



Study of Co–Sn and Ni–Sn alloys prepared in molten chlorides and used as negative electrode in rechargeable lithium battery

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ABSTRACT

Ni₃Sn₂ and several Co–Sn alloys prepared by electrodeposition in molten LiCl–KCl were studied as anode materials in rechargeable Li-ion battery. In the case of Ni₃Sn₂, the charge–discharge curves do not exhibit any plateau in contrast with Co–Sn alloys. For Ni₃Sn₂, the reversible capacity and the coulombic efficiency tend to constant values of about 225 mAh/g and 85%, respectively, after subsequent cycles. Among the studied Co–Sn alloys, the best electrochemical performances was observed when CoSn₂ was used as anode material: the reversible capacity and the coulombic efficiency observed after 60 cycles were about 530 mAh/g and 96%, respectively. Whatever the alloys, SEM investigations performed before and after cycling do not reveal any significant difference between the original material and the cycled material, indicating a good stability of the electrodeposited films upon cycling.

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1. Introduction

In the field of energy storage, attractive studies are devoted to the synthesis of new classes of anode materials as alternatives to graphite for the emergence of new generation of lithium batteries with higher performances than conventional one. Among them, tin-based compounds have received a particular attention [1–35] since the charge–discharge cycle accompanying the lithiation reaction involved Li_xSn alloys formation with a maximum *x* value of 4.4, giving rise to a maximum theoretical capacity value of 993 mAh/g. This value is about 2.7 times higher than the theoretical one obtained with graphite anode (372 mAh/g). Nevertheless, in spite of these remarkable performances, Sn cannot be practically used due to (i) detrimental volume change and high mechanical strain during the alloying/de-alloying process, and (ii) to a huge irreversible capacity during the first cycle leading to a poor cycle life [1–17]. Even if recent improvements have been obtained with a nano-architected Sn anode which delivers very high cycle life and good power performance compared to planar tin films [18], main attention has been devoted to the study of binary tin-alloys (M_xSn_y) as reliable candidates instead of pure Sn. In these alloys,

M is an inactive electrochemical matrix vs. lithium reaction which buffers drastically the volume expansion/contraction during the lithium alloying process. Subsequently, studies have been focused on the preparation of Ni–Sn [9,10,16,19–31], Co–Sn [16,29,32–39] and Cu–Sn [7,40–48] alloys.

Among available methods to synthesize Sn–Ni and Co–Sn, the electrochemical deposition process presents several advantages notably the control of the thickness, morphology and composition of the deposited films by adjusting the operating conditions. In addition, the films electrodeposited onto a substrate can be used directly as electrode materials without any binder and/or adjuvant. Usually, tin alloys used as anode material in Li battery are electrodeposited in aqueous solutions but it requires in most of cases a further annealing at moderate or high temperature. Recently, we have proposed a new electrochemical route for the synthesis of tin-based alloys in molten salts. The use of such media does not allow gaining in terms of energy credits but it allows reducing the number of steps required usually for the preparation of the alloys. Thus, Ni–Sn and Co–Sn alloys were prepared from the electroreduction of Ni(II) or Co(II) and Sn(II) species in molten LiCl–KCl [49,50] giving rise to Sn-based alloys with well-defined composition. For these two systems, it has been shown that the electrochemical reduction of these three ions occurs in a single two-electron step and the rate of the process is diffusion controlled. Our approach allows the preparation of Ni–Sn and Co–Sn alloys with different compositions depending on the operating conditions, without any further *ex situ* heat-treatment as usually found necessary according to the literature.

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The aim of the present paper is to study the electrochemical performances of tin–nickel and tin–cobalt alloys prepared in molten LiCl–KCl and used as anode materials in rechargeable lithium battery. At first, the structural and morphological characteristics deduced from SEM and XRD measurements of Ni–Sn and Co–Sn alloys will be discussed. Then, the electrochemical performances of the prepared Sn-based alloys as anode materials in organic electrolyte will be studied by coupling electrochemical results and SEM analyses before and after lithiation.

2. Experimental

The experimental procedure to prepare Ni–Sn and Co–Sn alloys in molten chlorides LiCl–KCl (Sigma–Aldrich) was described in detail elsewhere [49,50]. Briefly, it consists in the present case of the reduction of Sn(II) onto a reactive substrate (Co or Ni electrode), giving rise to Co–Sn or Ni–Sn alloys, respectively. Tin-based alloys were prepared in molten chlorides mixture with the eutectic composition (58.2:41.8 mol%). The powders were melted in a glass crucible placed in a cell made of an outer glass envelope. The salts were dried under vacuum at 120 °C during about 12 h and then heat-treated very slowly up to 450 °C under Cl₂ atmosphere. After fusion, Cl₂ was passed through the molten salt during 2 h to remove traces of impurities, notably oxygenated and hydrogenated species. Then, all electrochemical measurements were performed under Ar atmosphere and the temperature of the molten salt was controlled using a chromel–alumel thermocouple. SnCl₂ powder (Acros, ultra pure > 99%) was introduced into the crucible after drying during one night at 120 °C under vacuum. All electrodes used in this study were provided by Goodfellow. The auxiliary and reference electrodes were composed of a graphite rod and a Cl₂/Cl[−] reference [51], respectively. Depending on the experimental conditions such as temperature of molten LiCl–KCl and deposition potential, different compositions can be obtained. In this work, we focused our attention on the electrochemical performances of samples prepared using the experimental conditions given in Table 1.

