Short communication

Studies on capacity fading mechanism of graphite anode for Li-ion battery[☆]

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Abstract

It is of great importance to improve the electrochemical performance of graphitic anode materials since they are dominantly used in practical lithium ion battery and still will be the main component as anode material in the future. By SEM, XPS, Micro-Raman and EDX analyses of graphite electrodes before and after discharge/charge cycle, it is found that capacity fading is strongly related to the dispersion of conductive. Homogeneous dispersion of conductive resulted in good cycle performance. However, for the poorly fabricated electrode, with heterogeneous dispersion of conductive, it gives rise to the formation of imperfect SEI film in the first cycle and subsequent continual decomposition of the electrolyte, leading to large amounts of nonconductive surface deposits consisting of Li_2CO_3 and LiF. As a result, its irreversible capacity is high and capacity retention is poor. Thus, homogeneous dispersion of conductive is necessary to obtain good performance for graphitic anode electrode. The formation of Li_2CO_3 and LiF during repeated cycling is attributed to the inhomogeneous distribution of the overpotential throughout the fabricated electrode.
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1. Introduction

With the development of lithium ion battery, various kinds of anode materials have so far been studied [1], however, graphite materials are dominantly used in the practical batteries and will still be used as the major component in the future because of its low cost, appropriate potential profile and developed technology [2–4]. Even high capacity materials such as Si or Sn are used in the future it is expected that the practical material will be at least a composite with graphite. Therefore, the improvement of the performance of graphite is quite important.

Recently, a new kind of graphite anode material, designated as special spherical graphite (SSG), came into the market of China.

This material presents good electrochemical performance. For example, its reversible capacity is high, >350 mAh g^{-1} in the first cycle, and retains >86% initial reversible capacity after 500 cycles [5]. It looks very promising. However, its capacity still fades. Here we used SSG as anode material to investigate its capacity fading mechanism by scanning electronic microscope (SEM), Micro-Raman, X-ray photoelectronic spectroscopy (XPS), and energy dispersive X-ray (EDX).

2. Experimental

The anode material we chose for the study is special spherical graphite powder from a company in China. The powder was prepared by twice coating with carbons and detailed performance was reported in another place [5]. The powder was coated on a copper current collector sheet (15 μm thick) with vapor grown carbon fiber (VGCF) as a conductive and poly(vinylidene fluoride) (PVDF) as a binder in *n*-methyl pyrrolidone solvent. Both well- and poorly fabricated electrodes were prepared. In the former case, VGCF was dispersed homogeneously on the surface of
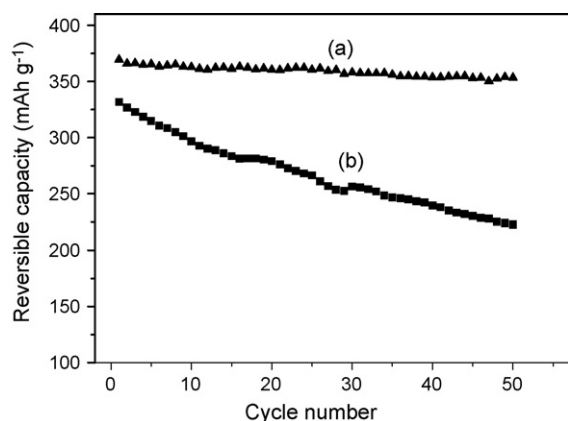
Fig. 1. Cycle performance of SSG graphite electrodes in an electrolyte of EC/DMC (1:1 by v/v) containing 1 M LiPF$_6$ at constant charge current density of 2.2 mA cm^{-2} (2*C*). (a) Well-fabricated electrode and (b) poorly fabricated electrode.

SSG particles, and in the latter one, the dispersion of VGCF was inhomogeneous. The coated sheet was heat-dried, roll-pressed, and punched into 1 cm diameter disk, and used as the working electrode. The electrochemical evaluation was performed with discharge/charge in an electrolyte of EC/DMC (1:1 by v/v) containing 1 M LiPF$_6$ between 0.04 and 1.5 V. The charge was performed at a constant current density, 2.2 mA cm^{-2} (about 2*C*).

SEM and EDX analysis were performed with a scanning electron microscope of JEOL (JEM 2011). Prior to the analysis, the samples after cycling were rinsed with pure solvent of DEC and dried in a glove box filled with dry argon. XPS analysis was done by PHI 5000C ESCA system. Micro-Raman was performed with LABRAM-1B Raman spectrometer at room temperature with 632.8 nm line of He and Ne laser for excitation.

