Short communication

Performance improvement of lithium ion battery using PC as a solvent component and BS as an SEI forming additive

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Abstract

The electrochemical behavior of propylene carbonate (PC)-based electrolytes with and without butyl sultone (BS) on graphite electrode and the performance of lithium ion batteries with these electrolytes were studied with cyclic voltammetry (CV), energy dispersive spectroscopy (EDS), as well as density functional theory (DFT) calculation. It is found that the co-insertion of PC with lithium ions into graphite electrode can be inhibited to a great extent by adjusting the composition of solvent in electrolytes. With the application of PC in the electrolyte without any additive, the discharge capacity of lithium ion battery is improved under high temperature or low temperature, however it decays under room temperature compared with the battery without PC. This drawback can be overcome by using BS as a solid electrolyte interphase (SEI) forming additive. BS has a lower LUMO energy and can be more easily electro-reduced than other components of solvent in electrolyte on a graphite electrode, forming a stable SEI film. With the application of BS in the electrolyte, the discharge capacity and cyclic stability of lithium ion battery is improved significantly under room temperature.
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1. Introduction

Due to their high discharge voltage and high energy density, lithium ion batteries become more and more popular as a power source for advanced portable electronics, and both experimentalists and theoreticians are attracted to this area for relevant chemistry problems [1–7]. A typical lithium ion battery system consists of a graphite anode, a transition metal oxide (such as $LiMn_2O_4$, $LiCoO_2$, $LiNiO_2$, etc.) cathode and a nonaqueous organic electrolyte, which acts as an ionic path between electrodes. The electrolytes used in commercial lithium ion batteries are prepared by dissolving $LiPF_6$ into binary or ternary solvents, which are of the mixtures of non-cyclic carbonates, including dimethyl carbonate (DMC), ethyl (methyl) carbonate (EMC) and diethyl carbonate (DEC), with ethylene carbonate (EC). The performances of lithium ion battery are closely related to the solvent composition of electrolyte and utilization of additives [8–10]. It is generally known that a solid electrolyte interphase (SEI) film forms on electrode surface at low potential during the first reduction step in EC based electrolyte [11,12]. Nevertheless, EC has a poor low temperature performance because of its high melting point (about 36.4 °C), which makes lithium ion batteries of EC-based electrolytes cannot meet the requirements of high technology application such as electric vehicle (EV), military and aerospace mission [13–16].

Propylene carbonate (PC) is an attractive solvent for nonaqueous electrolyte for lithium ion battery, especially for low temperature operation, because of its low melting point (about −48.8 °C), which can lower the eutectic point of solvent with EC. Unfortunately, PC is not widely used as a component of solvent in lithium ion batteries, since PC can easily decompose on graphite electrode surface and co-insert into graphite electrode with lithium ions, which makes graphite electrode exfoliate significantly and reduces the reversible capacity of graphite electrode or even causes the cycling performance of graphite electrode to lose completely.

In this paper, the performance improvement of Li-ion battery was considered by using the electrolyte with PC as a component of solvent and with butyl sultone (BS) as an SEI film forming additive.

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2. Experimental

2.1. Electrolyte preparation

Carbonates, EC, PC and EMC, were purified by distilling and with molecular sieve till the purity was higher than 99.9%, which was determined with GC-14C (SHIMADZU). $LiPF_6$ was the product of Stella Chemical (Osaka Japanese). Electrolyte solutions were prepared by dissolving $1\,mol\,L^{-1}$ $LiPF_6$ in the mixture solvents in a dry glove box ($H_2O < 1$ ppm) filled with high purity argon. Water and free acid contents in the electrolyte were controlled below 20 ppm, which were determined by Karl-Fisher 831 Coulometer (Metrohm) and Karl-Fisher 798 MPT Titrino (Metrohm).

