# Enhanced reversible lithium storage for nano-Si with a <10 nm homogenous porous carbon coating layer

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## ARTICLE INFO

## ABSTRACT

Nano-Si composite with a <10 nm homogenous porous carbon coating layer was fabricated by a facile approach with phenolic resin as carbon source, Pluronic 123 (P123) as pore forming agent and cetyl-trimethyl ammonium bromide (CTAB) as surfactant. The composite electrode exhibited a high lithium storage capacity of 960 mAh $g^{-1}$ over 100 cycles at 1 A $g^{-1}$ and could maintain reversible capacities of 810 mAh $g^{-1}$ at 0.5 A $g^{-1}$ over 400 cycles. The superior electrochemical performance could be due to the homogeneous and unique porous thin carbon shell for Si.

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## 1. Introduction

Due to the highest lithium capacity (4200 mAh $g^{-1}$ vs. $Li_{4.4}Si$), the ideal insertion/extraction potential (less than 0.5 V vs. $Li/Li^+$), abundant and low cost, Si has become the focus of the next generation of negative electrode materials for lithium ion battery [1,2]. However, due to the low intrinsic conductivity of Si and the serious volume effect (400% volume expansion) in the Li ion extraction/insertion process, it is not ideal to use it as anode material for Li-ion batteries directly. In addition, it is difficult to form a stable surface solid electrolyte (SEI) film on Si surface, which is also an important reason for the decrease of charge-discharge efficiency and the increase of capacity degradation. At present, in order to solve these problems, the main strategy is to prepare a buffer matrix for nano-Si with good conductivity [3].

Up to now, kinds of materials were used as buffer matrix to improve the electrochemical performance of Si anode, such as carbon materials [4,5], metals [6,7], metal oxides [8,9], conducting polymers [10,11] and so on. Among them, the carbon materials have become the first choice because of many advantages, such as wide range of sources, low price, good conductivity and good coating effect [12,13]. The Si/carbon composite structure usually can be divided into three types: coating, embedding and dispersion.

Compared these three kinds of composite structure, due to the higher Si content in composite and superior electrochemical performance, carbon coated core-shell composite has become the most widely Si anode coating method.

Although the core-shell Si/C composite structure has been widely studied, but the design and optimization of the structure and composition of the coating are still few studied. The power battery requires that the electrode materials must have high reverse capacity, high rate performance and excellent cycle performance. Thus, the electrode materials should satisfy the high electron and ionic conductivity, excellent chemical and electrochemical stability. These properties are closely related to the coating structure. Therefore, with the development of the battery technology, the electrode materials have higher requirements on the coating structure of Si composite. The structure design of coating layer should take into account the interaction and balance between the content and thickness, structure, morphology, distribution and porosity of the composites.

The carbon coating layer requires the formation of a homogeneous conductive network on the Si nanoparticle surface. Homogeneous conductive coating layer can significantly improve the electronic conductivity of electrode, and ensure that the electronic and Li ion uniformly and quickly transport to the electrode surface, and eliminate the internal imbalance and polarization within electrodes, thus improving the rate performance. Secondly, the thickness of the coating layer is also an important factor in

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designing Si composite structure. High carbon content is beneficial to control Si volume expansion, but it also increases the difficulty of Li ion transport and affects the rate performance of the electrodes. Therefore, the thickness of carbon layer should be controlled below 10 nm, which could be conducive to keep better ionic and electronic conductivity [14–16]. However, when the carbon layer thickness reduced to several nanometers, the coating uniformity was not ideal. In addition, due to the decrease of the coating thickness, the mechanical strength of the coating structure is poor and easy to be damaged for the electrode material when experiencing huge volume effect.

Furthermore, to further improve the properties of Si based materials, it is necessary to increase the pore structure in the composites. The existence of pore structure can not only be used as a buffer space of Si volume expansion and contraction to maintain the integrity and stability of electrode structure and reduce the electrode deformation, but also provide high contact area between Si and electrolyte to improve the Li ion diffusion rate. However, for Si composites, the existence of the porous structure, especially the heterogeneous pore structure will inevitably affect the mechanical strength of the coating structure. This is a new challenge for the preparation of Si based composites.

The above analysis shows that it is necessary to fabricate carbon structure with suitable thickness and uniform pores on the Si nanoparticle surface to ensure that the electrode has high electronic and ionic conductivity for Si-carbon composite anode electrode. Hu et al. [17]. prepared Si@SiO$_x$/C nanocomposites with 10–20 nm thick carbon shell, displaying reversible capacity of 600 mAh g$^{-1}$ at 1 A g$^{-1}$. Park et al. [18]. reported Si nanoparticles trapped in ordered mesoporous carbon composite presented reversible capacity above 700 mAh g$^{-1}$ over 50 cycles at 2 A g$^{-1}$. Shao et al. [19]. prepared nano-Si/porous-C spherical composite. The thickness and pore size of carbon shell was 15–20 nm and 3–5 nm, respectively. This electrode displayed reversible capacity of 1607 mAh g$^{-1}$ at 0.4 A g$^{-1}$ over 100 cycles. However, this process needed to experience hydrothermal reaction with a high temperature (180 °C for 6 h) and be protected by inert gas. Otherwise, nano-Si was very easy to be oxidized during high temperature hydrothermal reaction. Therefore, it is urgent to develop a new method to prepare uniform porous carbon layer coated nano-Si at lower temperature.

