



In situ microscope FTIR spectroscopic studies of interfacial reactions of Sn–Co alloy film anode of lithium ion battery

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ABSTRACT

Sn–Co alloy thin films with high IR reflectivity were prepared by electroplating on a copper substrate and served as anodes of lithium ion battery. The interfacial properties of the Sn–Co alloy anode in an electrolyte of 1 M LiPF₆/EC + DMC (1:1, vol.%) during discharge/charge (or lithiation/delithiation) processes were investigated by using in situ microscope Fourier transform infrared reflection spectroscopy (in situ MFTIRS). The results demonstrated that the solvation/desolvation reactions of lithium ions with solvent molecules in discharge/charge processes vary with the concentration of both solvated and free solvent molecules, leading to the shift of C=O, C–O and C–H IR bands. The effect of solvation/desolvation, which provides a possibility to probe the lithiation/delithiation processes by in situ MFTIRS, is observed and analyzed clearly. The solid electrolyte interphase (SEI) layer on a cycled Sn–Co alloy anode has also been investigated by ex situ MFTIRS, which determined that the main chemical composition of the SEI layer is ROCO₂Li. The current studies are of significance in understanding the interfacial reactions involving in lithium ion battery at molecular level.

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1. Introduction

Sn anode exhibits a super specific capacity (993 mA h g⁻¹), and therefore attracts extensive attentions as an alternative material to carbon anodes of lithium ion batteries (LIBs). The Sn anode suffers nevertheless a high degree of volume expansion/contraction during lithium alloying/dealloying reactions, resulting in a poor cycle performance [1]. To improve the cycleability of Sn anode, intensive efforts have been made through the synthesis of nano-sized/porous materials [2,3], or by use of Sn-based intermetallic alloys with inactive host matrix. It has shown that the inactive component can buffer, to some extent, the volume change caused by Sn component and thus increases the cycling stability. Many Sn-based intermetallic alloys such as Sn–Co [4], Sn–Ni [5], Sn–Cu [6] and Sn–Sb [7] were investigated. Though electrochemical properties of these Sn-based alloys have been improved effectively, the interfacial reactions were rarely reported.

The reactions occurring in the interfaces between electrodes and nonaqueous electrolyte include insertion/extraction of lithium ion, decomposition of electrolyte and formation of solid electrolyte interphase (SEI) layer. The interfacial properties are the key issue relating to the cycling ability, life time, chemical and physical

stability and reversible capacity of a LIB. In addition, the interfacial reactions on Sn-based electrodes are evidently different from those of carbonaceous anodes that were intensively studied by using various methods. The investigation of the interfacial phenomena of Sn-based alloy at a molecule level is of importance for the development of LIBs.

The applications of Fourier transform infrared spectroscopy (FTIRS) in studies of LIBs are significant, since it can provide information at molecular level [8]. The chemical compositions of SEI layers on various materials of LIBs, aged or cycled in different electrolytes, were examined by ex situ FTIRS [9–13]. In situ FTIRS investigations focusing on the reduction/oxidation of various electrolytes were carried on LIBs electrodes [14–18] or nonactive [19,20] materials. On the traditional LIBs powder electrode materials, however, the strong absorption of IR light makes it difficult to be studied by FTIRS due to a low reflectivity for incident IR radiation in most cases. Fortunately, Sn or Sn-based alloy thin film electrodes prepared by electroplating have a high IR reflectivity, so that IR spectra with high signal-to-noise ratio can be obtained, which provides detail information concerning the evolutions of species involving in the interfacial reactions.

We have studied the interfacial reactions of a Sn anode by using a FTIR microscope system to perform in situ infrared reflection measurements [21], and demonstrated that the processes of lithium insertion/extraction can be well-characterized by in situ

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microscope FTIR spectroscopy (MFTIRS) through the solvation/desolvation effects. In this paper, Sn–Co alloy thin film electrodes were further prepared by electroplating. Interfacial reactions and SEI layer on the Sn–Co alloy thin film anodes were investigated by both in situ MFTIRS and ex situ MFTIRS. The lithiation/delithiation processes of lithium with Sn–Co anode, the solvation/desolvation of lithium ions with solvent molecules and the chemical composition of SEI layer were characterized and analyzed.

2. Experimental section

2.1. Microscope Fourier transform infrared spectroscopy (MFTIRS)

MFTIRS studies were carried out on a Nexus 870 FTIR spectrometer (Nicolet) and a microscope (IR-Plan[®] Advantage, Spectra-Tech Inc.) equipped with an HgCdTe detector (MCT-A) cooled with liquid N₂. The in situ MFTIRS cell and the array of copper substrate electrodes were detailed in our previous paper [21]. A KBr disc was used as IR window. Different structures or composition of metal/alloy thin films can be deposited electrochemically on Cu substrates of the array. In this study, interfacial reactions of Sn–Co alloy thin film anode and copper substrate electrode were compared under the same experiment conditions, by using lithium foils as both reference and counter electrodes. The in situ FTIR spectrum is defined as:

$$\frac{\Delta R}{R}(E_S) = \frac{R(E_S) - R(E_R)}{R(E_R)} \quad (1)$$

where $R(E_S)$ and $R(E_R)$ are single-beam spectra collected at sample potential E_S and reference potential E_R , respectively. The E_S was varied step by step with an interval of 0.10 V, and single-beam spectrum was collected at each E_S after a polarization of 800 s at the

E_S in order to establish a stable interface. Each single-beam spectrum was acquired by collecting and coadding 400 interferograms at a spectral resolution of 4 cm⁻¹.

