Short communication

A high capacity, template-electroplated Ni–Sn intermetallic electrode for lithium ion battery

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ABSTRACT

In this paper we describe a Ni–Sn intermetallic material obtained via template electroplating synthesis. The structure and the morphology of this material are investigated by X ray diffraction (XRD) and Scanning Electron Microscopy (SEM) analyses. We demonstrate that Ni–Sn behaves as a sub-micrometric electrode showing a favourable response when cycled in a lithium cell. The results here reported suggest that the template electroplating is a promising synthetic approach that can lead to an optimized structure and morphology of the Ni–Sn electrode, such as to confer it a role of a high capacity anode in advanced lithium ion batteries.

1. Introduction

Due to their high capacity, lithium-alloying intermetallic electrodes, such as Ni–Sn and Co–Sn, have received attention as anodes to use in lithium ion batteries as alternatives to graphite [1–3]. The electrochemical alloying process involves the tin metal, while the Ni or the Co act as electrochemically inactive matrices to buffer the volume variations during the electrochemical Li–Sn alloying process [4,5]. Among the various intermetallic combinations investigated, the Ni–Sn revealed to be the most promising one in terms of capacity and cycle life [6,7]. In a previous paper we demonstrated that a remarkable increase in the cycle life of the electrode was obtained by passing from a micro-size [8] to a nano-structured morphology [9,10].

In this paper we report a new synthesis approach based on the direct utilisation of a template polycarbonate membrane in order to achieve an optimized, one step Ni–Sn electroplating process. This has allowed us to obtain Ni–Sn intermetallic electrodes characterized by a sub-micrometric fine morphology. We show that these electrodes offer a stable electrochemical behaviour when cycled in a lithium cell.

2. Experimental

Basically, the Ni–Sn synthesis procedure involved the use of a template polycarbonate porous membrane (Whatman®, pore size 100 nm) placed on a copper foil which was used as the current collector for the Ni–Sn electroplating in a two-electrode cell. An aqueous solution, formed by $NiCl_2$ 0.075 M, $SnCl_2$ 0.175 M, $K_4P_2O_7$ 0.5 M, glycine 0.125 M and NH_4OH 5 ml l^{-1} [6,8] was used as the electroplating bath and a Sn foil as the counter electrode. The current and time conditions were monitored by using a Maccor Series 4000 Battery Test System. The Ni–Sn intermetallic was deposited using a capacity of 1.8 coulomb cm^{-2} (2 mA for 15 min). For comparison, a Ni–Sn was deposited in the same conditions but without the support of the polycarbonate template membrane. The structure of the samples was determined by XRD, using a Rigaku X-ray diffractometer D-max with Cu-Kα radiation source and their morphology by Scanning Electron Microscopy, SEM, using a Phenom FEI co. instrument.

The electrochemical response in a lithium cell was studied using the Ni–Sn as the working electrode, a 1 M $LiPF_6$ electrolyte solution in an ethylene carbonate-dimethyl carbonate, EC:DMC 1:1 (Merck Battery Grade) mixture soaked into a Whatman™ separator as the electrolyte and a lithium metal foil both as counter and reference electrode. The cells were cycled at room temperature at 0.8 C rate and between a 0.02 V and 1.5 V voltage limit. The electrochemical response was monitored under constant charge–discharge cycling conditions using a Maccor Series 4000 Battery Test System. The cyclic voltammetry was run at a 0.5 mV s^{-1} scan rate

