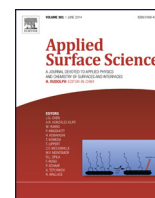




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Coaxial silicon/multi-walled carbon nanotube nanocomposite anodes for long cycle life lithium-ion batteries

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ABSTRACT

In this work silicon/multi walled carbon nanotube (MWCNT) composite anodes were produced via direct current (DC) magnetron sputtering of silicon onto carbon nanotube papers (buckypapers). The amount of silicon in the composite anodes was varied by using different sputtering powers of 150 W, 175 W, 200 W and the effect on the cell performance was studied. Phase analysis was conducted with X-ray diffraction (XRD) technique and Raman spectroscopy. Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) analyses were employed for morphological characterization of anodes. Energy dispersive spectroscopy (EDS) mapping was used to observe silicon distribution on the buckypapers. Cyclic voltammetry (CV) tests were carried out to reveal reversible reactions between silicon and lithium. Galvanostatic charge/discharge technique was employed to determine the cyclic performance of anodes. Electrochemical impedance spectroscopy technique was used to understand the relation between cyclic performance and internal resistance of cells. The results showed capacity retention of silicon anodes was improved with composite structure and higher capacity values were achieved than graphite anodes. The silicon/carbon nanotube composite produced with 150 W showed the best cycle stability after 100 cycles of galvanostatic charge/discharge tests with capacity value of 620 mAh g⁻¹.

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1. Introduction

Lithium-ion batteries (LIBs) are known to play already the most important role in the powering of portable electronic devices. Applications of rechargeable LIBs in mobile and stationary power storage has generated numerous researches to improve their energy density, power density and cycling life [1–3]. Compared with most other battery technologies, LIBs have the advantages of high energy density, long cycle life, high voltage, and excellent rate capability. However, there are still many challenges for further development of LIBs sufficient for electrical transportation with high energy density, long cycling life, excellent rate capability, low cost, etc. Therefore, much research has been focused on improving the electrochemical properties of Li ion batteries components such as anode, cathode, separator or electrolyte [4,5]. For the case of anode material, commercial graphite anode shows excellent capacity retention during cycling of battery. Although graphite as the anode possesses high coulombic efficiency, good cycling

stability and low cost, its theoretical capacity is only 372 mAh g⁻¹ which, clearly insufficient for powering of next generation electrical applications [6]. To meet the energy density requirements, many anode materials have been investigated including Si, Sn, Al, Ge and compounds including these elements [7]. Among them, silicon is the most attractive candidate since the possibility of forming Li₂₂Si₅ alloy (Li/Si = 4.4) according to the Li–Si phase diagram. Theoretically, Li₂₂Si₅ can deliver a specific capacity of 4200 mAh g⁻¹, which is 10 times higher than the graphite electrode [8]. Despite advantages, volume variation during lithiation is the major drawback of Li–Si alloys as it can reach 300% of its original volume via Li₂₂Si₅ formation, whereas only 10% of volume variation is observed for LiC₆. Volume variations caused by the lithiation of silicon leads the mechanical stress that causes cracking and pulverization of the anode which is responsible for loss of electrical contact between silicon particle thus low cyclability and rapid capacity fade [9].

In order to solve problems originated from volume variations of Si during cycling of battery, novel electrode architectures has been suggested by researchers such as nano sized and nanocomposite silicon materials and among them, most attractive ones are carbon nano tube composites. The superior mechanical properties of carbon nanotubes (CNTs) have received much attention, leading to many efforts to design materials that realize macro scale

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advantages through integrating these nano scale structures [10]. One of the most promising composite structures of silicon and carbon nanotube is unique coaxial structure. Coaxial type CNT reinforcement of the silicon matrix not only provides mechanical integrity via three dimensional interconnected webs and absorbs the mechanical stress caused by the volume variations of active silicon material but also provides high electrical conductive network. The advantages of this type of composites are the increased capacity of the metal alloying materials while using the CNTs as a scaffold to prevent pulverization and crumbling in the anode [11,12].

Although there are several studies related with CNT reinforced silicon based electrodes, to the best of our knowledge there is no study to investigate the electrochemical performances of the amorphous silicon coated MWCNT buckypaper nanocomposite negative electrodes by using magnetron sputtering. In this study, it is aimed to enhance electrochemical performance of silicon anodes via this novel coaxial Si/CNT composite structures. It is also aimed to increase the capacity retention of silicon anodes with producing optimized nanostructures using MWCNTs as both current collector and mechanical support component. A two-step composite production route was adopted for production of anodes. The first step was to produce the skeleton-like carbon nano tube reinforcement as paper form, which is called “buckypaper”. The second step was sputtering of Si onto a skeleton like structure of buckypapers via DC magnetron sputtering to achieve coaxial composite structure.

