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Production of Sn–Cu/MWCNT composite electrodes for Li-ion batteries by using electroless tin coating

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ABSTRACT

Cycling stability of pure tin electrodes were aimed to improve by using a suitable combination of copper and multiwalled carbon nanotubes (MWCNTs). For this purpose, firstly Sn–Cu composite powders were produced using an electroless process. Then, Sn–Cu/MWCNT composite electrodes were prepared with dispersing different amounts of MWCNT (10 wt.%, 20 wt.%, 40 wt.%) by high energy mechanical milling method. The surface morphology of the produced Sn–Cu/MWCNT composite powders was characterized using scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS) was used to determine the elemental surface composition of the composites. X-ray diffraction (XRD) analysis was performed to investigate the structure of the Sn–Cu/MWCNT composite powders. The electrochemical performance of Sn–Cu/MWCNT composite electrodes has been investigated by charge/discharge tests and cyclic voltammetry experiments. The cell discharge capacities were determined at a constant current in voltage range between 0.02 V and 1.5 V. AC Electrochemical Impedance Spectroscopy (EIS) analysis was also carried out to measure resistivity and Li-diffusion in the assembled cells. The amounts of MWCNTs were shown to be a crucial factor to improve Sn–Cu/MWCNT composite anodes for cyclability and reversible capacity.

1. Introduction

Lithium ion secondary batteries have the highest energy density in commercial batteries and are used for energy storage in many electric devices, such as mobile phones, laptop computers and digital cameras owing to the advantages of no memory effect, high operation voltage and superior volumetric/gravimetric energy density [1,2]. The most common anode material used in Li-ion batteries is graphite due to its low cost, availability and durability [3]. In graphitic anodes, the Li^+ insertion mechanism corresponds to the reversible, progressive intercalation of Li^+ ions between graphene layers to reach a theoretical capacity of 372 mAh g^{-1} if LiC_6 is formed, compared with a practical capacity of 350 mAh g^{-1} [4]. Recently, there has been tremendous interest and effort to the synthesis of tin-based compounds as alternatives to graphite materials, with the aim of improving the capacity and energy density of lithium ion batteries [2–4]. However, a large specific volume changing occurs during Li insertion and extraction reactions, which causes the electrode to fail by pulverization. As a result rapid capacity fading is observed [5–8]. Therefore, the main issue on the improvement of the Sn cycle performance is how to overcome the volume change and prevent the pulverization of particles. Therefore, many studies have been focused on tin-based intermetallic alloys such as Sn–Ni [9], Sn–Cu [10], Sn–Co [11], and Sn–Sb [12].

The interface between the active material and the inactive current collector has been found crucial for electrode performances. For this reason, to improve cyclic properties of Sn alloyed with these elements, which are inactive towards Li and hence function as a matrix and buffer the volume expansion. These alloy materials provided a longer cyclability than that of pure tin, but Sn-based alloy electrodes exhibit still dramatic loss in reversible capacity after several cycles. To enhance its electrochemical performance and cycle life, several carbonaceous nanocomposite Sn-based electrodes have been proposed [13,14]. Several carbon allotropes such as amorphous carbon, hard carbon, graphite, carbon nanofibers, CNTs and graphene were used because of their low volume changes as the negative electrodes in Li batteries. All the carbon based materials were known to be effective in terms of buffering of the stresses during the electrochemical cycling together with their specific electrochemical contribution and extremely high conductivities. The buffering effects are expected to be higher in the CNTs compared with layered morphologies, nanofibers and other particulate types of carbonaceous materials due to their excellent flexibility and extremely high modulus and fiber morphology. According to the composite mechanics rules, when the stress is stored in a matrix the load bearing capacity of the hollow fiber like morphologies are more beneficial than the layered geometries [15]. Multiwalled carbon nanotubes (MWCNTs), with their large internal cavity, high electrical conductivity, extensive surface area, and material flexibility should be good buffer materials to prepare

