

Short communication

Enhanced performance of Li-ion cell with LiBF₄-PC based electrolyte by addition of small amount of LiBOB

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Received 4 April 2005; accepted 30 April 2005

Available online 24 June 2005

Abstract

LiBF₄-PC based electrolytes have superior potentials in enhancing cycling performance of Li-ion cells at low temperature and at high current rate, respectively. However, their application is prevented because of the poor capability in enabling graphite to form a solid electrolyte interface (SEI). In this work, we found that addition of small amount of lithium bis(oxalate)borate (LiBOB) into the LiBF₄-based electrolytes could significantly promote SEI formation on the surface of graphite even in solutions with a high content of PC. This is attributed to the fact that LiBOB participates in the formation chemistry of the SEI. Results showed that 1–5 mol% LiBOB is sufficient to promote graphite cycling reversibly in 1.0 m LiBF₄ 1:1:3 PC/EC/EMC and 1.0 m LiBF₄ 1:1 PC/EC, respectively, while the excellent cycling performance of LiBF₄-PC based electrolytes at low temperatures was maintained.

Published by Elsevier B.V.

Keywords: LiBF₄; Lithium bis(oxalate)borate; Electrolyte additive; Solid electrolyte interface; Low temperature performance

1. Introduction

We recently focused on developing LiBF₄-based electrolytes for application of Li-ion batteries in a wide temperature range [1–5]. Compared with LiPF₆ that has been the only salt used in the currently commercial Li-ion batteries, LiBF₄ has such advantages as: (1) better thermal stability and lower sensitivity toward environmental moisture [1,2] and (2) its solution provides a much lower charge-transfer resistance, especially at low temperatures [3–5]. The latter feature, which also has been observed by other researchers in Li/LiMn₂O₄ half-cell [6], bestows LiBF₄-based electrolytes with much better performance at low temperatures, in spite of their relatively low ionic conductivity [3–5]. However, application of the LiBF₄-based electrolytes in Li-ion batteries is restricted, mainly because of their poor ability to form a protective solid electrolyte interface (SEI) on the surface of graphite and their relatively high freezing temperature due to inability to form a super-cooled solution [3]. Our approaches toward these two

hurdles were to use electrolyte additives [7,8] and to formulate new solvent systems [5].

In parallel efforts, we have found that lithium bis(oxalate)borate (LiBOB) has a unique chemical characteristic to form a stable SEI even in a pure PC solution [9,10]. Furthermore, the resulting SEI was able to withstand operation up to 70 °C [11]. Surface analyses by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR), respectively, on the SEI thus formed indicate that this unique property is attributed to the participation of LiBOB in the initial SEI chemistry [10,12]. On the other hand, the recognized concerns with LiBOB as the solute of Li-ion electrolytes are (1) its limited solubility in common electrolyte solvents such as linear alkyl carbonates, (2) its relatively inferior performance at low temperature and high current rate and (3) its extreme sensitivity to impurity and environmental moisture, which has been considered as one of the possible sources for gas generation during storage and cycling of Li-ion batteries. By reducing the content of LiBOB to 1–10 mol% versus the total of mixed salt, we found the unique capability of LiBOB in stabilizing SEI could be kept while its adverse effect was minimized [7,8].

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In this work, we used LiBOB to improve SEI formation on graphite in LiBF_4 -PC based electrolytes, and then evaluated the cycling performance of Li-ion cells with LiBOB-improved electrolytes. The effect of LiBOB as an electrolyte additive on the SEI formation and low temperature performance of such Li-ion cells is reported in this paper.

2. Experimental

LiBF_4 (Stella Chemifa Corp.) and LiBOB (Chemmetal, Germany) were dried at 100°C under vacuum for 8 h before use. Propylene carbonate (PC), ethylene carbonate (EC) and ethylmethyl carbonate (EMC, all from Ferro Chemical) were dried in sequence by 3\AA molecular sieves and neutral alumina. In a glove-box having oxygen and moisture levels below 10 ppm, 1.0 molality (m) electrolytic solutions with different salt and solvent compositions were prepared. Composition of the salt and solvent was expressed as a molar percentage and weight ratio, respectively.