2.2. Battery performances

Battery performances were determined with utilization of 063048-size batteries with nominal capacity of 700 mAh and 053048-size batteries with nominal capacity of 550 mAh using a programmable computer-controlled battery charge (BS-9300R type, Guangzhou, China). The cathodes and the anodes were made of lithium cobalt oxide ($LiCoO_2$) and graphite, respectively. The temperature was controlled with a WD4003 oven (Chongqing Yinhe experimental equipment Co. Ltd., China). The batteries were charged at constant current of 1 C rate to 4.2 V, followed by a constant voltage of 4.2 V until the current decreased to C/20 at room temperature. For room temperature performance determination, the charged batteries were discharged at 1 C rate to 3.0 V. For high temperature performance determination, the charged batteries were stored for 24 h at 60 °C and then discharged at 1 C rate to 3.0 V. For low temperature performance determination, the charged batteries were stored for 4 h at −10 °C and then discharged at 0.2 C rate to 2.7 V.

2.3. Voltammetry

A three-electrode cell was used for voltammetric measurements, with graphite as the working electrode and Li foils as counter and reference electrodes. The graphite electrodes were prepared as follows: carbonaceous mesophase sphere (CMS) was mixed with 8% (by weight) polyvinylidene fluoride (PVDF), and the mixture was rolled onto copper foil, pressed and dried at 120 °C for 14 h. Electrochemical measurements were carried out on Autolab (PGSTAT30, ECO Echemie B.V. Company).

2.4. DFT calculation

All the calculations were performed using the Gaussian 03 programs package [17]. The equilibrium and transition structures were fully optimized by B3LYP method using a 6-31 + G (d, p) basis set.

2.5. Surface analysis

The surface of the graphite was examined using an energy dispersive spectroscopy (EDS) detector (Oxford, INCA).

3. Results and discussion

3.1. Battery performance at low temperature and high temperature

Fig. 1a shows discharge curves of the Li-ion batteries using $1\,mol\,L^{-1}$ $LiPF_6$/EC:EMC = 2:5 (A) and $1\,mol\,L^{-1}$ $LiPF_6$/EC:PC:EMC = 2:1:5 (B) as the electrolytes at −10 °C. It can be seen from Fig. 1a that the battery with PC as solvent component shows better discharge performance than that without PC. On the one hand, the operating voltage of the battery with PC is higher than the battery without PC. For example, the voltage is 3.69 V at 200 mAh for the battery with PC, but only 3.51 V for that without PC. On the other hand, the discharge capacity is 499.1 mAh at −10 °C for the battery with PC, but only 477.7 mAh for that without PC. Both the power and capacity of the Li-ion batteries at the low temperature are significantly improved with the application of PC. This can be attributed to the fact that PC has a low-melting point and can lower the eutectic point of the solvents [18], and the low temperature con-
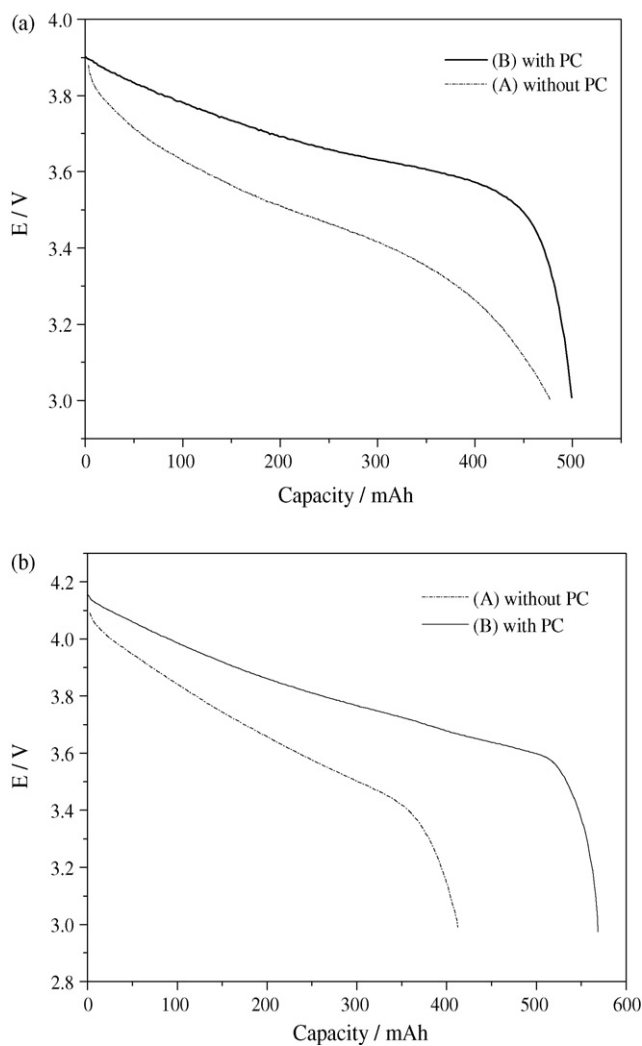

