

Si-doped composite carbon as anode of lithium ion batteries^①

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Abstract: Si-doped composite material was prepared by coating artificial graphite with the mixture of phenol resin and polysilicone and following with heat-treatment at 1 050 °C in an argon gas atmosphere. The structure and characteristics of the composite carbon were determined by means of XRD, SEM, BET surface area and electrochemical measurements. The new carbon material has a disordered carbon/graphite composite structure, with silicon doped in the disordered carbon. Compared with the pristine graphite, the electrochemical performance is improved for the Si-doped composite carbon with large reversible capacity of 312.6 mAh/g, high initial charge/discharge efficiency of 88.61%, and excellent cycle stability. The prototype batteries using the composite carbon as anode material have large discharge capacity of 845 mAh and high capacity retention ratio of 95.80% at the 200th cycle.

Key words: Li-ion battery; carbon; anode; Si-doped; capacity

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1 INTRODUCTION

Advanced rechargeable lithium ion batteries are attractive for use in consumable electronic and electric vehicles (EV) because of favorable combination of voltage, energy density, cycling performance, etc. Worldwide efforts have been devoted to the study of carbon materials as anodes in these batteries. Among a variety of carbon materials, graphite appears to be the most suitable candidate because of its high capacity, low and flat potential^[1, 2]. Nevertheless, there are still some problems with respect to the destruction of the carbon structure (exfoliation) during lithium intercalation and the resulting decrease of specific energy^[3-5]. Recently, some attempts to enhance the electrochemical performance have been made and much improvements have been achieved by mild oxidation^[6], Ni microencapsulation^[7], ball milling^[8] and addition of other elements such as B^[9], Si^[10] etc.

In the present work, disordered carbon/graphite composite material doped with Si is obtained by coating artificial graphite with the mixture of phenol resin and polysilicone and following with heat-treatment in an argon gas atmosphere. Application of the composite carbon material as anodes in lithium ion batteries is investigated.

2 EXPERIMENTAL

The pristine artificial graphite is provided by Xingtai Carbon Co., Henan province, China, which is made from petroleum coke. In a kneader, the finely ground artificial graphite powder was mixed with

phenol resin (10 %) and polysilicone (3% for Sample A and 5% for Sample B) dissolved in an organic solvent, stirred enough and hardened. The graphite coated with mixture of phenol resin and polysilicone was then heat-treated up to 1 050 °C in an argon gas atmosphere.

Powder X-ray diffraction (XRD) measurements were made with a Rigaku diffractometer equipped with Cu K_α radiation and a diffracted-beam monochromator. Brunauer-emmer-teller (BET) surface area measurements were made by using a Quantacrome monosorb surface area analyzer. Elemental analysis was performed by means of colorimetry method. Scanning electron micrographs (SEM) were obtained with a Hitachi S530 spectrometer. The average particle diameter was measured by using Malvern microplus particle size analyzer.

The Si-doped composite carbon material, acetylene black as electric conductor and poly(vinylidene difluoride) (PVDF) as binder were mixed together. The carbon electrodes were prepared by spreading the above mixture onto a copper foil substrate. The electrodes were then dried at 105 °C for 48 h under vacuum and pressed between two flat steel plates at about 20 MPa. The preparation of LiCoO₂ electrode was the same as that of carbon electrode except LiCoO₂ as active material and aluminum foil as current collector. A porous membrane (Celgard 2300) of 20 μm thickness was used as a separator, and the electrolyte was 1 mol/L LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio (EC: DMC = 1: 1).

Charge/discharge tests of carbon electrodes were

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performed in the three-electrode cells. The carbon was selected as the working electrode and the lithium metal served as both the counter and the reference electrode. Current density of 0.1 mA/cm^2 was used for the three-electrode cells between 0.005 V and 1.5 V .

