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Superior Li storage anode based on novel Fe-Sn-P alloy prepared by electroplating

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ABSTRACT

Novel ternary Fe-Sn-P alloys prepared by simple single-step electrodeposition are investigated as promising anodes for Li-ion batteries. The $Fe_{51}Sn_{38}P_{11}$ electrode, in particular, shows outstanding Li-storage properties, with initial specific discharge/charge capacities of 857.8 and 655 mA h g^{-1}, respectively. The reversible capacity remains stable at 427 mA h g^{-1}, even after 90 cycles, corresponding to a coulombic efficiency of 96% and a capacity retention of 65%. The cauliflower-like morphology of the above anode is well preserved after 90 cycles, suggesting that this alloy could significantly mitigate the electrode volume expansion by exerting a positive multiphase synergistic effect. The superior electrochemical performance of the ternary Fe-Sn-P alloys confirmed its potential as an alternative Li-ion storage anode; the large-scale suitability of the developed electroplating method provides an additional advantage.

1. Introduction

Rechargeable Li-ion batteries (LIBs), as well as supercapacitors, exhibit high power density, high safety, and long lifetimes, thereby playing an important role in our daily life because they are widely used in electronic devices, implantable medical devices, smart grid systems, and vehicles [1–5]. However, the accessible capacities of Li-ion batteries still cannot meet the fast-growing energy demand of newly emerging applications such as electric vehicles. Therefore, the development of anode materials with high capacities and superior cyclabilities as alternatives to graphite materials (372 mA h g^{-1}) for Li-ion batteries has become increasingly important. Among the various potential anode materials, phosphorus has recently attracted much attention because of its high theoretical discharge capacity (2596 mA h g^{-1}), unique puckered layer structure, and low Li intercalation potential (0.02–0.2 V) [6–8]. The puckered layer structure with a low stacking density of 30% can release structural strain and enable fast diffusion of Li^+, thus enhancing the electrochemical cycling stability. Because the electronic conductivity of P is rather poor, extensive research has been conducted on transition metal phosphides (MPs) that can effectively improve the overall electronic conductivity of the electrode, affording enhanced Li-storage properties [9–11]. However, the commercial application of MP anodes is hindered by their large volume changes upon Li insertion and extraction that result in particle pulverization and rapid capacity fading [12]. So far, various binary MPs such as MnP_4, FeP_x, CoP_3, Cu_3P, NiP_2, $SnP_{0.94}$, and Sn_4P_3 have been fabricated via high-temperature solid-state synthesis, ball milling, solution-phase techniques, and other traditional time-consuming and high-cost stepwise methods [7,9,12–18], which often require extreme operating conditions incompatible with practical applications.

In recent years, ternary metal phosphides (e.g., Sb-Co-P, Fe-Sb-P, and Sn-Ni-P) and even a quaternary Fe-Sn-Sb-P system have been explored as alternatives to binary MPs [19–22]. The introduction of inactive elements (Fe/Ni/Co) can not only effectively alleviate the mechanical stress induced by active phase (Sn/Sb/P) volume changes, but also enhance electron transfer and dynamic/mechanical strength. More importantly, these ternary/quaternary phosphides can be prepared via single-step electroplating, which is cost-effective and easy to scale-up, allowing facile film deposition onto substrates. In addition, the electroplating

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technique is flexible and adjustable, allowing one to control the composition, morphology, and thickness of the produced thin films via a simple variation of the current density and plating time.

Herein, we report a novel multiphase Fe-Sn-P composite via a facile single-step electroplating method. Five ternary Fe-Sn-P alloys of different compositions were electrochemically deposited on copper foil substrates; the optimal performance was observed for $Fe_{51}Sn_{38}P_{11}$. The Fe-Sn-P alloys were used to prepare a binder-free LIB anode, delivering high capacity and superior cycling performance. Thus, these alloys hold great promise as a superior Li storage anode.

2. Experimental section

2.1. Linear sweep voltammetry (LSV) characterization

All electrochemical analyses were conducted using an electrochemical workstation (CHI660C, Chenhua Instruments, China) and a three-electrode setup. A Pt sheet (exposed area = 2 cm^2) and a glassy carbon electrode (diameter = 0.5 mm) were employed as the counter and working electrodes, respectively, and the potential applied between them was regulated using a reference saturated calomel electrode (SCE).

2.2. Fabrication of Fe-Sn-P multiphase composite electrodes

Fe-Sn-P alloys were galvanostatically fabricated at room temperature using a potentiostat; the composition, content, and function of each reagent are listed in Table 1. The pH was adjusted to 1.5 by utilizing 1 M hydrochloric acid. All chemicals were of reagent grade and were dissolved in distilled water. A Pt foil with an area of 4 cm^2 was used as a counter electrode, with the SCE used as a reference. Fe-Sn-P electrodes were deposited on Cu foil circles (diameter = 1.6 cm, exposed surface area = 2.0 cm^2) at an applied current density of 8.85–44.25 A dm^{-2} for 2 min.

