

Electrochemical Performance of Pulse Electrodeposited Sn–Ni/MWCNT Composite Anode for Lithium-Ion Batteries

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Grain size, and MWCNT content in the electrolyte of nanocrystalline Sn–Ni/MWCNT composite deposits produced from a solution containing nickel chloride and tin chloride at constant electrodeposition conditions (pulse on-time T_{on} at 2.5 ms and pulse off-time T_{off} at 7.5 ms) but with different peak current densities were investigated. The structure of the electroplated thin film Sn–Ni/MWCNTs composite electrode is investigated by X-ray diffraction, scanning electron microscopy. Galvanostatic charge/discharge measurements were performed in the assembled CR2016 cells designed by using anode composite material produced by pulse electro co-deposition. These cells discharge capacities were cyclically tested by a battery tester at a constant current in voltage range between 0.02 and 1.5 V. The electrochemical results showed that the increase in the discharge capacity of the assembled cell was produced when compared with conventionally used graphite lithium-ion batteries.

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1. Introduction

Many studies have been focusing on replacing commercially used graphite anodes with other materials, with the aim of improving the capacity and energy density of lithium ion batteries. Among the candidate materials, Sn-based materials are particularly attractive as Sn has a high theoretical capacity of 994 mAh g^{-1} , which is much higher than that of graphite (372 mAh g^{-1}). However, the central problem for the practical application of a tin anode is the large volume change (about 300%) during Li^+ insertion/extraction, which results in fast pulverization of electrode and thus large irreversible capacity loss leading to poor cycling performance [1, 2].

In order to improve the performance of pure Sn electrodes, extensive attention has been paid on tin-based intermetallic compounds, such as Sn–Cu, Sn–Co, Sn–Ni, etc. These alloy materials can provide a longer cycleability than that of pure tin [2]. Ni atoms form a matrix around the Sn atoms; this structure can restrict the volume change of Sn during its electrochemical reaction with Li because the Ni matrix plays only a buffer role, i.e., it does not react with Li. However, since the volume change of Sn is not restricted completely, cracks are formed on the electrode surface during charging and discharging [3].

Recently, the nanocomposites of Sn-based alloy/carbonaceous materials were introduced to overcome this problem because of synergistic effect between carbonaceous materials and Sn [4]. Sn–Ni alloy can be prepared by different technique such as electrodeposition [5], sintering [6], ball milling [7]. In comparison, the electrodeposition presents significant advantages, particular

for the preparation materials of Li-ion battery. Electrodeposited anodes do not need conductive agents and binders, the microstructure of the deposits can also be significantly changed by well controlling the electrodeposition conditions, i.e., the chemical composition of the coating bath, the stirring conditions and the pulse current density [2].

Up to now, we did not find any report on about the synthesis and lithium storage performance of nanostructured Sn–Ni alloy/multiwall carbon nanotube (MWCNT) composites prepared by pulse electrodeposition.

In this paper, Sn–Ni/MWCNT composite was prepared for the first time by pulse electrodeposition on copper that is served as a current collector. The charge–discharge tests demonstrated that the electrode of nanocomposites of Sn–Ni/MWCNTs exhibited a relatively high capacity and excellent cycleability when it was used as an anode of a lithium battery.

2. Experimental

2.1. MWCNT functionalization

To obtain good deposition, MWCNTs should be dispersed uniformly in the plating solution, and suspension must be stable. This is because the MWCNTs were easily coalesced in aqueous solution due to their high surface energy. In this investigation, surface treatment of MWCNTs was carried out using a solution nitric acid/sulphuric acid to improve the dispersion of the CNTs into the electrodeposited Sn–MWCNT coating. The acid treatment not only removes most of the metal but also produces carboxyl, aldehyde, and other oxygen containing functional groups [8] on the surface of the MWCNTs and helps in the uniform dispersion of CNTs without any additional dispersing additive. The mixture was subsequently magnetically stirred at 100°C for 1 h. Then they

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were further collected on 0.2 μm filter, rinsed with distilled water, and dried at 100 °C for 4 h.

2.2. Pulse electrodeposition of Sn–Ni/MWCNT composite coatings

Sn–Ni/MWCNTs composite coatings were deposited from a chloride bath on the copper substrate. All chemicals are of analytical reagent grade, and analytic/chemical standards were used for the preparing of the bath solutions. The multiwalled CNTs were supplied by Arry Nano with the diameter of 50–60 nm and length of 10 μm . The electrodeposition solution was comprised of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (28 g/L), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (15 g/L), $\text{K}_4\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ (170 g/L), glycine (0.5 g/L). The composite coatings were prepared with a current density of 10, 20, 40 mA/cm^2 . The MWCNT concentration in the composite plating bath was 5 g/L. Coatings were produced under mixing of the electrolytes together with sonication during electrodeposition. A plating cell containing of the solution was immersed in a thermostatically controlled large volume water bath kept at a constant temperature of 50 °C. A high-purity tin was used as the anode. The copper substrate was then activated in 25% H_2SO_4 solution for ≈ 2 min. This activated copper substrate was placed parallel at a distance of 5 cm from the vertically oriented tin plate in the plating bath. Continuous stirring of the electrolyte was performed using a magnetic stirrer and sonication was conducted using an ultrasonic processor (UP400S) 20 kHz, at a power of 60 W, submerged at a fixed position within the plating solution in order to prevent agglomeration of MWCNTs in the electrolyte suspension. The duty cycle is defined as $t_{\text{on}}/(t_{\text{on}} + t_{\text{off}})$, where t_{on} is the pulse-on period, and t_{off} is the relaxation period.

