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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ARTICLE INFO

Article history:
Received 18 November 2014
Received in revised form 4 January 2015
Accepted 12 January 2015
Available online 13 January 2015

Keywords:
porous silicon particle
peanut shell
C/SiO2 coating
lithium-ion anode
electrochemical performance

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 \(\sim 400\%\) 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 columbic 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. Electrodos 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
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 \(\Omega\) 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 etching 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 independently and the porosity of it was \(\sim 70\%\) (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 reaction 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 \(\sim 0.85 mg\).

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 WITEC Raman system with an excitation at \(\lambda = 488\) nm. X-ray diffraction (XRD) patterns of the samples were obtained by a Rigaku Ultima IV with Cu Ka 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 isotherms were tested at 77 K in a range of relative pressure of 0.0001–0.99 P\(_0\) 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 \(\mu\)g.

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 LiPF\(_6\) 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 \(\mu\)m with pore depth on the order of \(\sim 100 \mu\)m (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 \(\sim 300\) nm (Fig. 2d). The pores formed process follows an interfacial two-electron transfer through an overall electrochemical reaction involving HF molecules [30–32]: \(Si^{2+} + \text{H}^+ + n \text{H}^+ \rightarrow SiF_2 + 2 H^+ + (2-n)e^- \). 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
be repeated for an entire silicon wafer, which can produce porous silicon film on a large scale.

After separation, the resultant fragile porous silicon film was mixed with PAN to form a PAN-coated, stable, peanut shell-like PSP slurry through a simple ball milling process, which was compatible with roll to roll electrode processing. As a result, a compact PAN layer was coated on the PSP in all directions and the PSP dispersed in the PAN binder matrix. The slurry was then spread on a copper foil current collector. To carbonize PAN and to produce a dense interaction between Si and carbon, the PAN-coated PSP electrodes

![Fig. 2. SEM images of the self-supported porous silicon film. (a) Top-view. (b) Back-side view. (c) Side-view. (d) A high magnification view of (c).](image)

![Fig. 3. (a) Raman spectra of PAN-coated PSP (black) and carbon-coated PSP (red). (b) Raman spectra of PAN-coated PSP. (c) XRD patterns for the PAN-coated PSP electrode before carbonization (black) and after carbonization (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image)
were annealed in an Ar atmosphere, which yielded the designed electronic network and porous silicon surface simultaneously. Pyrolyzed PAN has been reported to exhibit good mechanical and relatively high electrical conductivity properties at 700 °C [34,35]. During the heat treatment process, the color of the electrodes changed from dark yellow to black and no cracking occurred. Neither changes in the color of copper or folds were observed, no difference was found in the XRD patterns of the backside copper foil before and after annealed (Fig. S2). A similar carbonization process on copper foil was used in Refs. [16,33], no damage of copper was reported. The creation of a carbon layer coated on PSP helped to construct a stable SEI layer, while the PAN matrix converted to a carbon network on the whole current collector, improving the electrical conductivity and ensuring the interconnectivity of the PSP. As well, contact between the active material and copper current collector was improved.

