Electrodeposition and electrochemical properties of novel ternary tin–cobalt–phosphorus alloy electrodes for lithium-ion batteries

Ling Huang*, Yang Yang, Lian-Jie Xue, Hong-Bing Wei, Fu-Sheng Ke, Jun-Tao Li, Shi-Gang Sun*

Department of Chemistry, College of Chemistry and Chemical Engineering, State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University, Siming 422, Xiamen, Fujian 361005, China

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Porous Sn–Co–P alloy with reticular structure were prepared by electroplating using copper foam as current collector. The structure and electrochemical performance of the electroplated porous Sn–Co–P alloy electrodes were investigated in detail. Experimental results illustrated that the porous Sn–Co–P alloy electrode consists of mainly SnP0.94 phase with a minor quantity of Sn and Co3Sn2. Galvanostatic charge–discharge tests of porous Sn–Co–P alloy electrodes confirmed its excellent performances: at 50th charge–discharge cycle, the discharge specific capacity is 503 mAh g\(^{-1}\) and the columbic efficiency is as high as 99%. It has revealed that the porous and multi-phase composite structure of the alloy can restrain the pulverization of electrode in charge/discharge cycles, and accommodate partly the volume expansion and phase transition, resulting in good cycleability of the electrode.

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1. Introduction

Lithium-ion batteries (LIB) are widely used as a power supply for high performance electronic devices, such as mobile phones and notebook computers. To meet with the rapid increasing demand on specific energy density and safety of the LIB for diverse applications, the exploration of new electrode materials with better performances has become the key issue in development of the LIB [1,2]. Tin-based anode materials have received increasing attention as alternatives to carbon/graphite for LIB due to their high specific capacities and energy densities [3,4]. One major problem limiting the practical application of these materials is that they undergo severe volume changes during cycling, which results in disintegration of the electrodes and rapid capacity fading. Two effective approaches have been applied for improving cycle life of alloy anodes. One is to use intermetallic compounds or active/inactive composite alloy materials [5,6]. These materials exhibit longer cycleability than that of pure active materials. The inactive element can buffer the large volume change and as a barrier against the aggregation of active material into large grains during Li-ion insertion and extraction processes. However, Sn-based alloy electrodes of planar structure exhibit still rapid loss in reversible capacity after several cycles. Moreover, the introduction of the inactive material decreases the electrode energy density. Another effective approach is to use superfine materials [7]. These materials show better cycleability compared with bulk materials, because of their large surface area and short Li-ion diffusion length. However, superfine materials always aggregate severely and merge into large particles during lithium insertion and extraction. The aggregation leads to significant volume change in the electrode and a gradual decline of the electrochemical capacity. Besides above two approaches, the porous Sn-base alloys and porous current collectors were also proved the most effective methods to improve the capacity and cycleability [8,9].

Transition metal phosphides have been investigated recently as possible candidates for anode materials in lithium-ion batteries [10,11]. These materials show a large initial gravimetric capacity and a lower intercalation potential compared to the respective oxides. But preparation process of transition metal phosphides reported in above literature was very complicated. By far, there is little literature about the synthesis and application of porous Sn–Co–P alloy film electrodes for lithium batteries. In this study, porous Sn–Co–P alloy with reticular structure were prepared for the first time by electrodeposition on copper foam that is served as current collector. The charge–discharge tests demonstrated that the porous Sn–Co–P alloy electrodes exhibited a relatively high capacity and excellent cycleability when it was used as an anode of a lithium battery.

2. Experimental

2.1. Linear sweep voltammetry (LSV) of electrodeposition of Sn–Co–P alloy

Linear sweep voltammetry of the electrodeposition of Sn–Co–P alloy was carried out on an electrochemistry working station...
CHI660A (Chenhua Co., Shanghai, China). A conventional three-electrode cell was used. The solutions were deoxygenated with nitrogen gas. The working electrode was copper disc electrode, with a surface area of 0.28 cm². The reference electrode was saturated calomel (SCE), and all potentials are quoted with respect to this. A platinum counter electrode was used during linear potential sweep process. The electrolyte contained 75 g L⁻¹ Na₂SnO₃·3H₂O, 4 g L⁻¹ CoCl₂·6H₂O, 150 g L⁻¹ C₆H₄O₆KNa·4H₂O, 20 g L⁻¹ K₃C₆H₅O₇·2H₂O, and 2 g L⁻¹ NaH₂PO₄·4H₂O adjusted to pH 7.5 with the aid of NH₄OH. All these reagents are analytical reagents, and were purchased from Sinapharm Chemical Reagent Co. Ltd.

