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Short communication

Optimized Sn/SnSb lithium storage materials

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Abstract

We report the synthesis of SnSb-based intermetallic with improved morphology. The electrochemical characterization shows that these materials have a good electrode behavior in a lithium cell. Capacities exceeding 800 mAh/g with a charge–discharge efficiency approaching 100%, have been obtained. In addition, the percent of the initial irreversible capacity is moderate. The capacity decreases upon cycling quite likely due to a still not optimized electrode structure.
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1. Introduction

Large interest is presently devoted to improve the performance of lithium ion batteries in view of their expected applications in advanced technologies, such as multifunction cellular phones and, eventually, electric or hybrid vehicles. Indeed, although lithium batteries are commercially well established, there is still room for improvement, especially in terms of replacement of conventional electrodes with new materials having enhanced energy content. In this respect, it would be for instance advisable to replace the carbonaceous anode with compounds having larger specific capacity, for example, with lithium metal alloys. In fact, in principle these materials can store much more lithium than graphite, however, they suffer from limited cycle life due to the large volume changes occurring during the lithiation and delithiation process.

Consistent efforts have been devoted to identify and develop suitable alloy morphologies and compositions with the goal of controlling the volume expansion and thus, to allow battery operation of the lithium storage metals. Particularly promising is the approach proposed by Besenhard and co-workers [1–6] who have proposed the use of intermetallic alloys, such as SnSb, as optimized electrodes with controlled volume stresses. This strategy has been adopted by other laboratories with relevant results [7–11].

In the electrochemical process, one component of these electrodes alloys with lithium with the concomitant displacement of the second component from the intermetallic alloy; then, also this second component alloys with lithium [5]. This two-step process is highly beneficial since it leads to a composite of two finely inter-dispersed lithiated phases and in course, the non-reacting component can "buffer" the volume changes of the reacting one during its alloying with lithium, this finally leading to a good operational stability. Indeed, capacity delivery as high as 600 mA h/g has been reported for SnSb intermetallic electrodes in lithium cells [4].

In this work, we have extended the investigation of SnSb-based intermetallic electrodes originally proposed by Besenhard and co-workers [6], with particular emphasis on the optimization of their morphology with the aim of further improving their properties and performance as innovative electrodes for lithium ion cells. Capacities exceeding 800 mA h/g have been obtained for these improved materials. To our knowledge, this is the highest value so far reported for this type of electrode.

2. Experimental

The alloy powders were prepared by precipitation from aqueous solutions, basically following the procedure recommended in Ref. [1]. Two solutions have been used for the synthesis, namely solution A formed by 28 g/l $SnCl_2{\cdot}2H_2O$, 9.4 g/l $SbCl_3$ and 110 g/l trisodium citrate dihydrate; and solution B formed by 2.8 g/l NaOH, and 3.6 g/l $NaBH_4$. Aqueous HCl was used to wash the obtained powder; its

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concentration was 0.25 M. Particular care was devoted to control the synthesis and the annealing conditions since they are expected to have a great influence on the particle size and the morphology of the final compounds. For instance, in contrast to the procedure previously suggested [1], in this work the precursor solution has been added slowly, drop-wise to the $NaBH_4$ solution. This modification is expected to favor the completeness of the reaction with reduction of the amount of unreacted precursor in the precipitate and thus, the formation of a pure product. Also, to control the final morphology, the precipitate was dried in vacuum either at room temperature or at 210 °C. The morphology and the structure of the resulting materials were analyzed by Field-Emission Scanning Electron Microscopy, FE-SEM and by X-ray powder diffraction, XRD Cu Kα radiation, respectively.

The plasma ICP analysis of the materials gave a Sn:Sb percent ratio of 63:37, showing that, as reported in the literature [5], tin-rich compounds are obtained with the synthesis procedure adopted. Accordingly, the materials may be referred to as Sn/SbSn.

Composite electrodes were prepared by dispersing in *N*-methyl-2-pyrrolidone a blend of Sn/SnSb (active material), carbon black (conductive additive) and poly(vinylidene fluoride), PVdF (binder) in the weight percent ratio of 82:10:8. The slurry was then cast on a copper substrate using a Doctor Blade technique.

The electrochemical tests were run in laboratory-type cells having the alloy powder composite as the working electrode and lithium as the counter and the reference electrode. A 1 M $LiClO_4$ solution in ethylene carbonate–propylene carbonate, EC:PC, 1:1 weight percent, was used as the electrolyte. The electrodes were cycled between 0.02 and 2.00 V versus Li at a rate of 120 mA/g. A Maccor type 4000 battery cycler was used for this test.

Impedance analyses were run using a Solartron 2SS Frequency Response Analyser coupled with a PAR 362 Potentiostat as Electrochemical Interface. A frequency range of 30 kHz–10 mHz was used and the experiments were run and controlled by a computer.

