

## New anode systems for lithium ion cells

O. Crosnier<sup>a,\*</sup>, T. Brousse<sup>a</sup>, X. Devaux<sup>b</sup>, P. Fragnaud<sup>a</sup>, D.M. Schleich<sup>a</sup>

<sup>a</sup>Laboratoire de Génie des Matériaux, ISITEM, Nantes, France

<sup>b</sup>Laboratoire de Physique des Matériaux, UMR CNRS 7556, Ecole des Mines, Nancy, France

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### Abstract

Samples of small particle size bismuth and electroplated Ni–Sn alloy were tested as anodes for lithium ion batteries to highlight the effects of volume changes during charge and discharge on the cycling life of the electrodes. Bismuth was used for its relatively “high” potential of Li–Bi alloys formation (0.8–0.6 V) which prevents other components within the electrode from being electrochemically active versus lithium in this potential window. Electrochemical tests have shown that the capacity fade during cycling is largely dependant of the amount of Bi in the electrode. Electroplated Ni–Sn alloys were directly used as anodes and do not need to be reground nor mixed with additives. Different electroplating conditions, leading to different morphology, highlight the leading role of the particle size of the active materials used in the lithium ion cells. © 2001 Elsevier Science B.V. All rights reserved.

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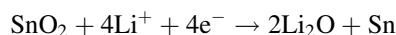
### 1. Introduction

Lithium battery technology has gone through a variety of changes in the last 25 years. In its initial form the cathode was composed of a metal disulfide, i.e. TiS<sub>2</sub> or MoS<sub>2</sub> [1–3], the anode was lithium metal, and the electrolyte was an inorganic lithium salt dissolved in an organic electrolyte. Approximately 10 years ago the lithium metal as anode was replaced by Sony due to the safety problems encountered by dendrite formation during cycling. At the same time to introduce lithium into the battery, and also add potential to the cell, the sulfide cathodes were replaced by a lithiated transition metal oxide. Thus was born the lithium ion cell using carbon as an anode and LiCoO<sub>2</sub> as the cathode. This battery has become a world standard especially in the areas of portable computers and mobile telephones where weight and volume are both extremely important, and the user is willing to pay an additional price for a superior energy storage device. Research has been undertaken by scientists throughout the world to both lower the costs of producing the battery, and to increase the volumetric and mass capacity of the battery. Efforts have been undertaken to replace LiCoO<sub>2</sub> as the cathode and carbon as anode in lithium cells. In this work we are interested in replacing carbon anodes, to

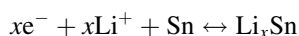
increase both the volumetric and mass capacity of lithium batteries.

Although there have been regular improvements in the carbon anodes since the initial incorporation of coke carbons, the limit to graphite intercalation is 372 mA h g<sup>-1</sup>. Recently Fuji released several patents [4,5] where the carbonaceous anode was replaced by a compound containing amongst other elements tin. The reversible capacity of this type of anode was substantially greater than for that observed in carbon electrodes. Although there has been some debate over the particular chemical reaction that occurs during the cycling of this electrode, there appears to be little doubt that there is a substantial irreversibility during the first cycle. Various authors have demonstrated that in the first cycle of simple tin oxides an irreversible reaction occurs with the formation of lithium oxide and metallic tin [6–9]. The metallic tin may then reversibly react with lithium to form a variety of alloys finally arriving at Li<sub>4.4</sub>Sn [10]. When the Sn is initially present as an oxide the tin oxide electrodes cycle quite well outside of the first reaction which has a substantial irreversible component:

(1) First irreversible reaction



(2) Subsequent cycles



\* Corresponding author. Tel.: +33-240-68-3161; fax: +33-240-6831-99.  
E-mail address: olivier.crosnier@isitem.univ-nantes.fr (O. Crosnier).