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superior composite anode materials [15,16]. Uysal et al. [9] fabricated a Sn–Ni/MWCNT composite by pulse electrodeposition. They indicated that the Sn–Ni/MWCNT composite anode provides a longer cyclability than that of Sn–Ni alloy. Huang et al. [17] reported that a Sn–Co/MWCNT composite anode prepared by reductive precipitation solution of chelating metal salts within a CNT suspension and the specific capacity of the Sn–Co/MWCNT composite anode was much better than the Sn–Co anode. Similarly, recently in a work published on Sn–Sb/CNT [18], improving the cycling performance of the Sn-based anode materials has been studied.

There are many methods of preparing structured nanoparticles, such as electroless plating, electrophoresis, electrodeposition and self-assembly [19,20]. In this study, to improve the cyclability and capacity performances of a Sn electrode, Sn–Cu composites were prepared for the first time by electroless coating of tin on copper powders. Subsequently Sn–Cu powders were reinforced with different amounts of MWCNTs by mechanical alloying to improve the interface bonding between the active material and the MWCNTs. To the best of the authors' knowledge there are no reports on the negative electrodes produced by electroless Sn coating on the ductile Cu surfaces and investigation on the effect of varying amounts of MWCNTs on the electrochemical performances of the Sn active materials. It is aimed not only to improve the electrode conductivity but also to contribute the buffering of high mechanical stresses caused by large-volume expansion during Li alloying.

2. Experimental details

Copper powders (60 μm diameters in size supplied by Alfa Aesar) and MWCNTs (supplied by Arry Nano with the diameter of 50–60 nm and length of 10 μm) were used in this experimental study for producing Sn–Cu/MWCNT nanocomposite electrodes. At the first step, the surface of pure copper powders were coated with tin by electroless deposition process. Before the Sn deposition process, the surfaces of pure copper powders were pretreated to obtain catalytic activity and then cleaned with acetone to remove any contaminants on the surfaces. Later, the surfaces of copper powders were micro-etched to provide sufficient bonding between Cu and Sn deposits. Following the micro-etching, copper powders were filtered and washed with distilled water several times and the pretreatment of copper powders was completed after drying of activated powders for 10 h in a vacuum oven at 60 °C. After the pretreatment process, the surfaces of Cu powders were coated with Sn by an electroless process. The basic composition of the bath, and the plating conditions are shown in Table 1. All solutions were prepared with de-ionized water and reagent grade chemicals. Plating process was carried out at 70 °C temperature and plating time was kept constant at 10 min for all samples. The pH value of the plating bath was controlled continuously during plating between 12 and 13 by using NaOH as a buffering agent. After the plating process, tin coated copper powders were washed up with distilled water and then dried at 60 °C in a vacuum oven for 12 h.

At the second step, the surfaces of the MWCNTs were prepared, since the nanocomposites based on the Sn–Cu powders reinforced with varying amount of MWCNTs. In this investigation, surface treatment of MWCNTs was carried out using a solution of nitric acid/sulfuric acid mixture to improve the dispersion of the CNTs into the Sn–Cu matrix. The acid treatment not only removes most of the metal catalyst but also produces carboxyl, aldehyde, and other oxygen containing functional groups on the surface of the MWCNTs and help in uniform dispersion of CNTs [21]. In the present investigation, MWCNTs were added into the solution of 2:1 nitric acid to sulphuric acid ratio in a glass bottle. The suspension was later filtered and neutralized with sodium hydroxide pellets. The MWCNTs were then subjected to a repeated process of rinsing by distilled water until a pH value of 7 was obtained. The suspension was then filtered and baked dry at 80 °C for 2 h to remove any residues. The third step was dispersing MWCNTs into Sn–Cu powders. Three different nanocomposite compositions were prepared; Sn–Cu/MWCNT composites with amounts of 10 wt.%, 20 wt.%, and 40 wt.% MWCNTs. To compare the effect of Sn–Cu/MWCNT composites, Sn–Cu electrodes were also prepared at the same conditions. MWCNTs and the Sn–Cu powders were placed in 250 ml stainless steel mixing jars for the fabrication of Sn–Cu/MWCNT nanocomposite electrodes. Ball milling was carried out at 400 rpm in a Fritsch P7 planetary ball mill with a ball-to-powder weight ratio of 10:1 using stainless steel milling balls having diameters of 10 mm. Methanol was added as a process control agent (PCA) in order to minimize cold welding of the copper particles and also to prevent powders sticking to the balls and the jar walls.