Standard graphite anode and LiNiO_2 -based cathode were provided by SAFT America. The electrode sheets were cut into discs of 1.27 and 0.97 cm^2 for the anode and cathode, respectively, and then dried at 120°C under vacuum for 12 h. Using Celgard[®] 3500 membrane as the separator, Li/graphite half-cell and graphite/ LiNiO_2 Li-ion cell were assembled and filled with $80\ \mu\text{L}$ of electrolyte. A Maccor Series 4000 tester was used for cycling tests. The cell was formed at 0.1 mA cm^{-2} for two cycles and then galvanostatically cycled at 0.5 mA cm^{-2} . The Voltage range for cycling tests was 0.002–1.5 V for the Li/graphite half-cell and 2.5–4.2 V for the Li-ion cell, respectively. A Tenney Environmental Oven Series 942 was used to control the temperature of the cell for cycling tests at low temperatures. In those tests, the cell was charged at 20°C , and then discharged at a specific temperature by storing the cell at a specific temperature for 6 h. A term of “relative capacity”, which is defined as the ratio of the capacity at a specific temperature to the capacity at 20°C , was used to describe the cycling performance at low temperatures.

3. Results and discussion

3.1. Li/graphite half-cell

Fig. 1 shows the effect of LiBOB on SEI formation of graphite in 1.0 m solution of LiBF_4 -LiBOB mixed salt in 1:1 PC/EC and 1:1:3 PC/EC/EMC, respectively. In the absence of LiBOB, the SEI cannot be formed at all in 1:1 PC/EC solution, as indicated by the perpetual plateau of cell voltage above 0.6 V, which is known to be the characteristic of solvent (mainly PC in this case) reductions (Fig. 1a). With addition of 1 mol% LiBOB, however, such reductions were effectively suppressed and intercalation of Li^+ ions into graphite occurred below 0.3 V. For 1.0 m LiBF_4 1:1:3 PC/EC/EMC electrolyte (Fig. 1b), significant solvent reductions were observable over a wide voltage range from 0.8 to 0.4 V although the cell voltage eventually went down to the potentials at which Li^+ ion intercalation underwent. These reductions were substantially eliminated by addition of as low as 0.5 mol% of LiBOB. Note that these three curves for 0.5, 1 and 2 mol% of LiBOB in Fig. 1b are so close that they are overlapped together. The observations above verify that the presence of small amount of LiBOB is very effective in suppressing PC reduction on the fresh surface of graphite.

To understand the mechanism of LiBOB facilitating SEI formation, we plotted differential capacities of graphite versus cell voltage in the inset of Fig. 1b. Without addition of LiBOB, the solvent reduction occurred over the whole voltage range from 0.83 to 0.20 V, as indicated by high background and two wide peaks at 0.73 and 0.54 V, respectively. With addition of LiBOB, the first peak at 0.73 V still was present although its area was substantially decreased, while the second one at 0.54 V completely vanished. Excellent consistency in the voltage ($\sim 0.73\text{ V}$) of the first peak for the solution without and with LiBOB, respectively, suggests that the first reduction peak around 0.73 V should be related to the solvents, instead of LiBOB.

It has been known that the SEI mainly consists of the reduced products of the electrolyte components. For example, the SEI formed in EC-based electrolytes is characterized

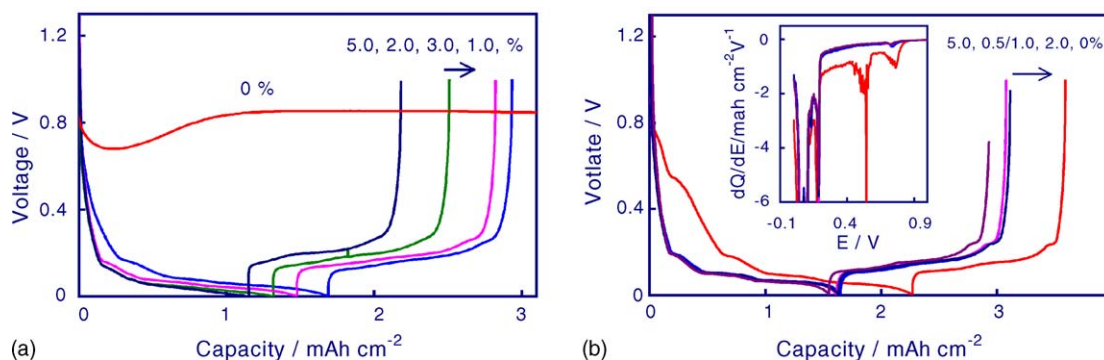


Fig. 1. Voltage–capacity curves of the first cycle for Li/graphite cells with different LiBF_4 -PC based electrolytes, in which the numbers present molar percentage of LiBOB in the mixed salt. Inset in (b) is a part of the plots of differential capacities vs. cell voltage. (a) 1.0 m LiBF_4 1:1 PC/EC and (b) 1.0 m LiBF_4 1:1:3 PC/EC/EMC.