In this alloy reaction there is a huge change in volume associated with both the initial decomposition reaction ( $V[\text{Sn} + \text{Li}_2\text{O}] = 2.12 \times V[\text{SnO}_2]$ ) as well as the reversible reaction proceeding to a final maximum lithium composition of  $\text{Li}_{4.4}\text{Sn}$  ( $V[\text{Li}_{4.4}\text{Sn} + \text{Li}_2\text{O}] = 4.07 \times V[\text{SnO}_2]$ ). This volume increase can cause major mechanical problems with the electrode during recycling, and unless very small particle size of the oxide is initially chosen the anode shows very poor cycling behavior. Of course this problem of poor cycling behavior has two particular components. There is a microscopic component due to the expansion and contraction of the individual active tin particles. This problem can be partially resolved by using very small initial particles so that the expansion and contraction does not cause crumbling of the active component; however, the use of small particles does not resolve the macroscopic problem associated with total volume expansion and contraction of the electrode during cycling. In the case of the tin oxide electrodes, the first cycle creates an amorphous  $\text{Li}_2\text{O}$  component and thus the electrode is able to withstand the mechanical deformations occurring during cycling. Eventually after continuous cycling, the tin particles become larger and either start to fail because they loose electrical contact or are no longer able to withstand expansion and contraction without breaking up. This phenomenon still can allow a simple  $\text{SnO}_2$  anode to cycle several hundred times before it starts to loose capacity; however, in this type of electrode system there is always a very large irreversible component on the first cycle due to the formation of  $\text{Li}_2\text{O}$ . If one chooses to use pure tin rather than the oxide to avoid the large irreversible behavior observed in the first cycle due to the formation of  $\text{Li}_2\text{O}$  one observes a rapid decline in cell capacity even if one selects small particle size tin. This capacity loss is probably due to the lack of a sufficiently flexible binder as the entire electrode undergoes a substantial volume change. The binders used in carbon

anodes are not sufficiently flexible in a system such as tin where very large volume changes are observed during cycling.

In this work we have examined the preparation of anodes by using either a Sn–Ni [11] alloy or examined the use of small particle size Bi with different percentages of carbon present in the anode. In the studies using the Sn–Ni alloy we have changed the electrochemical conditions to modify the morphology of the material. The Sn–Ni alloy shows less volume expansion than pure tin in passing to the fully lithium incorporated material; however, there is still substantial expansion. There is still doubt as to the exact chemical reaction pathway when the alloy reacts with lithium, and one can not yet say that the reaction pathway yields pure Ni metal and inserted Sn or if the reaction yields an alloy containing Li, Sn and Ni. In the use of pure Bi particles we have examined various mixtures of carbon and Bi in order to determine if simply decreasing the volume changes in an electrode can increase the cycle life. In this additional study on novel anodes we have kept the particle size of the Bi particles constant to avoid an additional complication due to microscopic modifications in the Bi particles.

## 2. Experimental procedures

Samples of small particle size bismuth were prepared by evaporating a bismuth ingot in a direct current (DC) arc plasma under an Ar– $\text{H}_2$  gas flow at reduced pressure. The fine powders were collected and stored in a glove box under high purity argon atmosphere. A complete description of the powders production was previously published [12].

Samples of Sn–Ni have been synthesized by electrolytic deposition on a copper foil using a standard electrolytic bath [13] of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  ( $250 \text{ g l}^{-1}$ ),  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  ( $50 \text{ g l}^{-1}$ ),

