



Short communication

Microstructure and electrochemical performance of Si–SiO₂–C composites as the negative material for Li-ion batteries

Zhiwei Lu, Lianqi Zhang, Xingjiang Liu*

National Key Laboratory of Power Source, Tianjin Institute of Power Sources, No. 18 Lingzhuangzi Road, Tianjin 300381, China

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ABSTRACT

Si–SiO₂–C composites are synthesized by ball milling the mixture of SiO, graphite and coal pitch, and subsequent heat treatment at 900 °C in inert atmosphere. The electrochemical performance and microstructure of the composites are investigated. XRD and TEM tests indicate that the carbon-coating structure of Si–SiO₂–C composites form in pyrolysis process, which can remarkably improve the electrochemical cycling performance. The coal pitch as carbon precursor and graphite demonstrate the same important effect on the Li-alloying/de-alloying property of the Si–SiO₂–C composites. The Si–SiO₂–C composites exhibit the electrochemical reversible Li-alloying/de-alloying capacity of 700 mAh g⁻¹ and excellent cyclic stability even at about the 90th cycle.

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1. Introduction

Recently, the researches on novel negative materials for the Li-ion secondary battery with the capacity superior to conventional carbon material attract considerable interest. Many electrode material families with high capacity including Si-based materials [1,2], alloys [3,4], metal nitrides [5], metal phosphides [6,7] and metal oxides [8,9], have been investigated intensively. Si is one of the most promising anode materials because of its high theoretical capacity (Li_{4.4}Si, 4200 mAh g⁻¹). However, a large volume change of Si particles during electrochemical alloying and de-alloying processes results in the deterioration of electrochemical cyclic performance, which inhibits the commercialization of the Si-based materials in Li-ion batteries. Nowadays, the silicon monoxide (SiO), one of the Si precursors in electrochemical Li-alloying reaction, has been reported to have better reversible electrochemical Li-alloying/de-alloying performance than the Si material, especially after heat treatment at high temperature [10].

It was reported that the electrochemically lithiated SiO process is associated with partial consumption of lithium to form lithium oxide as well as alloying of Si with Li⁺ [11]. The inert Li₂O buffers the large volume expansion on lithium insertion to some extent [12]. The SiO–C composites synthesized through directly ball milling SiO and graphite powders delivered high discharge and charge capacity

values of 1556 and 693 mAh g⁻¹, respectively, in the first cycle [13]. It is worth noting that the electrode also show a good reversible charge capacity value of 688 mAh g⁻¹ at the 30th cycle. At the same time, the superior electrochemical performances of the SiO-based anode material were obtained through heat treatment with precursors of carbon at high temperature. Morita et al. have found that nano Si cluster–SiO_x–C composite, prepared by heating disproportionation of silicon mono-oxide, graphite and the polymerization of furfuryl alcohol at 1000 °C, deliver reversible charge/discharge capacity of 700 mAh g⁻¹, even at 200 cycles [10]. The similar results were also achieved by Doh et al. and Kim et al. [14,15]. In addition, the Si–metal oxide–C composites synthesized by mechanochemical reduction of SiO [16–18] were also investigated. The commercialization of the SiO-based anode material for Li-ion secondary battery has made remarkable improvement by excellent electrochemical Li-alloying/de-alloying cyclic stability of the SiO-based composites.

In this paper, the composites anode was synthesized by ball milling SiO, graphite and coal pitch as carbon precursor, followed by heat treatment process at high temperature. The effect of the graphite and coal pitch on the electrochemical performance of the Si–SiO₂–C composites anode was investigated in detail by electrochemical test and microstructure analysis.

2. Experimental

The composite anode materials were synthesized by ball milling the SiO, graphite and carbon precursor (coal pitch), and a subsequent heat treatment process. The mass ratios of SiO/graphite/coal

* Corresponding author. Tel.: +86 22 23959613; fax: +86 22 23959692.
E-mail address: klpsc@yahoo.com.cn (X. Liu).