3. Results and discussion

The difference of cycle performance between the well- and poorly fabricated electrodes was shown in Fig. 1. For the well-fabricated electrode (Fig. 1a), it kept good capacity retention

Table 1
Data from XPS and EDX analysis for the surface of the SSG graphite electrode after 50 cycles

Atomic concentration (%)	C	O	F	Li
XPS data				
Part with VGCF	47.0	15.7	13.7	22.5
Part without VGCF	29.1	22.9	14.9	31.4
EDX data				
Before rinsing	50.1	41.8	8.1	–
After rinsing	92.2	7.5	0.3	–

after 50 cycles, and the reversible capacity still remains as 98% as that of 10th cycle. However, the capacity of the poorly fabricated electrode decreases sharply during its first 50 cycles (Fig. 1b), and after 50 cycles it is only 47% as that of its 10th cycle.

SEM micrographs after 50 cycles are shown in Fig. 2. There are white deposits on the surface of the electrodes. For the poorly fabricated electrode (Fig. 2b), the amounts of the deposits on the surface are much increased in comparison with that of the well-fabricated one (Fig. 2a). SEM analysis at different cycles shows that for the poorly fabricated electrode, after one cycle, the surface was already covered with the deposits and their amounts increased with cycling, concomitant with capacity fading.

Further EDX studies were performed focusing on the parts where VGCF is sticking and where there is no VGCF around on the surface of the well fabricated electrode after 50 cycles and are shown in Fig. 3. Results show that the surface where there is no VGCF around was covered by deposits consisting with O, F atoms, and the atomic concentrations of oxygen and fluorine are higher compared with those near to VGCF. It implies that the poor electrical contact between SSG particles and VGCF accelerates the formation of the deposits and the capacity fading. In contrary, the electrode with homogeneous dispersion of the conductive enjoys good electrical contact, suppresses the heterogeneous formation of the deposits and ensures good capacity retention.

The components of the white deposits were further investigated by XPS, Micro-Raman, EDX, and SEM. The data of XPS and EDX for the SSG graphite electrode after 50 cycles are sum-
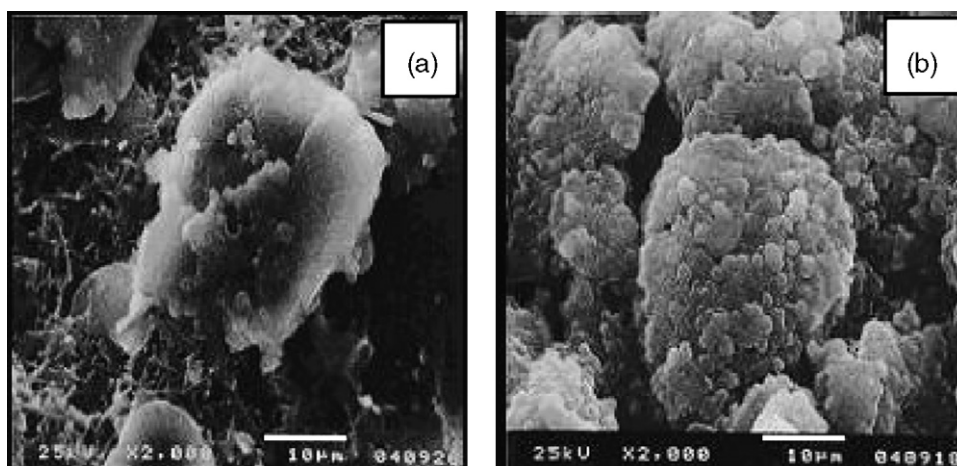

Fig. 2. SEM micrographs of SSG graphite electrodes after 50 cycles. (a) Well-fabricated and (b) poorly fabricated.
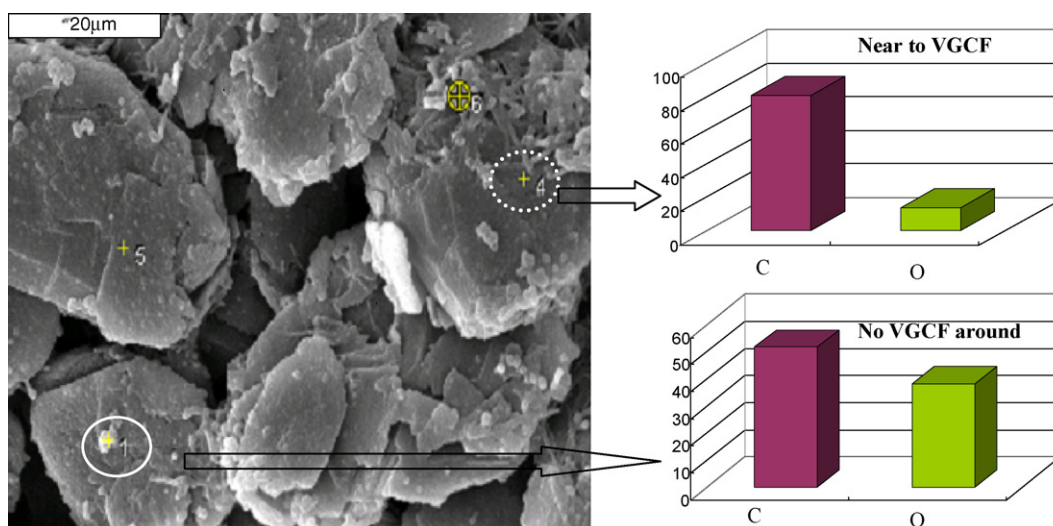
Fig. 3. EDX studies of the atomic concentrations comparison between the part where VGCF is sticking and that where there is no VGCF.