An EGG PAR apparatus was used for the electrodeposition of tin based alloys in molten LiCl–KCl. The electrochemical performances of the prepared tin-based electrodes alloys as anode materials in rechargeable lithium battery was studied in 1 M LiPF₆ in EC:DMC (1:1) solution (LP30, Merck) at room temperature in a glove box (water content ≤ 5 ppm) under argon atmosphere. The counter and reference electrodes were metallic lithium foils. All potential values will be referred to this Li/Li⁺ reference henceforth. The galvanostatic charge–discharge curves were performed using a potentiostat/galvanostat (VMP3 Bio-Logic) in the potential range: 0.01–3.0 V. Scanning electron microscopy images were obtained with a Jeol JEM 100 CX II scanning electron microscope equipped with a Jeol high resolution scanning attachment (SEM-FEG). The crystallinity of the deposits was investigated by X-ray diffraction using a Rigaku Ultima IV X-Ray diffractometer with a Cu K_α radiation ($\lambda_1 = 1.54059 \text{ \AA}$; scan rate: 1°/min). *Ex situ* XRD measurements were done to examine modifications occurring during the charge/discharge process. The preparation of the samples was

Table 1
Electrodeposition characteristics of the Ni–Sn and Co–Sn alloys in molten LiCl–KCl.

Samples	T (°C)	E vs. (Cl ₂ /Cl [−]) (V)	Time (min)
Ni–Sn	450	−1.48	30
Co–Sn-1	420	−1.48	10
Co–Sn-2	450	−1.52	15
Co–Sn-3	420	−1.50	15
Co–Sn-4	400	−1.48	15

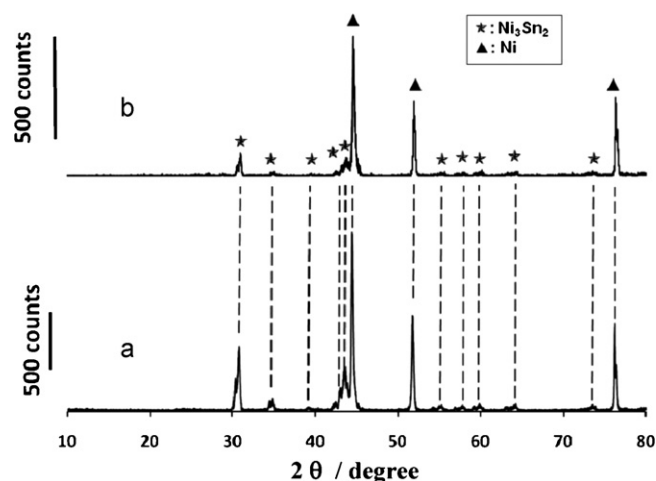


Fig. 1. XRD pattern of Ni₃Sn₂ electrodeposited in molten LiCl–KCl containing Sn(II). (a) Before cycling and (b) after cycling.

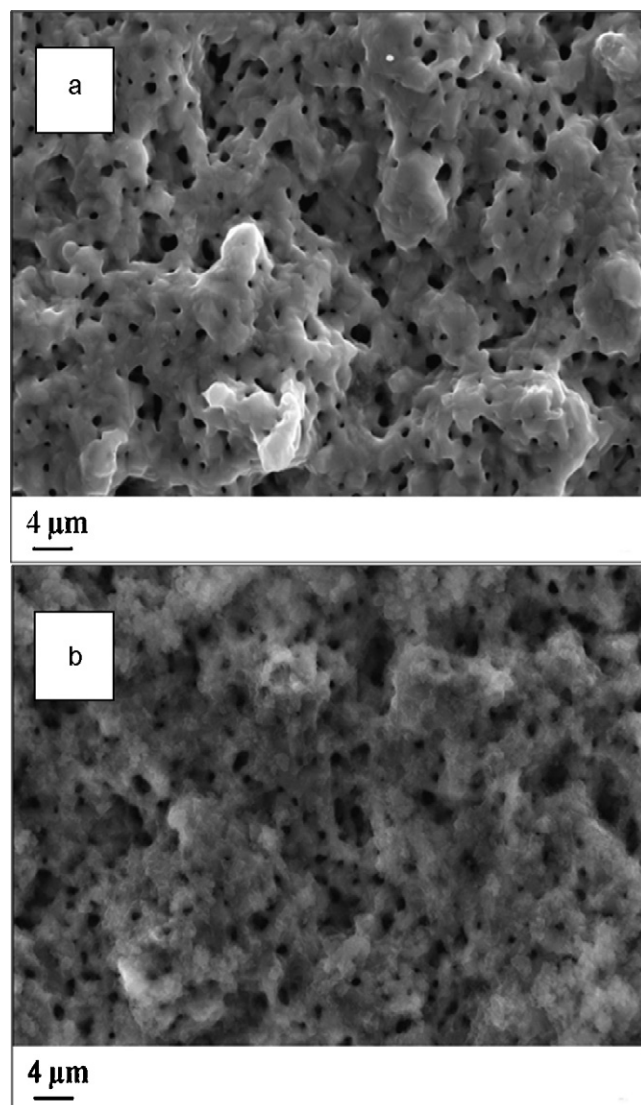


Fig. 2. SEM images of Ni₃Sn₂ electrodeposited in LiCl–KCl containing Sn(II). (a) Before cycling and (b) after cycling.

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