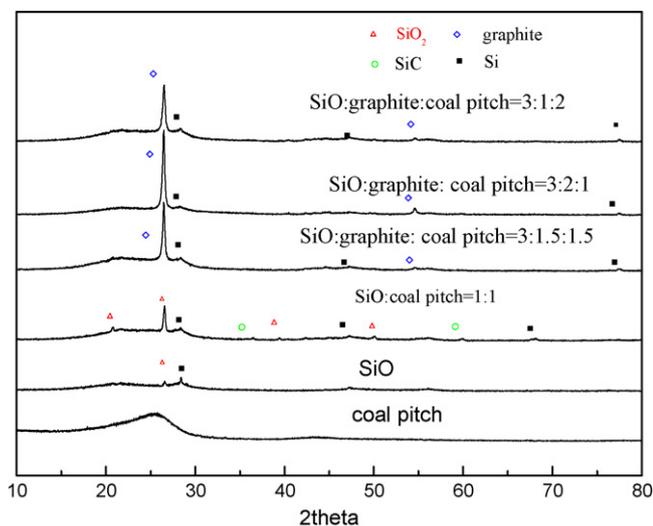


Fig. 1. XRD plots of Si-based composites after heat treatment at 900 °C.

pitch were set to 3/1.5/1.5 (sample A), 3/2/1 (sample B), 3/1/2 (sample C), respectively. Firstly, the ball milling process was performed with a mass ratio of ball to powders of 20:1 at 220 rpm under Ar atmosphere in a cyclohexane solution in a planetary Fritsch P-5 ball mill instrument for 30 h. Then the as-ball milled materials were dried and treated at high temperature of 900 °C at the heating rate of 3 °C min⁻¹ for 3 h in Ar atmosphere. The as-prepared samples were pulverized to 400 meshes. The microstructure analysis of the resultant composites was performed by X-ray diffractometer (XRD, Rigaku D/max-2500) and transmission electron microscopy (TEM, JEM-2010FEF).

The electrochemical characteristics of SiO-based composite materials were examined using CR2430 coin type cells with Li as anode. Electrodes were prepared by 70 wt% active material powder, 15 wt% acetylene black and 15 wt% polyvinylidene fluoride (PVDF). The cells were assembled in an air-dried room. 1.0 mol dm⁻³ LiPF₆ in a mixture of EC:DEC:DMC (1:1:1 in volume) was used as electrolyte for the coin cell. Charge–discharge measurements of the cells were carried out at a constant current of 100 mA g⁻¹ in the potential range of 0.00–1.20 V (vs. Li/Li⁺) using a LAND-CT2001A instrument. Cyclic voltammograms (CVs) conducted using a Salarton SI 1400 electrochemical workstation at 25 °C.

3. Results and discussion

The XRD patterns of SiO–graphite–coal pitch composites, SiO and coal pitch after heat treatment at 900 °C are shown in Fig. 1. In XRD pattern of the heated 50 wt% SiO–50 wt% coal pitch sample, the weak diffraction peaks of SiC, Si and SiO₂ are detected. This result indicates that SiO have been decomposed into SiO₂ and nanoparticle Si at high temperature, in agreement with previous reports [13–15,19]. Subsequently, the trace amount of SiC also forms at high temperature in the case of large quantity of carbon, which serves as the inert material in the electrochemical Li-alloying reaction. A broad peak is only detected in XRD pattern of heated coal pitch sample, indicating that the coal pitch can hardly form crystalline carbon at experimental temperature. Hence, the weak diffraction peak at 2theta value of 26.45° of the heated 50 wt% SiO–50 wt% coal pitch sample, which is hardly indexed as the carbon phase, can be indexed as the hexagonal phase of SiO₂. There are no obvious differences between the heated SiO–graphite–coal pitch and SiO–coal pitch composites. Except for the weak diffraction peaks of Si and SiO₂, the much stronger diffraction peaks detected at 2theta

value of 26.45° should be mainly indexed as graphite phase, and the intensity is consistent with the graphite content in the composites. This XRD results indicate that the Si–SiO₂–carbon composites form during ball milling and subsequent heating processes, and the additional reaction between Si and C is negligible at current experimental conditions. TEM images of the Si-based composites of sample A are presented in Fig. 2. According to mass-thickness contrast, the obvious non-crystalline carbon film with thickness of about 20–50 nm can be found coating on the Si–SiO₂ composite. Undoubtedly, the most of coal pitch should deposit and transform into amorphous carbon film on the surface of the Si-based composite during the ball milling and pyrolysis process. The coating carbon layer on the surface of electrode can not only supply the excellent conductivity capability, but also release the volume expansion during the electrochemical Li-alloying reaction of the electrode. At the same time, the component of graphite and Si–SiO₂ should mostly aggregate inside of Si-based composite, which denotes to the black area in the TEM images.