Ex situ MFTIRS measurements were carried out on a cycled sample in the same sealed IR cell without electrolyte. Before this measurement, a cycled Sn–Co alloy thin film anode was emerged from electrolyte, rinsed by DMC, and kept in a vacuum for 24 h. It was then transferred to the sealed IR cell. All above operations were carried out inside a glove box filled up with pure Ar gas. The result spectrum is calculated also by using Eq. (1), where the $R(E_S)$ and $R(E_R)$ stand for single-beam spectra collected on the cycled and pristine Sn–Co alloy thin films, respectively. Each single-beam spectrum was acquired by collecting and coadding 200 interferograms with 4 cm⁻¹ spectral resolution.

All battery cells in this study were assembled in the Ar-filled glove box. Measurements were carried out at room temperature. A 263 potentiostat/galvanostat (EG&G) was employed to control electrode potential. The electrolyte composes of a solution of 1 M LiPF₆ in a mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, vol.%), and was purchased from Guotai-huarong New Chemical Materials Co., Ltd. (Zhangjiagang, China). The coin cells were galvanostatically discharged and charged on a battery test system (NEWARE BTS-610, Neware Technology Co., Ltd., China). The potentials reported in this paper were referred to the Li⁺/Li electrode potential scale.

2.2. Preparation of Sn–Co alloy thin film electrodes

Electroplating of Sn–Co alloy films on copper substrate electrodes of the array (diameter = 1.1 mm, for both cyclic voltammetry and MFTIRS studies) and copper foils (diameter = 16 mm, thickness = 0.1 mm, for galvanostatically discharge–charge tests only)

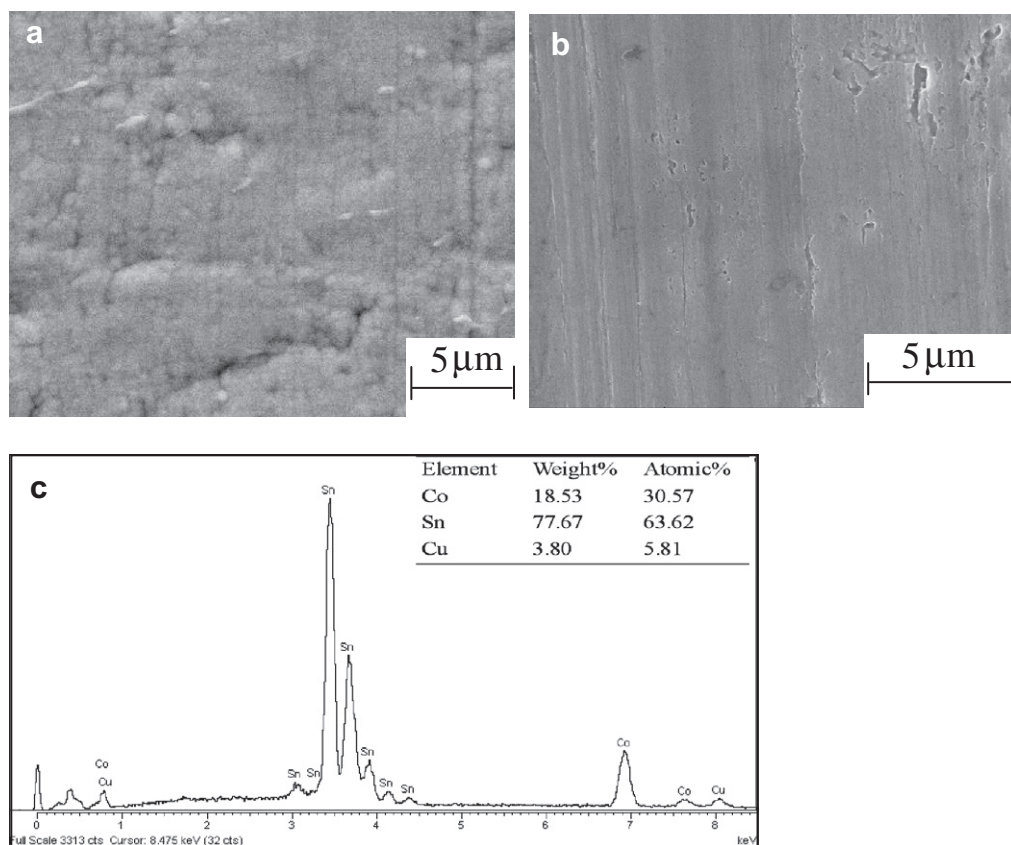


Fig. 1. SEM images of (a) Sn–Co alloy thin film electrode, (b) copper substrate electrode and (c) EDX analysis of Sn–Co alloy thin film electrode.

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