Prototype prismatic battery of 063448 size was prepared by assembling the carbon anode, LiCoO_2 cathode, electrolyte and membrane into a stainless-steel case. The charge/discharge characteristics and cycling performance of prototype batteries with different carbon anodes were investigated. The test procedures for the prototype batteries were as follows: 1) The batteries were charged to 4.2 V at a constant current of 800 mA (1C rate); 2) the voltage were held at 4.2 V until the current density decreased to $< 25 \text{ mA}$; 3) the batteries were rested for 10 min ; 4) the batteries were discharged at a constant current of 800 mA to 2.75 V , and 5) the cells were rested for 10 min ; then the cycles were repeated.

3 RESULTS AND DISCUSSION

3.1 Physical characteristics

Scanning electron micrographs (SEM) of the untreated artificial graphite and graphite coated with disordered carbon are shown in Figs. 1(a) and (b) respectively. These two micrographs show that surface morphology of the graphite is retained and becomes smooth after disordered carbon coating. Further-

more, the amount of small particles decreases and the particle sizes appear to increase after disordered carbon coating, which is also shown in Table 1. Therefore, we conclude that a thin film of disordered carbon is formed on the surface of graphite by coating the mixture of phenol resin and polysilicone and heat treatment at $1050 \text{ }^\circ\text{C}$. In other words, a new carbon material with disordered carbon/graphite composite structure is obtained.

Table 1 shows the results of elemental analysis and parameters of physical characteristics for the samples studied. The average diameter, specific surface area and tap density of composite carbon materials are larger than those of the untreated artificial graphite. The increase of average diameter is attributed to the reunion of some graphite particles and the reduction of small particles resulted from the modification. The formation of the disordered carbon film on the surface of graphite results in much larger surface area. The composite carbon has larger tap density for its smooth surface morphology and suitable particle size distribution, which is favorable for tight stack.

XRD measurements also exhibit the existence of disordered carbon in the composite carbon materials, which is shown in Fig. 2. For sample A and sample B, the ratios of intensity of (100) and (101) peaks to that of (002) and (004) peaks are increased compared to those of sample S0, indicating that the stacking of carbon on the surface of graphite is decreased because of a thin film of disordered carbon coated on the graphite.

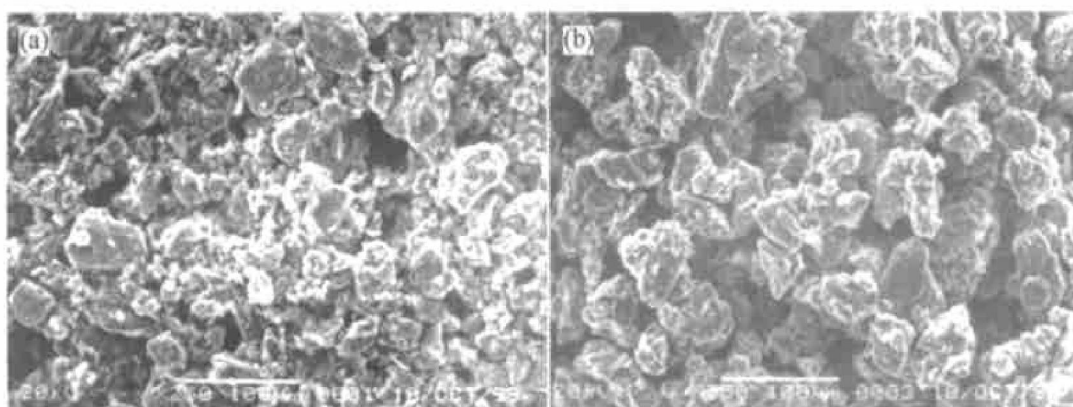


Fig. 1 SEM micrographs of artificial graphite(a) and composite carbon material(b).

Table 1 Results of elemental analysis and physical characteristics of samples

Sample No.	Polysilicone coating/ %	$w(\text{Si})/\%$	Average diameter/ μm	Specific surface area/ $(\text{m}^2 \cdot \text{g}^{-1})$	Tap density/ $(\text{g} \cdot \text{cm}^{-3})$
S0	Untreated	0	21.34	2.74	0.952
A	3	0.13	28.67	12.05	0.981
B	5	0.22	31.14	12.53	1.016