Cyclic curves of the SiO–graphite–coal pitch composites after heat treatment at the current density of 100 mA g⁻¹ are shown in Fig. 3. The maximal reversible capacities of the Si-based composites in the SiO/graphite/coal pitch mass ratio of 3/1.5/1.5 (sample A), 3/2/1 (sample B) and 3/1/2 (sample C) reach 730, 479 and 550 mA h g⁻¹, respectively. Obviously, the cyclic stability of the samples A and C is superior to the sample B. No remarkable capacity decay is detected in the cyclic curves of the samples A and C, and capacity retention ratio reach 90% even at almost 80th cycle. In a contrast, the electrochemical performance of the samples with low content of coal pitch remains poor. The sample B lost about 40% reversible capacity in 80 cycles. The heated 50 wt% SiO–50 wt% graphite composite demonstrate poor electrochemical capacity of 200 mA h g⁻¹. It is obvious that the coal pitch composition has an important influence on the electrochemical performance of the Si-based negative material. Just as indicated by TEM images, the addition of coal pitch into the SiO–graphite–coal pitch composite is beneficial to the formation of carbon-coating anode with excellent conductivity after heat treatment, leading to the high electrochemical cycle stability. Moreover, the cycling performance of 50 wt% SiO–50 wt% coal pitch composite is not satisfactory, whose reversible capacity reach about 700 mA h g⁻¹ and capacity retention reach 72% at 30 cycles. The rapid capacity degradation implies that proper amount of graphite also play the important role in the electrochemical Li-alloying cycles as the carbon precursor, resulting in the improved cycling stability of carbon-coating Si–SiO₂–C composites. The graphite material inside the Si-based composite, as indicated by TEM images, should enhance the conductivity capacity and release the volume expansion of Si–SiO₂ particles.

The charge/discharge curves of sample A at the current density of 100 mA g⁻¹ are present in Fig. 4. There is obvious difference between the first discharge potential curve and the subsequent ones of the Si–SiO₂–C composite, which Li-alloying processes conduct around 0 and 0.2 V, respectively. It is very clear that the irreversible phase transformation of silicon from crystalline to amorphous state by electrochemically-driven solid-state amorphization occur during electrochemical cycles [1,2,20,21]. That is to say, the crystalline Si is transformed from SiO during the heat treatment process, which is in agreed with the XRD results. In the case of the 50 wt% graphite–50 wt% coal pitch composite treated at the same experimental conditions (Fig. 5), a reversible electrochemical capacity and an irreversible capacity in the first cycle are obtain to 300 and 150 mA h g⁻¹, respectively. Considering the capacity of the Si–SiO₂–graphite–C composites of 700 mA h g⁻¹, it is confirmed that two electrochemical Li-alloying/de-alloying reactions with Si and carbon may be involved and the former reaction is dominant in Si–SiO₂–graphite–C composites.

