The Effect of Binder on the Electrochemical Property of Silicon/carbon Anode

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Abstract. In this research, needle coke, graphite and silicon nanosheet were bonded by pitch or glucose to prepare the Si/C composite anode. The influence of binder on the microstructure and electrochemical property of Si/C anode was discussed. The sample using pitch as binder has smooth surface and is densely coated by pitch. The silicon is exposed on the surface of Si/C compound using glucose as the binder. Compared with pitch-based Si/C anode, glucose-based Si/C anode shows higher initial capacity and coulombic efficiency, but it's capacity retention ratio is lower. The initial capacity, initial coulombic efficiency and capacity after 100 cycles of the glucose-based anode are 655.3 mAh/g, 70.3% and 474.0 mAh/g, respectively. Those of pitch-based anode are 555.8 mAh/g, 62.4% and 538.8 mAh/g, respectively. Using different binders leads to distinct microstructure, impedance and irreversible reaction, which finally causes the varying capacities and initial coulombic efficiency of anodes.

Keywords: Silicon/carbon anode, Lithium ion batteries, Binder.

1. Introduction

In recent years, increasing utilization of clean energy from wind and solar leads to a strong demand for energy storage devices with high efficiency.[1-5] Meanwhile, electrification of vehicles calls for suitable devices for energy storage. Lithium ion batteries have the advantages of relatively high energy density and environmental benefit. They have been considered as one of the major energy storage technologies, being used in the area of electric vehicles, portable electronic devices and grid scale energy storage.[6-8] Nowadays, the commercial graphite carbon anode with a theoretical capacity of 372 mAh/g is not able to meet the demand, and anodes with high capacity and long cycling life are in need. Silicon/carbon composites are regarded as excellent candidates for lithium ion battery anodes, because they show great potential to improve the energy density and cycling performance of anodes.[9-11] In the silicon/carbon composites, carbon is able to restrict the volume expansion of silicon and improve the electric conductivity of silicon.[12-14] Lots of methods have been proposed to prepare silicon/carbon composite anodes, such as embedding of silicon nanoparticles in a carbon framework[12, 15, 16], coating of carbon on bulk silicon particles[17], and combination of silicon and graphite[18, 19]. Using the binder is a simple and economical method to prepare silicon/carbon compounds. Binder can prevent the separation of silicon and carbon, contributing to raise the capacity and cycle life of anodes.

In this paper, pitch and glucose were used as binders. Needle coke, graphite and silicon nanosheet were bonded by the binder to prepare silicon/carbon composites. The influence of binders on the microstructures and electrochemical properties of silicon/carbon composites was investigated.

2. Experimental

2.1 Materials.

The needle coke and pitch with a softening point of 270 ºC were purchased from Ansteel Group CO., LTD.. The graphite and glucose were bought from Jining Keneng Carbon Material CO., LTD. and Sinopharm Chemical Reagent CO., LTD., respectively.

2.2 Preparation of Si/C Compounds.

In the preparation of Si/C compound by using pitch as the binder, 2 g needle coke, 2 g graphite, 0.5 g silicon nanosheet and 0.5 g pitch are firstly mixed by ball milling for 5 h. Then the mixture is heated to 600 ºC at a rate of 10 ºC/min, and kept at this temperature for 3 h under the N_2 stream. The product is named as Si/C-Pit.

As for the Si/C compound using glucose as the binder, firstly a mixture of 0.22 g needle coke, 0.22 g graphite, 0.06 g Si nanaosheet and 80 mL deionized water is ultrasonic treated for 6 h. Then 20 mL of 2.5 mg/mL glucose solution is added in the above mixture. After stirring for 3 h, the mixture is heated at 100 ºC for 4 h for drying. Finally, the dried mixture is heated to 600 ºC at a rate of 10 ºC/min, and kept at 600 ºC for 3 h under the N_2 stream. The product is named as Si/C-Glu.