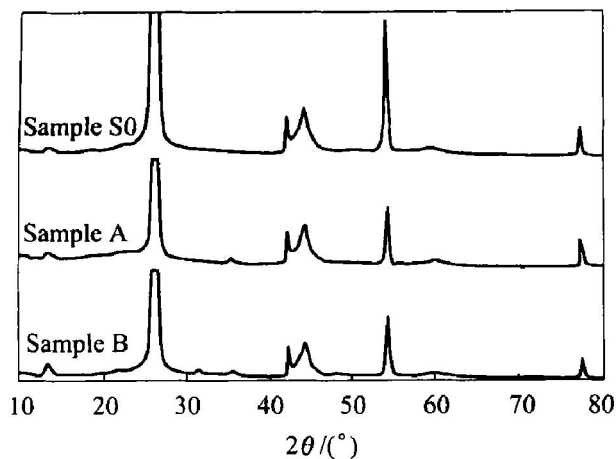


Fig. 2 XRD patterns for artificial graphite(S0) and composite carbon materials(A and B).

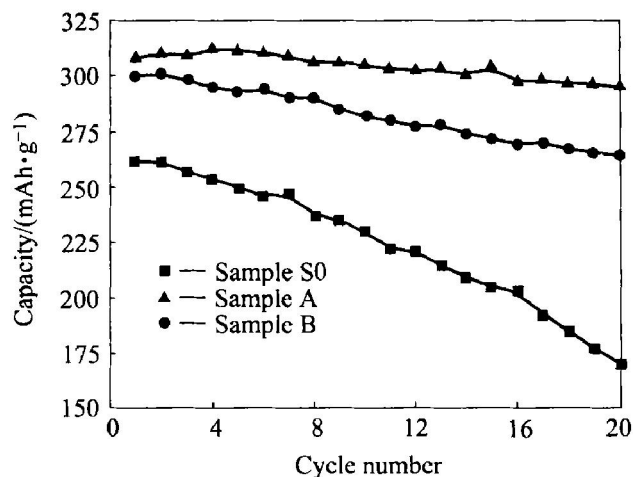


Fig. 3 Cycling performances of artificial graphite(S0) and composite carbon materials(A and B)

3. 2 Electrochemical performances

As results of the change in structure and surface characteristics, the electrochemical performances of modified graphite are improved. For composite carbon materials, the irreversible capacity is remarkably decreased and reversible capacity is increased compared with that of untreated graphite, which is shown in Table 2. Therefore, the coulombic efficiency at the first charge/ discharge cycle for the composite carbon electrodes is higher than that for the untreated graphite electrode. Fig. 3 shows that the composite carbon electrodes have improved cycling performance. After 20 charge/ discharge cycles, the capacity retention ratio of composite carbon electrodes is increased 23. 1%~30. 9% compared with that of untreated graphite electrode. In addition, the composite carbon coated with 10% phenol resin and 3% polysilicone has the best electrochemical characteristics among the three carbon materials.

The improved performances are attributed to the better SEI film formed on the surface of composite carbon electrode at the first charge/ discharge cycle. It is believed that the solid electrolyte interphase film results from the decomposition of the electrolyte on the carbon electrode during the initial charge/ discharge cycle. The electrochemical performances of carbon electrodes are remarkably affected by

the structure and characteristics of the SEI film. The studies^[11-13] conclude that the edge sites of graphite hexagonal arrays are the more active(catalytic) sites for electrolyte decomposition than those at basal plane. In the case of graphite, the hexagonal arrays form well-developed layer structures, and there is much difference between the basal plane and the edge sites. As to the composite carbon materials, the graphite is coated with a layer of disordered carbon, and the uniformity of surface structure is improved because of the well-distributed edge sites. Therefore, a thin, even and stable SEI film can be formed for the composite carbon during the first charge/ discharge cycle, which depresses the decomposition of electrolyte and keeps structure of carbon from deterioration. So low irreversible capacity loss and improved cycling capability are obtained for the composite carbon electrodes. Furthermore, the nanodispersed silicon in the disordered carbon layer has also increased the capacity of the composite carbon materials by alloying with lithium.