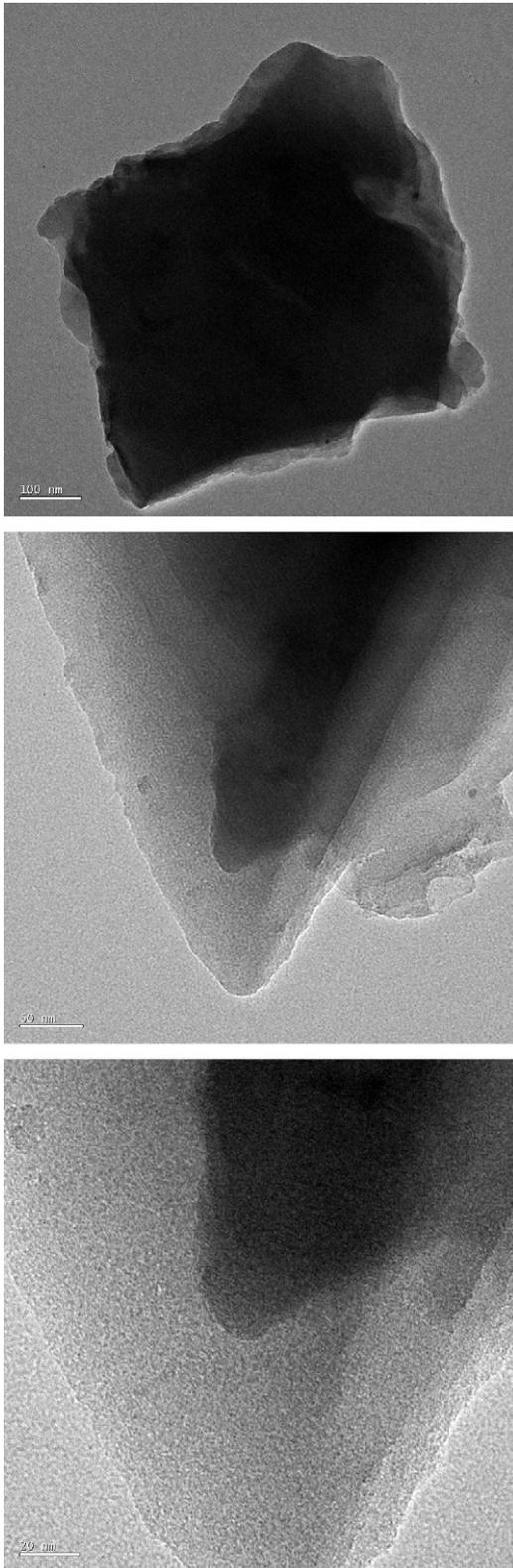


Fig. 2. TEM images of the Si-based composite with the SiO/graphite/coal pitch mass ratio of 3/1.5/1.5(sample A) after heat treatment at 900 °C.

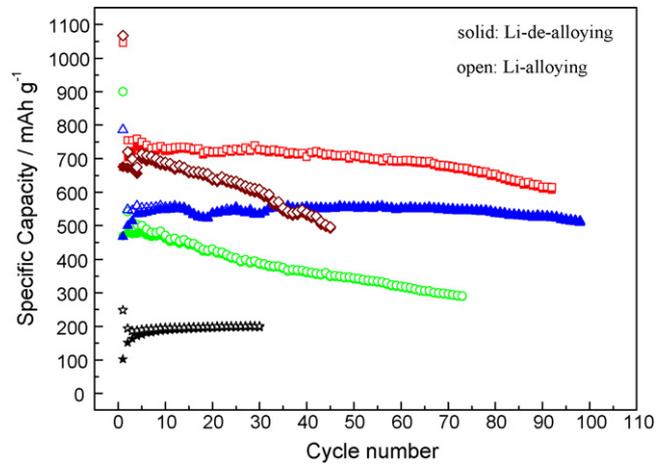


Fig. 3. Cyclic performance of the as-prepared Si–SiO₂–graphite–carbon composites at the current density of 100 mA g⁻¹ (◇: 50 wt% SiO–50 wt% coal pitch; ☆: 50 wt% SiO–50 wt% graphite; △: sample C; ○: sample B; □: sample A).

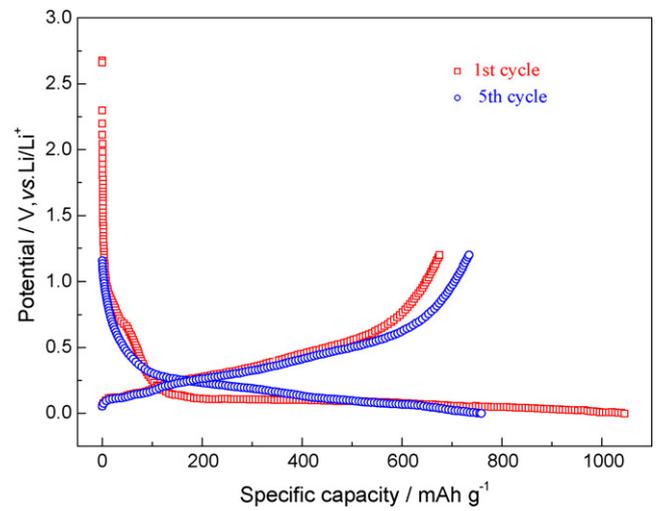


Fig. 4. Charge/discharge curves of heat treated Si composite (sample A) at the current density of 100 mA g⁻¹.

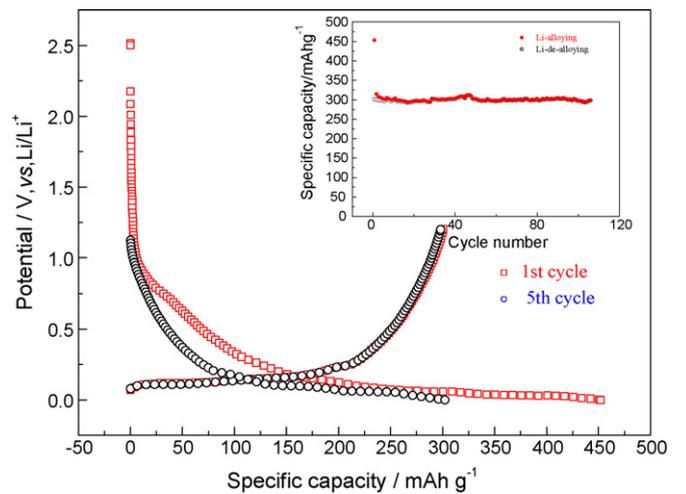


Fig. 5. Charge/discharge curves of heat treated 50 wt% graphite–50 wt% coal pitch composite at the current density of 100 mA g⁻¹. (Cyclic behavior of heat treated 50 wt% graphite–50 wt% coal pitch composite is inserted.)

