



High performance silicon carbon composite anode materials for lithium ion batteries

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ABSTRACT

Silicon and silicon containing compounds are attractive anode materials for lithium batteries because of their low electrochemical potential vs. lithium and high theoretical capacities. In this work the relationship between the electrochemical performance of silicon powders and their particle sizes was studied. It is found that the material with nano particle sizes gives the best performance. New silicon/carbon composite anode materials were synthesized and their structures and electrochemical performance were investigated. The results of these studies are reported in this paper.

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1. Introduction

There is a great interest in developing rechargeable lithium batteries with higher energy capacity and longer cycle life for applications in portable electronic devices, electric vehicles and implantable medical devices [1,2]. Many new materials have attracted attentions in recent years, such as $\text{Li}(\text{Ni},\text{Co},\text{Mn})\text{O}_2$, $\text{LiCo}_0.2\text{Ni}_0.8\text{O}_2$, LiFePO_4 , etc. for cathode [3,4] and $\text{Li}_2\text{Ti}_5\text{O}_{12}$, SnO/SnO_2 , and nano-alloy materials for anode [5–7].

Carbon-based materials are widely used in commercial lithium-ion batteries as the anode. However, the theoretical gravimetric capacities of these materials are limited (372 mAh g^{-1} , LiC_6). Intense research activities are underway to develop higher capacity anode materials for the next generation of lithium ion batteries. Silicon and silicon containing compounds are attractive candidates due to their high theoretical specific capacities (about 3580 mAh g^{-1} for $\text{Li}_{15}\text{Si}_4$ [8,9]).

In this work the relationship between the electrochemical performance of silicon powders and their particle sizes was studied. It is found that the material with nano particle sizes gives the best performance. New silicon/carbon composite anode materials were synthesized and their structures and electrochemical performance were investigated. The results of these studies are reported in this paper.

2. Experimental

Two kinds of silicon powders were used as starting materials: Yuan Tong (Zhejiang Wynca Chemical Group Co., Ltd., China) silicon powders (with average particle size less than $10 \mu\text{m}$), and Shenyang (Institute of Metal Research, Chinese Academy of Sciences) nanometer silicon powders. The particle sizes of Shenyang nanometer silicon powder are between 30 nm and 50 nm. Both of them have a silicon content higher than 99%. The Yuan Tong silicon powders were ball milled for 15 h in a high energy ball mill. After milling, the particle sizes were reduced to less than $1 \mu\text{m}$. Qingdao (Qingdao Taineng Graphite Co., Ltd., China) graphite powders (with $22 \mu\text{m D}_{50}$ particle size) were used as conducting agents.

Si/C composite powders were synthesized as following: pitch (Shanghai Dongdao Carbon Chemical industry Co., Ltd., China) was first dissolved in Pyridine, and then pure silicon powders were added to make the mixture. The solvent was evaporated (by heating) while the mixture was being stirred to get a solid blend. The blended precursor was heated to 1000°C under a nitrogen atmosphere at a heating rate of 3°C min^{-1} . After pyrolysis at 1000°C for 2 h, the furnace was cooled to room temperature. The final product, a Si–C composite material, was ground and sieved. The samples obtained were characterized by X-ray diffraction (XRD, X'Pert PRO, PANalytical). The morphology of the ball-milled powders was examined using a scanning electron microscope (SEM, JSM-6380LV, JEOL).

The electrode recipes using pure silicon powder as active materials were 20% Super-P (SP) + 20% poly(vinyl di-fluoride) (PVDF) + 80% pure silicon powders. The electrode recipes using Si/C composites as

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active materials were: 5% Super-P + 10% PVDF + 85% silicon carbon composite.

After coating, the electrodes were pressed and then dried for 8 h at 120 °C in an oven.

Several different recipes were used for the silicon carbon composites. The silicon powder contents in the composites were ranged from 1% to 7%, the carbon pyrolyzed from pitch was fixed at 6%, and graphite made up the remaining balance of the 87–93%.

Coin cells (LIR2430) were used to study the electrochemical performance of the pure silicon powder and composite Si/C materials. The electrodes were cut into discs (18 mm in diameter) with about 10 mg active materials. Coin cells were assembled in a dry room using Ube 25 μm separators, 1 M LiPF₆ in EC/DMC (1:1, by Vol.) as electrolytes, and Li foils as counter electrodes. The charging voltage limit was 2.0 V and the low voltage limit (discharge) is 0.005 V.

