



A Peanut Shell Inspired Scalable Synthesis of Three-Dimensional Carbon Coated Porous Silicon Particles as an Anode for Lithium-Ion Batteries



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ABSTRACT

A novel, economical ball milling and heat treatment of porous silicon based anodes was introduced to boost the electrochemical performance and cycle capacity of Li-ion batteries. The resultant peanut shell-like electrodes combined multiple advantageous features, including a continuous, flexible electrically conductive carbon network, a synergistic C/SiO₂ coating layer and improved interfacial contact, in a peanut shell structure with void space. The electrodes achieved an initial discharge capacity of 1909 mA h g⁻¹ with coulombic efficiency of 88.8% as well as a high reversible capacity of 1179 mA h g⁻¹ after 120 cycles at 0.1C. In addition, the material was capable of reaching a capacity of 493 mA h g⁻¹ even at the high charge rate of 4C. This work gives a compelling look at a novel and large-scale production method of fabricating next generation Si/C anodes for high-performance LIBs.

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1. Introduction

Silicon is a promising material for anodes in rechargeable lithium-ion batteries (LIBs) due to its high theoretical capacity, ten times that of graphite. This could help meet the ever-increasing requirements for use in various energy storage applications, including portable electronics, hybrid and electric vehicles, and grid-scale energy storage systems [1–4]. However, the implementation of Si in practical LIB electrodes has been hindered due to its large volume expansion of up to ~400% upon full lithiation, which causes serious mechanical fracturing that induces even total loss of contact with the current collector [4,5].

To boost its electrochemical performance, previous works have demonstrated that decreasing the feature size of Si to the nanoscale allows the material to bear the large volume changes without fracturing [5–12]. However, due to an unstable solid-electrolyte interface (SEI), the life of nanosized silicon is restricted to a hundred cycles. The deformation and degradation of the SEI layer during cycling leads to poor coulombic efficiency as well as the blocking of Li⁺ transport. Recently, electrodes made from nanosized silicon particles with SEI engineering have shown promising

results, with materials including double-walled silicon nanotubes, Si/C nanostructures [13–20]. However, creating nanostructured Si usually involves complex fabrication processes which come at a high cost [13,14,20], with the lack of controlled high-yield synthesis techniques for nanosized silicon being a large obstacle to industrial production. Electrodes based on the chemical etching of porous silicon may be an efficient approach to solving the aforementioned drawbacks. This method is simple and can be extended to silicon wafers and irregular industrial polycrystalline Si powders [21–25] for large scale synthesis. The porous structure provides space for volume expansion, which leads to a long cycle life. To improve electrical conductivity, one of the most commonly used strategies is adding a carbon or metal coating [26–29]. However, the synthesis processes usually involve high temperature chemical vapor deposition (CVD) or a noble metal [24,25,28,29]. Moreover, simultaneously engineering the electronic network and the surface of porous silicon still remains a great challenge.

In this work, taking advantages of electrochemical etching and ball milling processes, an anode of novel, 3D carbon-coated, peanut shell-like porous silicon particles was designed (Fig. 1). The comparatively simple synthesis process simultaneously engineered the surface of the porous silicon particles and the electrode matrix. During the ball milling process, a large scale porous silicon film fragments into smaller and smaller pieces while

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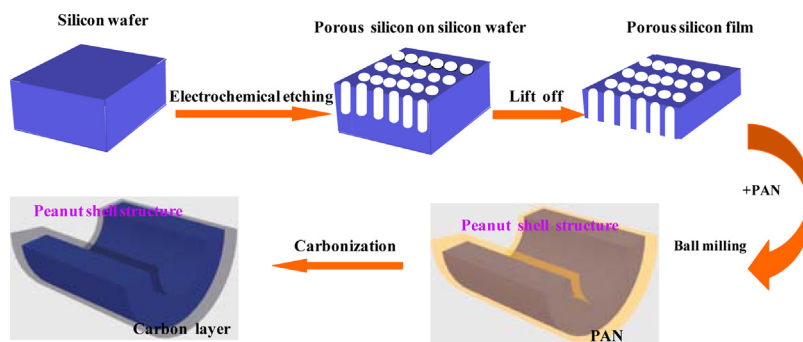


Fig. 1. Description of the fabrication process for carbon-coated peanut shell-like PSP.

polyacrylonitrile (PAN) is coated onto them. The benefits of this process include: (1) large scale fragile porous silicon film is converted to stable porous silicon particles (PSP) and the empty space inside the peanut shell structure is able accommodate the large volume changes of Si, leading to an excellent cycling performance; (2) a compact PAN layer is coated on PSP in all directions; (3) the PSP disperses in the PAN matrix so that PSP clusters are avoided. Moreover, the PAN coating layer and PAN matrix on the copper foil are converted into a carbon layer coated on the PSP and an amorphous carbon network respectively during carbonization process, which should improve the life of the electrodes. These functions synergistically improved cycle stability and rate capacity (432 mA h g⁻¹ at 0.3C over 400 cycles and 493 mA h g⁻¹ at 4C).

