹ (28Li/formula unit) can be developed in the 2–0.5 V range.

In the present work we have investigated BiSbO₄ which is another Aurivillius-related oxide. This is presented as an interesting material to be used in lithium primary batteries in view of the reaction characteristics with lithium; more precisely, it may be a very suitable and alternative cathode active material for batteries addressed to implantable cardioverter-defibrillators (ICDs). BiSbO₄ shows gravimetric and volumetric energy densities higher than those of SVO [12,13]. An additional advantage is (as it will be shown in the results section) that reduction proceeds through several plateaus, which could be used to predict lifetime of the battery.

2. Experimental

BiSbO₄ has been obtained by the solid state reaction method accordingly to the previously described procedure [14]. Bi₂O₃ and Sb₂O₃ (high purity grade) as powder raw materials were mixed in stoichiometric amounts and fired at 600 °C for 48 h in an oxidant air atmosphere. The mixture of reactants was grinded, pressed into pellets and heated at 850 °C for 12 h.

Structural characterization was first made by X-ray diffraction using a Bruker D8 high-resolution X-ray powder diffractometer with monochromatic Cu Kα₁ (λ = 1.5406 Å) radiation, obtained with a germanium primary monochromator and equipped with a posi-

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tion sensitive detector (PSD) MBraun PSD-50M. Diffraction patterns were analysed with the FullProf software [15].

The electrochemical characterization regarding the reaction of BiSbO_4 with lithium was carried out using Swagelok test cells [16] with the configuration: $\text{Li}/\text{electrolyte}/\text{BiSbO}_4$. A 5 mm diameter disk of lithium was used as the anode. The commercial solution Selectipur LP30 consisting of ethylene carbonate, dimethyl carbonate and LiPF_6 was used as the electrolyte. The cathode consisted of a powdery mixture (weight ratios are given) of active material (60%), carbon black (30%) and a binder (Kynarflex) (10%), which was pressed into 8 mm diameter pellets. A MacPile II system has been used for electrochemical studies. Potentiostatic experiments under quasi-equilibrium conditions were carried out by changing the potential step in intervals of ± 5 mV every 2 h, at 25 °C.

The structural changes upon reduction have been investigated by using an electrochemical cell suitable for *in situ* X-ray diffraction experiments in a conventional X-ray powder diffractometer operated in reflection mode. A beryllium foil was used as X-ray transparent window and as cathodic current collector at the same time. X-ray diffraction patterns were collected at room temperature from powdery samples and analysed using the profile matching feature of the FullProf software [15]. The cathode was placed below the beryllium window as 8 mm diameter pellets with the above mentioned composition for electrochemical runs. The cell was discharged at a constant current density of 0.3 mA cm^{-2} (ca. 1Li every 25 h) to a lower cut-off cell voltage of 0.2 V. Continuous X-ray diffraction scans were collected from 22° to 80° with a step time of 4 s. Step size was each 0.0366° (2θ).

3. Results and discussion

The X-ray diffraction pattern (XRD hereafter) of BiSbO_4 was fully indexed using the previously reported monoclinic unit cell (S.G. $I2/c$) in accordance with an Aurivillius-type structure (Fig. 1). Refined cell parameters are $a = 5.46804(7)$, $b = 4.88531(6)$, $c = 11.81895(16)$ Å, $\beta = 101.1228(1)^\circ$.

The crystal structure is shown in Fig. 2 as a layered structure in which the metal atoms, Bi and Sb, exhibit alternate layers. Sb is coordinated to six oxygen ions forming octahedra that share corners to form Sb-O_6 layers. There are three different Sb–O distances in those octahedra: 1.885, 1.936 and 2.046 Å. Bi atoms are located in the interlayer spaces, forming a distorted eight-fold coordination, with four different Bi–O distances between 2.174 and 3.022 Å.

