



A novel durable double-conductive core-shell structure applying to the synthesis of silicon anode for lithium ion batteries



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HIGHLIGHTS

- The etching of Al-Si alloy constructs a stable internal 3D skeleton.
- Ag particles synthesized in situ improve the internal conductivity of composites.
- The carbon layer stabilizes the structure and increases external conductivity.

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ABSTRACT

Si/C composites are currently the most commercially viable next-generation lithium-ion battery anode materials due to their high specific capacity. However, there are still many obstacles need to be overcome such as short cycle life and poor conductivity. In this work, we design and successfully synthesis an excellent durable double-conductive core-shell structure p-Si-Ag/C composites. Interestingly, this well-designed structure offers remarkable conductivity (both internal and external) due to the introduction of silver particles and carbon layer. The carbon layer acts as a protective layer to maintain the integrity of the structure as well as avoids the direct contact of silicon with electrolyte. As a result, the durable double-conductive core-shell structure p-Si-Ag/C composites exhibit outstanding cycling stability of roughly 1000 mAh g⁻¹ after 200 cycles at a current density of 0.2 A g⁻¹ and retain 765 mAh g⁻¹ even at a high current density of 2 A g⁻¹, indicating a great improvement in electrochemical performance compared with traditional silicon electrode. Our research results provide a novel pathway for production of high-performance Si-based anodes to extending the cycle life and specific capacity of commercial lithium ion batteries.

1. Introduction

With the ever-increasing growth of digital end devices and new energy vehicles, there is an urgent demand for lithium-ion batteries with longer cycle life and higher energy density [1,2]. Improving the energy density of cathode and anode materials is an effective way to further improve the energy and power density of commercial LIBs. As for anode materials, graphite is the most commonly used anode in the practical applications and currently, the capacity has been already implemented approaching to its theoretical density (372 mAh g⁻¹ for LiC₆) [3], which is still far from the growing energy requirement. Silicon (Si), with a particularly high theoretical capacity about 4200 mAh g⁻¹ (Li₂₂Si₅), low operating potential (< 0.5 V vs. Li/Li⁺), and natural abundance, is considered as the most promising substitution to the

commercialized graphite anode materials [4,5]. Nevertheless, the formation of lithium alloys, during the charge/discharge process, gives rise to serious volumetric expansion (~300%) of Si anode. Such a huge volume change will cause severe pulverization and peeling off in electrode, leading to the degradation of electrical contact between the silicon active material and the current collector. Even worse, simultaneously, the repeated volume change introduces the unstable solid electrolyte interphase (SEI) layer of Si particles [6–8]. All these unfavorable issues may induce the drastic fading in specific capacity or even overall damage to the electrodes, which hampers the commercial application of Si anode in LIBs.

To tackle the above drawbacks, tremendous modifications to the microstructure of Si itself have been proposed. Interconnected silicon hollow nanospheres and mesoporous silicon, which are capable of

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holding repeated huge volume change and relieve the volume stress without pulverization during charging/discharging process, have been in-depth research [9–12]. Silicon nanowires [13,14], silicon nanotubes [15,16], and silicon thin films [17,18] also exhibit significant effects on inhibiting the expansion of silicon in three dimensions. In addition to these silicon nanostructural modifications, the fruitful research on the modification of silicon anodes were based on the integration of silicon and carbon with diverse structural. The introduction of carbon can effectively offset the inherent poor conductivity of silicon, and further improve the coulombic efficiency. Amorphous carbon-coated silicon nanocomposites were synthesized via spray pyrolysis at a low-temperature, which retained a specific capacity of 1120 mAh g^{-1} beyond 100 cycles, with a capacity fading of less than 0.4% per cycle [19]. Carbon nanotubes (CNTs), thanks to their unique 1D structure, high conductivity and large specific surface area, have been used for ameliorate silicon-based anode [20]. Wang et al. reported the 1D heterostructures containing Si particles deposited on vertically aligned multiwall CNTs (VACNTs) via two-step liquid injection CVD process, which exhibited excellent reversible capacities (2050 mAh g^{-1}) and a high first coulombic efficiency (80%) [21]. Due to its superior electrochemical performance, in recent years graphene has been adopted to modify silicon anode to improve the comprehensive electrochemical performance [22–25]. Chang et al. successfully prepared a 3D multilayered Si/rGO nanocomposite anode, which shows an excellent reversible specific capacity (2300 mAh g^{-1} at 0.05 C, 700 mAh g^{-1} at 10 C) and superior capacity retention (87% capacity retention with a rate of 10 C after 152 cycles up to 630 mAh g^{-1}) [26]. However, although a large amount of researches focus on the reversible capacity of silicon-based anode, few works focus on improving the conductivity inside the silicon particles, which has a significant impact on the sustained stability during charge/discharge cycles.