3. Results and discussion

3.1. Performance of pure silicon powder

Scanning electron micrographs of the pure silicon powders were taken to compare the morphologies of different silicon powders used in this study. Fig. 1 shows the different morphologies of Yuan Tong silicon powder before and after 15 h milling in comparison with the Shenyang silicon powders. Before milling the Yuan Tong silicon powders have sharp particle edges as shown in Fig. 1(a). The edges become much smoother and the particles are more flocculated after ball milling. In contrast, the Shenyang silicon powder particles are flocculated even in the as received state. Of the three kinds of pure silicon powders, Shenyang nanometer silicon powders have the best particle size distribution consistency (between 30 nm and 50 nm). Both Yuan Tong silicon powders and milled Yuan Tong silicon powders have much wider particle size distributions.

Fig. 2 shows the XRD pattern of the three kinds of silicon powers. The red color is for Yuan Tong silicon powders, the blue one is for milled Yuan Tong silicon powders and the green one is for Shenyang nanometer silicon powders. All the three samples are crystalline. From the Full Wave at Half Maximum (FWHM) of the Bragg peaks in their XRD patterns, we can see that the crystal sizes of the Yuan Tong silicon is significantly reduced after ball milling, as expected. The crystal sizes of Shenyang nano-crystalline silicon sample are smaller than the Yuan Tong silicon powders, but almost the same as the milled Yuan Tong sample.

The results of the electrochemical performance for pure silicon powders are shown in Table 1 and Fig. 3. The reversible capacity of Yuan Tong sample is increased substantially by milling. The reversible capacity and first efficiency of Yuan Tong samples increased from 1058 mAh g^{-1} and 40.8% to 1811 mAh g^{-1} and 59.7%, respectively, through ball milling. Shenyang nanometer silicon sample shows the best performance among the three with

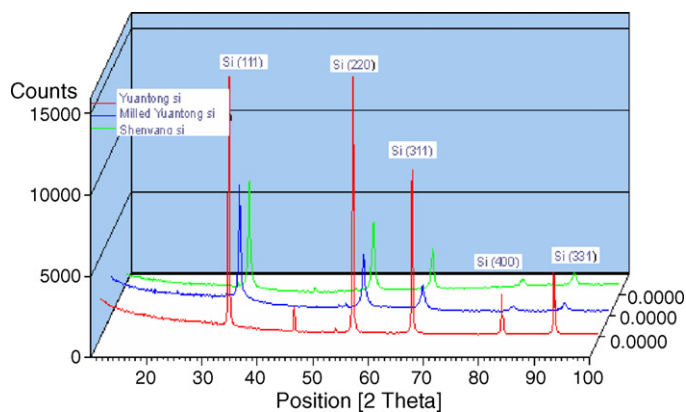


Fig. 2. XRD of silicon power.

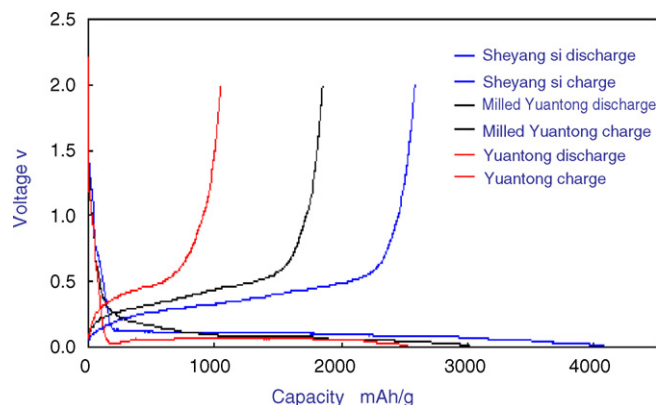


Fig. 3. Charge and discharge curve for silicon.

2465 mAh g^{-1} reversible capacity and a 64.0% first cycle efficiency, respectively.