marized in Table 1. XPS results show that the deposits consist of O, F and Li elements and the atomic concentrations of O, F and Li elements on the part without VGCF are higher than those of parts with VGCF. EDX study examined the difference of atomic amounts between the electrodes before and after rinsing with deionized water. It presents that the atomic amounts of oxygen and fluorine on the electrode before rinsing are much higher than those after rinsing. Measurement of SEM observation is consistent with the above results. After rinsing with deionized water, there are only graphite fragments and VGCF but no white deposits on the electrode surface, deducing that the deposits are water-soluble. Further research was done with Micro-Raman method. A strong peak was observed at 1090 cm^{-1} for the poorly fabricated electrode after cycling and rinsing by DEC. This peak is attributed to the vibration of CO_3^{2-} [6], demonstrating that the deposits include carbonates. From the above results, it is deduced that the deposits mainly consist of nonconductive Li_2CO_3 and other lithium salts, which are soluble in water and supposed to be formed by cathodic decomposition of the electrolyte.

It is known that SEI film is a protective solid electrolyte interface on the surface of graphite electrode, and plays a major role in determining battery electrochemical performance, including irreversible capacity, reversible capacity and cycle life [7,8]. Its formation is due to the cathodic decomposition of the electrolyte components at different potential with various rates, which consumes lithium ions and result in an irreversible capacity [9,10]. For the poorly fabricated electrode, the bad electrical contact gives rise to inhomogeneous polarization and heterogeneous potential distribution, thus the decomposition rates of the electrolyte components differ from place to place and an imperfect SEI film is formed. The decomposition of electrolytes continues and the amount of nonconductive deposits increases in the following cycles, resulting in a continual irreversible capacity and bad capacity retention. However, for the well-fabricated electrode with good electrical contact, it is another story. The

conductive is dispersed homogeneously providing a homogeneous potential distribution. The decomposition rates of electrolyte components are equal on the surface of electrode in the first cycle and a perfect SEI film is formed, which suppresses the further formation of the deposits and consumption of lithium ions in subsequent cycles and ensures good capacity retention.

4. Conclusion

Electrical contact is a main factor that influences the cycle performance besides the intrinsic properties of active electrode materials. Unfavorable electrical contact gives rise to the formation of an imperfect SEI film in the first cycle, resulting in a continual formation of the nonconductive deposits on the surface of the electrodes, high irreversible capacity and poor capacity retention. It means the capacity fading is accelerated by unfavorable electrical contact. Thus homogeneous distribution of conductive is necessary to obtain high performance for the graphite electrode.

References

[1] Y.P. Wu, X.B. Dai, J.Q. Ma, Y.J. Cheng, Lithium Ion Battery, Chemical Industry Press, Beijing, 2004, pp. 97–126.
[2] Y.L. Cao, L.F. Xiao, X.P. Ai, H.X. Yang, Electrochem. Solid-State Lett. 6 (2003) A30–A33.
[3] M.W. Verbrugge, B.J. Koch, J. Electrochem. Soc. 150 (2003) A374–A384.
[4] D. Aurbach, H. Teller, M. Koltypin, E. Levi, J. Power Sources 119–121 (2003) 2–7.

[5] H.P. Zhang, L.J. Fu, Y.P. Wu, H.Q. Wu, K. Endo, K. Sekine, T. Takamura, J. Power Sources, J. Appl. Electrochem., in press.

[6] G.F. Li, H. Li, Y.J. Mo, L.Q. Chen, X.J. Huang, J. Power Sources 104 (2002) 190–194.

[7] P. Arora, R.E. White, M. Doyle, J. Electrochem. Soc. 145 (1998) 3647–3667.

[8] M.C. Smart, B.V. Ratnakumar, S. Surampudi, Y. Wang, X. Zhang, S.G. Greenbaum, A. Hightower, C.C. Ahn, B. Fultz, J. Electrochem. Soc. 146 (1999) 3963–3969.

[9] E. Yair, Electrochem. Solid-State Lett. 2 (1999) 212–214.

[10] S.S. Zhang, M.S. Ding, K. Xu, J. Allen, T.R. Jow, Electrochem. Solid-State Lett. 4 (2001) A206–A208.