Raman spectra were used to characterize the chemical bond changes before and after annealing (Fig. 3a, 3b). Unsurprisingly, a strong peak at 520 cm⁻¹ was seen for the PAN-coated PSP, indicating the vibration of crystalline silicon. A peak at 964 cm⁻¹ was also visible, the peak shifted to the lower 919 cm⁻¹ after annealing. Because the second-order optical phonons vibrations of Si -Si bands is located around 1040 cm⁻¹ [16,28], the electrochemical etching of PS, the store of PS and the ball milling process were all in air. We attributed the shift of this peak to the oxidation of the silicon surface. The same phenomenon was observed in Ref. [16]. Three detailed peaks, at 2915 cm⁻¹, 2954 cm⁻¹ and 2985 cm⁻¹, were due to —CH and —CH₂ aliphatic stretching, corresponding to the hydrocarbon chain polymer backbone of the material [34,35]. A strong peak of —C—N triple stretching (2245 cm⁻¹) was due to the nitrile group side chain. Finally, —CH₃ and —CH bending (1458 cm⁻¹, 1362 cm⁻¹) peaks were observed and assigned to the polymer backbone. After annealing, the peak of crystalline silicon broadened and shifted to 506 cm⁻¹, demonstrating the presence of stress created by a difference in the thermal expansion coefficient between Si and C [36,37]. In addition, a new peak arose at 290 cm⁻¹, which may correspond to the Si-O-Si bending vibrations of silica [16,38]. The data confirmed that an amorphous carbon and silica coating layer was created during the annealing process. For the carbonized PAN, —CH and —CH₂ aliphatic stretching, —C—N triple stretch and —CH₂ and —CH bending peaks disappeared. Instead, carbonization of the PAN binder was evidenced by the appearance of carbon peaks at 1366 cm⁻¹ (D band, disordered) and 1591 cm⁻¹ (G band, graphene). The ratio of the D band to the G band was 2.8, corresponding to the structural disorder and defects of amorphous carbon [39].

XRD spectra (Fig. 3c) were collected of PAN-coated PSP before and carbon coated-PSP. As expected, before carbonization, Si and Cu peaks were observed. After annealing, the Si peaks shifted to lower diffraction angles, implying the presence of stress after annealing, which was consistent with the Raman results. In addition, a new peak of copper silicide was found. Because the electrode was heated at 700 °C for one hour, the presence of copper silicide was not unexpected. Since the silicon particles were coated by a carbon layer, this copper silicide only existed at the surface of

Fig. 4. (a) A low magnification SEM image of surface morphology of the carbon-coated PSP. (b) A high magnification view of (a). (c) A high magnification view of (a). (d) A low magnification TEM image of a carbon-coated peanut shell-like PSP. (e) A HRTEM image across the carbon-coated PSP edge. (f) A HRTEM image of the interface between the carbon layer and silicon. (g) X-ray photoelectron spectroscopy (XPS) spectra of the carbon-coated PSP electrode surface, 10 nm etched and 20 nm etched (high resolution scan for the element of C). (h) XPS spectra of the carbon-coated PSP electrode surface, 10 nm etched and 20 nm etched (high resolution scan for the element of Si). (i) Energy-dispersive X-ray spectroscopy (EDS) analysis of the carbon-coated PSP material (bare powders).
the copper current collector. The copper silicide may help to improve the cyclic performance and assist the following reasons [40]: (1) an enhanced adhenrence between the active material and copper foil; (2) the copper silicide interface causes less Si consumption and helps to form a stable SEI layer during cycling.

Fig. 4a-4f shows the surface structure and morphology of the carbon-coated PSP electrodes. During the ball milling process, the fragile porous silicon film fractured into smaller and smaller pieces. The fragment powders containing several half-tube like pores are called porous silicon particles (marked by the dash circle line in Fig. 4a). Controlling the ball milling condition, the single half-tube like pore just owns a peanut shell structure. The dispersed PSP with void space remained interconnected via the carbon network and a uniform carbon layer was coated on it (Fig. 4a, 4b). Also, Fig. 4c shows an exposed carbon layer coated PSP, where the carbon layer and the PSP could be clearly distinguished. There were void spaces inside the carbon shell, so that silicon could expand inside the carbon framework to occupy the void spaces with little volume change of the overall electrode. The Nitrogen adsorption (Brunauer-Emmett-Teller) measurement indicated that the surface area of the carbonized PAN coated PSP is 20.4 m² g⁻¹ (Fig. S3). In addition, the coated carbon layer helped to stabilize the SEI layer during cycling. A low magnification TEM image of the carbon-coated PSP is shown in Fig. 4d, with an amorphous carbon-coated on a peanut shell-like PSP visible along with a coherent interface, a clear example of the theoretical sketch of the PSP structure. Under high magnification, it could be seen that the coated carbon layer was ~15 nm thick (Fig. 4e), which could act as an electrolyte barrier. As a result, SEI formed mostly outside the carbon layer and decreased the consumption of Si. As well, the carbon thickness between adjacent PSPs was more than 15 nm, so the carbon between PSP functioned as both a conducting network and a mechanical backbone. A SiO₂ layer with a thickness of ~3 nm was found between the carbon layer and silicon, which was consistent with the Raman results. Clearly, the carbon layer and SiO₂ were interconnected by a coherent structure as shown in Fig. 4f. The FFT pattern of the area in Fig. 4f corresponds to Si (111) with a plane spacing of 0.321 nm, which confirms that Si remains