3. Results and discussion

Fig. 1 shows the FE-SEM images of two sample alloys, one obtained after drying at room temperature (Fig. 1A) and the other annealed at 210 °C (Fig. 1B). The pictures clearly show dramatic differences in the morphology of the two samples. The sample dried at room temperature is formed of single, nanosized particles while large aggregates appear in the annealed sample.

Fig. 2 shows the X-ray diffraction patterns of the two samples. Peaks specific as SnSb and Sn are seen for both samples. However, the annealed sample also shows peaks of SnO. In addition, sharper peaks are observed for this sample, this indicating its higher degree of crystallinity.

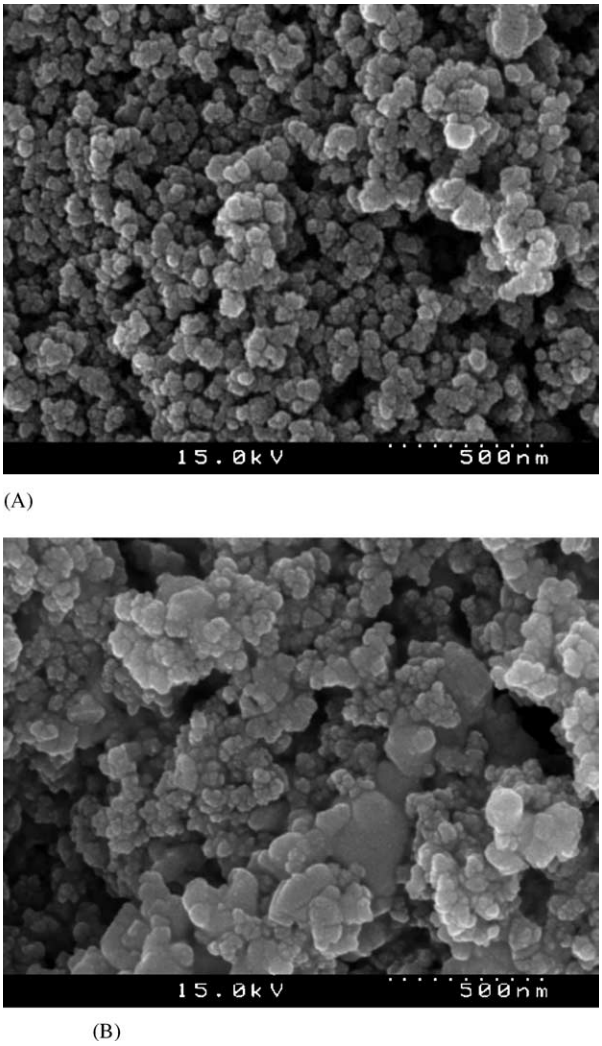

Fig. 1. FE-SEM images of as prepared (A) and annealed (B) Sn/SnSb powders.

Fig. 3 shows the voltage profiles of the initial cycling of the Sn/SnSb electrodes in a lithium cell. Both the responses of the annealed and of the non-annealed samples are shown. The multi-plateau behavior reflects the characteristics of the electrochemical process which is associated with the

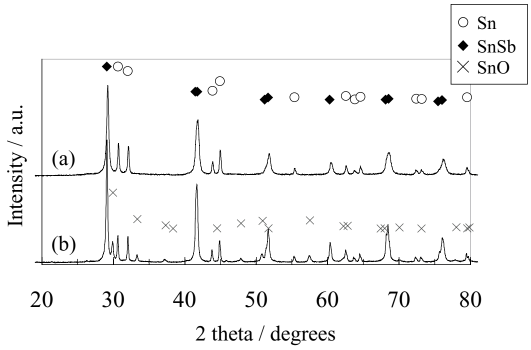

Fig. 2. XRD patterns of as prepared annealed (b) and non-annealed (a) Sn/SnSb powders.

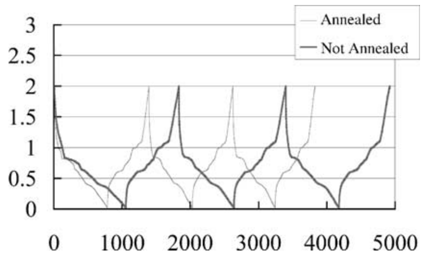

Fig. 3. Initial voltage profiles of Sn/SnSb electrodes made with annealed and non-annealed powders. Room temperature. Voltage range: 0.02–2.00 vs. Li. Current rate: 120 mA/g.

various lithium alloying (charge)–lithium de-alloying (discharge) stages [1]. The voltage trend of the two samples are similar, with the only difference being the annealed sample shows a plateau around 1 V which can probably be attributed to the process associated with the tin oxide impurity [5], see Fig. 2.

