

Effects of modification on performance of natural graphite coated by SiO₂ for anode of lithium ion batteries

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Abstract: A stable silicon dioxide film was coated on the surface of natural graphite anode by sol-gel method with Si(OCH₂CH₃)₄, and effects of modification on performance of natural graphite were investigated. The structure and properties of graphite samples were determined by X-ray diffractometry(XRD), scanning electron microscopy(SEM), energy-dispersive X-ray spectroscopy(EDS) and electrochemical measurements. The modified graphite shows mainly the layer structure, and silicon dioxide film is amorphous. Compared with the pure natural graphite, the modified graphite exhibits the higher specific capacity of 366 mA·h/g. After 40 charge-discharge cycles, the capacity retention ratio of the modified graphite reaches 99.55%, while that of natural graphite is only 83.04%. The results indicate that the surface modification of natural graphite by SiO₂ is effective for improving the electrochemical performance of the natural graphite anode for lithium ion batteries.

Key words: lithium ion battery; silicon dioxide; anode material; graphite

1 Introduction

Many types of carbonaceous materials have been studied as anodes of lithium ion batteries during the past several years. Graphitic carbon materials are mainly used as the anodes in commercial cells, because they appear to have high specific capacity, charge/discharge reversibility, low and flat working potential similar to that of lithium metal[1–5]. However, graphite powders are employed as the anode electrode, and they suffer from a large irreversible capacity loss during the first cycle due to the formation of solid electrolyte interface(SEI)[6–7]. This film prohibits the solvated lithium ions from passing through, but lithium ion can move from the electrolyte solution into the graphite[8–9]. The intercalation of solvent molecules can result in exfoliation of graphite, consequent destruction of the graphite structure and the poor cycling characteristics[5,8–9]. Therefore, surface structures of carbon materials are significant to the formation of this membrane and consequently the electrochemical performance. Recent research on the improvement of graphite's surface structures mainly includes coating

other materials and surface modification to help the formation of more compact and conductive SEI film[8,10–12].

In this work, modified graphite material was obtained by coating SiO₂ with tetraethyl orthosilicate (TEOS) in sol-gel method followed with heat-treatment in an argon atmosphere. The microstructure and electrochemical characteristics of the modified graphite materials as anodes in Li/C cells were investigated.

2 Experimental

The natural graphite/SiO₂ spheres were prepared by the hydrolysis of tetraethyl orthosilicate(TEOS). Typically, an appropriate amount of natural graphite submicrospheres was dispersed in the mixed-solution of 50 mL anhydrous alcohol and 0.017 mol TEOS. And then, 15 mL distilled water was added. To motivate the hydrolysis of TEOS, a little amount ammonia solution was also added into the reaction system to adjust the PH value of the solution to around 9. The mixture solution was heated to 40 °C, and kept stirring for 1 h. Then, the right amount of TEOS was introduced and the temperature of the mixture was raised to 80 °C to evapo-

rate and concentrate it. Subsequently, the wetted graphite was dried in oven at 110 °C. These precursors were calcined at 650 °C in argon atmosphere for 3 h. This pretreated graphite powders were used for electrochemical measurements. For comparison, natural graphite was used without pretreatment. According to the formula, the mass ratio of SiO₂ to C was 5:95.

The powder X-ray diffraction (XRD, Rint-2000, Rigaku) measurement using Cu K_α radiation was employed to identify the crystalline phase of the synthesized material. The morphology of modified graphite powders was observed by scanning electron microscope (SEM, JEOL, JSM-6380LV) with an accelerating voltage of 20 kV. The chemical composition characterization of modification graphite powders was measured by Energy Disperse X-ray Spectrometric Microanalyzer (EDS, EDS-GENESIS 60S) with a spectrum resolving power less than 132.0 eV.

The electrochemical characterizations were performed using CR2025 coin-type cell. For anode fabrication, the prepared powders were mixed with 5% LA133 and 5% acetylene black (mass fraction) in deionized water until slurry was obtained. And then, the blended slurries were pasted onto a copper foil current collector, and the electrode was dried at 65 °C for 12 h in vacuum. A Celgard 2300 porous membrane of 20 μm in thickness was used as a separator, and the electrolyte was 1 mol/L LiPF₆-EC/DMC (1:1 in volume fraction). Li/C cells were assembled in an argon filled glove box. Electrochemical characteristics of the graphite electrodes in Li/C cells were tested at a constant current density of 0.1 mA/cm² between 0.001 V and 2.000 V.

