



XPS and ToF-SIMS study of Sn–Co alloy thin films as anode for lithium ion battery

Jun-Tao Li^a, Jolanta Swiatowska^b, Antoine Seyeux^b, Ling Huang^c, Vincent Maurice^{b,*}, Shi-Gang Sun^{c,*}, Philippe Marcus^{b,*}

^a School of Energy Research, Xiamen University, Xiamen 361005, China

^b Laboratoire de Physico-Chimie des Surfaces, CNRS (UMR 7045), Ecole Nationale Supérieure de Chimie de Paris (Chimie-ParisTech), 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

^c State Key Laboratory of Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

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ABSTRACT

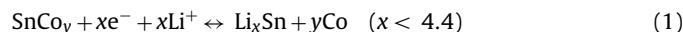
Sn–Co alloy films were prepared by electroplating on copper and used as anode material of lithium ion battery. Cyclic voltammetry and galvanostatic discharge/charge measurements were combined with surface analysis by X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). The results show the buildup of a solid electrolyte interphase (SEI) layer formed by reductive decomposition of electrolyte during the first Li–Sn alloying cycle. The layer is constituted of a mixture of Li_2CO_3 , ROCO_2Li , lithium oxalates, and/or ROLi , and its chemical composition is modified during the electrochemical multi-cycling process with increase of the Li_2CO_3 content. Multi-cycling also fractures the SEI layer. ToF-SIMS results revealed an incomplete initial alloying process of lithium ion with Sn, limited by mass transport through a Co layer and dividing the Sn–Co layer alloy into a fully lithiated outer part and an essentially non-lithiated inner layer during the first discharge. The volume expansion/shrink associated with the alloying/dealloying reaction irreversibly cracks and splits up the Sn–Co alloy into particles with interstitial voids filled by the SEI layer. Multi-cycling amplifies this division of the Sn–Co layer without material loss and stabilizes discharge/charge capacity.

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1. Introduction

Sn-based alloys are considered to be very promising alternative anodes for lithium ion batteries (LIBs) because of their higher specific capacity than commercially used carbon anodes and their better cycling ability than pure tin anodes [1–3]. Moreover, Sn-based alloy anodes do not suffer from the so-called co-intercalation observed on graphite anodes [4]. The Sn-based anodes alloy two or more elements. The active component, tin, reacts with lithium, whereas the other elements act as an electrochemically inactive buffer accommodating the volume changes. However, large volume changes are inevitably associated with alloying/dealloying reactions, and are the main origin for severe stress-induced fracture, which leads to the loss of contact between particles and significant capacity fading on cycling. Nanostructures, core-shell structures and amorphous structures of Sn-based alloy electrodes have been synthesized in order to improve their durability and to minimize dimensional changes and pulverization failure induced by discharging/charging [5–8].

Alloying with cobalt is expected to increase the ductibility of the material and the volume variation accommodation, to stabilize the reduced tin atoms in the lithiation stage, and thus to improve the electrochemical cycling stability [9]. The interest for Sn–Co alloy anodes has risen since the commercialization by a Japanese company of the Co–Sn–C component anode, composed of small grains of Sn–Co in a C matrix [10]. Co–Sn binary [11–16] and Sn–Co based ternary [16–21] alloys synthesized by various methods have been the subject of many electrochemical studies. It has been reported that four intermetallic phases are present in the Co–Sn binary alloy: CoSn , CoSn_2 , Co_3Sn_2 and CoSn_3 [22,23]. The alloying/dealloying reaction is the following:



Despite the progress of electrochemical performance of Sn–Co binary anodes, the mechanisms of interfacial reactions are not yet completely known. Questions still remain regarding the formation, stability, variation and composition of the solid electrode interphase (SEI) layer, as well as the morphological and phase structural changes of Sn–Co alloy anodes during discharge/charge, which are key issues for the cycling ability, the lifetime, the chemical and physical stability and the reversible capacity of LIBs. In addition, the electrochemical reactions always start at the interface between the

* Corresponding authors. Tel.: +33 01 44 27 67 38; fax: +33 01 46 34 07 53.

