Short communication

An electrochemical investigation of a Sn–Co–C ternary alloy as a negative electrode in Li-ion batteries

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Abstract

This work reports an electrochemical investigation of a Sn–Co–C ternary electrode which supposedly is similar to that adopted in a new lithium-ion commercial battery. The electrode, obtained by mechanical-milling of Sn, Co and C (graphite), and having the $Sn_{31}Co_{28}C_{41}$ composition, shows very promising electrochemical characteristics both in terms of specific capacity and rate. The practical relevance of this electrode is demonstrated by using it as anode in a new type of lithium-ion battery which cycles with a good capacity and with a high coulombic efficiency.
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1. Introduction

The recent announcement from a Japanese company of the launch in the market of a new lithium-ion battery [1], has given further impulse to the research in the continuously progressive field of lithium power sources. Although the composition of the new commercial battery is not yet totally disclosed, there are indications that it may employ an electrode combination which differs from the standard graphite–lithium cobalt oxide one. In particular, it has been reported that the anode material is formed by a Sn–Co–C ternary alloy [2]. One may reasonably assume that in this alloy the main electrochemical active material is tin while the two other elements act as a supporting components in order to buffer the large volume variations which occur in the course of the Li–Sn alloying–dealloying electrochemical process [3].

The reciprocal and combined role of cobalt and carbon, however, may be more complex than that of a mere buffering action. This aspect has been carefully studied by Dahn and co-workers who, by using combinatorial and high-throughout analysis, investigated Sn–Co–C thin film libraries extending over hundred different compositions [4]. These authors suggested that carbon has multi-fold actions which include promotion of amorphic-

ity, increase of specific capacity and stabilization of the Li–Sn alloy on the atomic scale [5]. These positive effects of carbon are supported by the third cobalt component which prevents the formation of intermetallic carbides over the entire useful composition range, thus finally avoiding the precipitation of tin out of the composite [6].

Despite the progress achieved by the above cited authors, the properties of the Sn–Co–C ternary alloy when used as an electrode in lithium cells are not yet fully clear. Questions remains on the exact nature of the electrochemical process, as well as on the retention of the structure upon prolonged cycling. In a previous work, we have reported an electrochemical study of a Sn–Co–C ternary electrode prepared by high energy milling in a appropriate composition range, selected as 0.31, 0.28, 0.41 molar ratio [7]. We demonstrated that, in accordance with the results of Dahn and co-workers [5], this electrode has a very promising response in lithium cells and thus, that it can be profitably used as anode in a complete lithium-ion battery [7]. In this work we have further refined the electrochemical investigation of this material with the aim of completing the evaluation of its practical potentiality.

2. Experimental

The Sn–Co–C ternary compound was prepared by ball milling using a Spex Mixer-Mill mod.8000, equipped with

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stainless steel vial and spheres. A powder charge of 8 g containing commercial micrometric Sn (Johnson Mattey, 325 mesh, 99.8 purity), Co (GoodFellow, 45 mesh e, 99.8 purity) and C (Graphite, Aldrich), with a molar ratio of 0.31, 0.28 and 0.41, respectively, was treated with two 8 g balls. The powder was milled for 102 h. To avoid metal oxidation during milling, powder handling as well as vial charging and sampling were performed under purified Ar atmosphere, in a MBraun glove box having O_2 and H_2O contents at ppm levels.

The structure evolution of the reagents and the completion of the alloy formation was controlled by XRD, using a Rigaku DMax diffractometer equipped with Cu Kα radiation and a graphite monochromator in the diffracted beam.

