

Silicon/Needle Coke Composites as Efficient Anodes for Lithium Ion Batteries

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Abstract. In this research, a facile method was reported to prepare silicon/carbon composites by heating Si nanosheets and coal-based needle cokes in the assistance of binder glucopyranose. The microstructures and electrochemical performances of samples were analyzed. It was found that Si nanosheets adhered to needle cokes forming silicon/carbon composites. Compared with needle cokes, the composites showed higher capacity and initial coulombic efficiency. Also, they improved the cycle stability of silicon materials. The silicon/carbon anode had a reversible capacity of 381.8 mAh/g at a current density of 100 mA/g after 170 cycles. In our work, relatively inexpensive Si nanosheets and coal-based needle cokes with low price were employed as the silicon and carbon sources respectively. Therefore, this method provides a possible strategy to reduce costs of silicon/carbon anodes, accelerating their commercial applications.

1. Introduction

Lithium ion battery, one of the major rechargeable energy storage device, has dominated wide applications in electric vehicles and portable electronic devices.[1-5] To improve the energy density of lithium ion battery, the anode material with high specific capacity has always been a hot topic.[6, 7] Silicon with high specific capacity of 4200 mAh/g and low working potential is the most promising candidate for the next generation lithium ion battery anode.[8, 9] However, the huge volume change of silicon during the Li insertion/extraction processes hinders its practical application as the anode material.[10, 11] In order to suppress the volume expansion of silicon, preparation of silicon/carbon composites has been developed.[12, 13] Such composites are able to improve the electronic conductivity of electrodes and alleviate the volume expansion of silicon.[14, 15] To fabricate silicon/carbon anodes, various strategies have been reported, for example, synthesis of silicon/carbon microspheres through chemical vapor deposition, composite of silicon nanowire, graphene and carbon nanotube, coating of carbon on silicon nanoparticles, and preparation of silicon/carbon particles through chemical etching.[16, 17] However, the current methods are relatively costly[18-20] (such as expensive raw materials and instruments) and complicated[21-23] (such as magnesiothermic reduction and electrospray), which severely limits the commercial application of silicon/carbon anodes in lithium ion batteries. Thus, developing a low-cost and facile method to synthesize silicon/carbon anodes is critical. In this work, relatively inexpensive Si nanosheets and coal-based needle cokes

were chosen as the raw materials. The silicon/carbon composite was prepared through simply heating of a mixture of Si nanosheet, needle coke and binder glucopyranose. Furthermore, the microstructures and electrochemical performances of the obtained composites were explored.

2. Experimental

2.1 Materials

The Glucopyranose and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd.. The coal-based needle coke was bought from Ansteel Group CO., LTD.. Its volatile, ash content, density and sulfur residue value were 5.2%, 0.01%, 1.41 g/cm³ and 0.45%, respectively.

2.2 Preparation of Silicon/Carbon Composites

The needle coke (0.475 g), silicon nanosheet (0.025 g), and glucopyranose (0.05 g) were added into ethanol (80 mL), followed by stirring of this mixed solution at room temperature for 3 h. Then the mixed solution was dried at 100 °C for 12 h. Finally, the mixture was heated at a rate of 5 °C/min to 600 °C, and kept at this temperature for 3 h under the protection of nitrogen. The product was denoted as Si/Nc-600. The sample Si/Nc-900 was prepared at the same condition but the heating temperature was changed to 900 °C. For comparison, samples Nc-600 and Nc-900 were produced through heating of pristine needle cokes at 600 °C and 900 °C respectively, without addition of Si nanosheets.

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2.3 Characterization

The X-ray diffraction (XRD) and atomic force microscopy (AFM) were conducted by Bruker D8 Advance with a Cu K radiation source of 1.5405 Å and Park NX20, respectively. The scanning electron microscopy (SEM) and element mapping were conducted by Gemini 560. The coin cells (CR2025) were used to analyze the electrochemical performances of samples. The active material, Super P and sodium alginate were mixed with a weight ratio of 7:2:1 in water to prepare a slurry. The working electrode was prepared by spreading the above slurry onto copper foil and dried at 120 °C for 12 h. A solution of 1 M LiPF₆ in ethylene (EC) and dimethyl carbonate (DMC) (v:v=1:1) was used as the electrolyte, and the counter electrode was the lithium foil. The charge/discharge tests were carried out in a voltage range from 0.01 to 2 V at room temperature.

3. Results and Discussion

Figure 1a shows the SEM image of the coal-based needle coke. Its size ranges from 2-10 μm. The Si nanosheet has a flaky morphology with the length of several micrometers and the height of 2-4 nm (figure 1b,c). As shown in the XRD pattern of the Si nanosheet, strong peaks of d₍₁₁₁₎, d₍₂₂₀₎ and d₍₃₁₁₎ were observed at 28.48°, 47.32° and 56.14°, respectively, demonstrating the crystalline structure of Si nanosheet (figure 1d).