2. Experimental procedure

2.1. Buckypaper and anode production

Multiwalled carbon nano tubes (MWCNT) with 50 nm diameter were purchased from Ary Nano for buckypaper production. A three-step production method was adopted for buckypaper production. First step was purification of carbon nanotubes via thermal (350 °C 1 h) and acidic (in HCl for 1 h at room temperature) treatment to get rid of impurities like amorphous carbon and metallic catalyst particles arisen from production techniques of carbon nanotubes. Second step was covalent functionalization of carbon nanotubes in order to add functional groups at the tips and defective side zones of nanotubes for enhancing the strength of buckypapers. Functionalization with sulphuric/nitric acid mixture at 3:1 ratio was employed to nanotubes. After functionalization process, homogenous dispersion of functionalized carbon nanotubes was prepared via ultrasonic homogenization with sodium dodecyl sulfate (SDS) addition [13]. At the last step, flexible and binder-free buckypapers were obtained by the vacuum filtration of carbon nanotube dispersion through 220 nm pore size PVDF membrane. A detailed description has been given in our previous study about production of buckypapers [14]. The thickness and diameter of produced buckypapers were measured as 10 μm and 16 mm, respectively.

For composite electrode production, direct current (DC) magnetron sputtering technique was used. Silicon was sputtered onto buckypapers from high purity silicon target (2 in., 99.99%, Kurt Lesker Company). Before starting the coating process, coating chamber was evacuated to 10^{-4} Pa by a turbo molecular pump and then back filled with argon up to 0.5 Pa pressure. The distance between the Si target and the buckypaper substrate was 13 cm, and no external heating was applied to the substrates during deposition. 150 W, 175 W and 200 W DC powers were employed for the deposition with a constant time of 10 min. A glass substrate was installed to the sample holder in the coating chamber to be able to calculate the amount of active material (silicon) in the nanocomposite electrodes by simple volume–density relational algebra with measuring the silicon layer thickness. In addition to composite anode

production, pure thin film silicon anodes were produced via sputtering of silicon onto stainless steel substrates in order to observe the performance difference between composite anodes and silicon thin film anodes.

2.2. Characterization

Phase analysis and crystal structure investigations of composite anodes were carried out via XRD (Rigaku D/MAX 2000 X-ray generator and diffractometer with Cu K α radiation) and Raman Spectroscopy techniques (Kaiser Raman Rxn System). For morphology analyses of the nanocomposite anode structures, FESEM (Jeol JSM-7000) and TEM (Tecnai G2 F20 S-TWIN) analysis were carried out. Energy dispersive spectroscopy (EDS) mapping was employed to reveal silicon distribution on the surface of buckypapers.

2.3. Electrochemical characterization

CR2016 coin type test cells were assembled in an argon filled glove box for electrochemical characterization of anodes. Si/MWCNT nanocomposites and silicon thin films were used as anode (working electrode) and metallic pure lithium foils as a counter electrode. 1 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by wt.) solution was chosen as the electrolyte. Micro porous polypropylene (PP) membrane (Cellgard 2400) was used to prevent the contact of two electrodes (separator). Galvanostatic charge/discharge tests were carried out with a MTI BST8-MA Battery analyzer between 0.2 and 2.0 voltage range using constant current density. Cyclic voltammetry analyses were conducted at a potential window of 0.01–2.0 V and with 0.5 mV s⁻¹ scan rate via electrochemical work station (Gamry Instruments Reference 3000). Electrochemical impedance spectroscopy tests were carried out for fresh composite anodes and after 100 galvanostatic charge/discharge cycles with electrochemical workstation (Gamry Instruments Reference 3000) from high to low frequency rate of 1000 kHz to 0.1 Hz.

3. Results and discussion

Fig. 1 shows the buckypaper pictures obtained after vacuum filtration. No remarkable defects were detected; observations showed that produced buckypapers are continuous and can be folded just like a paper. As a result of binder-free production procedure, obtained buckypapers are suitable to use as anode materials. It could be seen from FESEM images; buckypapers consist from MWCNT networks and have a high degree porous structure.

Fig. 2 shows the scheme of silicon/MWCNT nanocomposite anode structure. After sputtering process carbon nanotube surfaces has been coated with silicon in limited depth through the buckypaper. The structure exhibits MWCNT skeleton which wrapped by silicon layer which is consisting from very fine nano silicon particles and has high degree of porosity which could be understood from scanning electron microscopy analysis.

3.1. FESEM, TEM and EDS analyses

As mentioned in experimental procedure, silicon/carbon nanotube composite anodes were produced via direct deposition of silicon on buckypapers. FESEM images of silicon/MWCNT nanocomposite anodes are represented in Fig. 3.

As it can be seen obviously from FESEM images, silicon was deposited homogeneously on carbon nanotubes. Composite structure consists of a thin silicon layer at top and carbon nanotube network under the silicon layer. Furthermore, it is understood that porous structure which is provided by the buckypaper production

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