Amorphous carbon-coated prickle-like silicon of micro and nano hybrid anode materials for lithium-ion batteries

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ABSTRACT

Carbon coated prickle-like Si particles (PS@C) are prepared by metal-assisted chemical etching and subsequent coating with an amorphous carbon film carried out by thermal chemical vapor deposition (CVD). The electrochemical characteristics of PS@C employed as anode material for lithium-ion batteries are investigated in order to find a relationship between interfacial properties and electrochemical performance. The unique morphology of prickle-like Si (PS) having empty space can accommodate volume expansion during the lithiation and delithiation. Additionally, an amorphous carbon coating layer with a thickness of 10–15 nm deposited onto the PS prepared by thermal CVD is investigated as an effective way to enhance the cycle stability and rate capability of the PS electrode due to improved interfacial characteristics. The micro and nano hybrid structure of the PS material combined with the 12 wt.% amorphous carbon layer plays an important role in enhancing the electrochemical performance.

1. Introduction

As a prospective anode material for lithium-ion batteries, Si has been considered as an alternative to carbon-based anodes for next generation lithium-ion batteries because of its natural abundance, availability, environmental friendliness, and most importantly its low discharge potential and high theoretical capacity (4200 mA h g^{-1} in Li$_{4.4}$Si) [1]. However, the practical application of Si anodes has so far been mainly hindered by its low electrical conductivity, low lithium diffusion rate and enormous volume change (300–400%) occurring during the discharge (lithiation) and charge (delithiation) process [2]. The volume change causes bulk Si to be pulverized and lose electrical contact with the conductive additive or current collector, and can also lead to the instability of the solid electrolyte interphase (SEI) [3]. The latter issue encourages continuous consumption of Li-ions for reformation of the SEI layer caused by the breakage of the silicon surface with the progress of the cycle, which leads to an increase in irreversible capacity. In order to improve the cycling stability of Si anodes, great efforts have been made to mitigate the pulverization of Si and improve the stability of the SEI layer. These efforts include the development of Si materials composed of nanostructures, porous structures, or nano-composites,

the addition of coating layers, and the application of electrolyte additives and novel binders [4–8]. These studies investigate the fact that morphology, volume change, conductivity and surface characteristics of the Si-based electrode materials play a key role in producing high performance active material as anode in lithium-ion batteries. In particular, carbon coating the surface of the active material is very useful due to its nature of forming a stable SEI, structural integrity, and high electric conductivity [9,10]. Accordingly, the well-defined uniformity of carbon layer is of high importance for the electrode performance.

Since the nanostructured materials have a small size and large surface area, they are expected to inherently provide short diffusion length for lithium-ions, large interfacial area between the electrodes and the electrolyte, and large alleviation of lattice stress during the operation in lithium-ion batteries. Studies of Si as an anode material are leaning toward almost the whole nanostructure area [11–13]. The nanostructuring of electrodes has been demonstrated to result in lithium-ion batteries with superior electrochemical performance, i.e. higher storage capacity, higher rate capability, and excellent cycling performance. In contrast, the high surface area of nanostructured materials may result in undesirable side reactions with the electrolyte under certain conditions, leading to a significant fading of Li storage capacity and, therefore, poor cycling performance. To avoid these undesired problems, various surface modification or morphologies have been investigated such as hollow, core–shell, nanotube, and nest structures [14–17]. On the other hand, when micro-sized Si (10 μm) is fabricated as an anode to be made into a cell, it has a discharging capacity of only

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about 3260 mA h g^{-1}, and a charging capacity of 1170 mA h g^{-1}, indicating an initial coulombic efficiency of 35%. When the cell is continuously charged and discharged over 5 cycles, its discharge capacity rapidly decreases to about 300 mA h g^{-1}, which results in poor cycling performance due to internal resistance caused by volume change [18]. Therefore, micro and nano hybrid materials enable us to use the advantages of each component and to make up for the imperfection.

In another approach, Yoo et al. [19] have synthesized Si nanotubes via surface sol–gel reaction and magnesium reduction. The empty space in the cores of nanotube accommodates the large volume changes which results in an improved cycle performance. Chen et al. [15] have also shown that Si core-hollow carbon shell nano-composites with tunable buffer voids tolerate physical stress during charge and discharge of cells. Metal-assisted chemical etching of bulk Si powders is rarely reported and attractive for its unique nanostructures [20–25]. In this work, prickle-like Si (PS) of micro and nano hybrid material is prepared via metal-assisted chemical etching and used as an anode material for lithium secondary batteries. Their electrochemical characteristics are investigated in comparison to pristine bulk Si and amorphous carbon coated prickle-like Si (PS@C).