Cyclic voltammetry and galvanostatic cycling tests were performed in suitable electrochemical cells where the $Sn_{31}Co_{28}C_{41}$ sample was set as the working electrode with a lithium counter electrode. The $Sn_{31}Co_{28}C_{41}$ electrode was formed as a thin film by a doctor-blade deposition on a copper substrate of a slurry composed of 80% $Sn_{31}Co_{28}C_{41}$ (active material), 10% PVdF 6020, Solvay Solef (binder) and 10% SP carbon (electronic support). The counter electrode was a lithium metal foil and the electrolyte a 1 M $LiPF_6$ solution in an ethylene carbonate-dimethyl carbonate, EC:DMC 1:1 (Merck Battery Grade) soaked on a Whatman™ separator. The cyclic voltammetry of the Li/$Sn_{31}Co_{28}C_{41}$ cell was performed at a 100 μV s^{-1} rate and within a 0.01–2 V voltage limit using a PAR 362 potentiostat. The galvanostatic cycling tests were performed at various C-rate regimes (1C corresponding to a current density value of 1.18 mA cm^{-2} g^{-1}) and within a 0.01–1.5 V voltage limits, using a Maccor Series 4000 Battery Test System.

The specific capacity of $Sn_{31}Co_{28}C_{41}$ electrode was estimated considering both Sn and C (graphite) as the active elements. Cobalt is not considered in this calculation since its role is merely mechanical in buffering the volume changes which accompany the electrochemical process of tin. Under these condition, the capacity is assumed to be given by the relation: $(0.31 \times M_{Sn} \times 993 + 0.41 \times M_C \times 372)/(0.716 \times M)$, where M_{Sn} = Sn molecular weight = 118.7 g mol^{-1}; M_C = C molecular weight = 12 g mol^{-1}; M = $Sn_{0.31}Co_{0.28}C_{0.41}$ molecular weight = 58.2 g mol^{-1}, considering 0.72% (w/w) amount of active elements (Sn, C) in 1 mol of $Sn_{0.31}Co_{0.28}C_{0.41}$. The resulting value is 920 mAh g^{-1}, where the contribution of carbon (graphite) is calculated as 44 mAh g^{-1}.

The complete lithium-ion cell was formed by using the $Sn_{0.31}Co_{0.28}C_{0.41}$ electrode as the anode, the quoted 1 M $LiPF_6$ EC:DMC 1:1 solution as the electrolyte and lithium iron phosphate, $LiFePO_4$ as the cathode [8]. The latter was deposited as a thin film on an aluminium substrate by doctor-blade deposition of a slurry composed of 85% $LiFePO_4$ (active material), 5% PVdF 6020, Solvay Solef (binder) and 10% SP carbon (electronic support). The cell was cycled at 1C rate (i.e. 0.22 Ag^{-1} cm^{-2}) and under 2–3.8 V voltage limit, using a Maccor Series 4000 Battery Test System as the controlling instrument.
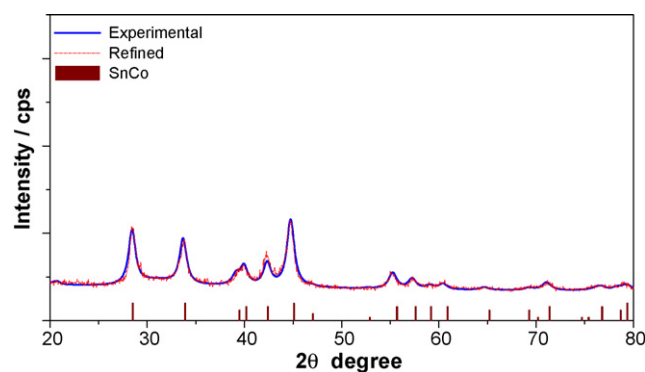

Fig. 1. XRD patterns and related Rietveld refinement for the $Sn_{31}Co_{28}C_{41}$ ternary compound.

3. Results and discussion

The ternary alloy electrode material examined in this work was obtained by high energy ball milling of a mixture of Sn, Co and C (graphite). Work originally carried out by Dahn and co-workers [5,6] and more recently in our laboratory [7], demonstrated that only few selected compositions of this alloy have structural and morphological properties such as to assure a proper electrochemical behaviour. One among these is the composition having the 0.31, 0.28 and 0.41 molar ratio, to which this work has been directed. For sake of simplicity, the 0.31, 0.28, 0.41 compound is hereafter named $Sn_{31}Co_{28}C_{41}$.