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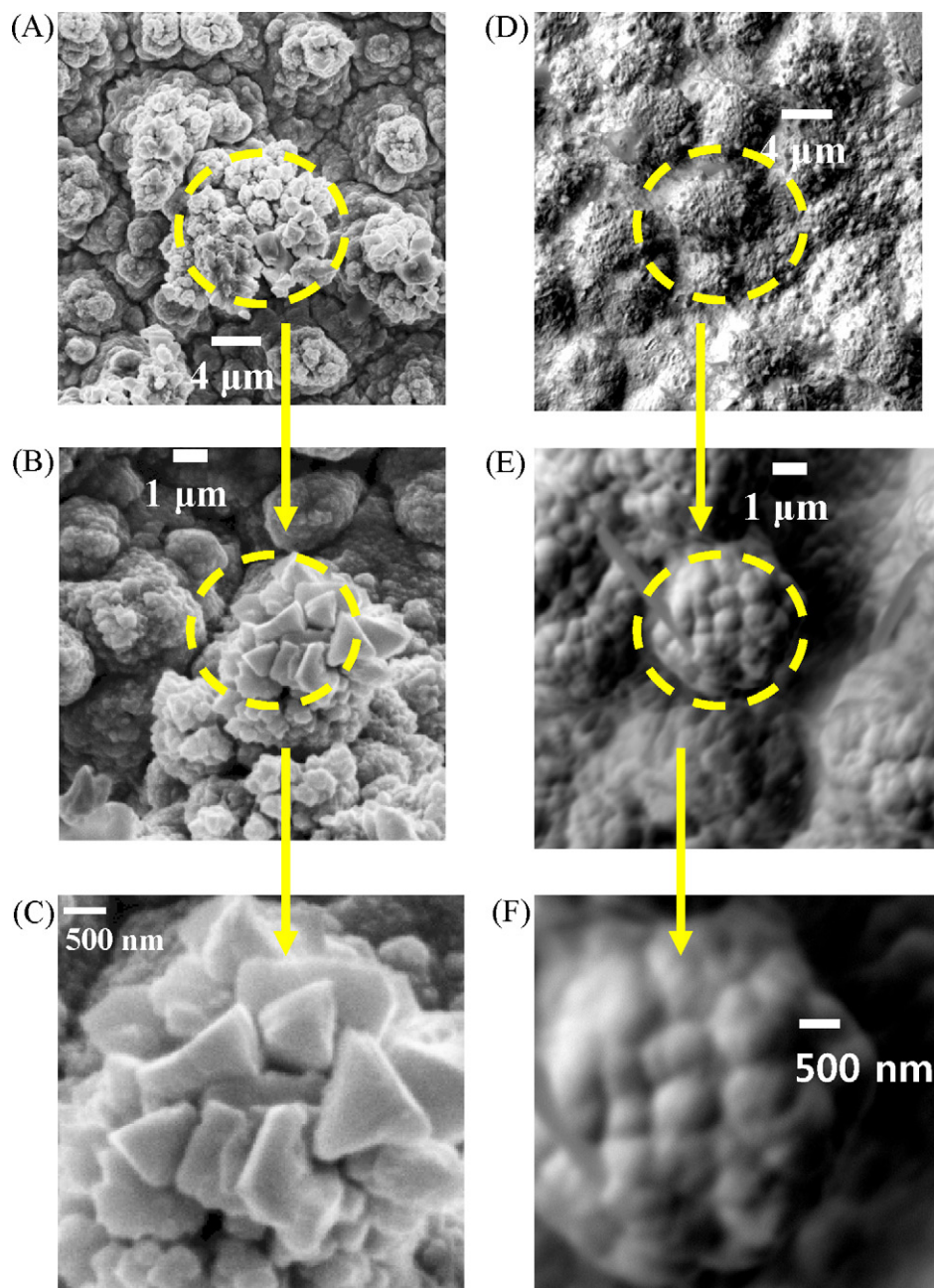
Fig. 1. SEM image with increasing magnification of top views of the Ni–Sn intermetallic electroplated using standard conditions (A, B and C) and by the support of the template porous polycarbonate membrane (D, E and F).

within 0.02–1.5 V vs. Li potential limits using a VMP Biologic instrument.