3. 3 Performance of prototype batteries

Prototype prismatic batteries of 063448 size with different carbon anodes were assembled and performances of the prototype batteries were meas-

Table 2 Electrochemical performances of different carbon electrodes and prototype batteries

Sample No.	Three electrode cells				Prototype batteries of 063448 size		
	Charge capacity/(mAh·g ⁻¹)	Discharge capacity/(mAh·g ⁻¹)	Coulumbic efficiency/%	Capacity retention (20cycles) / %	Discharge capacity/(mAh·g ⁻¹)	Average discharge voltage at 1C rate/ V	Capacity retention (200cycles) / %
S0	347.5	262.4	75.55	64.89	774.5	3.652	63.08
A	352.8	312.6	88.61	95.78	845	3.718	95.80
B	351.6	303.7	86.38	88.00	-	-	-

ured to gain more insight into the electrochemical characteristics of Si doped composite carbon material.

Because of the low irreversible capacity loss and good SEI film formed at the first charge/discharge cycle, the prototype batteries using composite carbon anodes have larger discharge capacity, higher discharge voltage and more excellent cycling performance in comparison with those using untreated graphite anodes, which is shown in Fig. 4, Fig. 5 and Table 2. Therefore, the Si doped composite carbon is an attractive anode material for lithium ion batteries.

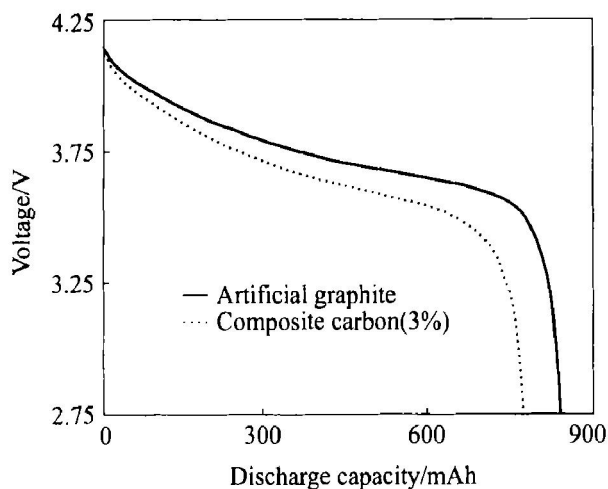


Fig. 4 Discharge curves of prototype batteries at 1C rate

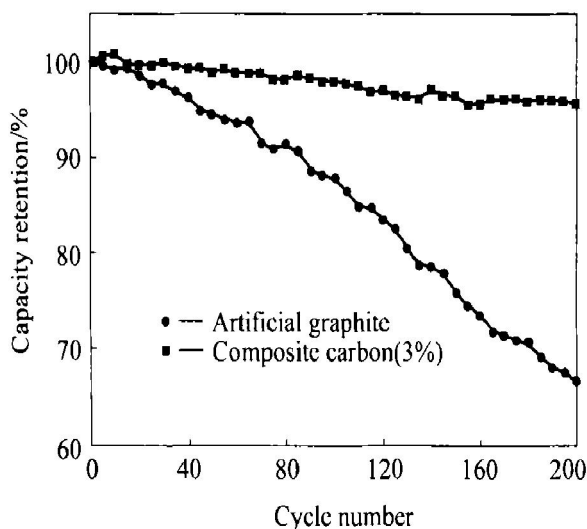


Fig. 5 Cycling performances of prototype batteries in fast charge/discharge pattern

4 CONCLUSIONS

1) Composite carbon materials doped with Si have been prepared by coating the artificial graphite with the mixture of phenol resin and polysilicone and heat treatment at high temperature. A layer of disordered carbon is formed on the surface of graphite.

2) The Si doped composite carbon materials have improved electrochemical characteristics compared with

the untreated graphite. Because of the better SEI film formed on the surface of the composite carbon, the electrodes have larger reversible capacity and coulombic efficiency at the first charge/discharge cycle, and better cycling capability.

3) Prototype prismatic batteries of 063448 size were assembled to gain more insight into the electrochemical characteristics of different carbon materials. The prototype batteries using composite carbon anodes have larger discharge capacity, higher discharge voltage and more excellent cycling performance.

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