Power capability improvement of LiBOB/PC electrolyte for Li-ion batteries

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Abstract

Lithium bis(oxalto)borate (LiBOB) is quite effective to prevent vigorous decomposition of propylene carbonate (PC) at the graphite anode of a Li-ion battery during Li insertion. PC is a very good solvent that is inexpensive, has high conductivity and a low melting point; however, the power capability of PC electrolyte containing LiBOB is unsatisfactory.

In an attempt to improve the power capability of the LiBOB/PC electrolyte, mixed electrolytes containing both LiBOB and $LiClO_4$ were examined. An integrated fiber felt of highly graphitized carbon was used as the working electrode and the performance was evaluated by cyclic voltammetry (CV), constant current followed by constant voltage charge (CCCV) and constant current discharge. The CV produced a stable peak for Li extraction, but the peak height was as low as half that obtained in a conventional electrolyte such as a 1:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) containing 1 M $LiClO_4$. However, the peak height in PC, containing 1/49 M LiBOB and 1 M $LiClO_4$, became 1.5 times higher than that in PC containing 1 M LiBOB. The peak height was increased further using a 1:1 mixture of PC and acetonitrile (AN) containing 1/49 M LiBOB and 1 M $LiClO_4$, although the cycleability was poor. A similar tendency was observed with the CCCV test. The CV peak height was plotted against the ionic conductivity of several solvents and showed no linear relationship, implying that the reaction activity was influenced by the solid electrolyte interphase (SEI) formed. The charge transfer resistance was evaluated by impedance spectroscopy. The results revealed that not only the surface film resistance but also the charge transfer resistance was markedly increased in the electrolyte containing LiBOB; however, they were reduced by the addition of $LiClO_4$.
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1. Introduction

The production number of Li-ion secondary batteries is still increasing rapidly because of their superior performance in satisfying the strong demands of various portable electronic appliances. As the active material for the anode, highly graphitized carbons are most widely used because of their high reversibility and reliability. The electrolyte used for the graphitized carbon anode is a mixture of ethylene carbonate (EC) and other solvents like diethyl carbonate (DEC) or dimethyl carbonate (DMC).

On the other hand, propylene carbonate (PC) is an attractive solvent for Li-ion batteries because it has high conductivity at low temperature and is inexpensive. However, it has a serious problem in that it decomposes vigorously when in contact with graphitized carbon at potentials less than 1 V versus Li/Li^+. The decomposition is believed by some to be caused by the absence of a stable solid electrolyte interphase (SEI). Therefore, it is worthwhile to explore a condition where graphitized carbon can be used in an electrolyte comprised of pure PC. Many studies have so far been conducted for the suppression of PC decomposition. Shu et al. proposed to add crown ether (12 crown 4) to the PC electrolyte [1]. Aurbuch et al. reported on the effective influence of carbon dioxide [2] and Besenhald and co-workers showed that the decomposition was suppressed very efficiently by the

addition of ethylene sulfite into the PC-based electrolyte [3]. In the absence of any additives, however, no work appears to have been reported on the stable performance of graphitized carbon in an electrolyte based on pure PC, except for the paper by Jeong et al. [4]. Jeong et al. reported that lithium bis(perfluoroethylsulfonyl)imide in PC can effectively stabilize graphite materials without additives. However, the concentration of the imide was as high as $2.72\,mol\,dm^{-3}$. In addition, the power capability for Li insertion/extraction reaction appears restricted [4] even though the dissolution of the Al current corrector is much suppressed [5].

Recently, a new Li salt, lithium bis(oxalto)borate (Li-BOB), was developed in Germany and USA. Xu et al. have reported that LiBOB can effectively stabilize graphite materials in PC-rich or even pure PC electrolyte [6,7]. However, in our preliminary measurement using LiBOB, the performance of a graphite anode in PC containing LiBOB was insufficient for providing high power capability compared to a conventional electrolyte. In this paper, we present the improvement of performance in the electrolyte containing LiBOB and PC while maintaining stable performance without decomposition of the electrolyte.