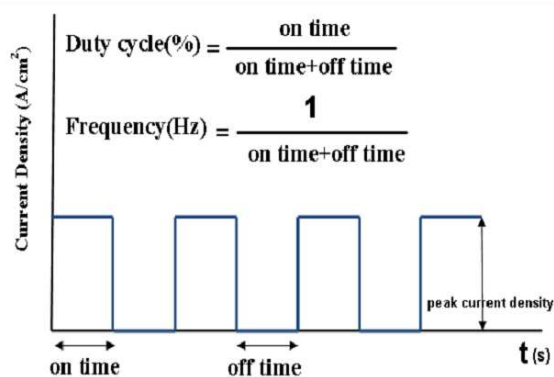


Fig. 1. Schematic diagram of the wave shape of pulse deposition.

A current waveform for the pulsed electrodeposition is illustrated in Fig. 1. The conditions of the pulse method were as follows; the bath temperature was kept at 50 °C and the pH was adjusted at 8.5. Duty cycle was of 25%, frequency — of 100 Hz, deposition time — of 3.0 min. Three different types of Sn–Ni/MWCNT nanocompos-

ite films are prepared with different peak current density in the electrolyte. After co-electrodeposition, Sn–Ni/MWCNT composite electrodes were cut into cylindrical coupons at about 16 mm in diameter and dried.

2.3. Characterizations of composites

The crystal structure and surface morphology of the composite coatings were examined with X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. Coin type CR2016 test cells were assembled in argon filled glove box. The co-deposited Sn/MWCNT nanocomposites were used as a working electrode, Li foil 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) as the electrolyte. The working and counter electrodes were separated with polypropylene (PP) separator. Charge–discharge characteristics were obtained at 293 K (room temperature) between 0.02 V and 1.5 V at a constant current of 50 mA/g .

3. Results and discussion

Figure 2 shows the surface morphologies of the Sn–Ni/MWCNT composite electrodes obtained at peak current densities of 20, 40, 60 mA/cm^2 . These coatings were produced with constant duty cycle (25%) and pulse frequency (100 Hz). The bath temperature was 50 °C, and the MWCNT concentration in the composite plating bath was 5 g/L. It reveals that by increasing the peak current density from 20 to 60 mA/cm^2 , the content of MWCNTs in the deposit increased. Surface roughness remarkably increased with increasing average current density, and a spherical morphology was observed at high peak current density (Fig. 2c). A relatively smooth

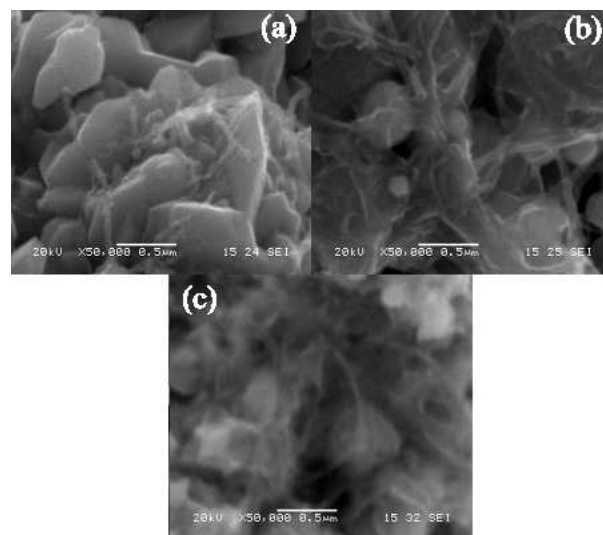


Fig. 2. SEM micrographs of Sn–Ni/MWCNT composite coatings obtained at constant frequency and duty cycle (100 Hz and 25%), peak current density of (a) 20 mA/cm^2 , (b) 40 mA/cm^2 , and (c) 60 mA/cm^2 .

surface morphology was obtained at low peak current density (Fig. 2a). MWCNTs were incorporated into the Sn–Ni matrix for whole peak current density. Spherical Sn–Ni electrodeposition incorporating MWCNTs was typically formed at peak current density of 40 mA/cm². Arai et al. [9] studied Cu/MWCNT composite materials by electrodeposition. They found that the surface morphology of the films was affected by the current density, and a bumpy morphology surface was obtained at a high current density.