E-mail addresses: vincent-maurice@chimie-paristech.fr (V. Maurice), sgsun@xmu.edu.cn (S.-G. Sun), philippe-marcus@chimie-paristech.fr (P. Marcus).

electrode and the electrolyte. Therefore, a better understanding of the interfacial reactions as well as the phenomena occurring inside the bulk electrode are prerequisite for further improvements of the Sn–Co alloy anodes for their commercial application. Up to now, the morphological and phase structural changes on Sn-based anodes have been extensively studied by in situ XRD and Mossbauer spectroscopy, which could probe the structure of electrode materials at the atomic level [24–27]. The application of the X-ray photoelectron spectroscopy (XPS) to characterize cycled Sn-based alloys has been reported by several research groups [28–32]. In addition, the interfacial reactions on the tin anode have been investigated by in situ Fourier transform infrared reflection spectroscopy (in situ FTIRS) [33–34].

XPS has been applied to investigate the chemical composition of the SEI layer formed on various electrode materials by analysis of the valence band and the core level regions of C, O, Li and F [35–40]. However, this technique provides information on the chemical composition of the first few nanometers at the electrode surface whereas some of the interesting issues relate to its bulk composition. Secondary ion mass spectrometry (SIMS) has an excellent sensitivity to lithium [41]. More recently, Time-of-Flight SIMS (ToF-SIMS) has been applied to depth-profile cycled electrode materials with a good depth resolution bringing information about the SEI layer and the distribution of species in the bulk materials [38,42–45].

Here we present a combined investigation by XPS and ToF-SIMS of electroplated Sn–Co alloy anode cycled in 1 M LiClO₄/PC. The interfacial mechanisms related to the formation and modification of the SEI layer during cycling are addressed, as well as the morphological changes of the electroplated layer related to the alloying/dealloying interfacial reaction.

2. Experimental

2.1. Preparation of Sn–Co anode

Electroplating of Sn–Co alloy films were carried out on copper foils (area = 2.6 cm², *l* = 0.1 mm) in a bath containing 75 g L⁻¹ Na₂SnO₃·3H₂O, 2.5 g L⁻¹ CoCl₂·6H₂O and the additives (150 g L⁻¹ C₄H₄O₆KNa·4H₂O, and 20 g L⁻¹ K₃C₆H₅O₇·H₂O), which act as the complexing agents. All these reagents are analytical reagents, and were purchased from Sinapharm Chemical Reagent Co. Ltd. The bath temperature was kept at 55 °C and its pH was adjusted to 7.5 via addition of HCl. The electrolyte was not deaerated. Titanium foil was used as counter and reference electrodes. A constant current density of 1.0 A dm⁻² was applied for 5 min leading to the deposition of ~1.9 mg of alloyed films. After electroplating, the prepared electrode was transferred to an anhydrous ethanol bath and rinsed in ultrasonic bath for 1 min. The thickness is estimated to be 820 nm by considering the Co–Sn alloy density ($\rho = 8.91 \text{ g cm}^{-3}$) [26]. Scanning electron microscopy (SEM) observation and energy dispersive X-ray spectroscopy (EDS) analysis, presented in Fig. 1, illustrate that a continuous Sn–Co alloy film is produced with Sn and Co atomic ratio of 62 and 28%, respectively (~Sn₂Co).