### 2.2. Preparation of porous Sn–Co–P alloy electrode

Sn–Co–P alloy electrode was prepared by electroplating using copper foam as current collector. The copper foam was rinsed by dilute H₂SO₄ (10 wt.%) prior to electroplating. The composition of electroplating bath contains 75 g L⁻¹ Na₂SnO₃·3H₂O, 4 g L⁻¹ CoCl₂·6H₂O, 150 g L⁻¹ C₆H₄O₆KNa·4H₂O, 20 g L⁻¹ K₃C₆H₅O₇·2H₂O, and 2 g L⁻¹ NaH₂PO₄·4H₂O. The mixture was stirred at 50 °C. A platinum-plated Ti mesh was served as anode. The electroplating was lasted for 10 min with a current density of 10 mA cm⁻². The pH value was adjusted to 7.5. The thickness and diameter of porous Sn–Co–P alloy electrode were measured about 1.2 mm and 1.3 cm. The number of pores per linear inch (PPI) was 110. The diameter of planar copper foil was 1.3 cm.

### 2.3. Structural analysis of porous reticular Sn–Co–P alloy electrode

The morphologies and phase structure of the electroplated Sn–Co–P films before and after charge–discharge cycles were investigated by using field emission scanning electron microscopy (XL30SEM system) and X-ray diffraction (XRD, Philips X’Pert Pro Super X-ray diffractometer, Cu Kα radiation, at 2 min⁻¹ scan rate). The electrodes subjected to electrochemical cycling and used for SEM imaging were washed three times in DMC to remove electrolyte and to avoid LiPF₆ deposition.

### 2.4. Electrochemical charge–discharge tests

Electrochemical charge–discharge behaviors were investigated directly using 2025 coin cells assembled in an argon-filled glove box. To remove water, the test electrodes were dried at 105 °C for 12 h in vacuum atmosphere before measurements. The cell was made from a porous reticular Sn–Co–P alloy cathode and a lithium anode. The electrodes were separated by a separator material (Celgard 2400). The electrolyte reservoir was made from LiPF₆ (1 M) in a mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) 1:1:1 (vol.%). Provided by Guotaifuhuang, Zhangjiagang, China). The cells were galvanostatically charged and discharged in a battery test system (NEWARE BTS-610, Neware Technology Co. Ltd., China) with a current density of 25 mA g⁻¹ during initial four cycles, followed by a current density of 50 mA g⁻¹ for a cut-off voltage of 0.05–1.5 V (versus Li⁺/Li) at room temperature.

### 3. Results and discussion

Fig. 1 shows the linear sweep voltammetry (LSV) of Sn–Co and Sn–Co–P alloy deposition. The electrode potential was swept from −0.1 to −1.4 V versus SCE, at 10 mV s⁻¹ potential sweep rate. The curve (a) of Fig. 1 presents the LSV obtained in a solution of 150 g L⁻¹ C₆H₄O₆KNa·4H₂O, 20 g L⁻¹ K₃C₆H₅O₇·2H₂O, and 2 g L⁻¹ NaH₂PO₄·4H₂O. The reaction current is not observed in this region, which indicates that electrochemical reduction of H₃PO₄ did not occur. The curve (b) of Fig. 1 presents the LSV obtained in a solution of 75 g L⁻¹ Na₂SnO₃·3H₂O, 4 g L⁻¹ CoCl₂·6H₂O, 150 g L⁻¹ C₆H₄O₆KNa·4H₂O, and 20 g L⁻¹ K₃C₆H₅O₇·2H₂O. It can be found that Sn–Co deposition started at a potential of approximately −0.85 V vs SCE. As the potential became more negative, the current density increases. So curve (b) of Fig. 1 indicates that Sn–Co alloy deposition can be obtained in above solution. The curve (c) of Fig. 1 shows the LSV obtained in a solution of 75 g L⁻¹ Na₂SnO₃·3H₂O, 4 g L⁻¹ CoCl₂·6H₂O, 150 g L⁻¹ C₆H₄O₆KNa·4H₂O, and 20 g L⁻¹ K₃C₆H₅O₇·2H₂O. At a potential more negative than −1.0 V, the current densities show a speedy increase. A comparison of curve (b) and curve (c) in Fig. 1 indicate that at some potential, the current density of curve (c) is larger than that of curve (b), which is ascribed to co-deposition of phosphorus and tin–cobalt alloy.