The XRD patterns of the Sn–Ni/MWCNT composite coatings produced at different peak current densities are presented in Fig. 3a. The XRD peaks were attributed to Ni₃Sn₄, and it was confirmed that Ni₃Sn⁴ is the predominant phase in the deposited composite film. As expected for Sn–Ni/MWCNT composites prepared at different peak current density for pulse electrodeposition, the peaks of all samples can be ascribed to both Ni₃Sn₄ phase and Ni_xSn_y metastable phase according to literature data [3, 10]. This might be due to the existence of a small amount of the Ni_xSn_y metastable phase, although it was not detected by XRD.

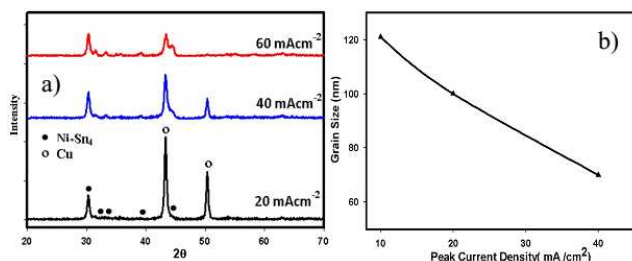


Fig. 3. Effect of peak current density (a) on phase structure, (b) on grain size of Sn–Ni/MWCNT composite coatings produced at constant duty cycle 25% and frequency (100 Hz).

The average grain size of the coatings was calculated from the diffraction peak width using the Scherrer equation. The MWCNT concentration in the composite coating increases with increasing the peak current density from 20 mA/cm² to 60 mA/cm². Moreover, the grain size of composite coating was found to decrease with increased peak current density in the electrodeposited composite materials (Fig. 3b). As it is well known, as the peak current density is increased the rate of formation of nuclei will be greater than the growth and the deposit will become finer-grained [11]. Moreover the presence of MWCNTs in a metal deposit may induce smaller grains due to a large increase of nucleation sites. The carbon nanotubes provide more nucleation sites and, hence, slow up the crystal growth; subsequently, the corresponding Sn–Ni matrix in the composite coating has a smaller crystal size [12, 13].

Figure 4 displays the cycling stability of the Sn–Ni/MWCNT composite electrodes produced different peak current density at a current density of 50 mA g^{−1} and potential between 0.02 and 1.5 V. As shown in Fig. 4, the

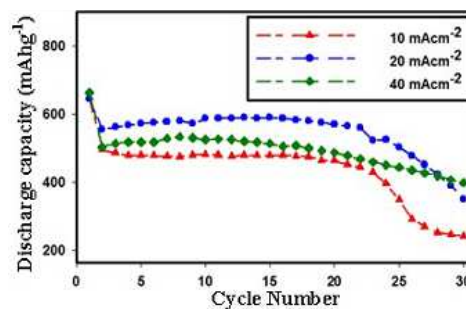


Fig. 4. Effects of peak current density on cycle performance of Sn–Ni/MWCNT composite electrode.

Sn–Ni/MWCNT (10 mA/cm²), composite electrode exhibited poorer cycle performance than Sn–Ni/MWCNT (40 mA/cm²) composite electrodes. When the peak current density increases to 40 mA cm^{−2}, the charge capacity of the composite electrode is 512 mAh g^{−1} at the 30th cycle, whereas that of the Sn–Ni/MWCNT (10 mA/cm²) composite electrode has decreased to 260 mAh g^{−1}. It appears that the improvement in the Li⁺ capacity and cycle performance of the Sn–Ni/MWCNT (40 mA/cm²) composite electrode is primarily due to the good dispersibility of the nanosized particles, indicates that the MWCNT, as well as the Ni nanoparticles, effectively restrains the aggregation of the Sn in the nanocomposite matrix, against the volume expansion of the tin anode. Based on the above results, it is concluded that Sn–Ni/MWCNT nanocomposite can effectively buffer the volume expansion of the micro-sized Sn particles and thus stabilizes the structure of the material. In this deposited Sn–Ni/MWCNT composite electrode, there are many interfaces between the nanocrystalline particles (Sn and Ni) and the MWCNT. These interfaces are the most probable sites for Li storage. In addition, the high electron conductivity of the metallic nanoparticles and their plentiful interfaces with the MWCNT also ensure the high-rate performance of this Sn–Ni/MWCNT composite anode.

4. Conclusions

Sn–Ni/MWCNT nanocomposite coatings were deposited from a plating tin and nickel chloride bath using pulse electrodeposition. The main conclusions of the investigation are as follows. The surface morphology of the composite coating was affected by the peak current density, and a relatively smooth surface was obtained at a lower current density. The co-deposition of MWCNT in a tin electrolytic coating depends on the peak current density in bath. The MWCNT concentration in the composite coating increases with increasing the peak current density from 10 mA/cm² to 40 mA/cm². A high reversible capacity, and fairly good cyclability was achieved for Sn–Ni/MWNT (40 mA/cm²) electrodes.

Acknowledgments

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