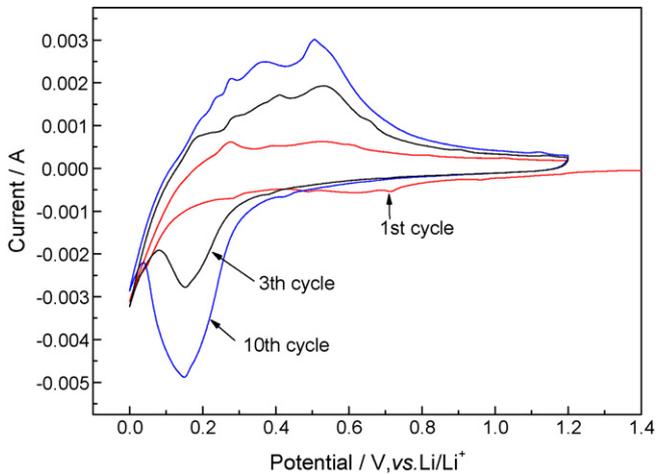


Fig. 6. CV plots of the heat treated Si-based composite (sample A) at the scan rate of 0.1 mV s^{-1} .

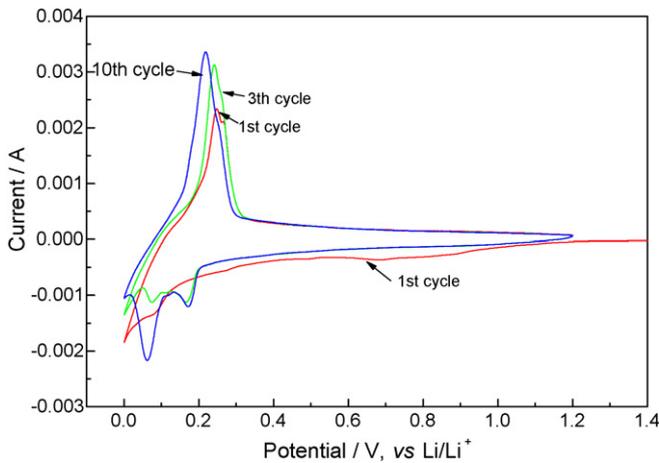


Fig. 7. CV plots of the heat treated 50 wt% graphite–50 wt% coal pitch composite at the scan rate of 0.1 mV s^{-1} .

In order to investigate the electrochemical mechanism of the electrochemical alloying/de-alloying reaction, cyclic voltammograms (CVs) of sample A are shown in Fig. 6. There are multiple peaks and activation processes in the CV curves of Si-composite. Compared with the CV curves (Fig. 7) of the 50 wt% graphite–50 wt% coal pitch composite after heat treatment, it is confirmed that the irreversible cathodic peaks located around 0.4–1.0 V in the first cycle should be related to electrolyte decomposition and SEI formation on the surface of carbon materials; two close anodic peaks located at 0.2 V should related to the electrochemical Li insertion reactions of carbon. In the subsequent cycles, two anodic peaks, located at 0.35 and 0.50 V, respectively, become gradually clear in the anode branches of CV curves, which can be attributed to the de-alloying process of Li_xSi alloys with different compositions [22].

Moreover, the remarkable peaks located at 0.15 V in the cathodic branches of the CV curves, which gradually increase with cycles, should correspond to the multiple electrochemical Li-insertion process of the active Si and carbon components in the Si-based composites. The anodic peaks area of active Si composite is much larger than that of the carbon component, meaning the electrochemical Li-alloying/de-alloying of active Si component is dominant in the electrode reaction.

4. Conclusions

In this work, the Si–SiO₂–carbon composites are synthesized by ball milling the mixture of SiO₂, graphite and coal pitch and subsequent pyrolysis process. The microstructure analysis indicates the as-prepare sample has the carbon-coating structure, which not only buffer the volume change during the Li-alloying/de-alloying reaction of Si particle, but also deliver excellent conductivity. The Si–SiO₂–carbon composite prepared in the SiO₂/graphite/coal pitch mass ratio of 3/1.5/1.5 (sample A), demonstrates excellent cyclic stability at 90 cycles, and the reversible capacity reach ca. 700 mAh g^{-1} . By analysis of CV and charge/discharge curves, it is confirmed that two electrochemical Li-alloying/de-alloying reactions with Si and carbon may be involved and the former reaction is dominant in the carbon-coating Si–SiO₂–graphite–C composites.

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