2. Experimental

2.1. Carbon materials

As an anode active material, an integrated felt of graphitized carbon fiber (Melblon 3100, Petoca Materials) was used, avoiding conventional coated electrodes that use some binders and conductive additives that cause capacity fading due to the loosening of contact between the active materials and the electronic conductor materials. The felt was sandwiched between sheets of Ni mesh or expanded metal, requiring no such binders and no coating process.

2.2. Test electrode fabrication

As an anode active material, the felt was cut into 1 mm thick 1 cm × 1 cm square sheet and heated at 250 °C for 1 h in a vacuum to remove physisorbed water and contaminants and used for the test electrode. The test electrode was fabricated by sandwiching the treated felt sample between two larger size Ni expanded metal sheets. The rims were spot-welded at several points to ensure the specimen was securely fixed. A Ni wire was spot-welded to one periphery of the Ni expanded sheets in advance for use as a lead wire.

2.3. Electrolyte

A 1:1 (v/v) mixture of EC and DMC containing 1 M LiClO$_4$ was provided by Tomiyama Chemicals. This electrolyte is one of the standard electrolytes for Li-ion batteries. A PC electrolyte containing 1 M LiClO$_4$ (electrolyte A) provided by Tomiyama Chemicals was used for examining the

decomposition of graphite. PC electrolyte containing 1 M LiBOB (electrolyte B) was prepared by dissolving a corresponding amount of LiBOB (Chemetall GmbH, Germany) into PC. Electrolyte B was mixed with electrolyte A to prepare several electrolytes having different LiBOB concentrations with molar ratios of LiBOB:LiClO$_4$ being 1:25, 1:50, 1:75, 1:100 and 1:150.

2.4. Electrochemical measurements

A cylindrical Pyrex glass cell with a three-electrode system was used for the measurements. Pure metallic Li foils were used as reference and counter electrodes. Cyclic voltammetry (CV) was conducted at a potential sweep rate of $1\,mV\,s^{-1}$. A Hokuto Denko Potentio-galvanostat Type HA-151 was used for the electrochemical evaluation. Constant current followed by constant voltage charge (CCCV) was also conducted with a loading current at 0.5 C rates for charging and discharging. All the measurements were performed at room temperature in a glove box filled with dried Ar.

3. Results and discussion

3.1. Effect of LiBOB

Fig. 1 shows the CVs with a sweep rate of $1\,mV\,s^{-1}$ in three electrolytes: (a) EC + DMC containing 1 M LiClO$_4$, (b) PC containing 1 M LiClO$_4$ and (c) PC containing 1 M LiBOB. Fig. 1(a) shows typical CVs for graphitic carbons where well-defined peaks of Li insertion/extraction currents are recognized. In contrast, as shown in Fig. 1(b), vigorous decomposition of PC was observed to occur continuously. However, when LiBOB was used in place of LiClO$_4$, the PC revealed quite stable CV features, as shown in Fig. 1(c), which shows stable insertion and extraction of Li. The CV peak currents, however, are poor when compared with the results obtained for a conventional electrolyte (Fig. 1(a)). Such a depression in the peak heights is a major issue for practical applications. In order to improve the depressed power capability by maintaining a decomposition-preventing effect, the cooperation of a conventional salt with LiBOB was utilized.
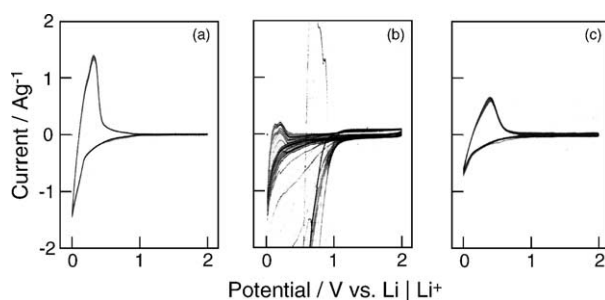