Fig. 1. Discharge curves of Li-ion battery at −10 °C (a) and 60 °C (b) with electrolyte (A) $1\,mol\,L^{-1}$ $LiPF_6$/EC:EMC = 2:5 and (B) $1\,mol\,L^{-1}$ $LiPF_6$/EC:PC:EMC = 2:1:5.

ductivities of the electrolyte is determined by the eutectic point [8].

Fig. 1b shows discharge curves of Li-ion batteries using $1 \, mol \, L^{-1}$ LiPF$_6$/EC:EMC = 2:5 (A) and $1 \, mol \, L^{-1}$ LiPF$_6$/EC:PC:EMC = 2:1:5 (B) as the electrolytes at 60 °C. The battery with PC as solvent component also shows better discharge performance than the battery without PC at 60 °C. The discharge capacity is 568.7 mAh at 60 °C for the battery with PC, but only 412.6 mAh for that without PC. Furthermore, the discharge voltage of the battery with PC is higher than that without PC. For example, the operating voltage is 3.76 V when the battery with PC discharged at 300 mAh, but it is only 3.5 V for that without PC.

3.2. Discharge capacity and cycling stability at room temperature

Fig. 2 presents discharge capacity and cycling performance of Li-ion batteries using $1 \, mol \, L^{-1}$ LiPF$_6$/EC:EMC = 2:5 and $1 \, mol \, L^{-1}$ LiPF$_6$/EC:PC:EMC = 2:1:5 at room temperature. It can be seen from Fig. 2 that the battery using the electrolyte with PC as solvent component shows poorer discharge performance and cycling stability than that without PC. The initial capacity of the battery without PC is 893.7 mAh, larger than that with PC, which is only 859.1 mAh. The capacity of both batteries decreases as the cycling number increases. However, the capacity of the battery without PC keeps at 876 mAh (98% of the initial capacity) after 50 cycles, while that of the battery with PC keeps at 818.6 mAh (95.3% of the initial capacity). Apparently, not only capacity but also cycling stability of the Li-ion battery using the electrolyte with PC as component at room temperature decays compared with that without PC. This can be attributed to PC decomposition that consumes a higher amount of lithium ions at the cathode [19]. However, this drawback of PC can be overcome by using electrolyte additives, which can
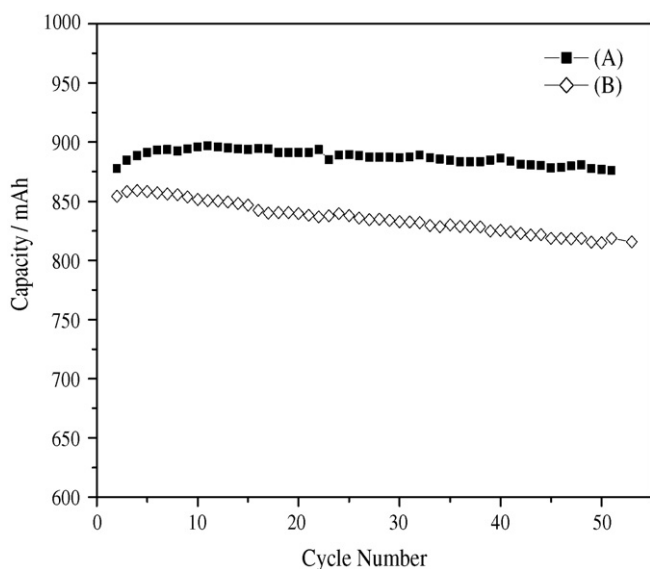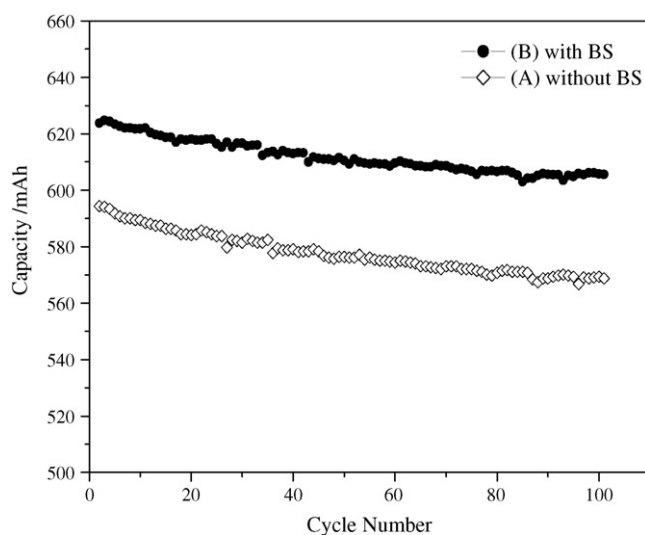
Fig. 3. Cycling performance of Li-ion batteries using $1 \, mol \, L^{-1}$ LiPF$_6$/EC:PC:EMC = 1:1:3 as electrolyte without (A) and with (B) 1 wt.% BS at room temperature.