The structural characteristics of the compound were investigated by XRD. The patterns reported in Fig. 1 demonstrate that the mechanical treatments carried out in the Spex mill resulted in the formation of a nanostructured alloy and that the related broadened signals pertains to the CoSn phase (JCPDS 2-559). The Rietveld refinement analysis evidenced the nanocrystalline nature of the coherent diffraction domains of the phase, these being of about 12 nm.

The electrochemical process of the $Sn_{31}Co_{28}C_{41}$ electrode in a lithium cell was first investigated by cyclic voltammetry. It is expected that tin is the main electrochemically active element, while cobalt and carbon basically act as supporting elements to buffer the large volume changes which accompany the Li–Sn alloying–dealloying process. The cyclic voltammetry profiles reported in Fig. 2 reveal that this electrochemical process is preceded by a series of secondary processes. Indeed, a substantial difference is observed between the first and the subsequent cycles. The high voltage peaks in the first cathodic scan may be reasonably associated to the decomposition of the electrolyte with the associated film formation on the electrode surface. In this respect, we may ascribe the peak at about 1.4 V to the passivation of tin [9,10] and that at about 0.8 V to the passivation of carbon [11,12]. Both these peaks are absents in the subsequent anodic scan, this supporting our interpretation.

The peak with a voltage value lower than 0.5 V, can be associated to the lithium alloying process in nanostructured tin:

$$4.4\,Li + Sn \leftrightharpoons Li_{4.4}Sn \tag{1}$$

Also for this peak, we observe a relevant difference between the first and the subsequent cycles. We may notice from Fig. 2
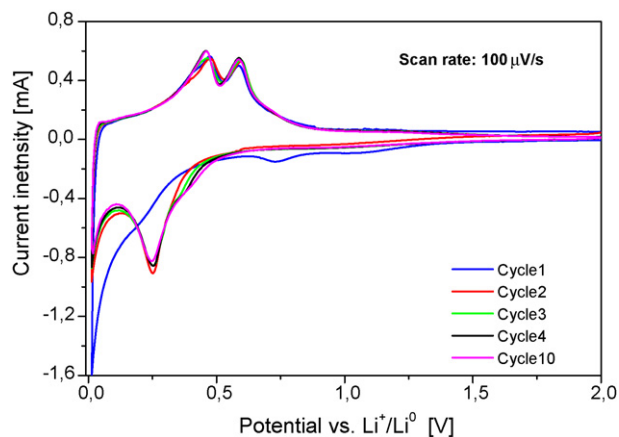
Fig. 2. Cyclic voltammetry of the $Sn_{31}Co_{28}C_{41}$ electrode in a lithium cell. EC:DMC 1:1 $LiPF_6$ electrolyte. Scan rate 100 $\mu V\,s^{-1}$, voltage limits: 0.01–2 V. Room temperature.

that in the first cathodic scan (lithium alloying) the peaks are broad and shifted to low potentials. We may ascribe this to an initial Sn–Co structural re-organization promoted by the first Li–Sn alloying step [13]. Indeed, in the second scan the peaks become sharper and remains reproducible for all the subsequent cycles reflecting the reversible nature of process (1). To be noticed that this is a multi-step process associated to the various alloying stages of lithium in tin. When using nanostructures electrodes, as in the case here under study, these steps overlap and not all of them are distinguishable in the related voltage profile [14]. We see from Fig. 2 that only two peaks are clearly distinguished in the voltammogram and that they are sharper in the anodic scan, this finally suggesting that the kinetics of the dealloying reaction are faster than those of the reverse alloying reaction. Finally, the voltammogram shows that, in the cycles following the first one, the peaks are reproducible overlapping one on each other.

