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Three-dimensional silicon/carbon core–shell electrode as an anode material for lithium-ion batteries

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HIGHLIGHTS

- 3D Si@C electrodes are prepared by thermal decomposition and laser ablation.
- The appropriate combination of active material (Si@C) and electrode architecture is most important.
- 3D Si@C electrodes exhibited 1200 mAh g^{-1} over 300 cycles and 1170 mAh g^{-1} at 8 A g^{-1}.
- Core–shell 3D channel architecture mitigate volume expansion during cycling.

ABSTRACT

Practical application of silicon anodes for lithium-ion batteries has been mainly hindered because of their low electrical conductivity and large volume change (ca. 300%) occurring during the lithiation and delithiation processes. Thus, the surface engineering of active particles (material design) and the modification of electrode structure (electrode design) of silicon are necessary to alleviate these critical limiting factors. Silicon/carbon core–shell particles (Si@C, material design) are prepared by the thermal decomposition and subsequent three-dimensional (3D) electrode structures (electrode design) with a channel width of 15 μm are incorporated using the laser ablation process. The electrochemical characteristics of 3D Si@C used as the anode material for lithium-ion batteries are investigated to identify the effects of material and electrode design. By the introduction of a carbon coating and the laser structuring, an enhanced performance of Si anode materials exhibiting high specific capacity (>1200 mAh g^{-1} over 300 cycles), good rate capability (1170 mAh g^{-1} at 8 A g^{-1}), and stable cycling is achieved. The morphology of the core–shell active material combined with 3D channel architecture can minimize the volume expansion by utilizing the void space during the repeated cycling.

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1. Introduction

Rechargeable lithium-ion batteries (LIB) are considered to be the most encouraging energy storage technology for the next-generation portable devices, electronic vehicles (EV), and hybrid electric vehicles (HEV). Graphite with a theoretical specific capacity of 372 mAh g^{-1} is currently used as state-of-the-art anode material in commercial LIB. The growing demand for energy integration systems has promoted efforts to develop next-generation LIB with higher capacity and energy density. High-performance materials used in LIB include silicon-based materials, which are among the most promising materials for electrodes in large rechargeable batteries, because of their exceptionally high specific capacity (3572 mAh g^{-1}), low redox potential between 0.2 and 0.4 V (vs. Li/Li$^+$), and low reactivity with nonaqueous electrolytes [1,2]. Unfortunately, silicon (Si) undergoes huge volume changes (up to 300%)

during the insertion and extraction of Li-ions. The electrical contacts among Si and the conductive agent, film delamination, and destabilized solid electrolyte interphase (SEI) formation are affected by the Si expansion/compression by repeated cycling, triggering the critical fading mechanisms known as the pulverization of the active material [3]. Specifically, the low electrical conductivity of Si discourages its use in high-performance batteries, which rely on a low internal electrical resistance. Therefore, the implementation of Si-based anodes is still controversial due to the abovementioned facts.

To alleviate the pulverization issue, significant efforts have been directed to produce various Si nanostructures owing to the fact that nanostructured materials show better capability to withstand mechanical stresses from the volume changes than the corresponding bulk materials [4]. In particular, Chan et al. [5] reported that Si nanowires improve electrochemical performance due to efficient fast electron transfer, reduction of physical stress, good contact with current collector, and short diffusion length of Li ions. Park et al. [6] reported the importance of contact points between Si and carbon because of electrode polarization in their study. In addition, diverse strategies (methods) for reduced volume changes have been used including Si-embedded hollow carbon structures (template-assisted chemical etching) [7], Si nanotubes (magnesium reduction) [8], Si hollow spheres (chemical vapor deposition) [9], Si-embedded graphene (plasma enhanced chemical vapor deposition) [10], and bundle silicon (metal-assisted chemical etching) [11] to prepare Si electrodes. A majority of studies on Si as anode material are focused on the design of the active material. Recently, 3D architectures for LIB electrodes are in the limelight. Yue et al. [12] reported the fabrication of 3D Si–SnO$_2$ composite core–shell nanorod arrays as anode material for LIB by nanosphere lithography combined with inductive coupled plasma dry etching. Although the active material has a homogeneous morphology and good mechanical structure, the manufacturing processes are complex and expensive. The use as the electrodes in commercial LIBs is therefore unlikely from a practical point of view. Consequently, for the commercialization, an ideal Si-based anode should be elaborately designed and fabricated to possess a favorable morphology, excellent conductivity, stable SEI formation, and good electrical contact with the current collector.