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**Fig. 5.** The electrochemical performance of carbon-coated PSP electrode. (a) Cycling performance of the carbon-coated peanut shell-like PSP electrode (red) and PAN-coated PSP electrode (black) at 0.1C. (b) Voltage profile of carbon-coated PSP electrode at 0.1C. (c) Long-term cycling performance of carbon-coated PSP electrode at 0.3C. (d) AC impedance spectra for the PAN-coated PSP cell (red) and carbon-coated PSP cell (black) after 2 cycles at 0.1C. (e) Rate capability of carbon-coated PSP electrode. (f) Cyclic voltammograms for PAN-coated PSP and carbon-coated PSP electrodes. All the electrodes were tested between 2.5 V and 0.005 V. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
crystalline after annealing. However the plane spacing of carbon-coated Si (111) became larger than the standard plane spacing of Si (111) (0.314 nm), this was consistent with Raman and XRD results, further demonstrating the formation of stress between Si and C. X-ray photoelectron spectroscopy (XPS) patterns of the carbon-coated PSP electrode surface, 10 nm etched and 20 nm etched were tested (Fig. 4g and 4h). High resolution scan for the element of carbon (C 1s) shows the appearance of C—C, C—H, and C=C (284.5 eV) [41]. The high resolution scan for the element of Si (Si 2p) indicates a native silica on the surface (SiO$_2$ 2p, 103.3 eV) of porous silicon particle (Si 2p, 99.3 eV) [29]. The C 1s peak of 10 nm etched sample receded, which was almost the same with the peak of 20 nm etched sample. The signal may come from the 3D carbon network and the carbon layer on side walls even the surface carbon layer (~10 nm) the porous silicon particles etched. The peak strength of SiO$_2$ 2p decreased and the peak strength of Si 2p increased with the etching depth increasing. This is due to the SiO$_2$ layer etched, the fresh Si exposed. Because the rough electrode surface and the SiO$_2$ layer on the side wall of PSP, there is still a weak peak of SiO$_2$ even 20 nm of the surface etched. This result further confirmed the depth profile of the 3D carbon and SiO$_2$ coating on the porous silicon particle. A similar confirmatory result is found the energy dispersive spectroscopy (EDS) of carbon-coated PSP as shown in Fig. 4i. The contents of C, N, O, and Si were found in the active material, the O is due to the surface SiO$_2$ upon Si core. Fig. 5 shows the electrochemical performance of the carbon-coated PSP electrodes in half cells. The gravimetric capacity was calculated using the mass of total electrode, considering the SiO$_2$ and amorphous C may contribute to the total capacity [42,43]. After annealing, the contents of C, H and N were 42 wt%, 1 wt% and 10 wt% respectively as calculated through elemental analysis, which is consistent with the EDS analysis results. The rest 47 wt% was the mass of Si/SiO$_2$. Fig. 5a shows the cycling performance of the carbon-coated PSP electrode at 0.1C (1C = 1880 mA h g$^{-1}$) and between 2.5 V and 0.005 V. The cycling capacity of the amorphous carbon electrode was shown in Fig. 5S. The first discharge capacity (delithiation process) was 1909 mA h g$^{-1}$ with a coulombic efficiency of 88.8%. For comparison, PAN-coated PSP electrodes were tested at the same conditions. The first coulombic efficiency for a PAN-coated PSP electrode was only 62.1% with a discharge