The electrochemical response of the $Sn_{31}Co_{28}C_{41}$ electrode was further tested by cycling it in a lithium cell. Fig. 3 shows the voltage profiles of typical charge (lithium alloying)–discharge (lithium dealloying) cycles at a moderate C/4 rate. As already mentioned, the main electrochemical process is assumed to be the lithium alloying–dealloying in tin, see (1). However,
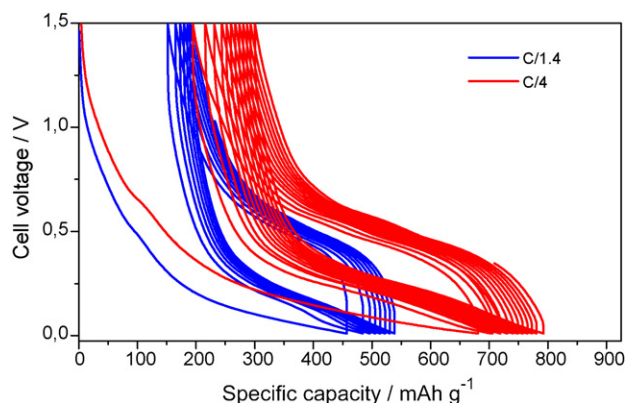
also a contribution of the carbon (graphite), which involves the reversible lithium intercalation–deintercalation process:

$$6Li + C \leftrightarrows Li_6C \tag{2}$$

has to be considered.

An initial irreversible capacity, about 28%, is clearly noticed from Fig. 3. As suggested by the cyclic voltammetry data, this may be associated to capacity losses due to electrolyte decomposition and electrode structural reorganization. Following the first cycle, the profiles overlap and the charge–discharge efficiency approaches 100%. Under this reversible condition, the specific capacity assumes a stable value of 500 mAh g^{-1}, which, considering the weight fraction of Sn and C in the $Sn_{31}Co_{28}C_{41}$ electrode, is the value expected on the basis of the combination of processes (1) and (2).

Fig. 3 also reports the cycling profiles obtained at a high rate of C/1.4. The voltage shape is similar to that obtained at the lower rate and the reversible capacity, although lower, is still at a 350 mAh g^{-1} level. This suggests that the electrode has a good rate capability, as indeed demonstrated by Fig. 4 which shows the trend of the delivered capacity versus the inverse of the C cycling rate. A relevant value of specific capacity, i.e., higher than 400 mAh g^{-1}, is obtained at cycling rates lower than C/2. By decreasing the rate to C/5, the specific capacity raises up to 500 mAh g^{-1} and this values remains stable for all the tested lower rates. We may then conclude that the polarization is mostly of ohmic type and thus, that the performance of the electrode may be further enhanced by the optimization of its structure and composition, e.g. in terms of proper balance between the active material ($Sn_{31}Co_{28}C_{41}$), the binder (PVdF) and the electronic conducting (carbon) components.

All the above results concur in demonstrating the promising feature of the $Sn_{31}Co_{28}C_{41}$ ternary alloy as an electrode in advanced lithium-ion batteries. The best way to confirm this is to assemble it in a complete lithium-ion battery prototype and test its behavior. In a previous paper we reported the response of one example of these prototypes, formed by coupling a $Sn_{31}Co_{28}C_{41}$ anode with a $LiN_{0.5}Mn_{1.5}O_4$ cathode [7]. In this work we extend the analysis by combining the $Sn_{31}Co_{28}C_{41}$ anode with a $LiFePO_4$ cathode. Fig. 5A reports some typical

Fig. 3. Voltage vs. specific capacity of a $Sn_{31}Co_{28}C_{41}$ electrode cycled at C/1.4 and at C/4 in a lithium cell. EC:DMC 1:1 $LiPF_6$ electrolyte. Room temperature.
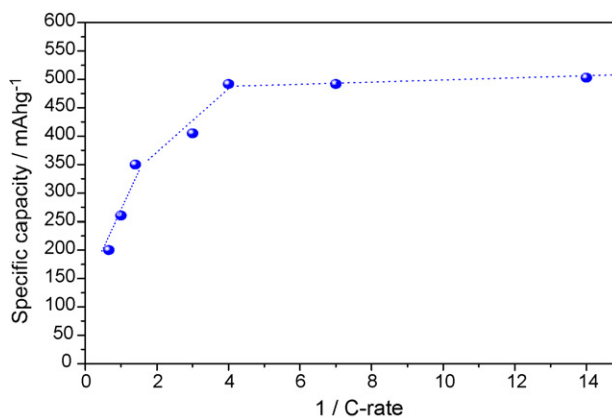

Fig. 4. Specific capacity vs. 1/C-rate of a $Sn_{31}Co_{28}C_{41}$ electrode in a lithium cell. EC:DMC 1:1 $LiPF_6$ electrolyte. Room temperature.