In this work, Si/C composite with homogenous porous carbon coating layer was obtained under mild conditions with phenolic resin as carbon source, P123 as pore forming agent and CTAB as surfactant. The structural characterization and effect of the porous carbon shell on the electrochemical properties were investigated.

## 2. Experimental section

0.5 g P123 (Aldrich, EO20PO70EO20, Ma = 5800) and 0.2 g nano-Si (Xuzhou Jiechuang New Material Technology Co. Ltd. (China)) were ultrasonically dispersed in the 28.6 mL deionized water and 71.4 mL ethanol for 1 h. 1.2 g CTAB, 0.175 g resorcine and 0.15 ml 25 wt % ammonia were added into the above suspension and heated at 45 °C for 30 min under stirring. Then, 0.15 ml formaldehyde was added and heated at 45 °C for 3 h. The precipitate was filtered and dried to obtain Si@PF resin. Then the Si@PF resin was calcined at 800 °C for 3 h in Ar to obtain Si@porous carbon composite. For comparison, Si@C was obtained by calcining Si@PF resin without P123. In the following case, the reaction time of all reactions was 3 h, unless special instructions were given.

The scanning electron microscope (SEM) with an energy-dispersive detector (EDS) and transmission electron microscope (TEM) were performed on Nova NanoSEM 450 scanning electron microscope and JEM-2100F transmission electron microscope,

respectively. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were carried out on X'Pert3 Powder diffractometer and ESCALAB 250Xi XPS, respectively. Attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectra of 670–4000 cm$^{-1}$ were observed on a Nicolet Magna 550 spectrometer at resolution of 4 cm$^{-1}$. Raman spectroscopy was performed on a Jobin-Yvon Lab-Ram high-resolution spectrometer with 532 nm diode laser. Thermal gravimetric analysis (TGA) analyses were obtained with a NETZSCH STA 449C analyzer (Germany) in air atmosphere at 40–800 °C.

The electrochemical measurement was carried out with the coin cells (CR2025). The anode electrode was made from the obtained material, acetylene black and carboxymethyl cellulose binder (70:15:15, wt.%) on Cu foil. The electrolyte was 1 M LiPF$_6$ with 5% fluoroethylene carbonate in ethylene carbonate/diethylene carbonate/dimethyl carbonate (1:1:1 V/V/V). The capability of the cells was evaluated on a Shenzhen Neware battery cycler (China) within 0.01–1.5 V. Workstation (Zennium/IM6, Zahner, Germany) was used to measure cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). EIS was measured by applying an alternating voltage of 5 mV over the frequency ranging from $10^{-2}$–$10^5$ Hz and at an equilibrium potential of 0.18 V (vs. Li/Li$^+$) at 25 °C.

## 3. Results and discussion

ATR-FTIR spectra of nano-Si, Si@C (after and before carbonated) and Si@porous C (after and before carbonated) were shown in Fig. 1. The spectrum of nano-Si showed Si−O−Si bending vibrations at 810 cm$^{-1}$, stretching vibration at 1060 and 1240 cm$^{-1}$ and O−H stretching vibration at 3400 cm$^{-1}$ [20]. Before carbonated, nano-Si was coated by phenolic resin layer. Before carbonated, Si@C and Si@porous C showed the characteristic spectrum of PF resin at 3330 cm$^{-1}$ for the intermolecular hydrogen bond, peaks at 2920, 2860 and 843 cm$^{-1}$ for vibrations of methylene linkages, peaks at 1617, 780 cm$^{-1}$ for the vibration of benzene ring, 1360 cm$^{-1}$ for O−H in-plane deformation vibrations, 1230 cm$^{-1}$ for stretching vibration of C−O, and 1086 and 1154 cm$^{-1}$ for stretching vibration of CH$_2$−O−CH$_2$ [21–23]. Furthermore, it is seen that the bands at 1456 and 1103 cm$^{-1}$ were attributed to the vibrational modes of PEO in the P123 crystalline phase [24,25]. However, after being carbonated, these typical characteristic peaks of resin layer and
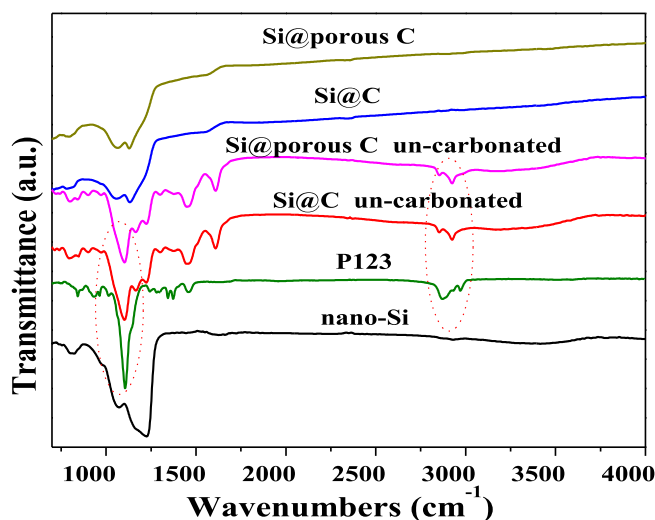


Fig. 1. ATR-FTIR spectra of nano-Si, Si@C (after and before carbonated) and Si@porous C (after and before carbonated).