The major factors affecting the electrochemical performance are the crystallite sizes and crystallite size distributions of these three samples. When the crystallite size is reduced by milling the Yuan Tong sample, the performance improved compared with the unmilled counter part. Comparing with the milled Yuan Tong sample, the Shenyang sample shows superior performance due to its better crystal size distribution, even though the average crystal size of these two are similar. Reports in the literature showed that amorphous silicon sample has a better electrochemical performance than crystalline silicon [5,10]. In this work we demonstrated that smaller sizes and better particle size distribution can also improve the electrochemical performance for crystalline silicon samples.

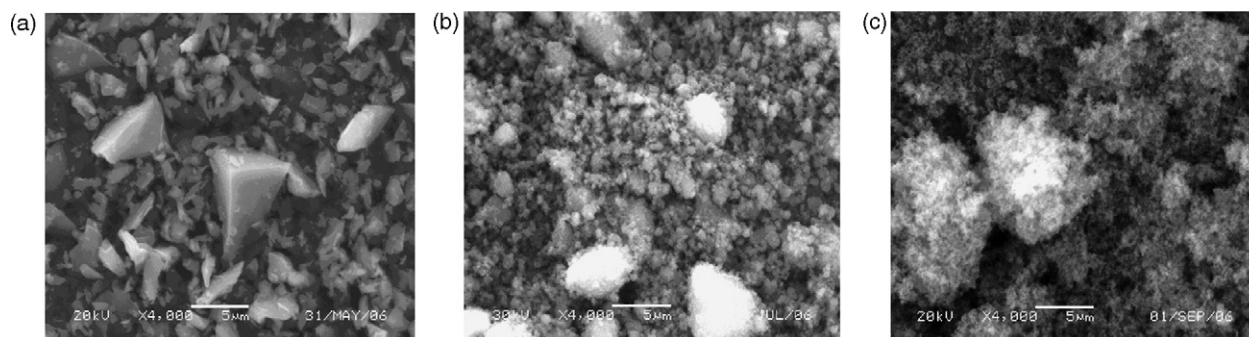


Fig. 1. SEM of silicon power: (a) Yuan Tong silicon powder before milling; (b) Yuan Tong silicon powder after 15 h milling; (c) Shenyang nanometer silicon powder.

Table 1
The electrochemical performance of the tree type silicon samples.

Silicon powder type		First discharge capacity (mAh g^{-1})	First charge capacity (mAh g^{-1})	First efficiency (%)
Yuan Tong	Before milling	2591	1058	40.8
	After 15h milling	3033	1811	59.7
Shenyang nano-particles		3853	2465	64.0

Table 2
The electrochemical performance of silicon carbon composite materials.

Recipe Si:graphite:pitch	Discharge capacity (mAh g^{-1})	Charge capacity (mAh g^{-1})	First cycle efficiency (%)
1:93:6	421	358	85.2
2:92:6	445	378	84.9
3:91:6	467	398	85.3
4:90:6	460	386	83.9
5:89:6	461	383	83.0
6:88:6	472	393	83.1
7:87:6	579	478	82.6

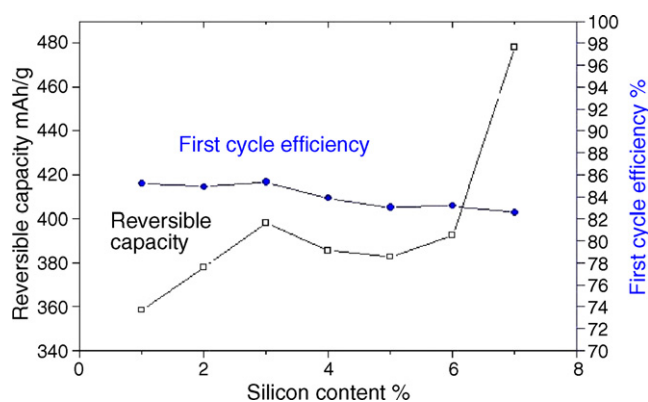


Fig. 4. The relationship between silicon content and performance.

3.2. Performance of silicon/carbon composite

In order to find out the optimized amount of silicon carbon composites for the best electrochemical performance, several different recipes were used with silicon powder content ranged from 1% to 7%, the carbon pyrolyzed from pitch was fixed at 6%, and graphite for the remaining 87–93%. Table 2 and Fig. 4 show that the reversible capacity goes up and the first efficiency goes down with increasing silicon content. The highest first discharge capacity of 579 mAh g^{-1} was obtained at 7% silicon content. The reversible capacity increased from 358 mAh g^{-1} to 478 mAh g^{-1} when the silicon content went from 1% to 7%, while the first cycle efficiency decreased from 85.2% to 82.6%. The data show that the reversible capacity increases significantly in the studied range of silicon content while the first cycle efficiency decreases gradually. The data shows that more silicon added into the carbon can be used to increase the reversible capacity if the small reduction of the first cycle efficiency is acceptable.