3. Results and discussion

Standard electroplating of Ni–Sn on a cupper substrate from aqueous solution leads to a morphology formed by micrometric crystals [8]. When prepared in this morphology, Ni–Sn electrodes show a limited cycling stability in a lithium cell. With the aim of addressing this issue, we have prepared the Ni–Sn intermetallic materials by electroplating on a Cu substrate covered by a sub-micron, porous polycarbonate membrane. The idea was to use the membrane as a medium capable to control the growing of the crystals, so that to model the resulting Ni–Sn electrode surface in the form of sub-micrometric spheres. Fig. 1, comparing the Scanning

Electron Microscopy (SEM) top view images with increasing magnifications of Ni–Sn intermetallic samples obtained by standard preparation method (Fig. 1A–C) with those of samples obtained by template method (Fig. 1D–F), demonstrates that for the latter the grains coalescence on the top of the electrode is indeed prevented. Also with the support of literature data [11] we believe that this effect is associated with the nature of the template polycarbonate membrane and with its pore size. However, even under these optimized conditions the template electroplated electrode still shows some aggregation, in particular in its lower side. Accordingly, additional work is in progress in our laboratory to increase the template efficiency for optimizing the Ni–Sn intermetallic morphology.

Fig. 2 reports the XRD analyses of the two Ni–Sn intermetallic samples electroplated using either the standard or the template conditions. The patterns evidence that the standard sample is
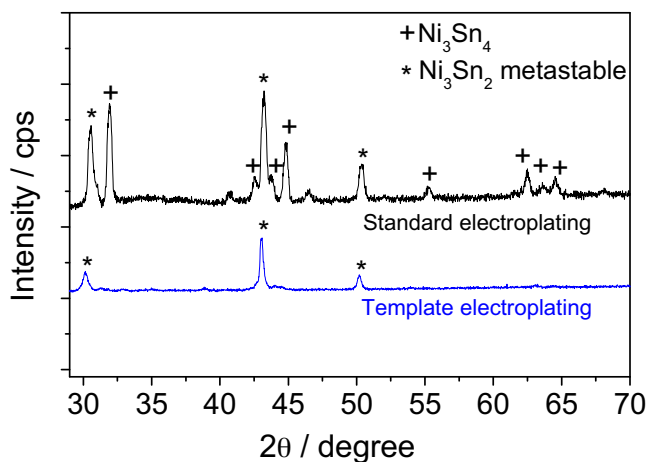
Fig. 2. XRD patterns of the Ni–Sn intermetallics electroplated using standard and template conditions.

formed by a crystalline Ni_3Sn_4 phase (JCPDS # 04-0845) accompanied by metastable Ni_3Sn_2 phases (JCPDS # 07-0256, 06-0414), while only the metastable Ni_3Sn_2 phase is observed for the template sample. The particular structure of the latter may be attributed to a different nucleation mechanism promoted by the local current density distribution associated with use of the template membrane [8,12].

The structural and morphological difference of the two samples reflects in a difference in their electrochemical responses when tested as electrodes in lithium cells. Fig. 3 shows the cyclic voltammetry, CV, profiles run at a $0.5\,mV\,s^{-1}$ scan rate of the standard and of the template Ni–Sn electrode, respectively. In both cases the electrochemical process is expected to evolve by a first irreversible activation step:

$$Ni_xSn_y + 4.4yLi^+ + 4.4ye^- \Rightarrow yLi_{4.4}Sn + xNi \qquad (1)$$
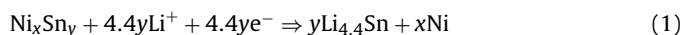
where $x = 3$, $y = 4$, and $x = 3$, $y = 2$ for Ni_3Sn_4 and Ni_3Sn_2, respectively, followed by the main, reversible, steady-state electrochemical process:

$$Li_{4.4}Sn \Rightarrow Sn + 4.4Li^+ + 4.4e^- \qquad (2)$$

$$Sn + 4.4Li^+ + 4.4e^- \Rightarrow Li_{4.4}Sn \qquad (3)$$

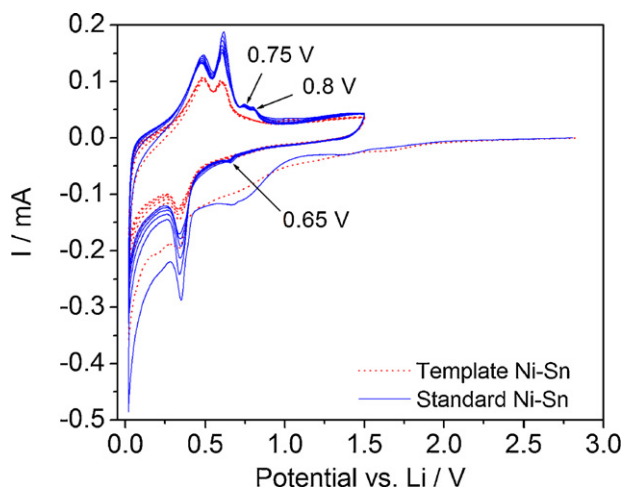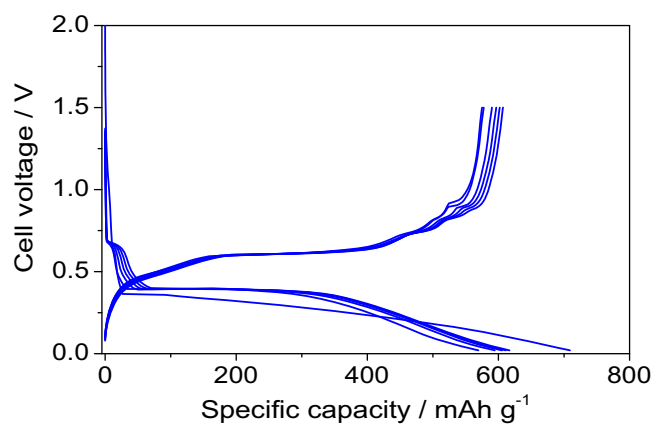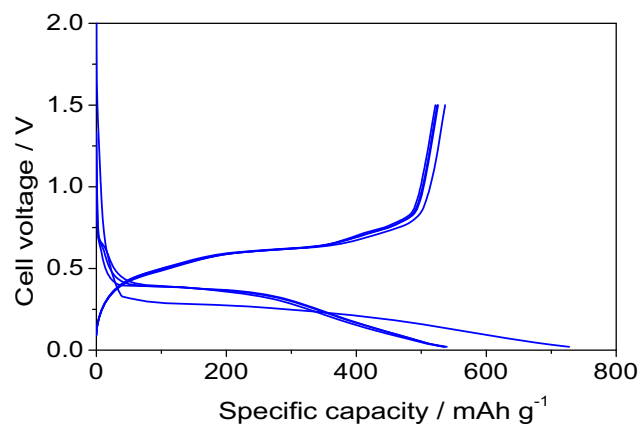**Fig. 3.** Cyclic voltammetry profiles run at a $0.5\,mV\,s^{-1}$ scan rate within a 0.02–1.5 V potential window of the Ni–Sn intermetallics electroplated using standard and template conditions and used as working electrode in a lithium cells.
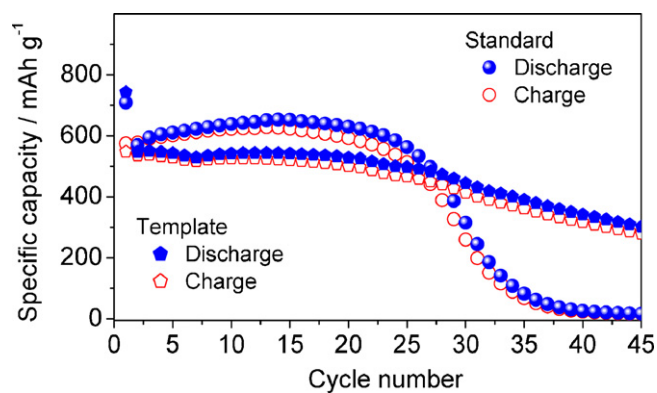

(A)

(B)

Fig. 4. Voltage profiles of the Ni–Sn intermetallics electroplated using standard (A) and template (B) conditions and used as working electrode in lithium cells cycling at 0.8C-rate ($1C = 993\,mA\,g^{-1}$) within 0.02–1.5 V voltage limits.