Fig. 1. Cyclic voltammograms of mesophase carbon fibers. Sweep rate: $1\,mV\,s^{-1}$. In (a) 1 M LiClO$_4$/EC + DMC, volume ratio EC:DMC = 1:1; (b) 1 M LiClO$_4$/PC and (c) 1 M LiBOB/PC.
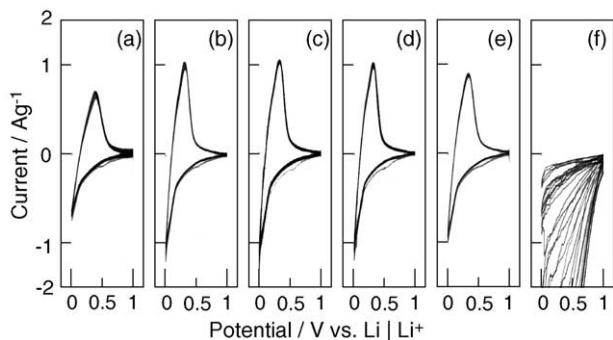
Fig. 2. Cyclic voltammograms of mesophase carbon fibers in PC. Sweep rate: $1 \, mV \, s^{-1}$. (a) Only LiBOB; (b) molar ratio LiBOB:LiClO$_4$ = 1:25; (c) molar ratio LiBOB:LiClO$_4$ = 1:50; (d) molar ratio LiBOB:LiClO$_4$ = 1:75; (e) molar ratio LiBOB:LiClO$_4$ = 1:100 and (f) molar ratio LiBOB: LiClO$_4$ = 1:150.

For the purpose of improving the power capability which can be estimated from the CV peak height, the effect of the amount of LiClO$_4$ coexisting with LiBOB was examined. Fig. 2 shows CVs obtained in six PC electrolytes containing LiBOB/LiClO$_4$, where the molar ratios of LiBOB:LiClO$_4$ are (a) 1:0, (b) 1:25, (c) 1:50, (d) 1:75, (e) 1:100 and (f) 1:150, respectively. Compared to the results obtained with LiBOB alone (Fig. 2(a)), the mixed electrolyte showed increased power capability in the absence of PC decomposition. Increased charge/discharge currents and improved cycleability can be realized as shown in Fig. 2(b–e). In Fig. 2(c), the electrolyte with a molar ratio LiBOB:LiClO$_4$ = 1:50 gave the highest peak current. This indicates there is a possibility that LiBOB can be used as an effective additive in PC electrolyte, to provide improved power capability. The amount of LiBOB was reduced further to a molar ratio of 1:150, but unfortunately electrolyte decomposition could not be prevented (Fig. 2(f)) with such a low content of LiBOB.

In order to analyze the cause of suppressed peak heights in an electrolyte of LiBOB/PC containing no LiClO$_4$, impedance spectroscopy was performed on three electrolytes of: (a) EC + DMC containing 1 M LiClO$_4$, (b) PC containing 1 M LiBOB and (c) PC containing LiBOB and LiClO$_4$, molar ratio LiBOB:LiClO$_4$ = 1:50. The results are shown in Fig. 3. In the case of simple system of LiBOB in PC (curve (b)), the charge transfer resistance as well as the film resistance were very high as compared with those of conventional electrolyte (a), whereas the modified electrolyte (c) revealed much suppressed impedance both in film resistance and charge transfer resistance, implying that the reaction site is activated to provide improved power capability.

3.2. Relationship between conductivity and power capability

Important factors influencing the power capability are not only the number and the activity of the reaction sites but also the conductivity of the electrolyte in contact with the electrode. An examination was made of the relationship between
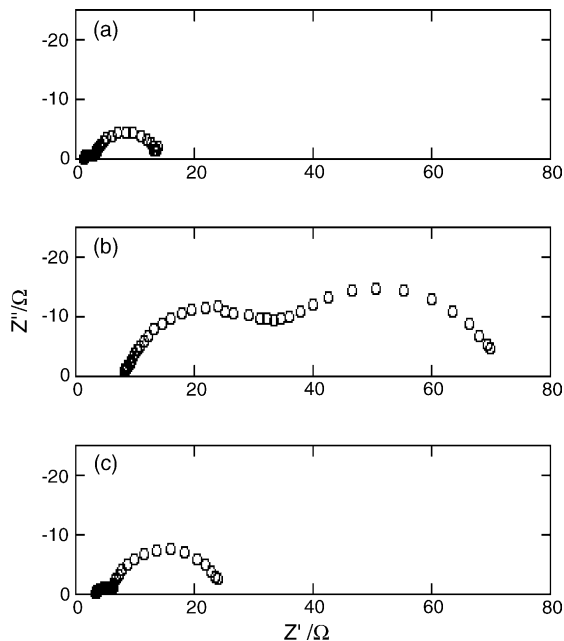

Fig. 3. Nyquist plots of mesophase carbon fibers during the Li extraction at 0.24 V in several electrolytes. In (a) 1 M LiClO$_4$/EC + DMC, volume ratio EC:DMC = 1:1; (b) 1 M LiBOB/PC and (c) LiBOB + LiClO$_4$/PC, molar ratio LiBOB:LiClO$_4$ = 1:50.

the CV peak height and the conductivity of the electrolyte where the CV was obtained.