capacity of 1185 mA h g$^{-1}$. The remarkably high coulombic efficiency of the first cycle may be attributed to the uniform C/SiO$_2$ coating layer, which acted as an electrolyte barrier so that SEI formed mainly outside the PSP and consumed less Si. Moreover, the C/SiO$_2$-coated peanut shell-like PSP anode showed high capacity retention and the cell began to stabilize around 60 cycles. For example, the reversible capacity of the 68th cycle was 1209 mA h g$^{-1}$ and the capacity of the 117th cycle was 1179 mA h g$^{-1}$ with a coulombic efficiency over 98% between these two cycles. The capacity attenuation per cycle was ~0.6 mA h g$^{-1}$, less than 0.05% of 1209 mA h g$^{-1}$. The same phenomenon was observed at a higher charge rate of 0.3 C (Fig. 5c), where the reversible capacity of the 57th cycle was 752 mA h g$^{-1}$ and the discharge capacity could still maintain 432 mA h g$^{-1}$ even after 400 cycles, with a coulombic efficiency over 98%. This favorable long life cycling performance was probably due to the stable C/SiO$_2$ shell and conductive carbon matrix which bound the electrode together. Moreover, the C/SiO$_2$ coating layer played a synergistic role, with the higher surface area anchoring the carbon shell and increasing both electrical and ionic conductivity through the SiO$_2$ layer [16]. The SiO$_2$ also interacted with Li, forming a stable Li$_2$Si$_2$O$_5$ phase during cycling which possibly help to release the strain related to the volume expansion [43]. Finally, the C/SiO$_2$ shell around the PSP functioned as a stable SEI layer and was able to improve the efficiency and cycling duration. The impedance of the PAN-coated PSP electrode and carbon-coated-PSP after 2 cycles at 0.1C were tested (Fig. 5d). The impedance spectra are both composed of one semicircular arc at high frequency region, followed by a nearly vertical line against the real axis at low frequency region. These semicircular arcs can be assigned to charge transfer impedance of the electrodes. It is clear that charge transfer resistance of PAN-coated PSP electrode is much larger than the carbon-coated PSP electrode. A good electronic contact between porous silicon particle and amorphous carbon was obtained during the carbonization process, the charge transfer resistance improved. The lower charge transfer resistance may help to improve the rate capacity. As a result, the C/SiO$_2$-coated peanut shell-like PSP electrode exhibited excellent rate capacity as shown in Fig. 5e. At the current densities of 0.1C, 0.2C, 0.5C, 1C, 2C, and 4C, the discharge capacities at these rates were 1478 mA h g$^{-1}$, 1146 mA h g$^{-1}$, 901 mA h g$^{-1}$, 841 mA h g$^{-1}$, 682 mA h g$^{-1}$, and 493 mA h g$^{-1}$ respectively. Even at the high rate of 4C, a stable capacity of 493 mA h g$^{-1}$ was obtained, a third of the 0.1C capacity. We also investigated the thickness of carbon-coated PSP electrode by SEM (Fig. S4). The carbon-coated PSP electrode showed an initial volumetric capacity of ~1354 mA h cm$^{-3}$. Compared to these previously reported porous silicon anodes (shown in Table 1), the simple electrochemical etching (without any templates or noble metal) and ball milling and process described here is more compatible with current roll-roll electrode processes. Moreover, this technique engineered the electrode binder simultaneously. Note that, the gravimetric