2.3 Characterization.

Gemini 560 was utilized to conduct the scanning electron microscopy (SEM) and element mapping. The X-ray diffraction (XRD) spectroscope (Bruker D8 Advance) and Raman spectrometer (Horiva JY-HR800) were employed to analyze the microstructures. The coin cells were used to test the electrochemical properties of samples. For the preparation of working electrodes, active material, Super P and sodium alginate were mixed in water with a ratio of 7:2:1 (w:w:w), and then the mixed slurry was spread onto copper foil. A solution of 1 M $LiPF_6$ in ethylene and dimethyl carbonate (v:v=1:1) was applied as the electrolyte. The counter electrode was a lithium foil. The preparation of coin cells was conducted in a glove box under the protection of Ar_2. The Land BT2000 battery test system was used to analyze the charge/discharge properties of samples. The cyclic votlammetry (CV) test and electrochemical impedance spectroscopy (EIS) were performed on a VersaSTAT electrochemical station.

3. Results and Discussion

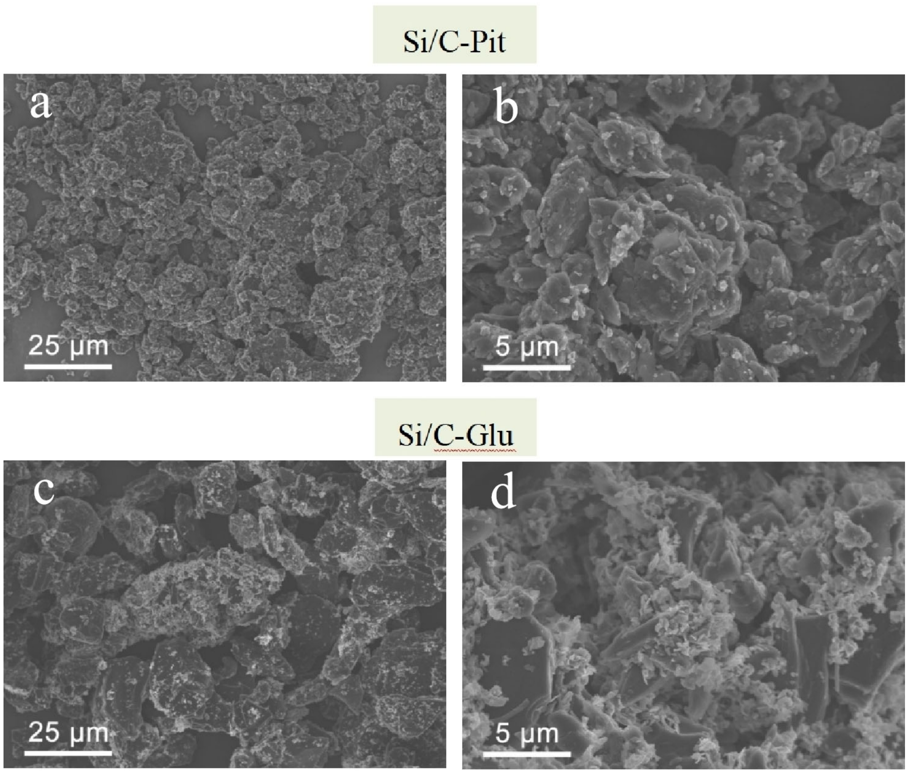

Figure 1. SEM images of (a, b) Si/C-Pit and (c,d) Si/C-Glu.

Figure 1 shows the typical SEM images of Si/C-Pit and Si/C-Glu. The silicon nanosheet, graphite and needle coke are bonded together by the carbonized pitch, forming the micro-scale particle (Fig.1 a and b). The surfaces of these particles are relatively smooth, indicating the surfaces of these particles are uniformly and densely coated by the pitch (Fig.1b). In SEM images of Si/C-Glu, the silicon nanosheet, graphite and needle coke are bonded together, forming the Si/C compound. The carbonized glucose particles and silicon adhere to the surfaces of these Si/C compounds (Fig 1c and d).