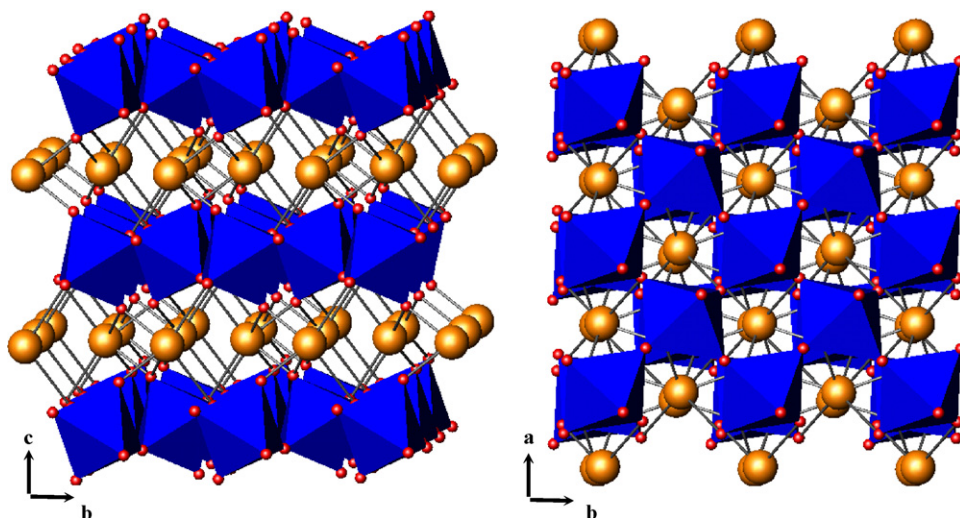


Fig. 2. Schematic crystal structure of BiSbO_4 , with slightly distorted SbO_6 octahedra (in blue on line) and BiO_8 coordination (Bi atom in yellow on line and O in red on line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

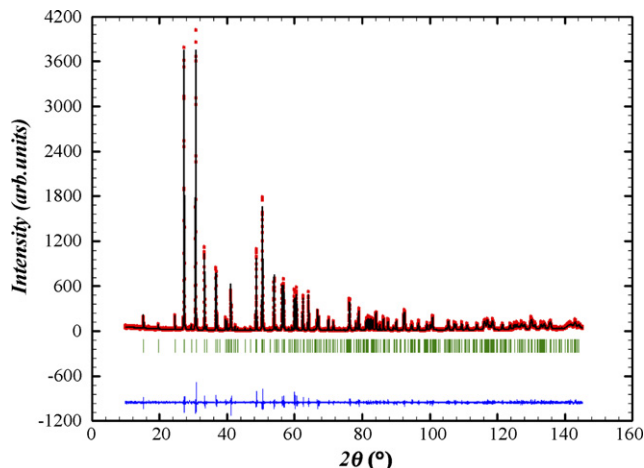


Fig. 1. XRD pattern of BiSbO_4 with observed, calculated and difference plot.

Regarding the electrochemical behaviour, Fig. 3a shows a typical discharge curve of a $\text{Li}/\text{electrolyte}/\text{BiSbO}_4$ cell down to 0.5 V. The data were obtained under quasi-equilibrium conditions (± 5 mV every 2 h). It can be seen that BiSbO_4 is able to react with ca. 18Li/formula unit through different reductive processes, which are evidenced by different pseudo-plateaus (indicated by I, II, III and IV) that are clearly separated in some cases by more abrupt changes of potential. The high specific capacity associated to the discharge process is comparable to those results obtained when some oxides are over reduced [17–19]. It is well known that for such cases reduction with lithium causes decomposition of the active material into a finely divided lithiated metal alloy phase, Li_xM , which is further electrochemically active, and an electrochemical inert metal oxide matrix. As intermediate step the formation of the corresponding metals can be supposed. In our case the electrochemical active lithiated metal phase will be assigned to Li_xM ($\text{M} = \text{Sb}, \text{Bi}$), and the electrochemical inert matrix would be Li_2O . The formation of these compounds is addressed below in view of our experimental results.