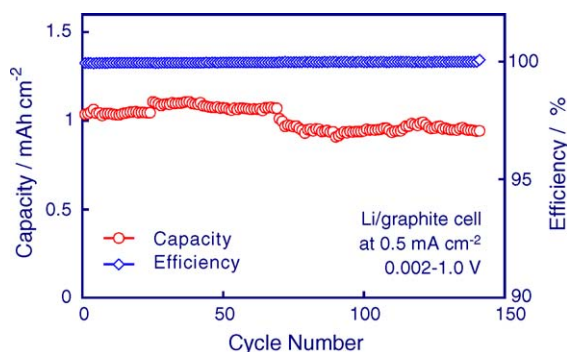
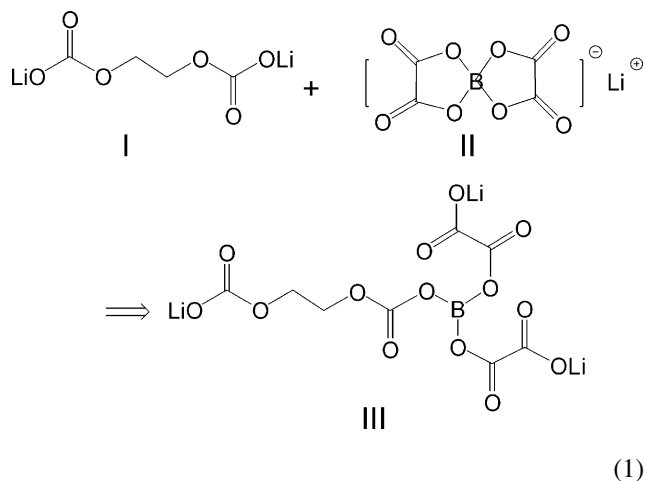


Fig. 2. Discharge capacities and cycling efficiencies of the Li/graphite cell with 1.0 m (0.98LiBF₄–0.02LiBOB) 1:1:3 PC/EC/EMC electrolyte.

by semicarboxylate-like products, such as compound (I) in Eq. (1) [13,14]. Independent analyses of XPS and FTIR have also verified that the SEI formed in LiBOB solution contains a large amount of LiBOB-originated molecular moieties [10,12], especially those like trigonal BO₃ esters and oxalic acid esters, both of which are realized as the rearranged products of LiBOB. Based on the knowledge above, we speculate that LiBOB stabilizes SEI probably through the rearranging reactions like Eq. (1) to form more stable compounds, such as (III), which are substantially insoluble in electrolytic solutions and probably have better morphology.



According to Eq. (1), it seems that LiBOB itself does not undergo reduction during SEI formation. Its role in stabilizing SEI is that it combines semicarboxylate-like products to form more stable compounds. A similar phenomenon also has been observed elsewhere [15], where a pre-coated oxalatorbate layer on the surface of natural graphite stabilizes SEI without reductions of itself.

After two forming cycles at low current density (0.1 mA cm⁻²), the Li/graphite cell with 1.0 m (0.98LiBF₄–0.02LiBOB) 1:1:3 PC/EC/EMC electrolyte was galvanostatically cycled at 0.5 mA cm⁻² between 0.002 and 1.5 V. Delithiation capacities and cycling efficiencies of graphite versus cycle number are plotted in Fig. 2, which shows that the capacities stayed at 0.92–1.1 mAh cm⁻²

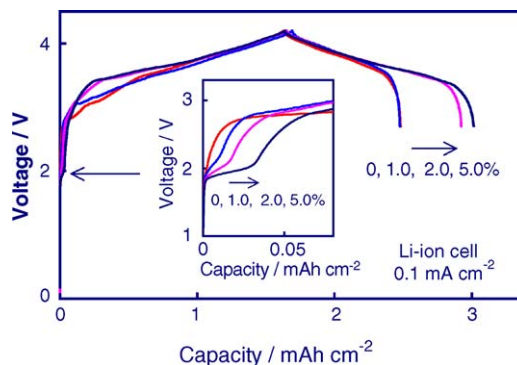


Fig. 3. Voltage–capacity curves of the first cycle for graphite/LiNiO₂ cells with different 1.0 m LiBF₄–LiBOB 1:1:3 PC/EC/EMC electrolytes, in which the numbers present molar percentage of LiBOB in the mixed salt.

and cycling efficiencies remained at 100%. Small changes in the capacities during cycling probably resulted from fluctuations in the room temperature. The results above reveal that addition of small amount of LiBOB is effective in promoting graphite to form a stable SEI with LiBF₄-PC based electrolytes.