The element analysis of Si/C-Pit and Si/C-Glu clearly shows silicon and carbon are uniformly distributed in these two compounds (Fig. 2). In the XRD patterns of Si/C-Pit and Si/C-Glu, the sharp peaks at about 26.5^{o} are assigned to the (002) facet of graphite (Fig. 3).[20] The diffraction peaks at approximately 28.4^{o}, which belong to the (111) facet of silicon, are observed in these two compounds (Fig. 3). The XRD patterns of Si/C-Pit and Si/C-Glu also demonstrate that these compounds are composed of silicon and carbon. In the Raman spectra, both Si/C-Pit and Si/C-Glu present peaks at about 514 cm^{-1} which attributes to the Raman scattering of silicon (Fig. 4).[21] However, the Raman scattering intensity of silicon in Si/C-Glu is higher than that in Si/C-Pit (Fig. 4). This is because the silicon exposes at the surface of the Si/C-Glu compound (Fig. 1 c and d). But in the Si/C-Pit compound, silicon is coated by carbonized pitch, which weakens the Raman scattering of silicon (Fig. 1 a and b). In the Raman spectra, the peaks at approximately 1346 and 1600 cm^{-1} belong to the Raman shifts of D and G band of carbon, respectively (Fig. 4).[22] These results above demonstrate that Si/C compounds are successfully prepared using pitch or glucose as binder.

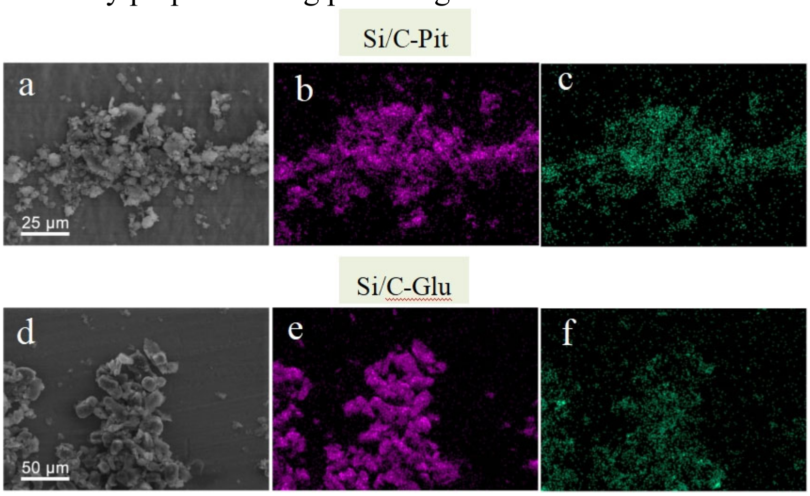

Figure 2. (a) SEM image and (b, c) the corresponding EDS mapping of Si/C-Pit. (d) SEM image and (e, f) the corresponding EDS mapping of Si/C-Glu. (C: purple, Si: green)

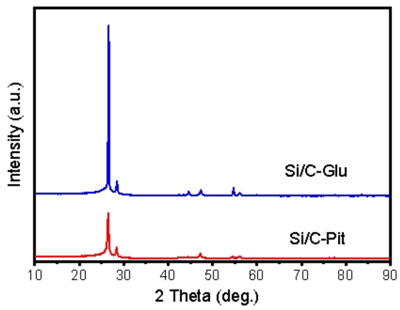

Figure 3. XRD patterns of Si/C-Pit and Si/C-Glu.

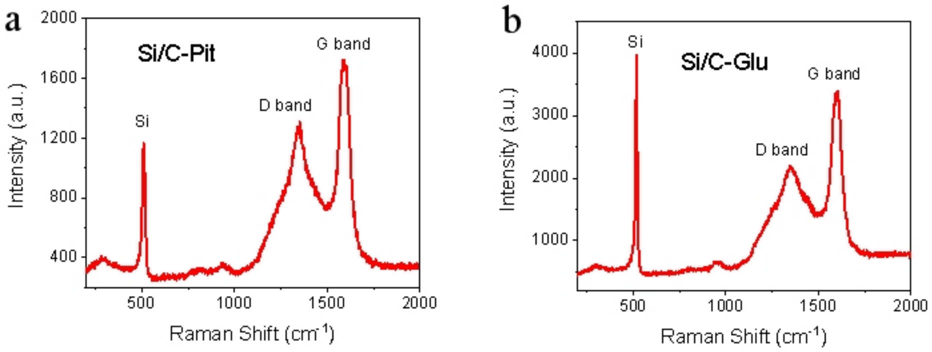

Figure 4. Raman spectra of a) Si/C-Pit and b) Si/C-Glu.