In order to obtain electrolytes having higher conductivity, an attempt was made to use the very low viscosity acetonitrile (AN). The composition of prepared electrolytes was: molar ratio LiBOB:LiClO$_4$ = 1:50, volume ratio PC:AN = 1:1. The CVs are shown in Fig. 4(a). The revealed CV peak height was higher than that obtained with a conventional electrolyte at the first cycle.

The cycle performance under CCCV condition is compared for results obtained with several electrolytes in Fig. 5,
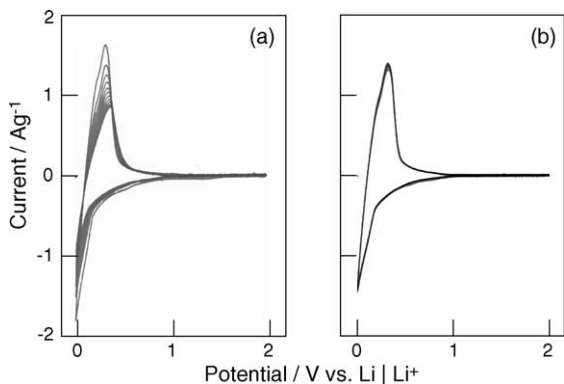

Fig. 4. Comparison of cyclic voltammograms of mesophase carbon fibers obtained in an acetonitrile containing electrolyte and a conventional electrolyte. Sweep rate: $1 \, mV \, s^{-1}$. In (a) LiBOB + LiClO$_4$/PC + AN, molar ratio LiBOB:LiClO$_4$ = 1:50, volume ratio PC:AN = 1:1 and (b) 1 M LiClO$_4$/EC + DMC, volume ratio EC:DMC = 1:1.
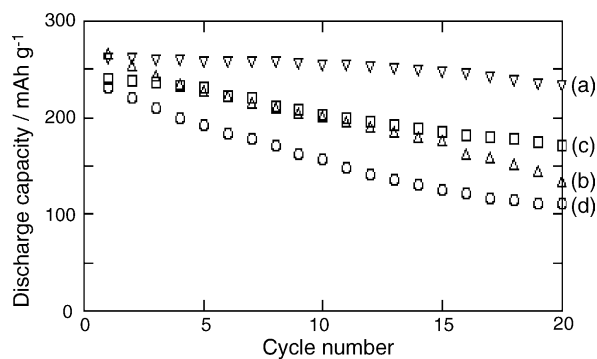
Fig. 5. Constant current followed by constant voltage charge/discharge cycle performance of a mesophase carbon fiber felt in several electrolyte at a 0.5 C rate. In (a) 1 M $LiClO_4$/EC + DMC, volume ratio EC:DMC = 1:1; (b) LiBOB + $LiClO_4$/PC + AN, molar ratio LiBOB:$LiClO_4$ = 1:50, volume ratio PC:AN = 1:1; (c) LiBOB + $LiClO_4$/PC, molar ratio LiBOB:$LiClO_4$ = 1:50 and (d) 1 M LiBOB/PC.
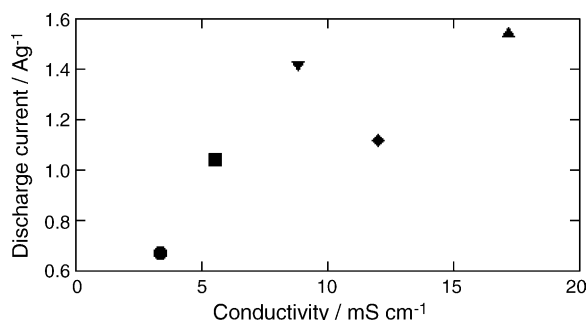