suppress PC decomposition and facilitate SEI formation [20]. In the following of this work, we recommended butyl sultone (BS) as an additive for the formation of SEI film to overcome the drawback of PC.

Fig. 3 compares discharge capacity and cycling stability of the batteries using $1 \, mol \, L^{-1}$ LiPF$_6$/EC:PC:EMC = 1:1:3 as electrolyte with and without BS at room temperature. It can be found that both discharge capacity and cycling stability are improved significantly with the application of BS. The initial discharge capacity of the battery with BS is 623.8 mAh, higher than that without BS, which is 594.4 mAh. The capacity loss of the battery with BS is only 2.9% (from 623.8 to 605.6 mAh) after 100 cycles, less than that without BS, which is 4.3% (from 594.4 to 568.8 mAh). This improvement can be ascribed to the formation of an SEI film on graphite in the electrolyte by the reduction of BS. Therefore, the drawback of PC causing the loss of capacity and the decrease of cycling stability can be overcome by utilization of BS.

3.3. Cyclic voltammograms of graphite electrode in the electrolytes with and without BS

Fig. 4 shows cyclic voltammograms of graphite electrodes in $1 \, mol \, L^{-1}$ LiPF$_6$/EC:PC:EMC = 1:1:3 with (b) and without (a) 1% BS. As we can see from Fig. 4a, during the first cathodic potential sweeping, a reduction peak appears at ca. 0.4 V, which is attributed to the reduction of EC, resulting in the formation of SEI film on graphite electrode. As the potential becomes more negative, the reduction current increases, which corresponds to the increasing of quantity of lithium ions inserted into graphite. During the second sweeping, the reduction peak at ca. 0.4 V can also be observed, although it is lower than that of the first cycle. This indicates that the SEI film, formed on graphite electrode at the first cycle, was not good enough to suppress the further reduction of solvents in the following cycles, which still leads to irreversible capacity loss.
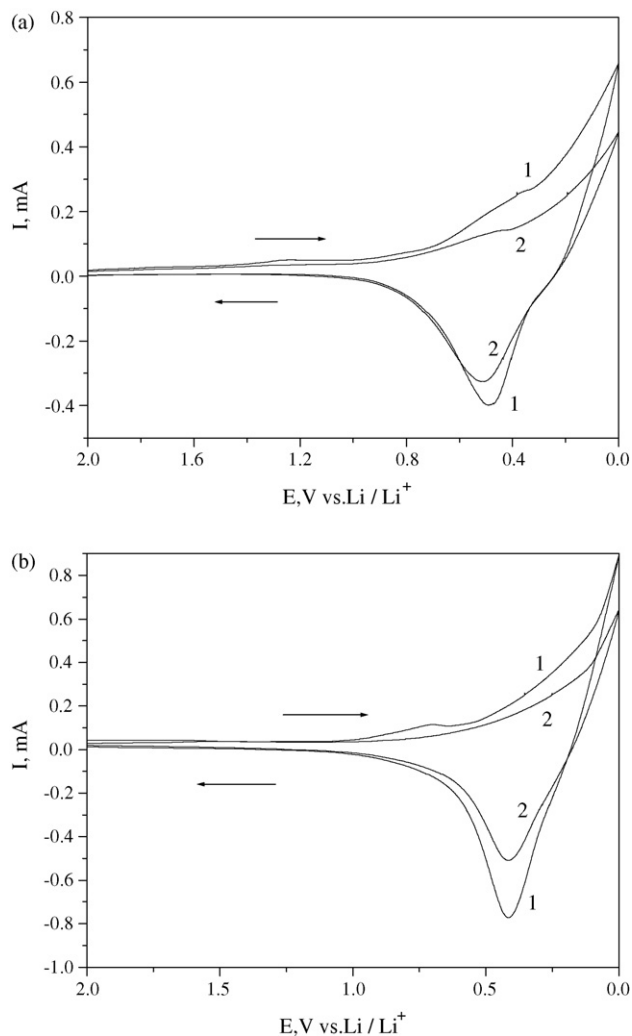
Fig. 2. Discharge capacity and cyclic stability of Li-ion batteries under room temperature, using electrolyte: (A) $1 \, mol \, L^{-1}$ LiPF$_6$/EC:EMC = 2:5 and (B) $1 \, mol \, L^{-1}$ LiPF$_6$/EC:PC:EMC = 2:1:5.