2. Experimental

PS obtained from bulk Si was synthesized via metal-assisted chemical etching. Therefore, commercially available Si powder (Kojundo co., 99.9%) was dispersed in etching solution that consists of 49 wt.% hydrofluoric acid (HF, 4.6 mol L^{-1}), 60 wt.% silver nitrate (AgNO$_3$, 0.04 mol L^{-1}) and de-ionized water. The etching solution is stirred mildly for 1 h in order to prevent the detachment of silver. After the etching process, residual silver nanoparticles were eliminated from the PS using a 50 wt.% HNO$_3$ aqueous solution, and the etched silicon powders are filtered out from the etching solution and dried in a vacuum oven at 80 °C for 5 h. The as-synthesized sample (PS) was transferred to a thermal chemical vapor deposition (CVD) reactor. The CVD was heated to 700 °C at a rate of 4.3 °C min^{-1}, and then stream of diluted gases of propylene and argon (10% C$_3$H$_6$, 90% Ar) at a flow rate of 100 cc min^{-1} was applied for 10 h to get a uniform carbon coating. After coating, the samples were cooled down to room temperature. The morphologies of pristine Si, PS, and PS@C were observed by scanning electron microscopy (SEM, NOVA NanoSEM200, FEI Corp.) and transmission electron microscopy (TEM, Tecnai, FEI Corp.) as well as chemically analyzed with energy-dispersive X-ray spectroscopy (EDX). The Brunauer–Emmett–Teller (BET) method using an N$_2$ sorption isotherm plot on a Micromeritics apparatus (ASAP 2010) was used to measure surface area, average pore diameter, and the change of total pore volume before and after etching and carbon coating. An investigation of the crystal structure was carried out using an X-ray diffractometer (XRD, Rigaku) equipped by Cu-K α (λ = 1.5418 Å) radiation in the 2 θ range from 10 to 90°. After the etching process, the chemical bonding of the remaining Ag was analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe). The structures of pristine Si, PS, and PS@C were obtained by Raman spectroscopy (Nicolet Almega XR dispersive Raman, Thermo electron co.) using a 632 nm excitation laser. A 50× microscope objective and an exposure time of 4 s combined with low laser power was used to avoid heating effects. The spectra were recorded at 4 cm^{-1} resolution between 4000 and 90 cm^{-1}. The laser spot has a diameter of about 2 μm on the sample surface. Elemental analysis (ES) by the CHN method was carried out to measure the carbon content. Therefore, the samples were burned in excess oxygen and then combustion products (carbon dioxide, water, and nitric oxide) were collected by various traps. Furthermore, the collected combustion products were weighed to calculate the unknown sample.

Electrochemical analysis were carried out using two-electrode cells with pristine Si, PS, and PS@C as the working electrode and lithium metal as counter electrode. The base electrolyte used was 1 M LiPF$_6$ dissolved in a 1:1:1 (*v/v*) mixture of ethylene carbonate, ethylmethyl and dimethyl carbonate. As reductive additive 30% vol fluoroethylene carbonate (FooSung co.) were added into base electrolyte. The working electrodes were fabricated by mixing 60% active materials (pristine Si, PS, and PS@C), 20% conductors (Denka black) and 20% binder (poly acrylic acid) onto a copper foil. The weight of the active materials in each electrode was around 1 mg. The coated electrodes were dried in a vacuum oven at 80 °C for 24 h. The CR2032 coin-type test cells were assembled in a dry room. The galvanostatic discharge–charge cycling was carried out by MACCOR cycle tester in the potential range of 0.05 to 2.0 V at various current densities of 100, 200, 400, 800 and 4000 mA g^{-1}. The electric current was calculated based on the amount of the active material, not including the weight of the additives in the electrode. Electrochemical impedance spectroscopy (EIS) experiments with the fully charged cells (up to 0.0 V) were performed using an impedance/gain-phase analyzer (Solartron SI 1260) equipped with an electrochemical interface (Solartron SI 1286). The AC amplitude was 5 mV over a frequency range of 1 mHz to 100 kHz.

3. Results and discussion

The synthesis process of PS@C is schematically presented in Fig. 1. Commercially available Si with an average particle size of 5 μm was used as raw material. The pristine Si for synthesis of micro and nano hybrid material was then added into the etching solution consisting of HF and AgNO$_3$. In a galvanic displacement process, the reduction of oxidizing metal ions (Ag) to metallic species, and the local dissolution of bulk Si powder occurred spontaneously on a silicon surface. The Si atoms act as a reducing agent for the metal ions in an aqueous HF solution. After the etching process, the color of pristine Si changed from dark gray to brown due to the formation of nanostructures (PS) with lower refractive index than that pristine Si. Carbon coating of the PS obtained from metal-assisted chemical etching is carried out via thermal CVD using gaseous polypropylene at 700 °C for 10 h. After the coating process the color changed from brown to black due to the carbon layer. The synthesis based on metal-assisted chemical etching is quick and easy, making it a cost efficient process to manufacture nanostructures with large surface areas at low temperature. Moreover, the produced quantities can be easily industrialized and are ultimately limited only by the dimensions of the vessel. Furthermore, carbon layers are well known for the formation of stable SEI layers on coated surfaces resulting in enhanced electrochemical performance [26,27].

Fig. 2 shows the SEM images of pristine bulk Si, surface-modified PS, and PS@C. Pristine bulk Si powders feature particle sizes of 5 μm and
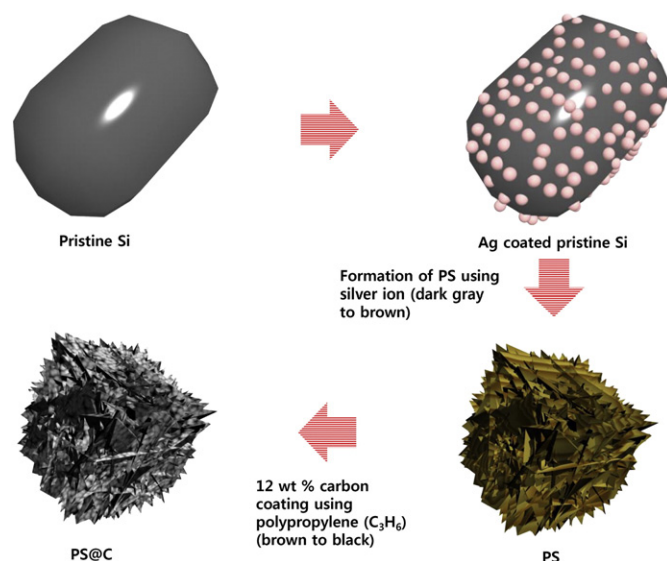

Fig. 1. A schematic illustration showing the synthetic process of PS@C.