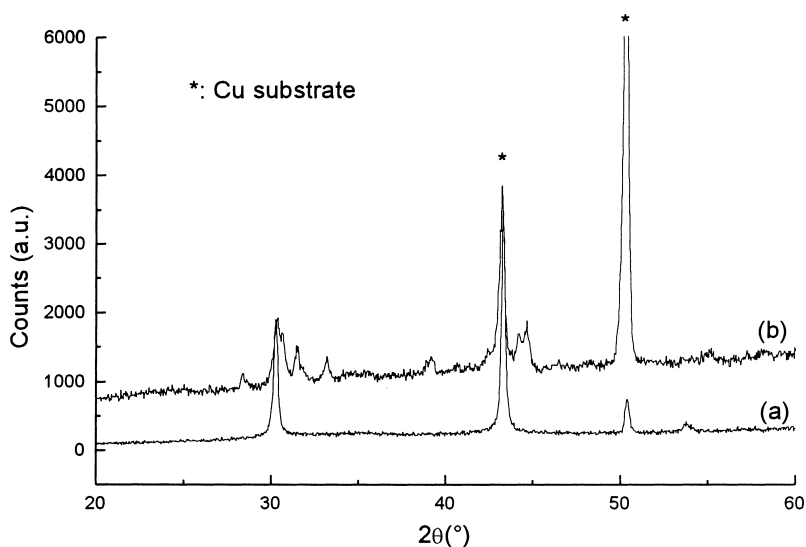


Fig. 1. XRD pattern of Ni–Sn alloy deposited at current densities of (a)  $100 \text{ mA cm}^{-2}$ ; (b)  $20 \text{ A cm}^{-2}$ .

$\text{NH}_4\text{F}:\text{HF}$  ( $40 \text{ g.l}^{-1}$ ) and  $\text{NH}_3$  35% ( $35 \text{ ml l}^{-1}$ ); the mixture was stirred at  $65^\circ\text{C}$ . The time of electrodeposition was 1 min with  $100 \text{ mA cm}^{-2}$  density of current, leading to a  $3 \mu\text{m}$  thick layer; then the films were dried 1 h at  $70^\circ\text{C}$ .

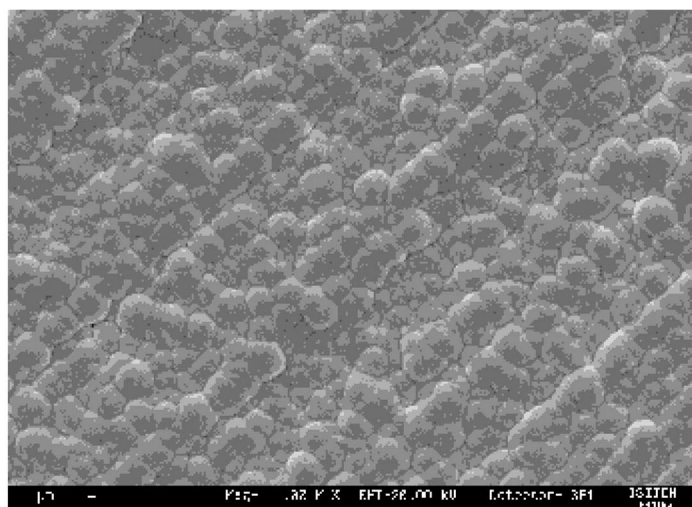
X-ray diffraction was performed on a Philips XRD 3100 using Cu  $\text{K}\alpha$  radiation. Morphology and composition of the films were determined by scanning electron microscopy (Leica Stereoscan 440 coupled with an EDX analysis).

Bi anodes of 2 mg were prepared by mixing the active material with SLM44 (Le Carbone Lorraine) and PVDF (Aldrich) as a binder, whereas Sn–Ni electrodes were tested as-deposited. Potentiostatic and galvanostatic measurements were performed on electrodes of 12 mm of diameter on a Macpile II in simple two-electrodes cells using a metallic