Fig. 4. Cyclic voltammgroms of graphite electrodes in $1 \, mol \, L^{-1}$ LiPF$_6$/EC:PC:EMC = 1:1:3 without (a) and with (b) 1 wt.% BS, scan rate 0.5 mV s^{-1}, the number in the plot indicating the cyclic number.

Different behavior appears in Fig. 4(b). During the first cathodic sweeping, there is a reduction peak in electrolyte containing BS at *ca.* 0.7 V, which should be attributed to the reduction of BS on the graphite electrode and the formation of SEI film. With the decreasing of potential, the cathodic current increases and the peak at *ca.* 0.4 V that appears in the electrolyte without BS disappears, which indicates that the SEI film formed from BS could effectively suppress the solvents decomposition on the graphite electrode. During the second sweeping, the reduction peak at *ca.* 0.7 V disappears. This indicates that a stable SEI film is formed from BS reduction at the first sweeping process and the decomposition of solvent on graphite electrode can be suppressed. With the comparison of the two anodic current peaks in the electrolytes with and without BS, it can be found that the anodic current peak potential (0.4 V) in the electrolyte with BS is lower than that (0.5 V) in the electrolyte without BS. This suggests that the de-intercalation potential is reduced by the addition of BS, which facilitates a higher potential plateau during the discharge process [21]. Thus, batteries with BS have higher capacity and cyclic stability.

Table 1
Results of DFT calculation

Compound	LUMO (eV)
Ethylene carbonate (EC)	−0.24
Propylene carbonate (PC)	−0.27
Ethyl (methyl)carbonate (EMC)	0.16
Butyl sultone (BS)	−0.38

3.4. DFT calculations on LUMO of solvents and BS

The lowest unoccupied molecule orbital (LUMO) level of a molecule has a tight relationship with its reduction ability [22]. The lower the LUMO level of a molecule is, the more easily the electron can be transferred into the molecule. Table 1 shows the LUMO levels of solvents, EC, PC and EMC, and the additive BS. It can be seen from Table 1 that the LUMO level of BS is much lower than those of carbonate solvents. This is why BS is reduced prior to the solvents.