2. Experimental

2.1. Preparation of freestanding porous silicon films

P-type Si (100) wafers with a resistivity of 8–12 Ω cm were used as substrates. The etching solution contained 40 ml HF (39 wt %) and 80 ml dimethylformamide (DMF). The electrochemical etching teflon cell contains a copper plate which connected to a constant-current source, a platinum wire counter electrode and a rubber ring with a diameter of 1.2 cm determines the region to be etched. The distance between the electrodes is 2 cm. First, a constant current density of 18 mA cm⁻² at room temperature was applied to etch silicon wafers with pores for 100 min. Next, the current density was increased to 66 mA cm⁻² for 40 min, leading to the generation of a transverse force that ruptured the porous silicon walls. As a result, the porous silicon film floated up independently and the porosity of it was ~70% (Supplementary Method 1).

2.2. Fabrication of the 3D carbon-coated peanut shell-like PSP electrodes

The porous silicon film was treated with a liquid PAN solution (10 wt% dissolved in DMF) and ball milled for 1 h at 200 r min⁻¹. The recipe contained 40 mg porous silicon film and 600 mg of the above liquid PAN solution. Following this, the mixed slurry was spread onto copper foil with a diameter of 14 mm for a current collector and dried for 3 h in a vacuum drying oven at 80 °C. The as-obtained PAN coated PSP electrodes were then heated in an Ar atmosphere at a rate of 5 °C min⁻¹ to 700 °C and held for 1 h. The carbon-coated PSP loaded on per electrode is ~ 0.85 mg.

2.3. Characterization

The morphologies of the electrodes were characterized by scanning electron microscopy (SEM) (HITACHI S-4800) and

transmission electron microscopy (TEM) (Philips Tecnai F30). Raman spectra were acquired using a WITTEC Raman system with an excitation at $\lambda = 488 \text{ nm}$. X-ray diffraction (XRD) patterns of the samples were obtained by a Rigaku Ultima IV with Cu K α radiation. A Vario EL III (Elementar, Germany) was used to analyze the elemental content of the carbon-coated PSP powders. X-ray photoelectron spectroscopy (XPS) spectra were acquired with PHI QUANTUM 2000 spectrometer. The nitrogen adsorption and desorption isotherm were tested at 77 K in a range of relative pressure of 0.0001–0.99 P/P₀ using a TriStar II surface area and porosity system (Micromeritics). The active mass was carefully weighted by a microbalance (METTLER TOLEDO XS3DU) with a resolution of 1 μg.

2.4. Electrochemical testing

For electrochemical characterization, the carbon-coated PSP electrodes were mechanically pressed and assembled into CR2025 coin cells as the working electrodes, with lithium foil being used as the counter electrodes. The electrolyte for all tests was 1 M LiPF₆ in ethylene carbonate (EC) and dimethylcarbonate (DMC) (1:1 by volume). The galvanostatic cycling of the assembled cells was tested on a Land CT2001A system between 0.005 V and 2.5 V at the temperature of 30 °C. The cells were also evaluated by impedance spectroscopy from 100 kHz to 10 mHz under AC stimulus with 10 mV of amplitude and no applied voltage bias. A four-channel multifunctional electrochemical work station (VersaSTAT MC, America) was used to record cyclic voltammetry data (CV) at a scan rate of 0.2 mV s⁻¹ between 0.005 V and 2.5 V.

3. Results and discussion

Scanning electron microscope (SEM) images of self-supported porous silicon film are shown in Fig. 2a–2d. The diameter of the pores is 1–2 μm with pore depth on the order of ~100 μm (Fig. 2a, 2c). The increase in current density during the etching process created a transverse force, which lead to isotropic etching at the pore tip and increasing pore depth. As a result, the thickness of the porous silicon walls at the tips became thinner and thinner until the walls separated from the substrate (Fig. 2b, 2d). The tips of the pores were larger than the top side. The top walls collapsed to a certain extent due to excessive etching during the process (Fig. 2a). However, the walls were smooth, straight, and regular with a thickness of ~ 300 nm (Fig. 2d). The pores formed process follows an interfacial two-electron transfer through an overall electrochemical reaction involving HF molecules [30–32]: $\text{Si} + 2 \text{HF} + n \text{h}^+ - \text{SiF}_2 + 2 \text{h}^+ + (2-n) \text{e}^-$, $\text{SiF}_2 + 4 \text{HF} - \text{H}_2\text{SiF}_6 + \text{H}_2$. Then an electrochemical polishing effect occurred at 66 mA cm⁻² so that the porous silicon film separated from the substrate [30–32]. The pore size and pore depth were also easily controllable by changing the etching current density and time (Fig. S1). The same processes can

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