Table 3
SP content effect on the electrochemical performance of composite.

Coin cell recipe	Capacity from all components (mAh g^{-1})		Si/C capacity (mAh g^{-1})		First cycle efficiency (%)
	Discharge	Charge	Discharge	Charge	
Si/C + 5% PVDF	473	284	497	299	60.6
Si/C + 5% PVDF + 5% SP	536	452	589	497	84.3
Si/C + 10% PVDF + 10% SP	512	423	615	508	82.6
Si/C + 15% PVDF + 15% SP	545	435	709	566	79.9
Si/C + 20% PVDF + 20% SP	534	413	747	578	77.3

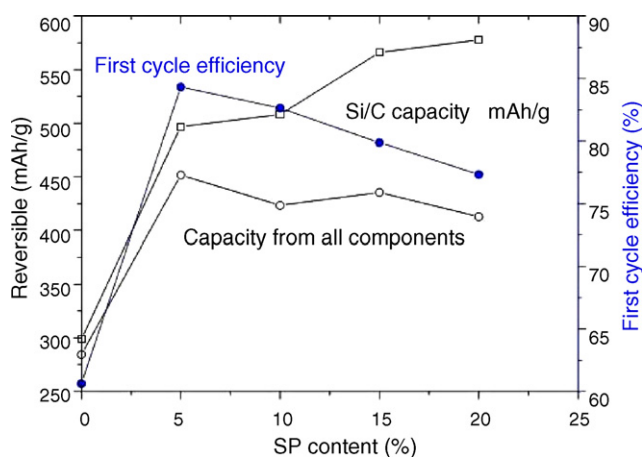


Fig. 5. SP content effects on the performance of composite.

The effects of the conductive agents were also studied. By comparing the results of the electrodes using Super-P and SFG-6, it was found that SP is more effective in increasing the conductivity than SFG-6, probably because of the higher surface area of SP makes better contact with the fine silicon powders.

In order to find out the effects of the content of the conductive agents on the electrochemical performance, samples with SP content varied from 0% and 20% at a fixed content (6%) of Si/C composite were studied. The first charge–discharge capacities and efficiency are shown in Table 3 and Fig. 5. The reversible capacity of the Si/C composite increases from 299 mAh g^{-1} to 578 mAh g^{-1} when SP content increased from 0% to 20%, however, the reversible capacity calculated for total materials in the electrode (all the components: Si/C + PVDF + SP, with the additional contribution from SP) reaches a maximum of 452 mAh g^{-1} when the SP content is 5%. When the SP content was increased above 5%, the reversible capacity of total materials in the electrode decreases although the

Table 4

The yields of pyrolyzed carbon after pitch carbonization and their electrochemical performances.

Pitch type	BTR pitch	Ningxia pitch	Shanghai pitch
Softening point (°C)	70	110	250
Yield of carbon (%)	29.8	46.4	59.2
Discharge capacity (mAh g ⁻¹)	247	298	324
Charge capacity (mAh g ⁻¹)	190	221	246
First cycle efficiency (%)	77.0	74.1	75.8

reversible capacity of the Si/C composite itself increases. Using our optimum recipe with 5% SP, the reversible capacity of the Si/C composite is 497 mAh g⁻¹ and the reversible capacity of total electrode is 452 mAh g⁻¹ with a 84.3% initial efficiency.

These results show that the electrochemical performance of the Si/C composite is worst with no SP at all and best with 5% SP. The benefits of SP can be attributed to the improved electronic contact of the Si/C composite by SP, while the higher irreversible capacity might be caused by the solid electrolyte interphase formation at the SP surface. Therefore the Si/C composite with 5% SP was used in coin cells for the rest parts of experiments.

Three different Chinese pitches (from BTR, Shanghai and Ningxia) were used to study the differences in cell performance of Si/C composites caused by pitches.