In this study, periodic 3D Silicon/carbon (3D Si@C) core–shell electrodes were fabricated using the thermal decomposition (material design) combined with the subsequent structuring of the electrode (electrode design) and then investigated as anode material for LIB. The rate capability of an electrode is dominantly determined by the electronic conductivity, lithium-ion diffusivity, and electrolyte accessibility in the electrode. The carbon shell allows faster electron injection from the current collector to the active material, providing an efficient electron transport along the 3D geometry. Moreover, side reactions between active materials and electrolyte can be minimized. The periodic arrays with void spaces can also reduce volume change during the insertion and extraction of Li-ions. Furthermore, electrolyte accessibility can be increased by the 3D architecture. The design of an active material and electrode configuration enables enhanced Li-ion diffusion kinetics, thereby improving in the rate capability of the electrodes.

2. Experimental

2.1. Synthesis of Si@C core–shell

Si powders (>100 nm, size distribution of 10–250 nm, and electronic conductivity of 6.7×10^{-4} S cm^{-1}) were purchased from Sigma–Aldrich. Si@C core–shell particles were prepared by loading the nanosized Si particles (1 g) on a ceramic boat in a conventional tube furnace, followed by their thermal decomposition of in an atmosphere of 10% C$_3$H$_6$ and 90% Ar gases at a flow rate of 100 cc min at 700 °C. The heating rate and holding time were 3 °C min^{-1} and 5 h, respectively. After the carbon coating, the tube was cooled down to room temperature. The pristine Si and Si@C particles were investigated by scanning electron microscopy (SEM, NOVA NanoSEM200, FEI Corp.) and transmission electron microscopy (TEM, Tecnai, FEI Corp.) equipped with energy-dispersive X-ray spectroscopy (EDX). Furthermore, the crystal structure was determined by X-ray diffractometer (XRD) using Rigaku X-ray diffractometer equipped with by Cu Kα ($\lambda = 1.5418$ Å) radiation in the 2 è range of 20–80°. The quality of the carbon coating was investigated by Raman spectroscopy (Wavelength of 632 nm, Nicolet Almega XR dispersive Raman Thermo electron Corp.) at a low laser power density and an exposure time of 4 s to avoid a laser-induced thermal impact during the measurement. The spectra were recorded at a resolution of 4 cm^{-1} between 3000 and 90 cm^{-1}. Carbon contents were measured by elemental analysis (EA). The samples were thermally decomposed in an excess of oxygen, and the combustion products such as carbon dioxide, water, and nitric oxide were collected. The elemental composition of an unknown sample can be calculated via the measurement of the mass of these combustion products.

2.2. Laser structuring process for 3D Si@C core–shell electrode

For the laser processing, an Yb doped-fiber laser (Tangerine, Amplitude Systemes) at a wavelength of 1030 nm integrated into a micromachining workstation (PS450-TO, Optec s.a., Belgium) was used. Second harmonic generation (SHG) and third harmonic generation (THG) modules wavelengths of 515 and 343 nm, respectively, were applied. The laser beam was focused on the sample surface via f-theta objectives at the focal distances of 100 mm and 56 mm for SHG and THG, respectively. The adjustable pulse duration was set to 370 fs using a repetition rate of 200 kHz. The structuring process was carried out under ambient air, and the ablated material was removed by an exhaust. After the slurry coating on a Cu foil, typical laser conditions applied to obtain 3D Si@C core–shell electrodes are as follows: laser wavelength (515 nm), 60% laser power (0.28 W), scanning speed (200 mm s^{-1}), and number of repetitions (5).

2.3. Cell fabrication

A working electrode was manufactured by applying coating slurries consisting of the pristine Si, Si@C, and 3D Si@C as the active materials (60 wt%), Denka black (DB) as the conducting agent (20 wt%), and poly acrylic acid (PAA, 20 wt%) as the binder dissolved in ethanol on a copper foil current collector. After the complete solvent evaporation, the electrode was rolled and dried in a vacuum oven at 60 °C for 6 h. The electrode loads of the active material with a thickness of 24 μm were in the range 0.6–1 mg cm^{-2}. All the specific capacities of Si@C and 3D Si@C core–shell electrodes before and after the laser ablation were calculated based on the total mass of active materials including the carbon layer. The test cells comprised a working electrode, lithium foil as the counter and reference electrodes, and a polypropylene (PP) membrane as the separator. The assembly of all the lithium-ion cells was performed in an argon filled glove box (<1 ppm of oxygen and water, Korea Kiyon) in a dry room at a relative humidity of ≤0.5%. The electrolyte was composed of 1.3 M LiPF$_6$ dissolved in a mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (3/7 v/v, Panax Etec) with fluorinated ethylene carbonate (30 vol%, FooSung) as the reductive additive. Galvanostatic charge–discharge cycling tests were investigated to analyze the electrochemical properties with