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Carbon thin-films/SiO_x nanowires complex using a polyvinylchloride (PVC) solution for lithium-ion batteries

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ABSTRACT

Carbon thin-films/SiO_x nanowires (C/SiO_x NWs) complex were fabricated by combining a simple electrospinning process combined with a carbon heat treatment method using a polyvinylchloride (PVC) solution as organic precursor. This material was investigated for use as the anode in lithium rechargeable batteries. The specific capacity of C/SiO_x NWs complex have exhibited 600 mA h/g when first cycled at 0.1 C rate which was higher than that for C/silica nanoparticles (C/silica NPs) complex, and the reversible capacity for the C/SiO_x NWs complex of approximately 360 mA h/g was retained after 30 cycles. The SiO_x NWs exhibited normal reversible capacities, which are adaptable in LIB.

Introduction

Lithium-ion batteries (LIBs) are representative of rechargeable batteries that serve as secondary battery systems and as batteries in modern technological devices; they represent the best currently available battery technology for military, electric vehicle and aerospace applications. Especially, carbon materials on the lithium-ion reactions in LIBs have been researched because lithium-ions have been confirmed to insert into the carbon material interior and in a stable state. Additionally, carbon materials exhibit a chemical reaction potential similar to that of lithium-ions in batteries. Furthermore, carbon materials exhibit only small changes in their crystal structure and have both high capacities and long lifetimes during lithiation and delithiation. Thus, carbon materials are useful in LIBs [1–9].

To increase the anode capacity, non-carbon anode materials with higher capacities than carbon, such as Al, Sn, Sb, and Si, have also been researched. Especially, silicon (Si) has been researched as an alternative anode material for LIBs because of its high theoretical capacity (~4200 mA h/g). However, Si anodes have problems that stem from their volume changing by as much as 300–400% during the lithiation and delithiation reaction of Si; these large volume changes structurally modify the Si phase and damage the solid-electrolyte interphase (SEI) [10,11]. In this case, carbon materials on the lithium-ion reactions in LIBs have been also used to overcome these drawbacks. Si and carbon complex exhibit synergistic effects, such as stabilizing the SEI layer, that enhance the conductivity of Si-based anodes. Such complex also exhibit reversible high capacities and long lifetimes because of buffer action of the carbon. These traits are required in batteries that power multifunctional electronic devices [12].

Specifically, Si nanowires (Si NWs) have been widely used in high-capacity electronic devices, despite having several problems, which include being expensive, multi-step and advanced fabrication process, highly reactive toward oxygen, and the drastic volume variation (around 300%) during repeated insertion and extraction of lithium ions leads to its remarkable capacity fading, While silica NWs have interesting electronic and optical properties. Additionally, they can be manufactured on a large scale because of the simple procedures and inexpensive equipment required. Additionally, silica nanowires exhibit various advantageous physical properties, including high stiffness and strength [13–16].

In this study, SiO_x NWs were fabricated by electrospinning to confirm their potential use in LIBs, their electrochemical characteristics were compared to those of silica nanoparticles (silica NPs). In addition, anodic complex were synthesized by carbon heat treatment with the silica NPs and SiO_x NWs. The effect of carbon

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heat treatment of the silica NPs and SiO_x NWs on the electrochemical performance was investigated in detail using electrochemical tests and nanostructural analyses.

Experimental

Materials

Tetraethyl orthosilicate (TEOS, Samchun, Korea, 98%), hydrochloric acid (HCl, Samchun, Korea, 35–37%), ethanol (Samchun, Korea, 98%), and polyvinylalcohol (PVA, Aldrich, San Louis, MO, USA, M_w = 85,000–124,000, 99%) were used in the electrospinning solution to fabricate the SiO_x NWs. Polyvinylchloride (PVC, Aldrich, San Louis, MO, USA, low molecular weight) was prepared as the carbon source material. Tetrahydrofuran (THF, Samchun, Korea, 98%) was used as the solvent for the PVC. Silica (SiO_2, Aldrich, San Louis, MO, USA, 99.8%) was used as silica NPs source to compare with capacity of SiO_x NWs.

SiO_x NWs fabrication by electrospinning

A mixture of 5 g of TEOS, 15 g of distilled water, and 40 g of ethanol was stirred in an Erlenmeyer flask for 1 h at 60 °C. A 7 wt% PVA solution was prepared using 2.1 g of PVA and 27.9 g of distilled water, which were mixed and stirred for 3 h at 60 °C. The TEOS mixture and 7 wt% PVA solution were mixed with a weight ratio of 40:7 and stirred 1 h at 60 °C. The TEOS mixture and 7 wt% PVA solutions were electrospun using an apparatus equipped with a power supply (NT-PS-25 K, NTSEE Co, Korea) [17,18]. The voltage, tip-to-collector distance (TCD), syringe pump rate, and collector speed were 15 kV, 10 cm, 1 mL/h, 400 rpm, respectively. The acquired electrospun fiber was heated for 1 h at 1000 °C in a nitrogen atmosphere at a heating rate of 4 °C/min to eliminate the PVA polymer.