3 Results and discussion

3.1 Characterization of graphite after modification

Fig.1 shows XRD pattern of graphite powders modified with SiO₂. The main diffraction peaks are the

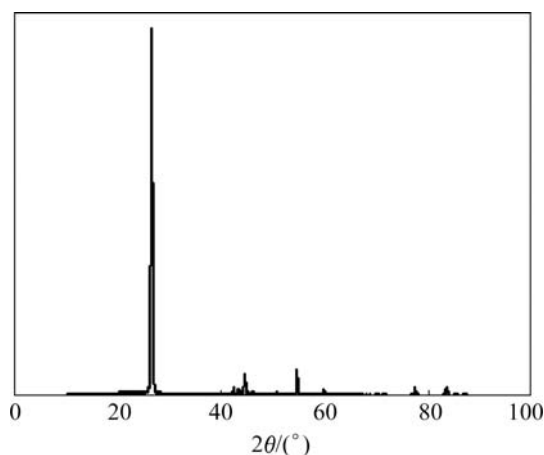


Fig.1 XRD pattern for modified graphite by SiO₂ after heat treatment at 650 °C for 3 h in argon atmosphere

same with graphite, demonstrating that the graphite powders are crystalline carbon and the crystal structure of the graphite is not affected by the pretreatment with SiO₂. It can be seen that the phase of SiO₂ was not detected in the SiO₂-coated graphite samples, which may be due to the fact that the silica is an amorphous material.

In addition, scanning electron micrographs (SEM) of the untreated natural graphite and modified graphite are shown in Fig.2. These four micrographs show that top-surface morphology of the graphite is retained, and the size and shape of the graphite are not changed. The surface of natural graphite is smooth. However, the modified graphite presents many white stripes clearly, and some white floccules can be seen on the surface of the treated graphite from Fig.2(c).

Fig.3 shows EDS spectra of natural graphite and modified graphite by SiO₂. Compared with that of un-coated graphite, the signal of C after being coated by SiO₂ is less than before obviously, but the peaks of Si and O rise remarkably. However, the peaks of S and Cl disappear after being modified, which indicates that the coated layer is SiO₂. From Table 1, we can see the detailed data of the element on the surface of graphite before and after modification. Therefore, based on the result of SEM and EDS, it can be confirmed that a SiO₂ film is deposited on the surface of natural graphite microspheres.

Table 1 EDS data of C, O, Si, Al and Cl contained on surface of natural and modified graphite

Element	Natural graphite		Modified graphite	
	w/%	x/%	w/%	x/%
C	97.16	97.97	93.08	95.51
O	2.49	1.89	4.37	3.37
Si	0.11	0.05	2.31	1.02
Al	0.18	0.08	0.24	0.11
S	0.02	0.01		
Cl	0.04	0.02		

3.2 Electrochemical performances

Fig.4 exhibits the initial charge (lithium ion deintercalation) and discharge (lithium ion intercalation) curves of anode for natural and graphite coated by SiO₂. Compared with the untreated graphite sample, the modified graphite samples have larger charge capacity, reaching 368.70 mA·h/g, but that of the natural graphite is only 358.71 mA·h/g. While, the coulombic efficiency of the coated material is slightly lower than that of natural one. Their efficiencies are 89.23% and 90.99% respectively. This displays that the irreversible capacity of the modified graphite is larger than that of natural one. Besides, the discharge voltage of natural graphite is