Softening points and carbonization yields of these three pitches are shown in Table 4. The carbonization was performed using a heating rate of 2 °C min⁻¹ to 1000 °C and soak for 2 h inert gas. The electrochemical performance of the three carbons produced from the pitches (carbon only, no Si powders at all) is also shown in Table 4. The first cycle efficiencies for the different pitches are not significantly different. However, the reversible capacities are quite different. The highest capacity is 246 mAh g⁻¹ for the Shanghai pitch, while the lowest capacity is 190 mAh g⁻¹ for the BTR pitch.

In order to evaluate the effects of the different of pitches on the electrochemical performance of the resulting Si/C composites, Si/C composites were made by using 10% of three different pitches with 10% silicon powder and about 80% graphite. The coin cell electrode recipe was 5% SP + 5% PVDF + 90% of above Si/C composites. Table 5 and Fig. 6 show that the electrochemical performance of Shanghai Pitch based Si/C composite is the best, with a reversible capacity of 454 mAh g⁻¹ and a first cycle efficiency of 80.4%. Reversible capacity and the first cycle efficiency of BTR pitch based Si/C composite is the lowest, with a 428 mAh g⁻¹ reversible capacity and a 76.9% first cycle efficiency, respectively. Ningxia pitch based composite is in the middle.

Fig. 7 shows the XRD patterns of the Si/C composites derived from the three different pitches. Table 6 gives the parameters of the crystallograms. All three Si/C composites have almost the same 2θ angle positions for the Bragg reflections of the graphite. The Full

Table 5

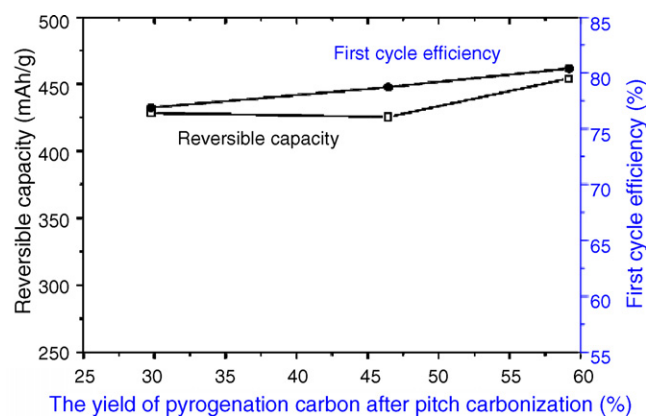
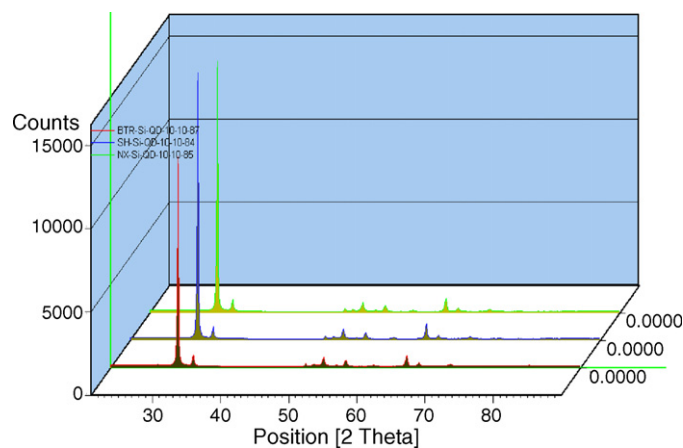
Performance of three different pitches.

Recipe	Discharge capacity (mAh g ⁻¹)	Charge capacity (mAh g ⁻¹)	First cycle efficiency (%)
BTR pitch:Si:graphite = 10:10:87	557	428	76.9
Ningxia pitch:Si:graphite = 10:10:85	540	425	78.7
Shanghai pitch:Si:graphite = 10:10:84	565	454	80.4

Table 6

The parameters of crystallogram of three different Si/C composites.

Sample	Pos. (°2Th.)	d-Spacing (Å)	FWHM (°2Th.)	Area (cts*°2Th.)	Backgr. (cts)	Height (cts)
BTR-Si-QD-10-10-87	30.9086	3.3569	0.2376	27854.81	1311.03	87925.5
NX-Si-QD-10-10-85	30.9097	3.3568	0.2126	28324.80	1049.00	104965.2
SH-Si-QD-10-10-84	30.9093	3.3568	0.1909	29698.65	1391.01	122415.2

**Fig. 6.** The performance of composite vs. yield of carbon.**Fig. 7.** The XRD of three different pitch composites.

Wave at Half Maximum (at 30.91°) of Shanghai pitch composite is the smallest, presumably because the crystallinity of Shanghai pitch based composite is the highest after carbonization.