The theoretical capacity of the Ni–Sn electrodes on the basis of the processes (1)–(3) is calculated to be of the order of $730\,mAh\,g^{-1}$ and $570\,mAh\,g^{-1}$ for Ni_3Sn_4 intermetallic and for Ni_3Sn_2 metastable, respectively.

The CV profiles of Fig. 3 clearly show the different response of the two samples. In particular, the electrode obtained under standard electroplating conditions reveals the expected low potential peaks in addition to one cathodic peak at about 0.65 V vs. Li and two anodic peaks at about 0.75 V and 0.8 V vs. Li. These additional voltammetric peaks, quite likely associated with a micrometric crystalline Ni_3Sn_4 phase [8–10], are not observed for the submicron, metastable, template electrode which has also a higher electrochemical reversibility.

The two Ni–Sn intermetallic electrodes were tested in lithium cells using a common EC:DMC, $LiPF_6$ liquid electrolyte. Fig. 4 shows the voltage profiles of the cell using the standard (A) and the template (B) Ni–Sn electrode, respectively. Following the first activation step (compare also Fig. 3) the voltage profiles are those expected for the electrochemical Li–Sn alloying/de-alloying processes (2) and (3), with a specific capacity of the order of $600\,mAh\,g^{-1}$ for the standard electrode (A) and $550\,mAh\,g^{-1}$ the template electrode (B). The difference in the capacity values is attributed to the different composition of the samples, as evidenced by the XRD of Fig. 2 and by the discussion of the reaction mechanisms (1)–(3). The related cell response shows that only the standard electrode evolved with the high voltage anodic and cathodic signatures associated with the crystalline Ni_3Sn_4, this confirming the CV response of Fig. 3.

Fig. 5. Capacity delivered upon cycling of the Ni–Sn intermetallics electroplated using standard (A) and template (B) conditions and used as working electrode in lithium cells cycling at 0.8C-rate (1C = 993 mA g⁻¹) within 0.02–1.5 V voltage limits.

Fig. 5 compares the cycling response at 0.8C-rate of the two electrodes in a lithium cell. For simplicity, the 1C-rate current is considered to be that of the pure Sn alloying reaction, i.e. 990 mA g⁻¹ associated with the mechanisms (2) and (3). Clearly, the template electrode shows a remarkably enhanced cycling stability. The superiority of this electrode can be associated with its improved sub-micrometric morphology and, in particular, with the fine particles distribution that provides a buffer action to control the volume expansion and contraction experienced by the active material during the electrochemical alloying-de alloying processes. An additional favourable aspect to assist the cell cycling behaviour is provided by the predominance of the Ni_3Sn_2 metastable phase which is known to be electrochemically more stable than the Ni_3Sn_4 crystalline phase [8]. Nevertheless, the template Ni–Sn intermetallic still suffers by some capacity decay upon cycling. SEM images taken on electrode samples after cycling are underway in our lab in order to better understand the reasons of this fault.

4. Conclusion

The results reported in this work demonstrate that Ni–Sn intermetallic electrodes electroplated under template conditions are characterized by an optimized structure and morphology that result in an enhanced electrochemical behaviour when they are cycled in lithium cells. Indeed, the template Ni–Sn electrode shows a reversible capacity of the order of 550 mAh g⁻¹. We believe that these results may be of interest for the lithium battery community since they disclose a new, simple route for the synthesis of lithium-metal alloy, intermetallic electrodes, characterized by high capacity and good cycle life.

Acknowledgement

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