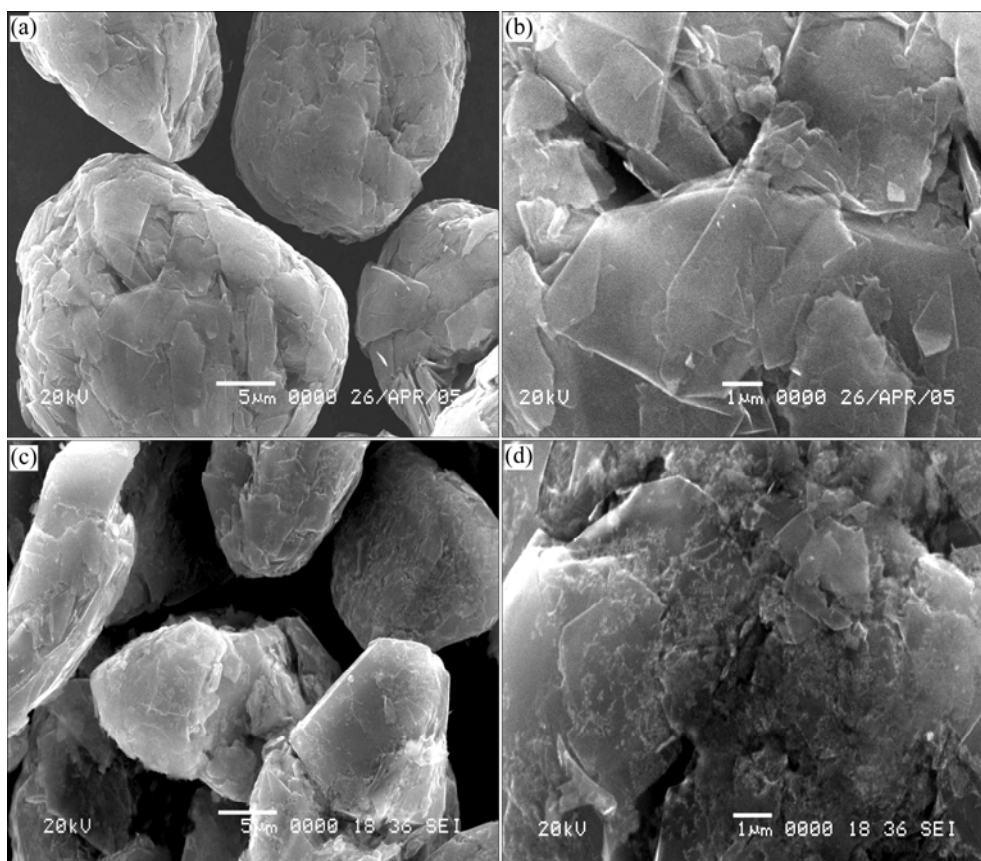


Fig.2 Typical SEM micrographs of section and surface of natural graphite ((a), (b)) and modified natural graphite by SiO₂ ((c), (d))

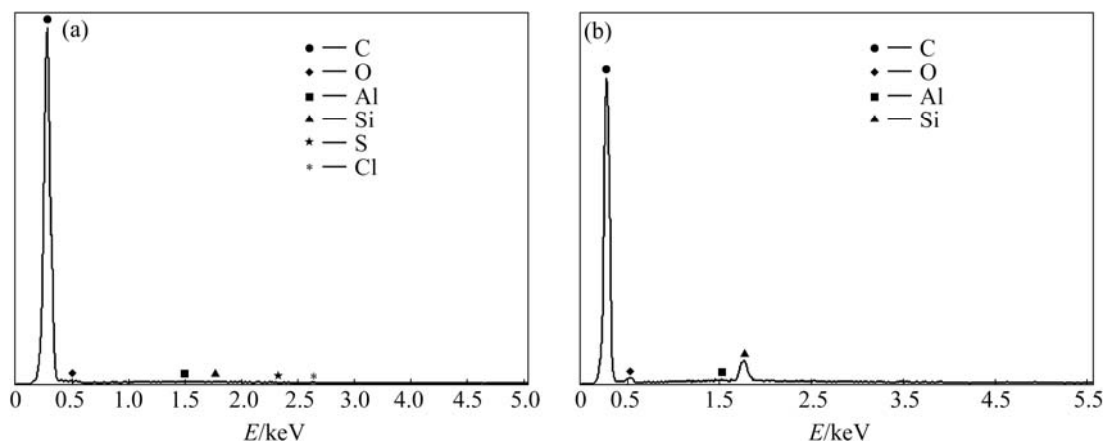


Fig.3 EDS spectra of natural graphite (a) and modified graphite (b)

lower than that of modified graphite below 0.8 V. This results from electrode polarization during discharge because SiO₂ film on the surface of the coated graphite is not a conductor, and the majority of the researchers agree with that 0.8 V is the voltage of formation of SEI layer [12–16]. This implies that modified graphite consumes more lithium ion to format SEI films.