3.5. Electron dispersive spectra

In order to understand the composition of SEI film formed on graphite in the electrolytes with and without BS, the graphite electrodes after the first cycle in the electrolytes with and without 1% BS were analyzed with EDS (all the graphite electrodes were washed with EMC before experiments). The results are shown in Fig. 5. A sulfur peak at *ca.* 2.2 keV was detected in the electrolyte with BS (Fig. 5B). This was not detected in the electrolyte without BS (Fig. 5A). Apparently, this peak is corresponding to the sulfur in the sulfurous compounds formed on the graphite electrodes during the reduction of BS. This suggests that the reduction products of BS take part in the formation of SEI film.

The effect of BS on lithium ion battery is very similar to that of propane carbonate [20]. With the results available, the possible mechanism for the reduction reaction of BS can be expressed as in Scheme 1. A radical anion coordinated with lithium ion (A) is formed at the first step of the reduction of BS with one electron
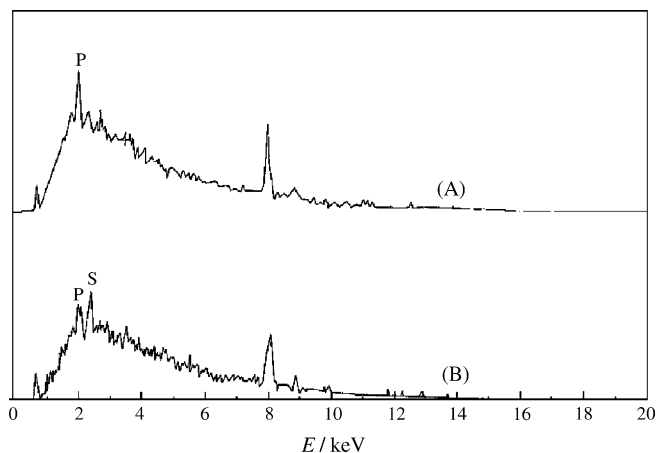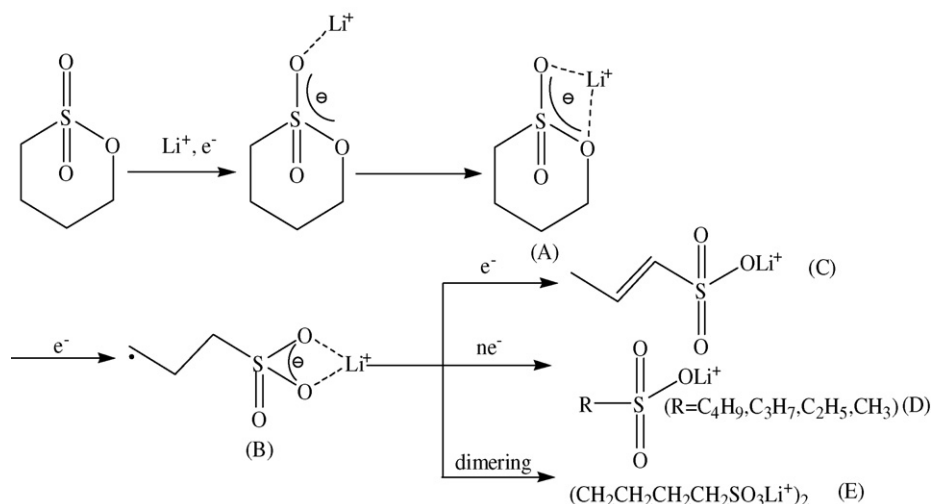

Fig. 5. EDS of graphite electrodes after the first cycle in $1 \, mol \, L^{-1}$ LiPF$_6$/EC:PC:EMC = 1:1:3 without (A) and with (B) 1 wt.% BS.

Scheme 1. Possible reaction paths for the reduction of BS on graphite electrodes.

transfer, followed by the formation of radical alkyl sulfonate (B) with another electron transfer. Several products may be formed from the radical alkyl sulfonate, for example (1) the formation of alkenyl sulfonate (C) due to the reduction of (B) with a one electron transfer accompanying the formation of the C=C bond; (2) the formation of alkyl sulfonate (D), R may be C_4H_9 in (D) when (B) is reduced with a one electron transfer and without the formation of the C=C bond, or C_3H_8, C_2H_5 or CH_3 when the reduction of (B) takes place with a more than two electron transfer accompanying the breakdown of a C–C bond in (B); (3) the formation of dimmer (E) due to the self-dimerization of (B).

