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Short communication

A new process of preparing composite microstructure anode for lithium ion batteries

Hai-peng Zhao[a,b,*], Chang-yin Jiang[a], Xiang-ming He[a], Jian-guo Ren[a]

[a] Institute of Nuclear & New Energy Technology, Tsinghua University, Beijing 100084, PR China
[b] Pingdingshan Institute of Technology, Henan 467000, PR China

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ABSTRACT

A composite material anode for lithium ion batteries (LIB) consisted of electrodeposited Sn–Sb alloy dispersing in a conductive micro-porous carbon membrane coated on Cu current collector was investigated. The composite material was obtained by directly electrodepositing Sn–Sb alloy on the micro-porous membrane electrode via micro-pores in it, which was prepared by casting a polyacrylonitrile (PAN) solution containing polyethylene glycol (PEG) on a copper foil and then immersing the copper foil into de-ionized water to perform phase inversion, following by heat-treatment. SEM examinations showed that the composite material consisted of isolated pillar-like structure SnSb electrodeposited on Cu current collector dispersing in a conductive micro-porous carbon membrane deriving from pyrolysis of PAN. Constant current charge and discharge tests using the composite anode showed stable coulombic efficiency and desirable cyclability. The reversible discharging capacity was 339.5 mAh g^{-1} after 50 cycles, corresponding to 78.6% of the discharge capacity retention.

1. Introduction

Lithium ion batteries are currently the best portable energy devices for the consumer electronics. Carbon materials (hard carbon, soft carbon, graphite, etc.) are commercially used as the anode material of lithium ion battery. In view of the fact that the theoretical capacity of carbon material is only 372 mAh g^{-1}, to get higher energy and power densities, a significant attention has been paid to investigation of many alloy materials. These alloy materials, such as Sn-based alloy, Si-based alloy, Sb-based alloy, etc., used as anodes for lithium ion batteries may exhibit larger specific gravimetric and volumetric capacities [1–4]. However, they have a common drawback, which is the pulverization of alloy caused by its volume expansion/shrinkage during the charge/discharge cycles of lithium ion batteries associated with the reversible reaction of Li. Such morphological changes results in severe cracking of electrode with loss of electrical contact between inter-particles, and particle and the current collector, resulting in poor charge/discharge cycling characteristics. Therefore, it is necessary to relieve such morphological changes to achieve satisfactory cycling performance. Many research findings have shown that abovementioned problems can be resolved to some extent by using nanocrystalline [5–7], porous materials [8] and by using multi-component instead of single-component materials like binary phases Cu_6Sn_5 [9–11], which due to their complex reaction mechanism help to relieve mechanical strain during charge and discharge of the material. However, macroscopical alloy particles will still suffer from pulverizing risk in long-term cycles as a result of the rapid loss of the reversible capacity. Although the introduction of nano-sized materials can strongly affect reversible capacity, it confronts still some unsolved problems such as the reaggregation of nanometer alloy particles during cycling. Nevertheless, when superfine alloy particles are dispersed in suitable supporting medium such as amorphous carbon network, the resulting composite materials should be very effective in maintaining dimensional integrity during cycling [12–14], where the carbon network acts as a barrier to prevent the aggregation between the nanometer alloy particles, and provides a void space where the particles experience a volume change.

Polyacylonitrile (PAN) is a linear and insulated macromolecule at room temperature. Thermally treated polymer of PAN shows a rich evolution of structural and electric properties, the chains undergoing cyclization to form a conjugated-chain chemical structure, resulting in electrical conductivity. Thus, PAN becomes conjugated conducting polymer by low temperature pyrolysis [15].

In the other hand, PAN is a very processable polymer, which can be dissolved in DMF or DMSO to form casting solution. After the casting solution cast on a glass plate was properly treated by phase inversion process, a microporous PAN membrane can be obtained. In the present study, we attempted to prepare composite material by electrodepositing Sn–Sb alloy on a template-like microporous

* Corresponding author at: Institute of Nuclear & New Energy Technology, Tsinghua University, Beijing 100084, PR China. Tel.: +86 10 89796036; fax: +86 10 89796031.
E-mail address: zhaohp05@mails.tsinghua.edu.cn (H.-p. Zhao).

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Table 1
Bath composition and operating conditions for preparing electrode

Materials	Concentration ($g L^{-1}$)
$SnCl_2 \cdot 2H_2O$	30
$SbCl_3$	2
$K_4P_2O_7 \cdot 10H_2O$	130
Tartaric acid	7
Gelatin	0.3
Temperature	44–50
Current density ($mA cm^{-2}$)	2
pH	7.5–8.2
No stirring	

membrane electrode, which was prepared by casting PAN solution on a copper foil following phase inversion in a non-solvent water, and then heat-treatment. The composite material with dispersed Sn–Sb alloy in conducting carbon network showed better cycle performance.

