Preparation of Three Dimensional Porous Silicon with Fluoride-Free Method and Its Application in Lithium Ion Batteries

Xueling Yang, Changhan Shi, Lulu Zhang, Gan Liang, Shijing Ni, and Zhaoyin Wen

Three dimensional porous silicon (PS) powder samples are synthesized by a fluoride-free method composed of high-temperature sintering and liquid extraction processes. As a conducting agent and strength supporter, amorphous carbon is incorporated into porous silicon using a hydrothermal technology. The microstructure and composition of PS and PS/Carbon composite are characterized by means of scanning electron microscopy (SEM) and X-ray diffraction (XRD). Electrochemical properties are investigated by cyclic voltammetry (CV) and galvanostatic charge/discharge tests. The experimental results indicate that reversible capacity and capacity retention of silicon anode can be significantly improved with the existence of 3D pores and amorphous carbon. More specifically, the PS and PS/Carbon electrodes deliver reversible capacity of 664.6 mAh g\(^{-1}\) and 608.7 mAh g\(^{-1}\) after 100 cycles.

© 2013 The Electrochemical Society. [DOI:10.1149/2.009310ssl] All rights reserved.

Manuscript submitted July 12, 2013; revised manuscript received August 6, 2013. Published August 14, 2013.

Lithium ion batteries (LIB) have become the most popular power sources for a wide range of applications due to their high energy density, high voltage, low self-discharge, and free maintenance. Developing new electrodes with higher capacity or higher energy density has been increasingly important due to the LIB miniaturization for portable electronic product development in aviation, military and automobile industries. Silicon with high theoretical capacity (4200 mAh g\(^{-1}\)) has been widely investigated as a candidate for next-generation high-energy-anode capacities. However, severe particle pulverization can be caused by large volume changes during repeated insertion/extraction reaction, resulting in a substantial capacity fading due to electrical disconnection. A variety of silicon structures and silicon-based composites have been designed to solve this problem. Examples include the use of mesoporous silicon nanowires, silicon nanotubes, porous silicon, and Si dispersed in an active/inactive matrix. Extensive studies have confirmed that the electrochemical performance of silicon can be effectively improved by designing it into three-dimensional (3D) porous structure. To all preparation methods of porous silicon, however, the use of the virulent and corrosive hydrofluoric (HF) solution is indispensable. Therefore, it is desired to seek a safer alternative method to replace the traditional preparation processes. In this work, we developed a simple fluoride-free method to synthesize 3D PS powder material and carried out the study on the electrochemical properties of 3D PS and PS/Carbon composite.

Experimental

3D porous silicon.— Silicon and magnesium powders were ground in ethanol to ensure homogeneous mixing. After drying, the mixture was heated to 500 °C for 8 h in argon atmosphere to obtain magnesium silicide (MgSi) powders. Then, MgSi powders were milled for 1 h in ethanol, followed by heat-treatment (1000 °C, 3 h) under vacuum (<50 Pa). After cooling to room temperature, the resultant was bleached in HCl solution, filtered and washed with deionized water until the PH value reached 7. Finally, the 3D porous silicon powders were obtained by further heat-treatment (1000 °C, 3 h) of the resultant in argon to remove volatile impurities. And the tap density of the 3D porous silicon powders was measured by the tap density measurement instrument (JZ-1, China).

Carbon-coated porous silicon.— To improve electronic conductivity, carbon was incorporated into 3D PS via a hydrothermal method. The carbon-coated porous silicon was synthesized by a hydrothermal reaction using glucose as carbon source. The suspension composed of 3D porous silicon powders and glucose solution was magnetically stirred under negative pressure for 3 h to facilitate the glucose solution entering into the pores. After the hydrothermal reaction (200 °C for 24 h), the resultant was filtered and heat-treated at 900 °C for 3 h in argon. The scheme for the sample synthesis process of 3D PS and PS/Carbon composite is shown in Figure 1.