The lithium insertion/extraction properties of the samples are presented in figure 5. As shown in figure 5a, the Si/C-Pit has a reversible capacity of 555.8 mAh/g in the first cycle at a current density of 100 mA/g. Its initial coulombic efficiency is 62.4% (Fig. 5c). The Si/C-Glu shows higher reversible capacity and coulombic efficiency in the first cycle. They are 655.3 mAh/g and 70.3%, respectively (Fig. 5b and d). The Si/C-Glu presents lower impedance than that of Si/C-Pit (Figure 6). The cyclic voltammetry curves of these two samples display reduction peaks at about 1.2 V in the first cycle, and these peaks disappear in the following cycles (Fig. 7). This phenomenon indicates that irreversible reactions occur between electrolyte and electrode. The peak intensity of Si/C-Pit at 1.2 V is higher that of Si/C-Glu, demonstrating more irreversible reactions occur in Si/C-Pit. Higher impedance and more irreversible reactions may lead to lower capacity and coulombic efficiency of Si/C-Pit in the first cycle.

However, Si/C-Pit remains a capacity of 538.8 mAh/g and Si/C-Glu only has a capacity of 474.0 mAh/g after 100 cycles (Fig. 5c and d). As we discussed above, the silicon is well coated by pitch in the Si/C-Pit, while the silicon is exposed on the surface of Si/C-Glu. Thus silicon in the Si/C-Glu is easier to pulverize and detach from electrode, resulting in poor cycling performance.