The different electrochemical processes are better recognized in Fig. 3b, where the incremental capacity $-dx/dE$ has been plotted versus potential. The maxima observed in the $-dx/dE$ vs. E curve, labelled as I', II', III' and IV' correspond to plateaus in the voltage–composition plot (marked as I to IV, respectively in Fig. 3a)

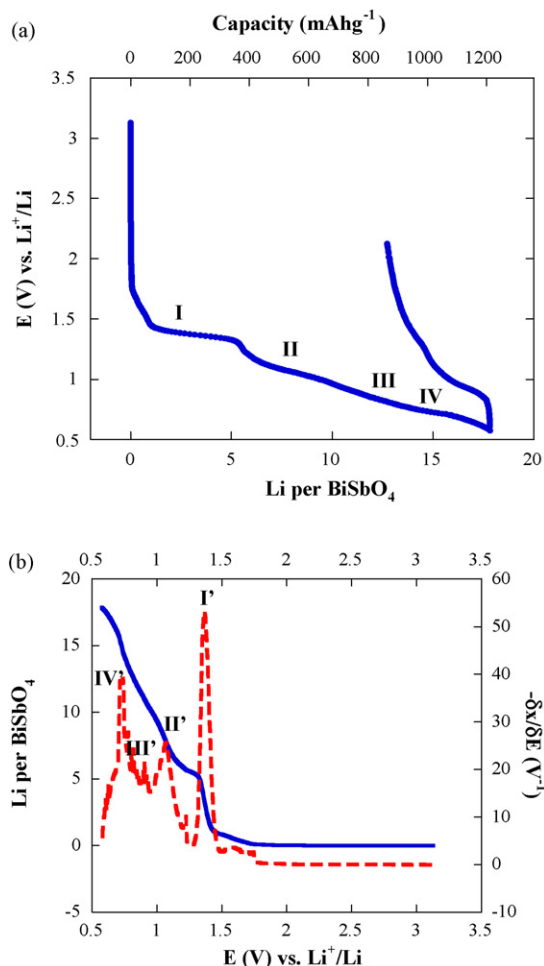
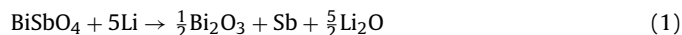


Fig. 3. (a) Typical voltage–composition variation obtained for the first discharge and first charge of a cell Li/BiSbO₄ at the rate of ± 5 mV every 2 h, (b) incremental capacity (discontinuous curve, red on line) and voltage–composition curve (continuous line, blue on line) for the first discharge. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

and are assigned to the transformation of the active materials through biphasic regions. During a two-phase transformation the electrochemical potential should be constant if the system is thermodynamically under equilibrium. The reaction of Li with BiSbO₄ starts with the reaction of 1Li/formula unit through likely a single phase region. The first pseudo-plateau is reached at 1.4V (region I) and at its end the reaction of ca. 5Li/formula unit has been completed. Then, after a narrow compositional region (regarding number of lithium that react) where again a continuous variation of potential seems to exist (likely a narrow single phase region), a second pseudo-plateau is detected at 1.2V (region II). The use of the incremental capacity–potential curve linked to the information taken from the voltage–composition curve allows to establish the limit of this second plateau that can be roughly estimated to be about 3 additional Li/formula unit. From here on, another two plateaus are evidenced from the presence of the corresponding maxima in the incremental capacity–potential curve, though no abrupt potential change can be detected between them. Approximate lithium quantities after plateaus II and III seems to be 3 and 4, respectively, although the separation of both regions is not clear.

For the two first and well defined plateaus a feasible model of reduction can be now proposed in view of the above mentioned quantities of lithium, the shape of the discharge curve and the oxidation state of bismuth and antimony. Regarding the latter note that

Bi^{III}Sb^VO₄ is assumed accordingly to Enjalbert et al. [20]. Therefore, at the end of region I (see Fig. 3a) the reaction may produce the partial reduction of the oxide BiSbO₄ with 5Li/formula according to the following reaction:



The reaction with 5Li/formula proceeds through two processes; the initial solid solution region ca. 1.5V and a wider two-phase region I ca. 1.4V. In agreement with the proposed reaction (1) we have to note that the reduction process of Sb₂O₅ to Sb, has been reported to proceed mainly through a plateau at 1.4V [21].