Table 1
Overview of electroless coating parameters for preparation of Sn–Cu coatings.

Bath composition	
$SnSO_4$ (Alfa Aesar, purity >%99)	40 gL^{-1}
$NaH_2PO_2 \cdot H_2O$ (Alfa Aesar, purity >%95)	20 gL^{-1}
$Na_3C_6H_5O_7$ (Alfa Aesar, purity >%98)	50 gL^{-1}
NH_4Cl (Alfa Aesar, purity >%99)	100 gL^{-1}
Glycine (Alfa Aesar, purity >%98)	0.5 gL^{-1}
Powder concentration	10 gL^{-1}
pH	12–13
Plating time	10 min
Temperature	70 °C

The surface morphology of the Sn–Cu and Sn–Cu/MWCNT nanocomposites was characterized by SEM (JEOL 6060LV) equipped with EDS. Possible growth planes and the crystallographic relationship of Sn–Cu/MWCNT composites were performed by XRD method using a Rigaku D/MAX 2000 X-ray diffractometer.

The Sn–Cu/MWCNT nanocomposites were tested as anode active materials in Li-ion battery CR2016 cells. To prepare the electrodes, 75 wt.% Sn–Cu/MWCNT nanocomposite powders and 10 wt.% carbon black were mixed with 15 wt.% PVDF binder dissolved in a N-methyl-2-pyrrolidinone (NMP) solution. The resulting slurry was cast on a copper foil, pasted using a doctor blade, and dried at 120 °C in a vacuum oven for 12 h. The sample on the copper foil was then cut using a cutter disc. For comparison, tin coated copper electrodes were also prepared using the same conditions. Coin type CR2016 test cells were assembled in an argon filled glove box, the prepared electrodes were used as working electrode, Li foil was used as counter electrode, and 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 in volume) was used as the electrolyte. The working and counter electrodes were separated with polypropylene (PP) separator. Charge–discharge characteristics of the electrodes were tested between 0.02 V and 1.5 V at a constant current of 150 mAh g^{-1} (C/5) based on tin and carbon nanotube weights by MTI Battery Tester.

3. Result and discussion

The bath solutions were prepared with NaH_2PO_2 as a reducing agent and sodium citrate ($Na_3C_6H_5O_7$) served as the complexing agent for the reduction process [22]. To investigate the tin deposition on the surface of the copper powders, SEM studies were performed. The SEM micrographs in Fig. 1a and b show the microstructure of the uncoated copper powders and Sn coated copper powders, respectively. The morphology of the irregularly sized pure copper powder is also illustrated in Fig. 1a. Fig. 1b shows the SEM images of Sn coated copper powders with an average particle size of 10–30 μm. As can be seen in Fig. 1b, copper particle surfaces were successfully coated with a continuous tin layer. Moreover, a relatively continuous uniform and dense tin layer is observed on the surface of the copper powders. Especially, Sn–Cu/MWCNT composite electrode developed cycling performance and capacity of Li-ion batteries. Copper cannot only be helpful to buffer the stresses caused by volume changes of Sn electrode during electrochemical reaction [23,24].

Distribution of Sn and Cu atoms was revealed by X-ray color mapping carried out with a SEM–EDS, as shown in Fig. 2. The EDS elemental