Characterization and electrochemical measurements.— The phase composition was analyzed by powder X-ray diffraction (Rigaku Ultima IV) with Cu Kα radiation (λ = 0.15406 nm) and at a scanning speed of 10° min\(^{-1}\). The accelerating voltage and electric current were set to be 40 kV and 40 mA, respectively. The morphology and structure of the as-obtained samples were characterized by field-emission scanning electron microscopy (FE-SEM, JSM-7500F, JEOL).

The working electrodes were prepared by mixing active material (raw Si, 3D PS or PS/Carbon) with CMC and acetylene black in a mass ratio of 3:1:1 in deionized water. The working electrode disks (diameter Φ = 14 mm) were dried in air at 60 °C and further heated at 120 °C for 12 h in vacuum, the loading of active material on the electrode is about 1.27 mg cm\(^{-2}\). 2025 coin cells were assembled using Celgard 2400 as separator, lithium foil as counter and reference electrode, and 1 M LiPF\(_6\)/EC+DMC+DEC, 1:1:1 in mass, 2% VC) as electrolyte. The cells were tested in the voltage range of 0.02 and 1.5 V (vs. Li\(^+\)/Li\(^-\)) at room temperature on a cell testing instrument (LAND CT2001A, China). Cyclic voltammetry (CV) measurements were performed on an electrochemical working station (CHI 614C) at a scanning rate of 0.05 mV s\(^{-1}\) within a voltage range of 0–1.5 V.

Results and Discussion

Figure 2 compares the XRD patterns of samples synthesized with different reaction steps. As shown in Figure 2a, the diffraction peaks of...
Mg$_2$Si indicate that the solid-state reaction ($Si + 2Mg \xrightarrow{500^\circ C} Mg_2Si$) is sufficient after a thorough grinding and homogeneous mixing of the reactants. Although magnesium powders (Si/Mg molar ratio of 1:2.2) were used abundantly, residual silicon can still be detected (see Figure 2a) because of strong volatility of magnesium. In the process of the vacuum heat-treatment, the milled Mg$_2$Si phase decomposed as follows:

$$Mg_2Si(s) \xrightarrow{\geq 700^\circ C} MgSi(s) + Mg(g)$$

$$MgSi(s) \xrightarrow{\geq 1000^\circ C} Si(s) + Mg(g)$$

With escaping of magnesium vapor from Mg$_2$Si in the reactions, there remains a large number of pores in newly formed elemental silicon. Except for diffraction lines of silicon, lines for MgO can also be seen in the XRD pattern of the sample heat-treated at 1000°C (Figure 2b). The XRD pattern for the 3D PS sample is shown in Figure 2c and it displays only diffraction lines of Si. This result indicates that the formation of the impurity Mg$_2$SiO$_4$, which is insoluble in HCl solution, is effectively suppressed under vacuum heat-treatment conditions. In Figure 2d, the XRD pattern for the as-obtained PS/Carbon composite is shown and it presents the same diffraction lines as that for the 3D PS sample, indicating that the produced carbon in the PS/Carbon composite could be in amorphous form.

Figure 3 compares the SEM images of raw silicon powders, 3D PS and PS/Carbon composite. After the fluoride-free treatment, the blocky particles of raw silicon with wide size distribution (Figure 3a) are turned into ultrafine grain with micropores, regular shape, and sleek edges (Figure 3b and Figure 3c), the tap density of 3D porous silicon powders is 0.703 g cm$^{-3}$. Compared with blocky silicon, porous silicon is more effective in generating Li$^+$ insertion/extraction because of the increased contact area and the reduced Li$^+$ diffusion path length. With the help of hydrothermal reaction, amorphous carbon is incorporated on the surface and in the pores of 3D PS (seen in Figure 3d). It is a well known method to cover the surfaces of silicon particles with amorphous carbon to improve electrical conductivity. Here for an interconnected conductive network, the existence of amorphous carbon in the 3D pores of silicon particles appears to be more important because the charge-transfer process would be improved effectively in the core area of the silicon particles.