SEM images of the three Si/C composites are shown in Fig. 8. Less silicon powders was observed on the surface of graphite for Si/C composite derived from Shanghai pitch than for those derived from the other two pitches. The higher carbonization yields of the Shanghai pitch may have covered more silicon powders.

Four different Si/C composites were tested in coin cells. In addition to the two in-house made composites using 84% graphite, 6% carbon from pitch and 10% of either Yuan Tong milled Si or Shenyang nano-Si, two other Si/C composites obtained from Supplier A and B were also tested. The electrode recipe was 5% SP + 5% PVDF + 90% Si/C composites, and the electrolyte was 1 M LiPF₆ in EC:DMC (1:1,

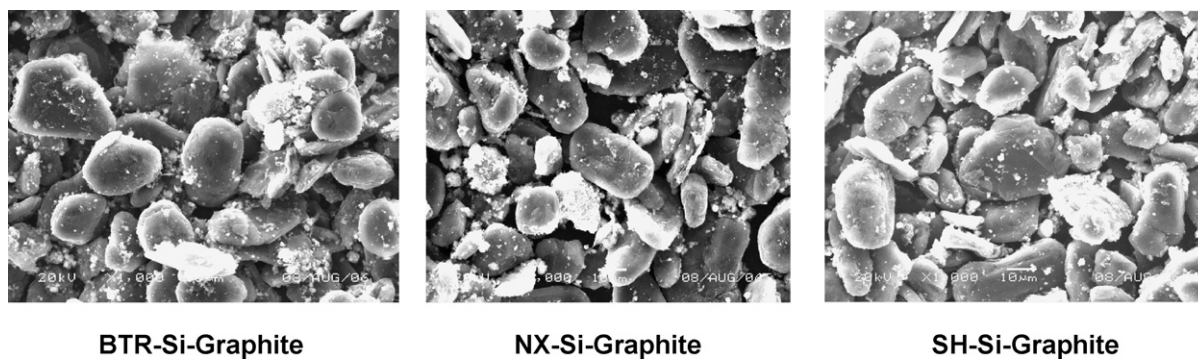


Fig. 8. SEM of three different pitch based composites.

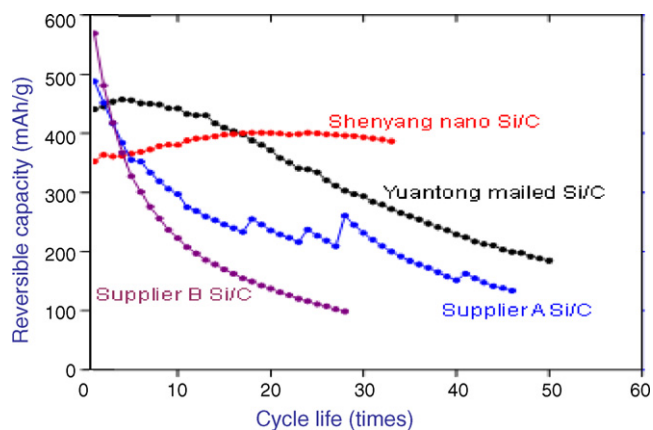


Fig. 9. Performance of four different Si/C composites.

by Vol.). Electrochemical performance results of the four different Si/C composites are shown in Fig. 9.

Fig. 9 shows that Shenyang nano Si/C composite has the best cycling performance. The initial capacity of the first cycle

of Shenyang nano Si/C composite was the lowest (only around 350 mAh g^{-1}), but increased as the cycling continues, reached the maximum (400 mAh g^{-1}) at 20th cycle, and kept in that level for more cycles with very low fading rate. The second best cycling performance is the Si/C composite from milled Yuan Tong Si powders. The initial capacity of the first cycle for this composite was 450 mAh g^{-1} , reached the maximum (480 mAh g^{-1}) at 5th cycle, but faded rather rapidly at a rate about 6 mAh per cycle. The initial first cycle capacities of composites from other suppliers (both A & B) were higher than the in-house made ones at 490 mAh g^{-1} and 590 mAh g^{-1} , respectively. However the fading rates for these two composites were quite large.