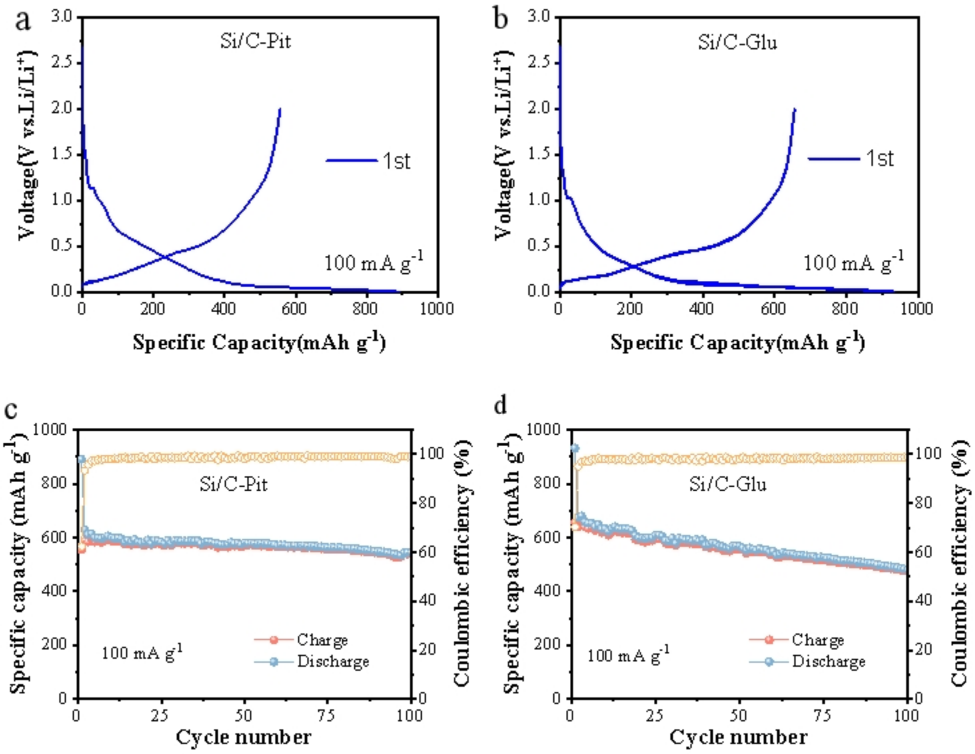

Figure 5. Charge and discharge profiles of a) Si/C-Pit and b) Si/C-Glu in the first cycle. Cycling performance and the corresponding coulombic efficiency of a) Si/C-Pit and b) Si/C-Glu. (current density: 100 mA g^{-1})

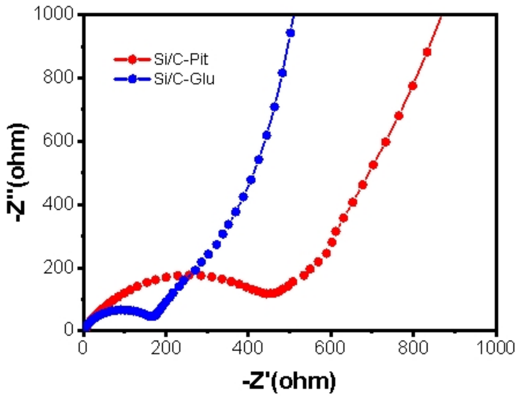

Figure 6. Electrochemical impedance spectroscopy of SiC-Pit and Si/C-Glu before cycling.

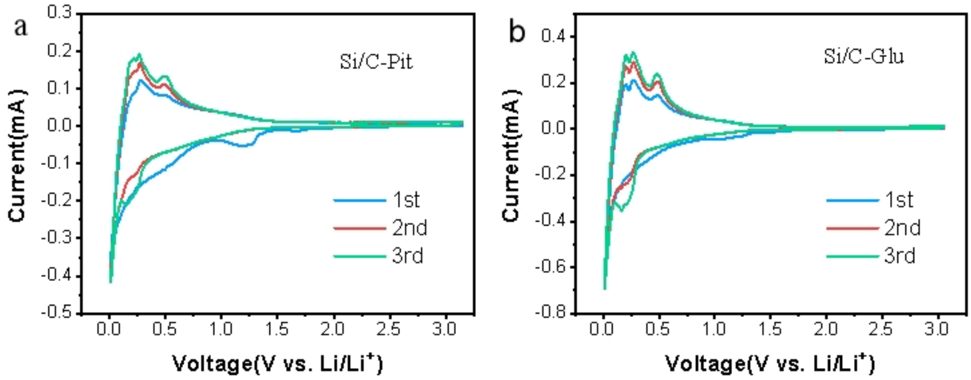

Figure 7. Cyclic voltammetry curves of a) Si/C-Pit and Si/C-Glu at the first 3 cycles.

4. Summary

In this paper, we discuss the effect of different binders (i.e. pitch and glucose) on electrochemical properties of Si/C anode matertials. The microstructure and element analyses demonstrate that needle coke/graphite/silicon nanosheeet compounds are prepared by using pitch or glucose as the binder. The surface of Si/C-Pit is smooth and it is densely coated by pitch, while silicon is exposed on the surface of Si/C-Glu. The sample Si/C-Glu using glucose as the binder displays higher initial reversible capacity and coulombic efficiency, which are 665.3 mAh/g and 70.0%. This is because Si/C-Glu has lower impedance and less irreversible reaction. However, the sample Si/C-Pit using pitch as the binder shows better cycling performance. The capacity of Si/C-Pit is 538.8 mAh/g, while that of Si/C-Glu is only 474.0 mAh/g after 100 cycles. The good cycling performance of Si/C-Pit is due to the dense coating of silicon by pitch. These results indicate that binders affect the microstructure, capacity, initial coulombic efficiency, and cycling performance of Si/C anode materials. This work provides a clue to adjust the electrochemical properties of Si/C anode materials for lithium ion batteries.

Acknowledgments

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