In this work we successfully synthesis p-Si-Ag/C composites via a modified silver mirror reaction followed by a chemical vapor deposition (CVD) process. The porous silicon (p-Si) is prepared via etching Al-Si alloy. A small amount of silver particles are *in-situ* synthesized inside the porous silicon, which can greatly improve the internal conductivity of silicon. The carbon layer outside the silicon particles provides external conductivity and ensure the stability of the integrated structure. This well-designed structure applied in silicon anode materials offers a stable specific capacity of around 1000 mAh g^{-1} after 200 cycles at a current density of 0.2 A g^{-1} .

2. Experimental

2.1. Material synthesis

Porous silicon was synthesized through etching Al-Si alloy followed by depositing silver particles by means of modified silver mirror reaction. After that, chemical vapor deposition (CVD) was conducted to cover a carbon layer and then the p-Si-Ag/C composites were obtained. Typically, commercial Al-Si alloy powder was immersed in 1 M HCl solution for 6 h with vigorous magnetic stirring to remove aluminum. Then the mixture was centrifuged and washed several times with DI water until the solution was neutral, and the powder was dried in vacuum at 60°C for 6 h. After that, 3.87 mL ammonium hydroxide was added dropwisely into 50 mL 0.01 M AgNO_3 solution until the yellow

sediment disappears. 1 g porous Si, 15 mL ethanol and 0.3 g Polyvinyl Pyrrolidone (PVP) were added into the solution in sequence. Then the mixture was magnetic stirring in water bath heating at 70°C for 24 h. The p-Si-Ag was successfully synthesized after centrifuging and drying process.

The as-prepared powder was put into a tube furnace with the atmosphere of $\text{Ar}:\text{C}_2\text{H}_2 = 40:20$ at 700°C for 30min. Finally, the p-Si-Ag/C composites were collected and as an active substance of electrode. The silver content of the composites prepared in this work is about 5.0 wt%.

2.2. Material characterization

The morphology and microstructure were characterized by scanning electron microscopy (SEM, Hitachi SU70) and transmission electron microscopy (TEM, JEOL JEM200CX) with energy dispersive spectrometer (EDS). X-ray diffraction (XRD, Rigaku D/max 2550 PC, $\text{Cu K}\alpha$) was operated to describe the crystal structure. The specific surface area and pore size were investigated by Brunauer–Emmett–Teller (BET, Autosorb-1-C) test. The carbon structures were studied on a Jobin Yvon Labor Raman HR-800 system using Ar-ion laser of 514.5 nm . Thermogravimetric analysis (TGA) of the composites was measured using a TA Q600 (TE, USA) apparatus from 25°C to 800°C at a heating rate of $10^\circ\text{C min}^{-1}$ in air. X-ray photoelectron spectroscopy (XPS, Escalab250Xi) test was investigated to research the bonding state between atoms.

2.3. Electrochemical assessment

In order to test the electrochemical performance of composites, the coin-type half cells (CR2025) were assembled in an argon-filled glove box with Li foil as a counter electrode. The electrode slurry was made via stirring the mixture consists of active material (p-Si-Ag/C), super-P, carboxymethyl cellulose (CMC) and styrene butadiene rubber (SBR) with the mass ratio of 7:1:1:1 for several hours. Then the slurry was coated on the copper foil at a mass loading of around 1.5 mg cm^{-2} . The as-prepared electrodes were dried at 120°C for 8 h under vacuum. The electrolyte of the half cells was 1 M LiPF_6 in a mixture of ethylene carbonate (EC) and diethylene carbonate (DEC) (v/v = 1: 1) with 5% fluoroethylene carbonate (FEC), and Celgard 2300 as separator. Cyclic voltammetry (CV) were conducted in the voltage range of 0.01–1.5 V via a CHI660C electro-voltammetry workstation at a scanning rate of 0.1 mV s^{-1} . The galvanostatic discharge–charge tests were carried out by Land Battery Test System with a potential window of 0.01–1.5 V. Electrochemical impedance spectroscopy (EIS) measurements were conducted by PARSTAT MC multi-channel electrochemical workstation with the frequency range from 100 kHz to 0.01 Hz. Furthermore, capacity was calculated based on the total mass of the composite.

3. Results and discussion

The synthesis procedure of p-Si-Ag/C composite is illustrated in Fig. 1. Inspired by the structure of fig in natural, a double-conductive core-shell structure are designed though the deposition of silver nano particles in the internal pores of porous silicon and followed by the external carbon coating. In the first step, Al-Si alloy powder is adopted

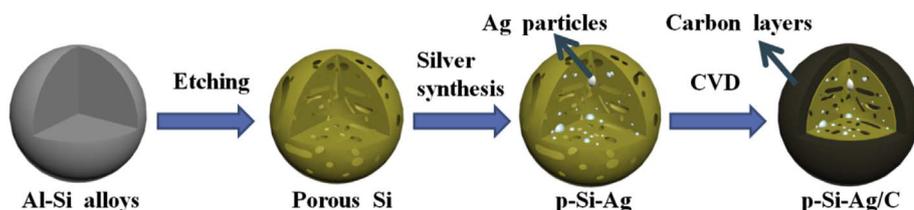


Fig. 1. Schematic illustration of the fabrication for double-conductive core-shell structure p-Si-Ag/C composite.

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