Carbon thin-films/SiO_x NWs and silica NPs complex

A mixture of 4 g of PVC dissolved in 100 mL of THF was stirred for 6 h at room temperature, and 1 g of SiO_x NWs or silica NPs was added to this 100 mL solution of 4 wt% PVC. The mixture was stirred for 3 h at room temperature, and the solid and liquid phases were separated by centrifugation at 2000 rpm for 1 min. The liquid was decanted out and the solid was dried at 60 °C for 6 h. The dried solid was placed in an alumina boat and heated to 900 °C for 2 h under a nitrogen atmosphere at a heating rate of 5 °C/min.

Analysis of the SiO_x and silica samples

Thermogravimetric analysis (TGA, Shimadzu, TGA-50H) was performed under air flowing at 10 °C/min to measure the carbon content. X-ray diffraction (XRD, D/MAX-2200 Ultima/PC, Rigaku International, Japan) was performed using Cu-K_α radiation; the sample were scanned over the 2θ range from 5° to 80° to investigate their crystal structure. X-ray photoelectron spectra (XPS) were obtained using a MultiLab 2000 spectrometer (Thermo Electron Corporation, UK) and were used to identify the elements present on sample surfaces. The thickness and morphology of the samples were analyzed by field-emission scanning electron microscopy (FE-SEM, Hitachi, S-4700) and ultra-high-resolution scanning electron microscopy (UHR-FESEM, Hitachi, S-5500) in conjunction with the energy-dispersive X-ray spectroscopy (EDX, Horiva, EX-250, Japan). An EDX map of C, O, and Si was collected over a focused region.

Electrochemical measurements

Electrodes were fabricated by mixing (Thinky mixer, ARE310) the final product powder, carbon black (CB, Timcal, as a conductive agent) and polyvinylidene fluoride (PVDF, Aldrich, St. Louis, MO, USA, as a binder) in *N*-methyl-2-pyrrolidone (NMP, Aldrich, St. Louis, MO, USA, 99%) in a weight ratio of 80:10:10. The slurry was uniformly plastered onto a copper foil current collector using a roll press operated at 0.7 m/min at room temperature, 25 °C and was subsequently dried under vacuum at 100 °C for 10 h. The electrode was assembled into pouch type half cells (electrode area 10 cm^2) with Li metal electrode and ethylene carbonate/dimethyl carbonate (1:1 v/v) with 1 M $LiPF_6$. The mass loading of active material was 2.5 mg/cm^2. Cyclic voltammetry (CV) were performed in a voltage range from 2.5 to 0.01 V (vs. Li/Li^+) at a scan rate of 0.5 mV/s using CH Instruments CHI660 C electrochemical workstation (Chenhua, Shanghai). The galvanostatic charge–discharge measurements were performed at room temperature on a LAND CT2001A (Wuhan) in the voltage range from 2.5 to 0.01 V (vs. Li/Li^+) [19].

Results and discussion

Synthetic process for the carbon thin-films/SiO_x NWs complex

A schematic of the preparation of the C/SiO_x NWs complex is shown in Fig. 1. The polymer solution was spun from the nozzle, which continuously formed SiO_x NWs with thin diameters. The subsequent pyrolysis of these electrospun fibers removed the PVA and organic material to form the crystallized SiO_x NWs. The PVC solution and SiO_x NWs were continuously mixed using a shaker, and the solid was separated from the solution using a centrifuge. The acquired solid was then heated to a high temperature. Finally, the thin, uniform, C/SiO_x NWs complex was easily and conveniently acquired.

Characteristic XRD patterns and thermograms for carbon thin-films/SiO_x complex materials

The XRD patterns of the C/SiO_x complex is typical of an amorphous Si–O–Si, Si–O–H, and Si–O–C phases (broad peak at 2θ = 20–25°), as shown in Fig. 2 [20,21]. The peak of SiO_x NWs was shown to the broadening band between 20° and 25°, and carbon heat treatment sample showed more intense peak. In results, the mixture of SiO_x and carbon peaks was higher than SiO_x NWs peaks by carbon heat treatment with the SiO_x NWs. Fig. 3 provides quantitative thermogravimetric information on the SiO_x NWs and silica materials (TGA, TGA/DSC 1 by Mettler Toledo). The TGA curves were obtained under an oxygen atmosphere by heating the samples from 0 to 1000 °C a heating rate of 10 °C/min. As shown in Fig. 3, the C/silica materials exhibited discernible thermal degradation at 500 °C. The weight loss for the C/silica NPs complex due to carbon removal as CO_2 gas under an oxygen atmosphere was approximately 2.5% at 500 °C. Only carbon weight was lost in the case of the C/silica NPs complex because the silica is an oxygen-stable material. Thus, the silica NPs did not lose weight. SiO_x NWs were synthesized and exhibited weak broadening peak, as previously confirmed by XRD. The C/SiO_x NWs complex experienced a weight loss of approximately 17.5% at 500 °C. Therefore, the carbon material was approximately 2.5–17.5% of the total weight of the SiO_x and silica materials with carbon heat treatment using the 4 wt% PVC solution (in THF) at 900 °C for 2 h. In contrast to the SiO_x NWs, the silica NPs surfaces were not well combined with the carbon material because of their high crystallinity and low reactivity with the carbon source materials.