2.3. Material characterization

The crystal structures of the deposited materials were investigated by powder X-ray diffraction (XRD; Philips X'pert Pro Super X-ray diffractometer, Netherlands, Cu K_α radiation, λ = 1.5408 Å) at a scan rate of 2° min^{-1}. The morphology and elemental composition of the electrodeposited films were determined by field emission scanning electron microscopy (SEM, Hitachi S-4800) coupled with energy dispersive X-ray spectroscopy (EDX). The binding energies of Fe, Sn, and P in as-prepared Fe-Sn-P alloys were determined by X-ray photoelectron spectroscopy (XPS, Quantum 2000 spectrometer, USA).

Table 1
Composition of the bath and electroplating conditions used for the preparation of Fe-Sn-P alloys.

Bath composition	Concentration (M)	Function
$SnCl_2{\cdot}2H_2O$(stannous chloride)	0.03	Source of Sn
H_3BO_3(boric acid)	0.60	Buffer agent
NH_4Cl(ammonium chloride)	1.00	Complex agent
$NaH_2PO_2{\cdot}H_2O$(sodium hypophosphite)	0.5	Source of P
$FeCl_2{\cdot}4H_2O$(ferrous chloride)	0.05	Source of Fe
Electro-deposition parameters	value	
Current density (A/dm^2)	8.85–44.25	
pH	1.5	
Temperature	Room temperature	
Plating time	2 min	

2.4. Electrochemical performance characterization

As-deposited Fe-Sn-P electrodes were heated to 80 °C under vacuum for 12 h, and their electrochemical behavior was characterized using a two-electrode cell; a lithium foil was used as a reference/counter electrode. All CR2025 coin cells were assembled in an Ar-filled glove box (with H_2O and O_2 levels being less than 2 ppm). The electrolyte corresponded to a 1.0 M solution of $LiPF_6$ in a mixture of diethyl carbonate (DEC), dimethyl carbonate (DMC), and ethylene carbonate (EC) (DEC:DMC:EC = 1:1:1 v/v/v) containing 2 wt% of vinylene carbonate (VC, provided by Guangzhou Tinci Materials Technology Co., Ltd., China). A Celgard 2400 polypropylene membrane was used as a separator.

Galvanostatic charge-discharge tests of Li/Fe-Sn-P half-cells were performed using a LAND-V34 (Wuhan, China) battery tester at a rate of 100 mA g^{-1} in a fixed voltage range of 1.5–0.02 V at room temperature. The cycled electrodes were dismantled in the glove box, washed with DMC and acetone for three times, and reserved in a special box sealed with epoxy resin glue prior to SEM measurements.

3. Results and discussion

Fe-P and Fe-Sn-P films deposited on the Cu substrate were characterized by cathodic LSV, which was performed in cathodic direction from −0.6 to −1.15 V at room temperature and a scan rate of 5 mV s^{-1} (Fig. 1a). Curve 1 (red line in Fig. 1a) was recorded in a solution of 0.6 M H_3BO_3, 1.0 M NH_4Cl, 0.5 M $NaH_2PO_2{\cdot}H_2O$, and 0.05 M $FeCl_2{\cdot}4H_2O$. A rapid increase in current density was observed between −1.09 and −1.5 V (vs. SCE), associated with Fe-P electrodeposition and simultaneous evolution of hydrogen, in agreement with a previous study [20]. Significant changes were observed upon incorporation of Sn^{2+} ions into the Fe-P system, such as the appearance of a new reduction peak at around −0.65 V (curve 2, black line). This peak was attributed to the deposition of Sn, as confirmed by SEM and EDX (inset) measurements (Fig. 1b). Ternary alloy deposition occurred at potentials more negative than −1.0 V. Under these conditions, curve 2 was observed to have a higher current density than curve 1 because of the electrodeposition of Sn on the Cu substrate. To confirm Sn deposition at −0.65 V, a thin film was deposited on the Cu substrate from the same solution at −0.65 V for 10 min. The corresponding SEM image in Fig. 1b shows numerous stripes on the thin film surface, without any other special features. As illustrated in the inset of Fig. 1b, EDX results demonstrate that the deposit obtained at −0.65 V consists of Sn, and the weak intensity of the Sn peak indicates the low amount of this metal. The peak of Cu was attributed to the Cu matrix. No peaks of other elements were observed, implying that pure Sn was deposited at around −0.65 V. When cathodic scanning was carried out at −1.5 V, a ternary Fe-Sn-P alloy was obtained. As shown in Fig. 1c, the SEM image reveals that the as-deposited Fe-Sn-P (denoted as $Fe_{51}Sn_{38}P_{11}$) exhibits uniform and compact packing without holes or cracks. It features cauliflower-like aggregates composed of nanoparticles, most of which are spherical and exhibit sizes between 50 and 1.5 μm. This cauliflower-like morphology provides more active sites for electrochemical reactions due to its large specific surface area, as compared to those of planar or spherical particles. This morphology effectively alleviates the volume expansion induced by repeated Li^+ insertion and extraction. Moreover, the elemental mappings of element Fe, Sn, and P shown in Fig. 1d–f confirm that these elements are homogenously dispersed in the composite without any impurity.

The reactions on the Cu surface can be expressed as follows [23]:

$$H_2PO_2^- + 2H^+ + e^- \rightarrow P + 2H_2O \quad (1)$$