After reaction (1) the reduction of “BiSbO₄” continues onward involving 3 additional lithium atoms. For this composition range, reduction begins through a narrow solid solution (ca. 1Li/formula unit) and is completed after a pseudo-plateau developed at 1.2V (2Li/formula unit). These two regions could go along with the complete reduction of the Bi(III) in (1/2)Bi₂O₃ obtained in reaction (1) to its metallic state, accordingly to reaction (2).



Previous works [22,23] have reported the electrochemical characteristic of Bi₂O₃ when used as the positive electrode in lithium cells: discharge leads to the reduction of the oxide to metallic Bi at about 1.4V at 24 °C. The lower value observed in our case for the reduction of BiSbO₄ may be due to the unfavourable effect of the composite obtained after reaction (1) that may increase the polarization of the cell due to the formation of Sb crystallites with high electrical resistivity.

Further reduction, seems only possible by considering the alloying of both Sb and Bi with lithium following Eqs. (3) and (4). Voltage variation profile does not present clear features that may allow proposing a reliable or unambiguous mechanism. In a very roughly manner a couple of pseudo-plateaus can be inferred to exist in view of the two maxima observed in the incremental capacity plot (see Fig. 3b) ca. 0.9 and 0.75V. Taking into account the reports on the alloying reaction of Bi and Sb at room temperature in lithium cells we suppose that in these last stages of reduction the following reactions take place: [24–26]



Reaction (3) is known to occur at 0.9V and it is at this voltage where we also detected a maximum in Fig. 3b. On the other hand, during the reduction process of Bi towards Li₃Bi (reaction (4)), the coexistence of two phases has been reported [24], Bi in equilibrium with LiBi around 0.77V and a second plateau, at 0.75V, showing another two-phase region, with coexistence of LiBi and Li₃Bi. This is in agreement with our observation of a wide maximum in the incremental capacity (see Fig. 3b) ca. 0.75V.

In any case the alloying of Bi and Sb in the 1–0.5V range only would account for 6Li/formula unit, while our observation is a capacity that corresponds to ca. 10Li/formula unit. However, we have to take into account that in this voltage range two other processes may occur; a contribution from carbon and the formation of the SEI (solid electrolyte interface) which is known to occur at 0.8 and slightly above 0.5V, respectively.

Having also into account the low voltage regions, the total specific capacity is very high, ca. 1250mAhg⁻¹. Therefore, higher than the value that corresponds to the theoretical specific capacity of SVO [27], 315mAhg⁻¹. Note that the formula weight of BiSbO₄ is smaller than that of Ag₂V₄O₁₁ but the former reacts with 18Li/formula unit while the latter with only 7Li/formula unit. However, regarding possible applications we need to compare also the output voltage. BiSbO₄ delivers the above mentioned capacity at

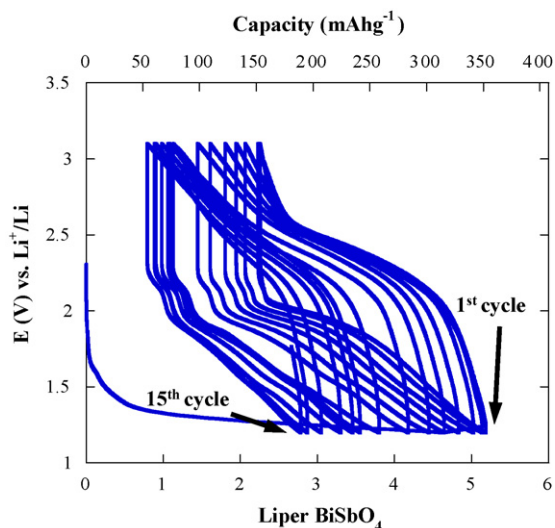
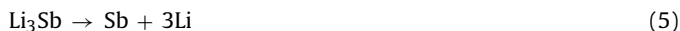


Fig. 4. Discharge curve down to 1.2 V and further cycling in the 1.2–3.1 voltage range (potential steps of ± 5 mV every 2 h).

an average voltage of 0.5 V much lower than that of SVO (1 V). Even if we limit the discharge of BiSbO_4 to 1 V the capacity of the here presented material is still superior being approximately 650 mAh g^{-1} . In this case 10Li/formula are used along the reduction. Therefore, BiSbO_4 may be considered a very interesting candidate for the development of primary lithium cells with applications in ICDs devices.