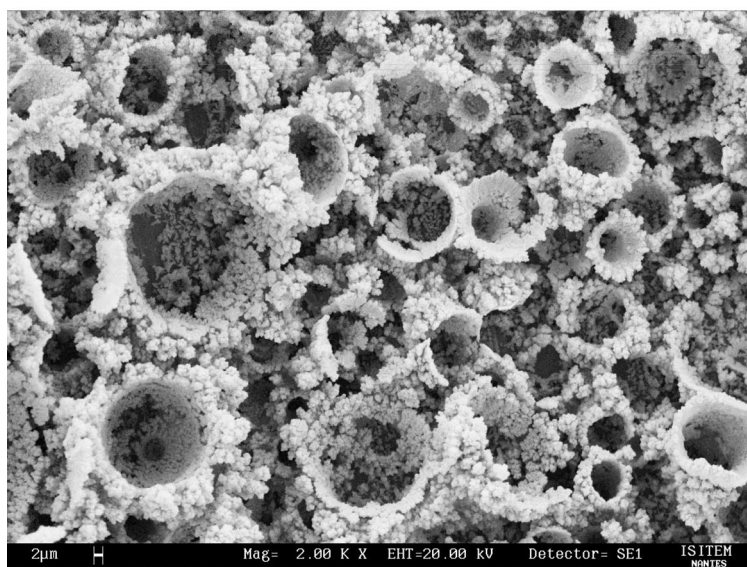
lithium foil (Aldrich) as both reference and counter electrode. The electrolyte was a 1 M solution of  $\text{LiPF}_6$  dissolved in EC/DEC 2:1 (Merck).

### 3. Results and discussion

The concentrations of Ni observed in the Ni–Sn alloy as well as the morphology of the electrochemically synthesized material were strongly influenced by the current density used in the synthesis. At low values of the current density ( $100 \text{ mA cm}^{-2}$ ) in order to obtain an alloy with a 1:1 ratio it was necessary to use an electrolytic solution containing a molar ratio of Sn–Ni of 1:0.2 whereas when a higher



(a)



(b)

Fig. 2. SEM picture of Ni–Sn alloy deposited at current densities of (a)  $100 \text{ mA cm}^{-2}$ ; (b)  $20 \text{ A cm}^{-2}$ .

fabrication rate was used ( $20 \text{ A cm}^{-2}$ ) it was possible to obtain the desired 1:1 Sn–Ni alloy from a solution containing a 1:1 molar ratio. In Fig. 1 is shown the XRD patterns for the Sn–Ni alloys prepared at “high” ( $20 \text{ A cm}^{-2}$ ) and low rate ( $100 \text{ mA cm}^{-2}$ ). It can be seen that only the use of low current density leads to the expected Sn–Ni single phase [14], which is rather a metastable composition outside the equilibrium range of  $\text{Ni}_3\text{Sn}_2$ . The peak at  $43.3^\circ 2\theta$  coincides with the position of both Cu substrate and Ni–Sn sample and is therefore a convolution of both signals. EDX analysis performed on large areas indicate a 52% Sn–48% Ni composition [15] for the low rate deposit. The use of high current density leads to a multiphase compound.

Scanning electron photographs shown in Fig. 2 clearly indicate that the rate of deposition changes the morphology of the alloy. The material prepared at higher rates shows a much smaller particle size (i.e. less than  $1 \mu\text{m}$ ) and higher porosity than the material prepared at the lower rate (particle size of  $5 \mu\text{m}$ ). Anodes of the low and high rate materials were prepared and cyclic voltametric experiments were performed in the voltage range 1.2–0.01 V versus lithium with 10 mV steps every 2 min. In Fig. 3 are shown the electrochemical cycling behavior of the electrochemically prepared alloys. It can be clearly seen that the specific capacity of the very dense thin film obtained with low density of current is much smaller than the capacity obtained with a high rate; however, the capacity is still smaller than the theoretical one ( $682 \text{ mA h g}^{-1}$  for  $\text{Ni}_{0.48}\text{Sn}_{0.52}$  composition). The better cycling behavior of the high current density ‘Ni–Sn’ sample may not only be due to the smaller particle size, but also to the higher porosity of the deposit, which

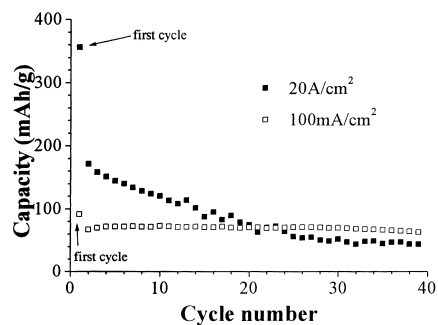


Fig. 3. Specific capacity vs. cycle number for Ni–Sn alloys.

allows for expansion, and due to the multi-phase character of the deposit.