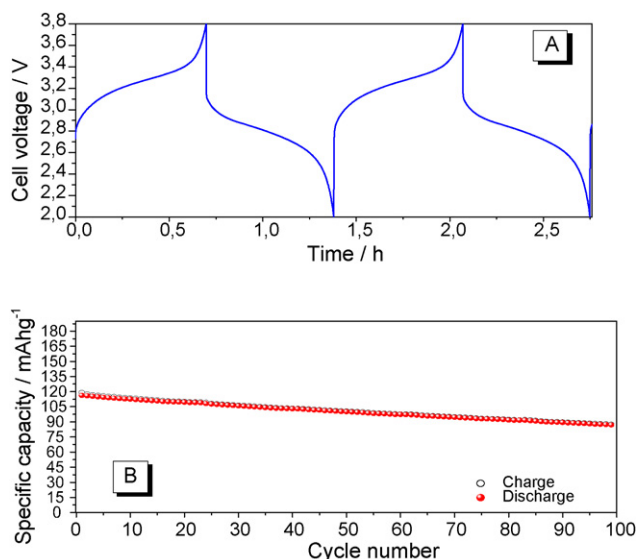Fig. 5. Voltage vs. time profiles (A) and specific capacity vs. cycle number (B) of $Sn_{31}Co_{28}C_{41}$/EC:DMC 1:1 LiPF$_6$/LiFePO$_4$ lithium-ion cell. Charge–discharge current density: 0.22 A cm^{-2} g^{-1} vs. LiFePO$_4$, about 1C rate. Room temperature.

voltage versus time profiles of this second type of battery, run at 1C rate. We see that the battery operates around a 3 V level, reflecting the electrochemical process which, still assuming that tin is the active material in the $Sn_{31}Co_{28}C_{41}$ alloy, is the lithium cycling transfer from the cathode to the anode:

$$Sn + LiFePO_4 \underset{discharge}{\overset{charge}{\rightleftarrows}} Li_x Sn + Li_{(1-x)}FePO_4 \qquad (3)$$
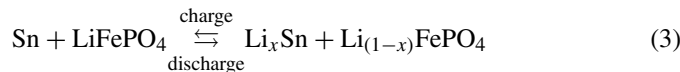
Since cathode limited, the maximum capacity of the battery is evaluated to be of the order of 170 mAh g^{-1} [15]. The first cycles give a capacity of 120 mAh g^{-1}, i.e. with about 70% of the maximum value. Fig. 5B, which reports the cycling response of the $Sn_{31}Co_{28}C_{41}$/LiFePO$_4$ battery, reveals a high charge–discharge efficiency but also a slight tendency of capacity loss upon cycling. This aspect, which may rise some concern on the effective cycling stability of the electrode, is under additional investigation.

4. Conclusion

The main goal of this work was the investigation of the electrochemical process of a ternary Sn–Co–C electrode which supposedly is similar to that used in a battery recently released by a Japanese company. We show that, when prepared in a proper composition, the Sn–Co–C composite electrode can operate in a lithium cell at capacity levels as high as 500 mAh g^{-1} and that it can be cycled at rates exceeding 1C still recovering 50% of its total capacity. The practical use of this ternary alloy as anode in advanced types of lithium-ion batteries, previously demonstrated in our laboratory [7], has been confirmed in this work. The batteries reflect the favourable property of the new anode in terms of reversibility and rate capability. Questions still remain on the capacity retention upon prolonged cycling.

Acknowledgements

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