Fig. 2 shows the XRD patterns of the as-deposited Sn–Co–P alloy electrodes. The XRD results indicate that the presence of three different phases: the main electrodeposited product of Sn₉P₄Sn, as evidenced by the several peaks at 2θ of 22.4°, 43.6°, 62.4°, 64.3°, 72.9°, and 79.5°, and Sn with minor quantity of Co₃Sn₂. The diffraction peak at 44.7° is assigned as peak of copper substrate. Therefore, multi-phase composite alloy film electrode was formed. As shown in Fig. 3a, the Sn–Co–P composite alloy electrode exhibits three-dimensional (3D) porous reticular structure, the active material is observed to have a dense structure on copper foam.
Fig. 4a shows the initial charge and discharge curve of the Sn–Co–P composite alloy electrode. It is clear from the figure that during charge, the potential of the electrodeposited Sn–Co–P composite alloy anode is dropped to 0.25 V versus Li+/Li immediately after starting the test, and decreased gradually to 0.05 V. During the discharge, compared to the electrodeposited pure Sn electrode, we can not observe multiple potential plateaus, corresponding to lithium insertion into the different Li$_x$Sn phases. It is considered that Sn metal cluster is hardly formed in the electrode before and during the initial cycle. Therefore, Li was inserted into the Sn–Co–P active material to form a multi-component alloy like Li–Sn–Co–P alloy instead of forming Li–Sn alloys. The electrode showed discharge capacity of 827 mAh g$^{-1}$ and Coulombic efficiency of 93% in the first cycle, indicating that there is low initial capacity loss in Sn–Co–P composite alloy anode.

Fig. 4b presents cycle behaviors of the as-deposited 3D porous Sn–Co–P composite alloy electrode. The discharge capacity for porous Sn–Co–P composite alloy anode was measured 650 mAh g$^{-1}$, and the coulombic efficiency was about 96% in 5th cycle. It decreases slowly to 503 mAh g$^{-1}$ in 50th cycle, but the coulombic efficiency increases to 99%. The capacity retention after 50 cycles was 77% of the 5th-discharge capacity. This value is far superior to that previously reported for the MnP$_4$ anode [10], which showed a capacity that rapidly decreased to 350 mAh g$^{-1}$ after only a few cycles. These results demonstrated that the porous Sn–Co–P composite alloy anode exhibits the good electrochemical lithium storage performance. As shown in Fig. 3b, pulverization phenomenon is hardly observed on the 3D porous Sn–Co–P composite electrode, which is attributed certainly to the porous structure. The multi-phase active material may swell in either upper or side directions during discharge in the moderate spaces provided by the porous structure, so that it can strongly stick to the substrate under much reduced stress and strain caused by its volume change. In addition to the accommodation of the volume expansion during charge–discharge cycles, the porous structure is beneficial for the diffusion of Li$^+$ insertion/extraction. Such properties can improve significantly the chargeability/dischargeability at large current densities.

4. Conclusions

In this work, a novel ternary Sn–Co–P alloy was electrodeposited with a facile method on foam copper substrate. Electrochemical experiment confirmed co-deposition of phosphorus and tin–cobalt alloy. X-ray diffraction demonstrated that the as-prepared Sn–Co–P alloy exhibits multi-phase structure. It has also been found that the electrode of porous Sn–Co–P alloy with multi-phase structure displayed a higher initial charge–discharge capacity and excellent cycleability. The porous and multi-phase structure of electrodes can buffer a large volume expansion caused by the change of stress during charge–discharge cycles, which lead the porous Sn–Co–P alloy anodes to exhibit a remarkable performance during charge–discharge processes.

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