XRD patterns taken after cycling between 10 mV and 1.2 V do not show any indication of the formation of either metallic nickel or tin. At this time from the XRD results it is not possible to say if the reaction involves a decomposition of the alloy into inactive Ni and active Sn and a subsequent recombination of the elements into an alloy or if the alloy remains undissociated during the reaction with lithium; however, as expected the “high” current density sample with the smaller particle size cycles better than the “low” current density, larger particle size.

Electrodes were also prepared from bismuth particles prepared by DC arc discharge. In Fig. 4 is shown a SEM photograph of the obtained particles indicating that the particles have a size of about 200 nm. Electrodes were prepared from these particles along with PVDF binder

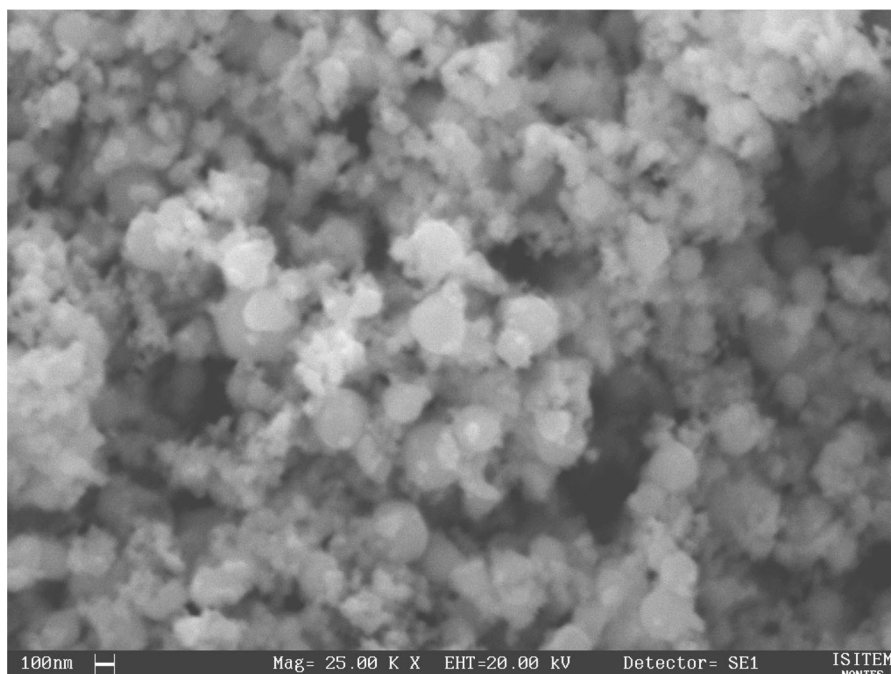


Fig. 4. SEM picture of Bi nanoparticles.