2.2. Electrochemical properties of Sn–Co anode

Cyclic voltammetry (CV) and galvanostatic discharge/charge studies were carried out in a glove box (Jacomex) under Ar atmosphere (O₂ and H₂O < 5 ppm). A conventional three-electrode glass cell was employed with Sn–Co alloy film as working electrode and Li foil (Aldrich) as reference and counter electrodes. All potentials given in this paper are referred versus the Li⁺/Li reference electrode. An Autolab (AUT30) potentiostat/galvanostat was used. The electrolyte was an organic, anhydrous solution of 1 M lithium perchlorate in propylene carbonate (1 M LiClO₄/PC, Aldrich). After

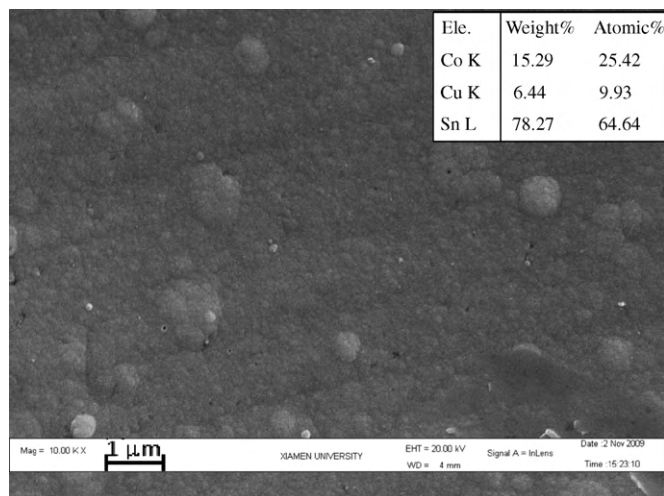


Fig. 1. SEM images and EDX analysis of Sn–Co alloy layer electrode on Cu substrate.

electrochemical treatment, the specimens were emerged from the electrolyte at applied potential, rinsed with anhydrous acetonitrile, dried in Ar flow and transferred directly from the Ar atmosphere of the glove box to the ultra-high vacuum XPS analysis chamber without exposure to air. For ToF-SIMS analysis, the specimen were stored in the glove box and transferred rapidly through laboratory air to the ultra-high vacuum analysis chamber prior to analysis.

2.3. X-ray photoelectron spectroscopy analysis

XPS analysis was carried out with a VG ESCALAB 250 spectrometer equipped with a UHV preparation chamber directly connected to the glove box [40]. Base pressure during analysis was $\sim 1 \times 10^{-9}$ mbar. An Al K α monochromatized radiation ($h\nu = 1486.6 \text{ eV}$) was employed as X-ray source. For all analyses, the take-off angle of the photoelectrons was 90°. High-resolution spectra of the Sn3d, Co2p, O1s, C1s and Li1s core level and valence band (VB) regions were recorded with a pass energy of 20 eV. The data processing (peak fitting) was performed with the Avantage software provided by Thermo Electron Corporation, using a Shirley type background subtraction and Gaussian/Lorentzian peak shapes. The binding energies were corrected by setting the C1s hydrocarbon ($-\text{CH}_2-\text{CH}_2-$ bonds) peak at 285.0 eV.

2.4. Time-of-flight secondary ion mass spectrometry depth profiling

Depth profiles were obtained using a ToF-SIMS 5 spectrometer (IonTof). The spectrometer was run at an operating pressure of $\sim 1 \times 10^{-9}$ mbar. A pulsed 25 keV Bi⁺ primary ion source was employed for analysis, delivering 1.8 pA of current over a 100 $\mu\text{m} \times 100 \mu\text{m}$ area. Sputtering was done using a 2 keV Cs⁺ beam giving a 100 nA target current over a 250 $\mu\text{m} \times 250 \mu\text{m}$ area. Data acquisition and post-processing analyses were performed using the Ion-Spec software. Negative ion profiles were recorded and analyzed.

3. Results and discussion

3.1. Electrochemical properties of Sn–Co alloy anode

Fig. 2a depicts some cyclic voltammograms (CVs) of the first 20 cycles recorded on Sn–Co alloy anode at 0.5 mV s⁻¹. The curves are very similar and nearly superimpose except the first cycle. In the first negative-going potential scan (NGPS), the current attributed to

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