4. Conclusions

The performance of lithium ion battery greatly depends on the nature of electrolyte. PC can easily decompose on graphite and co-insert with Li-ions into graphite electrode, which reduces the reversible capacity of graphite electrode. PC can be used as a component of electrolyte for Li-ion battery by adjusting the composition of the solvents. With the application of PC in the electrolyte, the discharge capacity of lithium ion battery is improved under high temperature or low temperature. However, the discharge capacity and the cyclic stability of lithium ion battery with PC are not so good as the battery without PC under room temperature. To overcome this drawback of PC, an SEI forming additive should be used. It is found that the performances of Li-ion battery can be significantly improved by the use of BS as the SEI forming additive. This improvement can be ascribed to the reduction of BS and the formation of a stable SEI film on the graphite electrode.

Acknowledgements

References

[1] J.M. Tarascon, M. Armand, Nature 414 (2001) 359.
[2] A. Schechter, D. Aurbach, H. Cohen, Langmuir 15 (1999) 3334.
[3] T. Eriksson, A.M. Andersson, C. Gejke, T. Gustafsson, J.O. Thomas, Langmuir 18 (2002) 3609.
[4] Y.X. Wang, S. Nakamura, K. Tasaki, P.B. Balbuena, J. Am. Chem. Soc. 124 (2002) 4408.
[5] Y.X. Wang, S. Nakamura, K. Tasaki, P.B. Balbuena, J. Am. Chem. Soc. 123 (2001) 11708.
[6] M.D. Levi, E. Markvich, D. Aurbach, J. Phys. Chem. B 109 (2005) 7420.
[7] D.S. Lü, W.S. Li, Acta Chim. Sin. 61 (2003) 225.
[8] L.F. Xiao, X.P. Ai, Y.L. Cao, H.X. Yang, Electrochim. Acta 49 (2004) 4189.
[9] K. Xu, Chem. Rev. 104 (2004) 4310.
[10] T.R. Jow, M.S. Ding, K. Xu, S.S. Zhang, J.L. Allen, K. Amine, G.L. Henriksen, J. Power Sources 119–121 (2003) 343.
[11] Y.X. Wang, P.B. Balbuena, J. Phys. Chem. B 106 (2002) 4486.
[12] D. Aurbach, J.S. Gnanaraj, W. Geissler, M. Schmidt, J. Electrochem. Soc. 151 (2004) A23.
[13] J. Fan, J. Power Sources 117 (2003) 170.
[14] M.C. Smart, B.V. Ratnakumar, S. Surampudi, J. Electrochem. Soc. 149 (2002) A361.
[15] R.A. Marsh, S. Vukson, S. Surampudi, B.V. Ratnakumar, M.C. Smart, M. Manzo, P.J. Dalton, J. Power Sources 97/98 (2001) 25.
[16] E.J. Plichat, M. Hendrickson, R. Thompson, G. Au, W.K. Behl, M.C. Smart, B.V. Ratnakumar, S. Surampudi, J. Power Sources 94 (2001) 160.
[17] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian Inc., Pittsburgh PA, 2003.

[18] M.S. Ding, K. Xu, T.R. Jow, J. Electrochem. Soc. 147 (2000) 1688.

[19] S.S. Zhang, K. Xu, J.L. Allen, T.R. Jow, J. Power Sources 110 (2002) 216.

[20] X.X. Zuo, M.Q. Xu, W.S. Li, D.G. Su, J.S. Liu, Electrochem. Solid-State Lett. 9 (2006) A196.

[21] M.Q. Xu, X.X. Zuo, W.S. Li, H.J. Zhou, J.S. Liu, Z.Z. Yuan, Acta Phys.-Chim. Sin. 22 (2006) 335.

[22] G.C. Chung, H.J. Kim, S.I. Yu, S.H. Jun, J.W. Choi, M.H. Kim, J. Electrochem. Soc. 147 (2000) 4391.