After cycling, the SEM images were taken again from the surface of Si/C composites as shown in Fig. 10. The morphologies of Shenyang Si/C and Yuan Tong Si/C composites are quite different. After cycling, the sharp edged large primary particles in Yuan Tong Si/C composite disappeared and agglomerated secondary particles formed. In contrast, the morphology changes in Shenyang Si/C composite are much smaller. This is attributed to the fracturing of large silicon particles in the Yuan Tong Si/C composite. The fractured particles with poor electrical contact cause the loss of capacity during cycling. Nanometer silicon powders are much more resistant to fracturing and have much better cycling per-

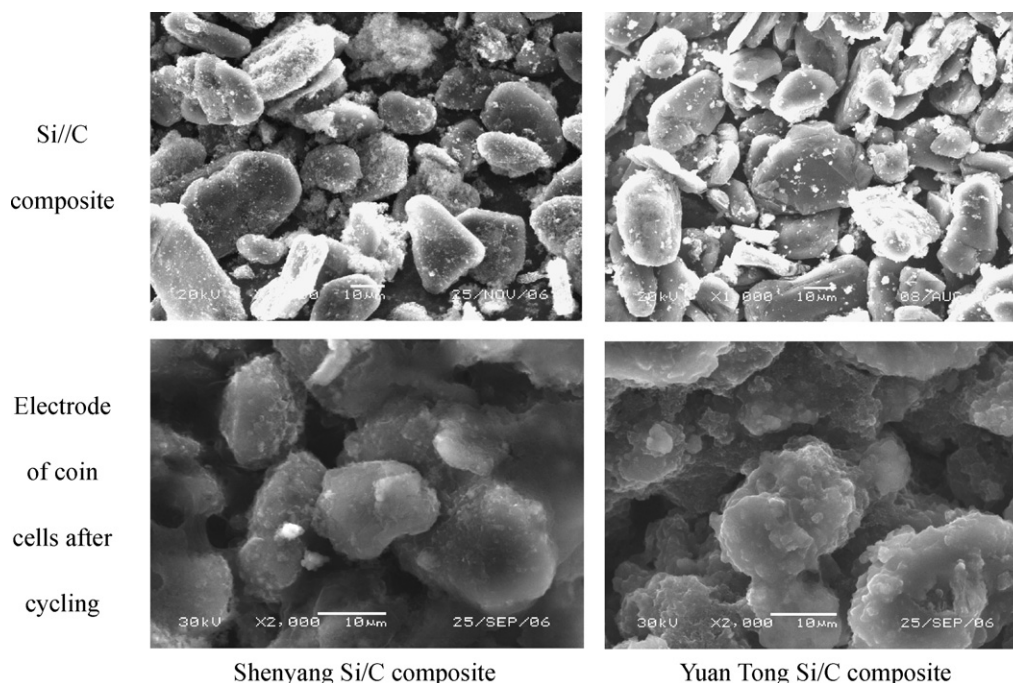


Fig. 10. SEM of Si/C composites before and after cycling.

formance than the sample containing large particle sized silicon powders.

4. Conclusion

The decreased particle sizes of the silicon crystal powders produced by ball milling can improve the reversible capacity and cycling performance of the Si/C composites, as shown for the Yuan Tong samples. The Si/C composite made from Shenyang nanometer crystal has even better electrochemical performance than the milled Yuan Tong sample. This might be attributed to the narrower particle size distribution of the Shenyang nanometer silicon powders.

Silicon and SP content also affects the performance of Si/C composite. SP can improve electronic contact but may cause higher irreversible capacity loss due to the SEI formation if too much is used. The type of pitches also affects the performance of Si/C composite. Shanghai pitch with higher softening point and high carbonization yield can cover more silicon particles, and exhibited better electrochemical performance than the others.

Compared with Shenyang nanometer Si/C composite, the particles in Yuan Tong Si/C composite is easier to fracture during cycling, result in poor cycling life. Si/C sample made from Shenyang nanometer crystal silicon powders has better electrochemical per-

formance than the milled Yuan Tong sample, probably due to narrower particle size distribution.

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