The cycle characteristics of natural and SiO₂-coated graphites in terms of charge capacity are presented in Fig.5. The SiO₂-coated sample displays better cycleability than the untreated counterpart. The modified

graphite demonstrates a capacity higher than 366.9 mA·h/g over 40 cycles, whereas the untreated graphite shows only 297.9 mA·h/g. The reversible capacity retention ratio of the modified graphite is 99.55%, while that of the untreated graphite is only 83.04%. Thus, the charge and discharge performances of the treated graphite are improved due to the better SEI film formed on the surface of composite graphite electrode at the first charge/discharge cycle[3,17–18]. Because the structure of SiO₂ synthesized is composed of steric network, it makes the SEI film fibrosis and its toughness is enhanced.

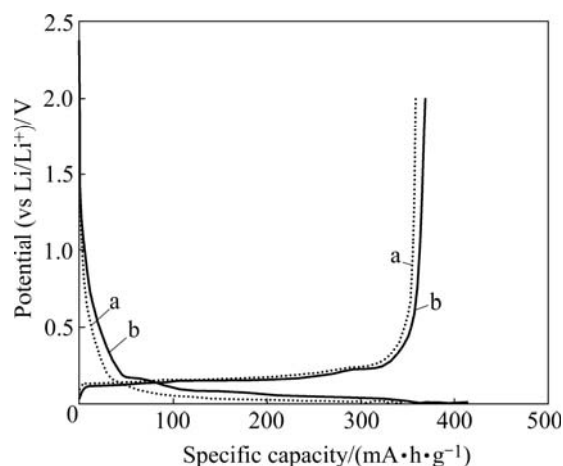


Fig.4 Charge-discharge curves of graphite (a) and modified graphite (b) electrodes in 1 mol/L $\text{LiPF}_6/\text{EC}/\text{DMC}$ electrolyte for first cycle at $0.1 \text{ mA}/\text{cm}^2$

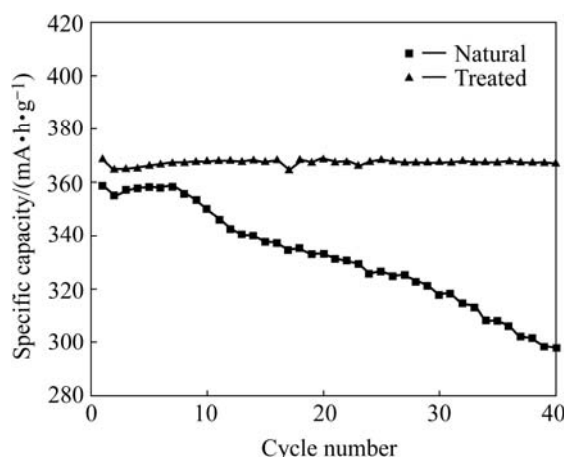


Fig.5 Cycling behavior of natural graphite and treated graphite

The SEI film is not destroyed during the cycle life test. It prevents lithium ion and electrolyte inserting the graphite layers together, so the cycle performance of modified graphite by SiO_2 is much better than that of untreated one.

4 Conclusions

1) Graphite- SiO_2 composite anodes are prepared by coating the natural graphite with TEOS and heat treatment at 650°C . A layer of amorphous silicon dioxide is formed on the surface of natural graphite.

2) The silicon dioxide coating results in a great improvement of the cell performance, such as higher reversible capacities and more excellent cycling performance for lithium ion cells. The graphite electrodes modified by 5% SiO_2 have much better electrochemical performances with a reversible capacity of $368.70 \text{ mA}\cdot\text{h}/\text{g}$. The Li/C cells with treated graphite anodes have improved cycling stability because of the better SEI film formed on the surface of the modified

graphite during the first cycle. After 40 charge-discharge cycles, the capacity retention ratio of the composite graphite electrodes reaches 99.55%, while that of the untreated graphite electrode is only 83.04%.