Figure 4 exhibits the CV curves for the raw Si and 3D PS samples at a scan rate of 0.05 mV s$^{-1}$ in the potential range of 0–1.5 V. For both samples, an obvious broad peak in the range of 0.4–1.0 V can be seen in the first reduction process and it disappears in the subsequent cycles, indicating the formation of solid electrolyte interphase (SEI) on the electrode surface.

For the 3D PS electrode, however, there are two peaks (near 0 V and 0.1 V) for reduction process after the first cycle and oxidation process (0.4 V and 0.55 V). The separation of redox peaks indicates different alloying/dealloying process between...
Si and Li$_2$Si$_5$, which is similar to the CV curves of electrode samples which used nano-silicon particles as active materials. For the raw Si electrode, the process of alloying/dealloying reaction on the surface and in the core of silicon particle is not synchronous due to Li$^+$ diffusional limitation. That’s the reason why the CV curves of raw Si electrode display superposition features (see Figure 4a). Furthermore, the response current peaks of the 3D PS electrode are much higher than those of raw Si, indicating that there exists a larger contact area for former during the electrochemical reaction.

The galvanostatic charge-discharge curves of raw silicon powders and 3D PS at different cycles are shown in Figure 5. For the raw silicon electrode, a reversible capacity of 2146 mAh g$^{-1}$ can be obtained in the first cycle, but only 9.5% of the first capacity (205 mAh g$^{-1}$) is kept after ten cycles. The fast capacity fading is not only related to particle pulverization caused by huge volume changes, but also due to severe polarization caused by a poor charge-transfer environment. After incorporation of 3D pores into silicon particles, however, the first reversible capacity increased from 2146 mAh g$^{-1}$ to 2954 mAh g$^{-1}$; and a high capacity of 1508 mAh g$^{-1}$ can be reversibly extracted in the 10th cycle. Such improvement of capacity due to the 3D pores in silicon particle can be mainly ascribable to the increase of surface area and the contraction of Li$^+$ diffusion path length. To our knowledge, the cyclic performance of the 3D PS with micron size is comparable with that of nano-sized silicon. This means that it is possible to produce high capacity silicon-based composite using much cost-effective micro silicon.

Figure 6 compares cyclic performances of 3D PS and PS/Carbon composite samples. As seen in Figure 6a, discharge/charge capacity of the 3D PS electrode experiences a rapid declining phase during the first 20 cycles and a reversible capacity of 664.6 mAh g$^{-1}$ can be obtained at the 100th cycle. Compared to the 3D PS electrode, the first discharge/charge capacity of the PS/Carbon electrode declines dramatically as a result of the decrease in silicon content, but a reversible capacity as high as 608.7 mAh g$^{-1}$ is kept after 100 cycles with only 0.69% of capacity loss ratio per cycle. Obviously, amorphous carbon in 3D PS also plays an important role in the improvement of cyclic stability similar to other silicon/carbon composite. For the PS/Carbon composite, therefore, improvement of cyclability can be attributed to effective self-absorption of volume changes, unitary conducting network distributed not only on the surface but also in the interior of silicon particle.
Conclusions

3D PS and PS/Carbon composite were prepared by high-temperature sintering followed by HCl bleaching and hydrothermal treatment. 3D pores were uniformly distributed in the micro silicon particles. The 3D PS electrode kept a reversible capacity of 664.6 mAh g$^{-1}$ up to 100 cycles, which is almost ten times higher than that of raw silicon electrodes. With the help of amorphous carbon, cyclic performance of the PC/Carbon composite was further improved, i.e. a reversible capacity of 608.7 mAh g$^{-1}$ can be obtained with only 0.69% of capacity loss ratio after 100 cycles. It is believed that this fluoride-free preparation technology for 3D PS will provide an alternative approach to improve the cyclability of silicon-based composite.

Acknowledgments

This work was financially supported by Natural Science Foundation of China (NSFC, 51272128, 50972075) and Excellent Youth Foundation of Hubei Scientific Committee (2011CDA093). Moreover, the authors are grateful to Dr. Jianlin Li at Three Gorges University for his kind support to our research.

References