Fig. 6. Relationship between conductivity of the electrolyte solution and the discharge peak height in several electrolytes containing LiBOB and $LiClO_4$. ●, 1 M LiBOB/PC; ■:, LiBOB + $LiClO_4$/PC, molar ratio LiBOB:$LiClO_4$ = 1:50; ▼, 1 M $LiClO_4$/EC + DMC, volume ratio EC:DMC = 1:1, ◆, 1 M LiBOB/volume ratio PC:AN = 1:1; ▲, LiBOB + $LiClO_4$/PC + AN, molar ratio LiBOB:$LiClO_4$ = 1:50, volume ratio PC:AN = 1:1.

where we see a similar tendency in the performance to that obtained with CV (Fig. 2) among the electrolytes tested: The best one is in the case of conventional electrolyte, followed by the modified electrolyte containing LiBOB and $LiClO_4$ (mixing ratio: 1:50). When an electrolyte having the salt molar ratio LiBOB:$LiClO_4$ = 1:50 and the solvent volume ratio PC:AN = 1:1 is used, the discharge capacity is larger than that obtained with a conventional electrolyte at the first cycle. These results appear to suggest that the power capability is strongly dependent on the conductivity of the electrolyte. Conductivity measurements of several electrolytes were plotted against the peak heights of the CVs. However, as shown in Fig. 6, the results do not show a simple linear relationship between the ionic conductivity and the CV peak heights. Fig. 3 indicates that the charge transfer resistance is more directly related to the power capability. The charge

transfer resistance is expected to relate to the physical chemistry of SEI. The reaction site activity is expected to depend on the nature of the SEI formed on the carbon surface where adsorption of BOB or some fragment of BOB is expected to influence the site activity. Recently, Xu et al. have reported on the SEI formed in a PC electrolyte solution containing LiBOB [8–10]. They pointed out that the SEI is formed by the electrochemical reduction of the BOB anion. The same SEI may also be formed in our experiment; however, the relationship between the SEI formation and power capability is not clear. This will be analyzed in future work.

4. Conclusions

The concept of mixing LiBOB/PC electrolyte with $LiClO_4$/PC is very effective because not only was PC decomposition prevented but also the power capability of LiBOB/PC electrolyte was increased. The prevention of PC decomposition is due to the SEI containing a LiBOB related substance formed on the graphite carbon surface.

The power capability of LiBOB + $LiClO_4$/PC electrolyte was improved by mixing with AN and the CV peak heights were higher than that in a conventional electrolyte at the first cycle, although the cycleability was not satisfactory.

Acknowledgment

References

[1] Z.X. Shu, R.S. McMillan, J.J. Murray, J. Electrochem. Soc. 140 (1993) 922.
[2] D. Aurbuch, Y. Ein-Eli, O.Y. Chusid, Y. Cermeli, M. Babai, H. Yamin, J. Electrochem. Soc. 141 (1994) 603.
[3] G.H. Wrodnigg, J.O. Besenhald, M. Winter, J. Electrochem. Soc. 146 (1999) 470.
[4] S. Jeong, M. Inaba, Y. Iriyama, T. Abe, Z. Ogumi, Electrochem. Solid-State Lett. 6 (2003) A13.
[5] L.J. Krause, W. Lamanna, J. Summerfeld, M. Engle, G. Korbra, R. Loch, R. Atanasoski, J. Power Sources 68 (1997) 320.
[6] K. Xu, S. Zhang, B.A. Poese, T.R. Jow, Electrochem. Solid-State Lett. 5 (2002) A259.
[7] K. Xu, S. Zhang, T.R. Jow, Electrochem. Solid-State Lett. 6 (2003) A117.
[8] K. Xu, U. Lee, S. Zhang, M. Wood, T.R. Jow, Electrochem. Solid-State Lett. 6 (2003) A144.
[9] G.V. Zhuang, K. Xu, T.R. Jow, P.N. Poss Jr., Electrochem. Solid-State Lett. 7 (2004) A224.
[10] K. Xu, U. Lee, S. Zhang, T.R. Jow, J. Electrochem. Soc. 151 (2004) A2106.