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<td>CVD deposited Si</td>
<td>Template + HCl etch</td>
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<td>2</td>
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capacity in our work was calculated using the mass of total electrode, the gravimetric capacity of Si/SiO₂ is estimated to be about twice as much as the above capacity.

To better understand the lithiation/delithiation processes, the PAN-coated PSP and carbon-coated PSP electrodes were tested with cyclic voltammotry between 0.005 V and 2.5 V (Fig. 5f). For the PAN-coated PSP electrode, the curves exhibited very similar to those obtained from standard crystalline Si⁴⁷,⁴⁸, which was consistent with the crystalline XRD results shown in Fig. 3c. The cathodic peak at ~0.17 V and the anodic peaks at ~0.35 V and ~0.51 V are characteristic of amorphous Si, and the cathodic peak at ~0 V is characteristic of both crystalline and amorphous Si⁴⁷–⁵³. On the first cathodic branch, only crystalline Si existed, so only one peak at ~0 V was observed. However, the crystalline Si converted to amorphous during lithiation, and hence, two anodic peaks of amorphous Si (at ~0.35 V and ~0.51 V) were observed in the subsequent anodic branches. For the carbon-coated PSP, inspection of the first cycle, a broad cathodic peak at ~0.5 V corresponds to SEI formation, implying that the carbon layer helps to form SEI layer. Subsequently, the current started to decrease at 0.25 V, which was assigned to Li reacting with C/SiO₂ [⁵¹–⁵³]. Also, a sharp peak of crystalline Si at ~0 V with a larger current density than that of PAN-coated PSP was observed. This further demonstrates that the electrical conductivity improved during the annealing process. Due to the existence of amorphous carbon, the anodic peaks (at ~0.35 V and ~0.51 V) were not separated, however the current density was larger than that of PAN-coated PSP as well. The anodic peaks became broader and stronger, which illustrated the transition from crystalline silicon to amorphous silicon during lithiation/delithiation processes [⁴⁸,⁴⁹]. As a result, the amorphization degree improved and the chathodic peak of amorphous Si (at ~0.16 V) was observed in the third scan.

After 400 cycles at the rate of 0.3C, the carbonized PAN-coated PSP electrode was opened and the electrode was soaked in DMC overnight to remove all residual electrolyte. SEM images of the electrode surface are given in Fig. 6a and 6b. Even after 400 cycles at 0.3C, the amorphous carbon network was still hold together and the porous silicon particles dispersed in the carbon without aggregation (Fig. 6a). Moreover, examining the peanut shell structure (Fig. 6b) after long life cycling revealed that 3D C/SiO₂-coated peanut shell-like PSP with void space could accommodate the large volume changes during lithiation/delithiation processes. In the XRD pattern of the carbon-coated electrode after 400 cycles (Fig. 6c), the diffraction peaks of crystalline Si disappeared, meaning the amorphous nature of silicon and this is consistent with the CV curves. However the peak of copper silicide still existed after 400 cycles, which further confirmed the stability of the C/SiO₂ coating layer and quality of interfacial contact during electrochemical cycling.

4. Conclusions

In summary, this technique is a promising approach to the industrial production of silicon anodes for high-performance LIBs, based on simple and economical ball milling and carbonization synthetic processes. The controlled electrochemical etching process enabled us to tune the morphologies of the porous silicon, with the resulting electrodes having multiple advantages including a binding, conductive carbon matrix, a SiO₂/C shell acting as a stable electrolyte barrier, a full contact between electrode and current collector, and a novel peanut shell structure with void space for problematic volume changes. These properties have the effect of promoting efficient electron transport and long life cycling. Under testing, the electrodes exhibited a high reversible capacity (1179 mA h g⁻¹ at 0.1C over 120 cycles and 432 mA h g⁻¹ at 0.3C over 400 cycles) as well as excellent rate capacity (493 mA h g⁻¹ at 4C) based on the total mass of the electrode. For large-scale production at a low cost, this technique using metallurgical-grade Si and bitumen together with chemical etching and carbon coating is promising for future implementation.
Acknowledgements

This work is supported by the National Natural Science Foundation of China under grant nos. 61176003, 61176002, and 121233004 the Fundamental Research Funds program for Fujian province, China, with grant no. 2012H0308, the National Basic Research Program of China under Grant nos. 2012CB933503 and 2013CB632103 as well as the Fundamental Research Funds for the Central Universities (2010120105).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2015.01.051.

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