Fig. 4 shows the cycle performance of the two samples reported in terms of the capacity delivered with cycle number. It may be clearly seen that the non-annealed sample cycles have a capacity consistently higher than the annealed ones. We assume that this is directly related to the difference in the morphologies of the two samples. Upon decrease in particle size, the electrode surface area increases and this enlarges the reacting zone, favoring the alloying process and thus, ultimately the achievement of high capacity.

The FE-SEM images of Fig. 1 show that the annealing treatment results in the agglomeration of the particles and thus to a reduction of the active electrode area, accounting for the depression in specific capacity observed in Fig. 4. We can then conclude that the performance of the Sn/SnSb intermetallic, is particularly sensitive to the preparation procedure with particular emphasis on the annealing temperature. We show here that by keeping this temperature low, electrode materials with optimized morphology are obtained. Indeed, specific capacity as high as 800 mA h/g were routinely delivered when this condition was fulfilled, as demonstrated by the results of Fig. 4.

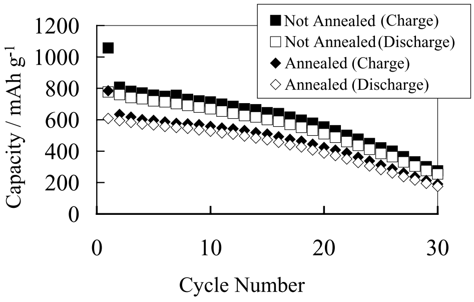

Fig. 4. Cycle performance of Sn/SnSb electrodes made with annealed and non-annealed powders. Room temperature. Voltage range: 0.02–2.00 vs. Li. Current rate: 120 mA/g.

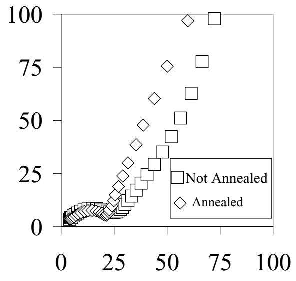

Fig. 5. Impedance spectra taken at open circuit of Sn/SnSb electrodes made with annealed and non-annealed powders. Room temperature. Frequency range: 30 kHz–10 mHz.

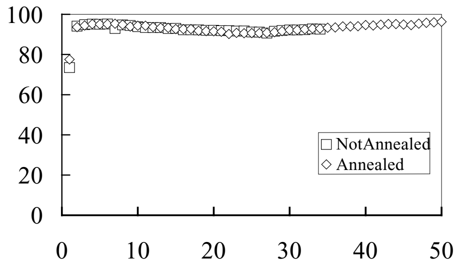

Fig. 6. Charge–discharge coulombic efficiency of a Sn/SnSb electrode formed by annealed and by non-annealed powders. Room temperature.

A high surface area is expected to be beneficial not only in terms of capacity but also in terms of the current rate of the electrode. A low particle size distribution results in a reduction of the lithium diffusion length and thus, in an enhancement of the kinetics of the electrochemical process. This is confirmed by Fig. 5 which compares the impedance response of the two differently thermally-treated samples considered in this work. The response is qualitatively similar for the two samples; there are however some significant differences in the width of the semicircle and in the trend of the low frequency Warburg line, which demonstrate the faster kinetics of the low temperature sample.

Finally, some discussion must be addressed to the charge–discharge efficiency of the Sn/SnSb electrodes here considered. After a value of about 75% in the initial cycle, the efficiency levels out at around 100%, see Fig. 6. An initial irreversible capacity is a common drawback for lithium metal storage electrodes and may be ascribed to various effects, which include electrolyte decomposition with the formation of an interfacial film, trapping initial lithium in structural defect sites, reduction of residual impurities, and others [5]. In this scenario, an irreversible capacity amounting to 25% in this work, is acceptable since much higher levels, for example, 50–65%, have been reported for similar materials [5].

4. Conclusion

In this work we have extended the investigation of lithium storage electrodes of the Sn/SnSb type originally proposed by Besenhard and co-workers [6]. We have shown that by properly controlling the synthesis conditions, an improved electrochemical response can be obtained. Indeed, the electrodes here prepared delivered values of initial capacity which are on average 200 mA h/g higher than those of samples prepared under the conditions usually reported in the literature. In addition to high capacity, these electrodes offer fast kinetics (average current rates of 120 mA/g can be routinely sustained in discharge), and are characterized by a comparatively low initial irreversible capacity. The capacity decreases upon cycling; however, we believe that this decay is associated to a not yet optimized electrode structure, rather that to an intrinsic default of the intermetallic electrode. Work is in progress to control this assumption and, eventually to define the best electrode composition to assure stable capacity delivery.

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