As shown in the initial discharge-charge curve of Si nanosheet, a long voltage plateau is observed below 0.45 V during the charging process, which is the extraction of lithium ions from Si (figure 2a). The charge capacity and coulombic efficiency of Si nanosheet are 1537 mAh/g and 72.4% in the first cycle at a current density of 100 mA/g, respectively (figure 2b). However, the reversible capacity of Si nanosheet fades dramatically to 282.1 mAh/g in the 50th cycle (figure 2b). After 170 cycles, it is only 56 mAh/g (figure 2b). Si nanosheet has high capacity but low cycle stability. The capacity fading may be caused by the volume expansion and pulverization of Si nanosheets.[13]

To improve the electrochemical performances of carbon materials and increase the cycle stability of silicon materials, the silicon/carbon anodes were prepared through heating of the mixtures of needle cokes and Si nanosheets at 600 °C and 900 °C, respectively. The obtained silicon/carbon composites were denoted as Si/Nc-600 and Si/Nc-900. Figure 3 presents the SEM images and elemental analysis of Si/Nc-600 and Si/Nc-900. Compared with the pristine needle coke, some small particles (about several hundred nanometers in size) are observed on the surfaces of Si/Nc-600 (figure 1a and 3a). The elemental analysis shows these small particles are Si (figure 3c,e). Similar results are observed in the sample Si/Nc-900 (figure 3b, d and f). The above results indicate that Si nanosheets are crushed to small particles in the stirring, and adhere on the surfaces of needle cokes by glucopyranose, forming the silicon/carbon composites.

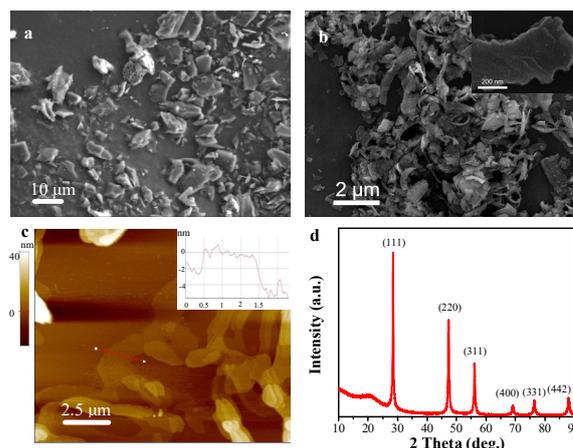


Figure 1. Typical SEM images of a) needle cokes, and b) Si nanosheets (inset: enlarged SEM image of Si nanosheet). c) The AFM image (inset: the corresponding height profile) and d) XRD pattern of Si nanosheets.

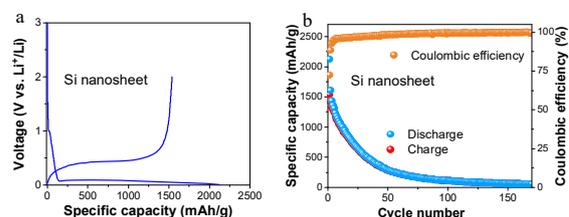


Figure 2. a) The initial discharge-charge curve and b) cycle performance and the corresponding coulombic efficiency of Si nanosheet. (Current density: 100 mA/g)

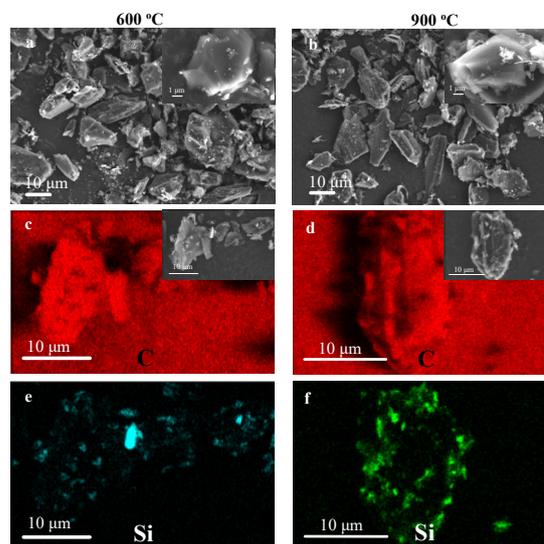


Figure 3. Typical SEM images of a) Si/Nc-600 and b) Si/Nc-900 (inset: enlarged SEM images). EDS elemental mapping images of c,e) Si/Nc-600 and d,f) Si/Nc-900 (inset: the corresponding SEM images).