Besides the investigation of BiSbO_4 during the first discharge and its possible application in primary lithium cells, the study will now be addressed to the possibility of recharging Li/ BiSbO_4 cells, i.e. the reversibility of the process involved during the first discharge and the evolution upon further discharge. In this connection Fig. 3a shows that the second discharge is not able to revert completely the reduction reaction. However, a reversible capacity is observed at low voltage which may correspond to the extraction of lithium from the Li_3Bi and Li_3Sb alloys, i.e. the de-alloying reaction. Indeed, 6Li atoms appear to be reversibly extracted during oxidation. This reversible capacity agrees with the oxidation (de-alloying) of the electrochemically active species Li_3Bi and Li_3Sb to form again the corresponding active metals inside the inert matrix, Li_2O , according to the following equations:



This type of process is well known to be reversible in some metals (as Sn [17,18] already mentioned), though a great deal of work needs to be done in order to optimize electrode microstructure and hence performances as it has been done in the case of the Sn-based negative electrodes that have finally been launched to the market.

An interesting feature of the first discharge is that only the plateau corresponding to the reduction summarized by reaction (1) is very well defined. Obviously the reconstruction of BiSbO_4 from the reduction products indicated in this equation is not possible as it can be deduced from the shape of the first charge curve presented in Fig. 4. Subsequent discharge–charge cycles from 3.1 to 1.2 V, this is the voltage range where reaction (1) has finished, are also shown in the same figure. Interestingly enough, after the first charge at 3.1 V, the cell exhibits a quite remarkable cyclability. The involved reaction may be the partial reoxidation of Sb and reduction of Li_2O in a similar way to that observed in the reduction of some simple oxides [5], in lithium cells.

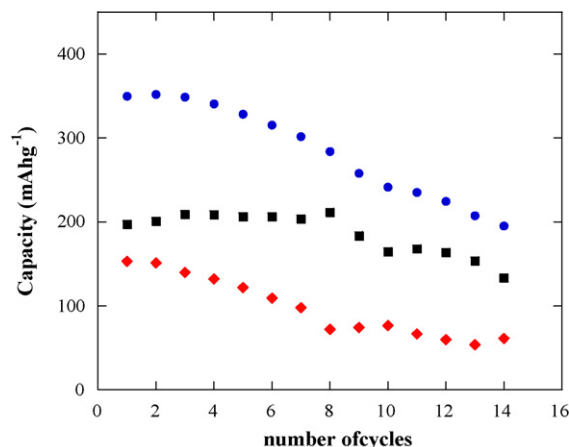


Fig. 5. Extended cycling of Li/ BiSbO_4 . (●) Capacity discharge at 1.2 V, (◆) capacity charge at 3.1 V, and (■) difference between both.

Variation of capacity upon cycling in this voltage range is depicted in Fig. 5. It can be seen that both discharge and charge capacity suffer from a fast decrease. After 14 cycles the starting capacity, 350 and 150 mAh g^{-1} at full discharge and charge, respectively, have decreased to 200 and 60 mAh g^{-1} , respectively, which means a decrease in more than a 40% and 60%. The loss due to polarization is high as can be deduced from the large difference observed between charge capacity and discharge capacity in each cycle. It seems then that the application of BiSbO_4 in rechargeable lithium batteries – similarly to the systems based on the reduction of a simple oxide to metals – will strongly depend on the electrode processing and its optimization.

To investigate the structural change during the discharge process, *in situ* X-ray experiments have been performed under galvanostatic conditions, using a home-made testing cell, with a beryllium window.