References

- [1] ZHANG Han-ping, FU Li-jun, WU Yu-ping, WU Hao-qing, TAKAMURA T. Research progress in anode materials for Li-ion batteries [J]. *Battery*, 2005, 35(4): 274–275. (in Chinese)
- [2] HANG S. Coke vs. graphite as anodes for lithium ion batteries [J]. *J Power Sources*, 1998, 75(1): 64–72.
- [3] MUKAI S R, TAKAHIRO H, MICHIIYA T, HAJIME T. Reduction of irreversible capacities of amorphous carbon materials for lithium ion battery anodes by Li_2CO_3 addition [J]. *Carbon*, 2004, 42(4): 837–838.
- [4] MEGAHED S, SCROSATI B. Lithium-ion rechargeable batteries [J]. *J Power Sources*, 1994, 51(1): 79–98.
- [5] LEE H Y, BAEK J K, JANG S W, LEE S M, LEE K Y, KIM M H. Characteristics of carbon-coated graphite prepared from mixture of graphite and polyvinylchloride as anode materials for lithium ion batteries [J]. *J Power Sources*, 2001, 101(2): 206–207.
- [6] BUQA H, GLOLB P, WINTER M, BESENHARD J O. Modified carbons for improved anodes in lithium-ion cells [J]. *J Power Sources*, 2001, 97/98: 122–123.
- [7] ZEMPACHI O, TAKESHI A, TOMOKAZU F, SHIGEKI Y, YASUTOSHI I. Lithium-ion transfer at interface between carbonaceous thin film electrode/electrolyte [J]. *J Power Sources*, 2004, 127(1/2): 72–75.
- [8] FU L J, LIU H, LI C, WU Y P, RAHM E, HOLZE R, WU H Q. Surface modifications of electrode materials for lithium ion batteries [J]. *Solid State Sciences*, 2006, 8(2): 113–128.
- [9] GUO H J, LI X H, WANG Z X, PENG W J, GUO Y X. Si-doped composite carbon as anode of lithium ion batteries [J]. *Trans Nonferrous Met Soc*, 2003, 13(5): 1062–1063.
- [10] LU Mi, YIN Ge-ping, SHI Peng-fei. Modifications of graphite material for negative electrode of Li-ion batteries [J]. *Battery*, 2001, 31(4): 195–197. (in Chinese)
- [11] XIE J N, VARADAN V K. Synthesis and characterization of high surface area tin oxide/functionalized carbon nanotubes composite as anode materials [J]. *Materials Chemistry and Physics*, 2005, 91(2/3): 274–280.
- [12] WU Y P, RAHM E, HOLZE R. Carbon anode materials for lithium ion batteries [J]. *J Power Sources*, 2003, 114(2): 228–236.
- [13] MA S H, LI J, JING X B, WANG F S. A study of cokes used as anodic materials in lithium ion rechargeable batteries [J]. *Solid State Ionics*, 1996, 86/88: 911–917.
- [14] KIM W S, CHUNG K, LEE C B, CHO J H, SUNG Y E, CHOI Y K. Studies on heat treated MPCF anodes in Li-ion batteries [J]. *Microchemical Journal*, 2002, 72(2): 185–192.
- [15] ENDO M, KIN C, NISHIMURA K, FUJINO T, MIYASHITA K. Recent development of carbon materials for Li-ion batteries [J]. *Carbon*, 2000, 38(2): 183–197.
- [16] WANG Y X, SHIMICHIRO N, MAKOTO U, PERLA B B. Theoretical studies to understand surface chemistry on carbon anodes for lithium-ion batteries: Reduction mechanism of ethylene carbonate [J]. *J Am Chem Soc*, 2001, 123(47): 11708–11718.
- [17] XU Zhong-yu, ZHENG Hong-he. Research progress on compatibility of electrolyte with carbon negative electrode in lithium ion batteries (Part I): Surface chemistry of carbon electrode and the compatibility of electrolyte with carbon negative electrode [J]. *Chinese Journal of Power Sources*, 2000, 24(3): 171–175. (in Chinese)
- [18] NI Jiang-feng, ZHOU Heng-hui, CHEN Ji-tao, SU Guang-yao. Progress in solid electrolyte interface in lithium ion batteries [J]. *Progress in Chemistry*, 2004, 16(3): 335–341. (in Chinese)

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