Figure 4a shows the initial discharge-charge curve of the Nc-600, which was obtained through heating of needle cokes without addition of Si nanosheets at 600 °C. Its charge capacity and coulombic efficiency are 352.9

mAh/g and 46.2% in the first cycle at a current density of 100 mA/g, respectively (figure 4a). Compared with Nc-600, the initial charge capacity and initial coulombic efficiency of silicon/carbon composite Si/Nc-600 are increased to 411.9 mAh/g and 54.7%, respectively (figure 4c). After 170 cycles, the reversible capacity of Si/Nc-600 declines to 336.2 mAh/g, but it is higher than that of Si nanosheet (figure 2b and 4e). When the heating temperature was increased to 900 °C, similar phenomenon was observed. Both the initial charge capacity and initial coulombic efficiency of Si/Nc-900 (345.6 mAh/g, 66.6%) are higher than those of Nc-900 (302.5 mAh/g, 54.8%) (figure 4b,d). The reversible capacity of Si/Nc-900, which is 381.8 mAh/g, is also higher than that of Si nanosheet after 170 cycles (figure 2b and 4f). These results suggest that the addition of Si nanosheets could improve the initial charge capacity and initial coulombic efficiency of needle cokes, because of the high initial charge capacity of Si nanosheets. The composites of needle cokes and Si nanosheets may restrict the volume expansion of Si, leading to the improvement of the cycle stability.[13]

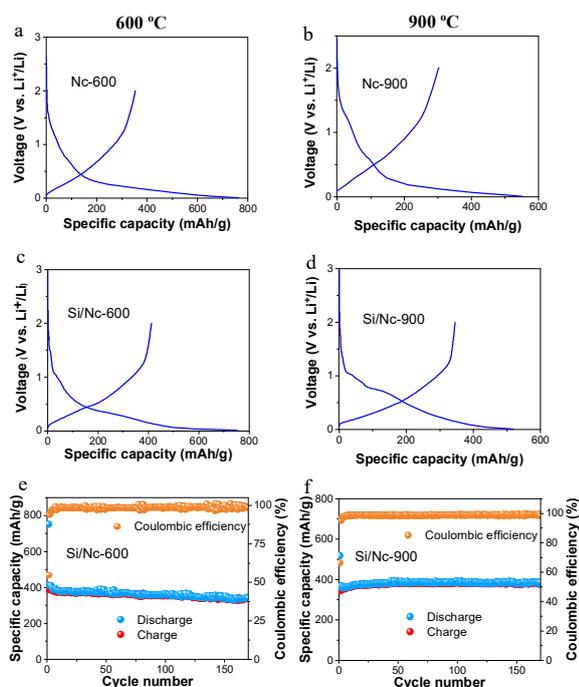


Figure 4. The initial discharge-charge curves of a) Nc-600, b) Nc-900, c) Si/Nc-600 and d) Si/Nc-900. Cycle performance and the corresponding coulombic efficiency of e) Si/Nc-600 and f) Si/Nc-900. (Current density: 100 mA/g)

In comparison with the Si/Nc-600, the Si/Nc-900 shows a little lower initial charge capacity but higher initial coulombic efficiency (table 1). This is because a higher heating temperature could cause the decrease of initial charge capacity and increase of initial coulombic efficiency of needle cokes, as reported in our previous work (table 1). After 170 cycles, the Si/Nc-900 (381.8 mAh/g) presents a better cycle stability than Si/Nc-600 (336.2 mAh/g, figure 4e,f). Maybe higher heating temperature benefits the combination of carbon and

silicon, resulting in improvement of cycle stability. But the exact reason is still under research.

Table 1. The electrochemical performances of Nc-600, Nc-900, Si/Nc-600 and Si/Nc-900.

Sample	Initial charge capacity (mAh/g)	Initial coulombic efficiency (%)
Nc-600	352.9	46.2%
Nc-900	302.5	54.8%
Si/Nc-600	411.9	54.7%
Si/Nc-900	345.6	66.6%

4. Conclusion

In this work, a low-cost method was provided to prepare the silicon/carbon anode by using the Si nanosheet with relatively low price and cheap coal-based needle coke as the raw materials. After the stirring and heat treatment, crushed Si nanosheets adheres to the surfaces of needle cokes, forming the silicon/carbon composites Si/Nc-900. This composite structure helps to improve the capacity and initial coulombic efficiency of needle cokes. Meanwhile, it benefits the cycle stability of silicon/carbon anode. After 170 cycles, the reversible capacity of Si/Nc-900 keeps at 381.8 mAh/g. This simple and low-cost fabrication process makes Si nanosheet/needle coke anode a candidate for the practical application in the Li-ion battery.

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