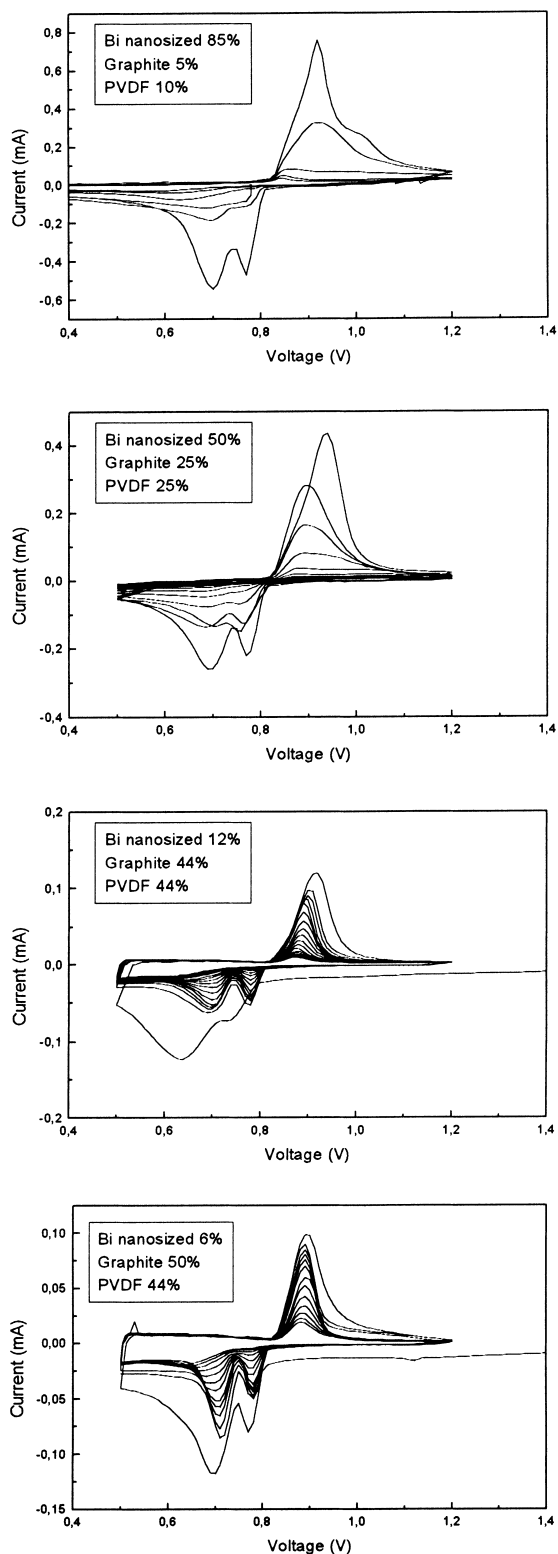


Fig. 5. Typical cyclic voltammograms of 2 mg Bi electrodes (12 mm of diameter) cycled with 10 mV steps in every 2 min between 0.5 and 1.2 V vs. Li.

and carbon. In this system it seems highly likely that the electrochemical reaction between lithium and bismuth can be written as follows:



In this reaction there should be no irreversible chemical reaction, and the loss in capacity upon cycling should be only a result of mechanical failure. In addition, as is shown in the electrochemical voltammetric cycling data (see Fig. 5) the voltage associated with the lithium incorporation into bismuth is at a potential higher than that associated with the lithium intercalation into carbon. This therefore allowed us to prepare several electrodes with different concentrations of carbon, binder, and bismuth without having our results modified by the presence of different carbon compositions. It is clear from the voltammetric results shown in Fig. 5 that the cyclability of the electrode, with the same PVDF binder, improves as the concentration of Bi decreases. In the case of pure bismuth going to  $\text{Li}_3\text{Bi}$ , the volume of the electrode will increase by a factor of 2.15. In our case, the volume expansion/contraction of the electrode composed of Bi, carbon and PVDF will be simply that associated with the bismuth present. As we decrease the amount of bismuth in the electrode the volume increase upon lithium uptake must also linearly decrease. It is quite clear from these results, that the simple, macroscopic expansion/contraction of the bismuth electrode plays an important role in the cycle life of a simple Bi electrode. However, by decreasing the amount of active material in the electrode, the theoretical capacity of the composite electrode is significantly decreased.

#### 4. Conclusions

In this study, we have examined two materials as possible anodes for Li ion batteries with theoretical capacities greater than graphitic carbon. In both cases we have started with materials that should not show the extremely high first cycle irreversibility that is observed in oxide materials. We have observed that the particle size of materials (Sn–Ni) that show a large volume change during lithium incorporation plays a vital role in cycle life, i.e., small particles are necessary if one wishes to obtain good cyclability. With pure metallic Bi particles of a specific size (200 nm) we have demonstrated that the value of macroscopic expansion/contraction of an anode also plays a vital role in cycle life. It is our feeling that it may be possible to obtain good cycle life in an alternative anode if one optimizes particle size, total volume expansion during lithium uptake and uses a binder that is more elastic than PVDF and related copolymers.

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