Fig. 6 shows a selected part of the XRD patterns collected during the reduction reaction of BiSbO_4 above described. They correspond to the reaction of BiSbO_4 with ca. 5Li/formula unit (equivalent to a discharge capacity of 350 mAh g^{-1}), down to 1.1 V within region I. Peaks marked with solid triangles and rhombuses correspond to Be (used as X-ray window) and BeO , respectively. It can be seen that the diffraction peaks coming from BiSbO_4 gradually disappear

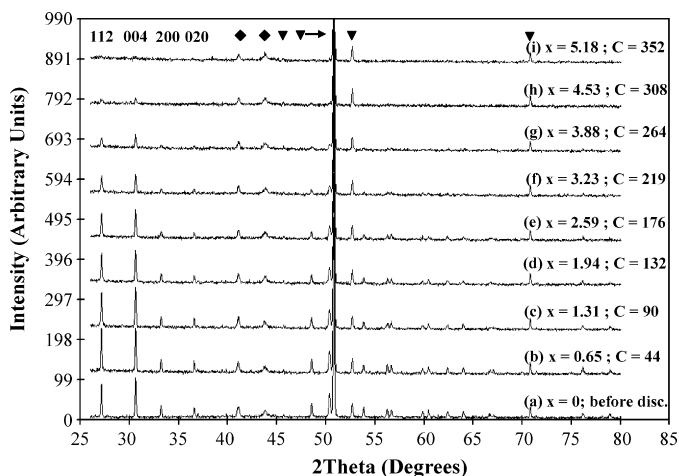


Fig. 6. Selected *in situ* X-ray diffraction patterns recorded during reduction under galvanostatic experimental conditions (0.15 mA as constant current). After $x = 5.18$ no change is observed. The capacity (C) is given in mAh g^{-1} . Besides (▼) Be and (◆) BeO diffraction peaks, only BiSbO_4 is detected.

as the reaction with lithium continues onward. For $x = 5\text{Li}/\text{formula}$ unit diffraction lines coming from BiSbO_4 have completely vanished from the X-ray pattern. On the other hand, no new diffraction peaks arise either upon further reduction that has been investigated down to 0.6 V. Bearing now in mind that no significant shift in diffraction lines is observed during reduction and that the variation of cell parameters for some selected discharged materials is negligible, it is clear that BiSbO_4 is being decomposed according to reaction (1) to amorphous phases. Taking into account other related cases of reduction of simple oxides [28–31], nanosized particles rather than amorphous phases are likely to account for the absence of diffraction peaks in the recorded patterns. Even more, a possible re-oxidation of Sb in the 1.2–3.1 V range, may be facilitated by the microstructure and particle size of the composite formed.

4. Conclusions

The electrochemical properties of BiSbO_4 as a new cathode electrode for lithium primary batteries, more specifically for ICD applications, have been unveiled. Comparing with the present state-of-art, specific capacity of commercialized SVO is surpassed by more than two times by BiSbO_4 , which delivers about 650 mAh g^{-1} at 1 V and more than 1250 mAh g^{-1} at 0.5 V. This behaviour points BiSbO_4 towards a promising cathode material for ICD batteries. The reduction reaction seems to proceed through the total reduction to Sb and Bi followed by alloying to Li_3M ($\text{M} = \text{Bi, Sb}$).

The use of BiSbO_4 as electrode for lithium rechargeable batteries is not so attractive. BiSbO_4 reacts with $5\text{Li}/\text{formula}$ at an average voltage of 1.4 V delivering a specific capacity of 350 mAh g^{-1} , but cells exhibit a progressive loss of capacity that could be possibly overcome by an appropriate optimization of electrode processing.

Acknowledgements

We thank Ministerio de Educación y Ciencia and Comunidad de Madrid for funding the projects MAT2004-03070-C05-01, MAT2007-64486-C07-01 and S-0505/PPQ/0358, respectively. Financial support from Universidad San Pablo-CEU is also acknowledged.

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