2. Experimental

The polymer PAN (its weight-average (M_w) values: about 1.5×10^5 g mol^{-1}) used in this study was synthesized by suspension polymerization in our laboratory. A homogenous casting solution of polyacrylonitrile (PAN) was obtained under the mechanical agitation by dissolving 1 g of PAN in 20 mL of dimethylformamide (DMF) solution in which about 5 mL of polyethylene glycol (PEG) was contained. After leaving still for certain time, the resulting viscous solution was cast by a home-made blade with a about 30 μm gap onto a rimmed Cu foil (thickness: 30–40 μm), which was treated in corrosive hydrochloric acid solution in advance. After exposed to air atmosphere at room temperature for appropriate time, the Cu foil was immediately immersed in a de-ionized water bath (a non-solvent coagulating bath) for at least 4 h to perform phase inversion. After the exchange of DMF and water by phase inversion, a substantial number of micro-pores were formed in the film coated on the Cu foil. The resultant was washed, rinsed and dried at 80 °C under vacuum for 24 h, successively. In the end, a white, opaque membrane was firm adhered to the Cu foil and thus a micro-porous membrane electrode was obtained.

The composite anode material for LIB was prepared by electrodepositing Sn–Sb alloy into the as-obtained micro-porous membrane electrode through membrane pores in it, where the membrane electrode was used as working electrode and a pure Sn plate as counter electrode. Compositions and operating conditions of a pH 8.5 electroplating bath are shown in Table 1. All electrodeposition runs were carried out at 44–50 °C without agitation. After electro-deposition, heat-treatment and preparation of tested anode foil were done as follows: the as-electrodeposited composite electrode foil as well as unelectrodeposited micro-porous membrane electrode were cut into circular sheets of diameter 1 cm and then put them into a quartz tube furnace. The heat-treatment was performed under the protection of nitrogen gas at appropriate temperature. Different temperature and time of heat-treatment were tried to optimize parameter of heat-treatment. Based on electrochemical performance and conduction of pyrolytic PAN, the proper temperature for heat-treatment of the electrode foils was carried out in the range of 250–350 °C under the atmosphere of N_2 for 14 h.

Electrochemical tests were performed on 2032-type coin cells with lithium metal (0.5 mm thick foil) as a counter electrode. The electrolytes used were 1 M $LiPF_6$ EC + DEC + DMC (1:1:1, v/v/v). The separator of cell was Celguard 2400. The cell assembly was performed in a glove box filled with argon gas (less than 2 ppm of water). The charge–discharge cycling of the coin cell was galvanostatically performed at a current density of 0.25 mA cm^{-2} with cut-off voltages of 0.02–2.0 V at room temperature. Cycle test was conducted using Land Battery Test System made by Wuhan Land Electronic Co. Ltd. In this study, the charging and discharging processes represent Li-de-insertion and Li-insertion processes, respectively. The amount of active materials in sample was calculated as follows.

Amount of active materials = total weight of anode sheet − weight of corresponding copper current collector or copper substrate, where corresponding copper current collector or copper substrate was the same treatment processes as that of the composite anode foil or unelectrodeposited micro-porous membrane electrode sheet.

Please note, herein, that PAN-pyrolyzed carbon was still regarded as active material in the composite electrode though its reversible capacity is very low. (The amount of Sn–Sb alloy in sample was calculated as follows: amount of active materials = total weight of anode sheet − weight of corresponding heat-treated unelectrodeposited micro-porous membrane electrode sheet.)

Crystal structures of samples were characterized by X-ray diffractometer (XRD, D/max-RB) using Cu Kα radiation. For the cross-section observation, the micro-porous membrane electrode foils were inlaid in an epoxy resin. The epoxy resin was cut, ground and dried to obtain cross-section of them. Before passing through SEM, the cross-section samples of the composite material had to go through the carbon coating process. After that, the samples were imaged and photographed by employing a scanning electron microscope (SEM: JSM6301, Hitachi, Ltd.) with energy dispersion X-ray spectroscopy (EDXS, ATW Link Isis300) with potentials of 15 kV in achieving magnification ranging from 100× to 50,000× to examine the membrane cross-section and the surface. The differential discharging capacity profiles during 1st, 2nd, 10th and 20th for the composite material anode derived from discharge/charge voltage versus capacity profiles of the composite material anode at the constant current density of 0.25 mA cm^{-2} cycled between 0.02 and 2.0 V (vs. Li/Li$^+$).

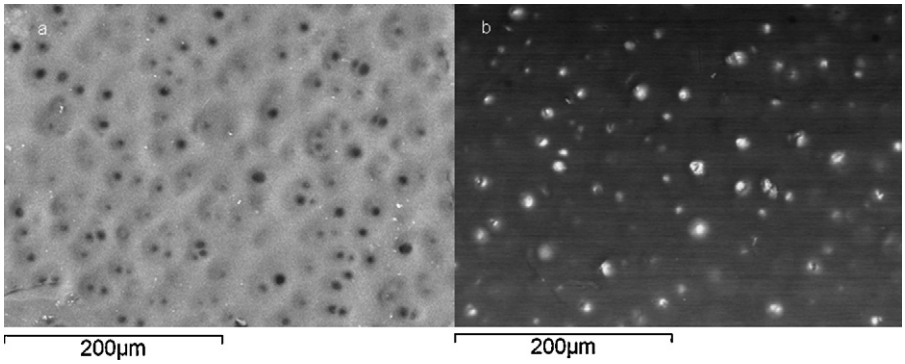

Fig. 1. the electrons back scattered images of surface morphology of microporous membrane electrode before (a) or after (b) electrodepositing.