3.2. Graphite/LiNiO₂ Li-ion cell

Effect of LiBOB on the performance of the first forming cycle for graphite/LiNiO₂ Li-ion cells is plotted in Fig. 3, which shows that the cycling efficiency increases with addition of LiBOB. It seems that there was no improvement as the content of LiBOB was less than 1.0 mol%. This phenomenon is different from that observed in Li/graphite cells (see Fig. 1). To compare this difference, we summarize cycling efficiencies of the first forming cycle for these two types of cells in Table 1. It is surprising that the cycling efficiency of the Li-ion cell decreased, as the content of LiBOB was 1%. Table 1 indicates that at least 5 mol% of LiBOB is necessary for the improvement of Li-ion cells although the data of Li/graphite cells shows much lower threshold value of 1%. We consider that the difference between Li/graphite and Li-ion cells is associated with the impurities contained in the LiNiO₂-based cathode. It has been long known that Li₂CO₃ impurity is inevitably present to the surface of LiNiO₂-based materials and its content increases with exposure time to air [16,17]. This trace amount of Li₂CO₃ may be responsible for the alleviation of effectiveness of LiBOB additive in Li-ion cells. It has been found that further improvement to the graphite anode no longer increases cycling efficiency of the first

Table 1
Cycling efficiencies of the first forming cycle

LiBOB (mol%)	Li/graphite	Graphite/LiNiO ₂
0	58.2	52.2
0.5	86.6	–
1	90.4	46.3
2	90.6	77.0
5	89.1	83.9

Electrolyte: 1.0 m (100 – x)LiBF₄–xLiBOB 1:1:3 PC/EC/EMC.

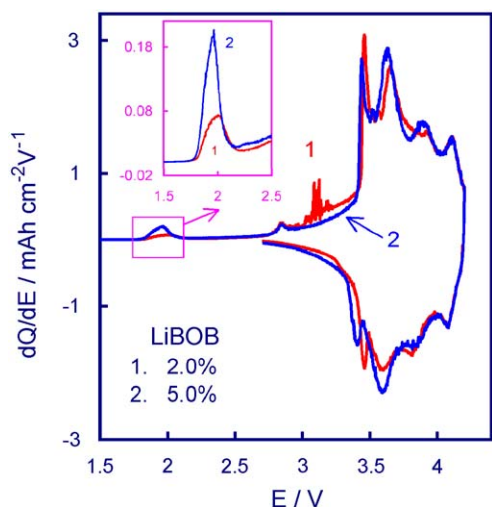


Fig. 4. Plots of differential capacities versus cell voltage for the first cycle of graphite/LiNiO₂ cells with different 1.0m LiBF₄-LiBOB 1:1:3 PC/EC/EMC electrolytes. (1) 0.98LiBF₄-0.02LiBOB and (2) 0.95LiBF₄-0.05LiBOB.

forming cycle for the graphite/LiNiO₂ cells. This is because LiNiO₂-based materials suffer from irreversible structural change during the first charging [18,19]. That is, parts of divalent nickel ions are collapsed into the sites of lithium ions as extra nickel ions. This process produces 10–20% irreversible capacities in the first cycle, which depends on the x value in LiNi_(1-x)M_xO₂ (M = transition metal such as Co).

It is interesting to note a very short voltage plateau at 1.8–2.0 V in the first charge process, and its length increases with the content of LiBOB (see inset in Fig. 3). This plateau, which corresponds to the small plateau of Li/graphite cell at ~1.6 V [20], is related to LiBOB, and it is not responsible for the stabilization of SEI. We spent much effort to understand the origin of this small plateau, and found that it was most likely related to the impurity contained in LiBOB, such as oxalate-like compounds. This conclusion is based on the following observations: (1) purifying LiBOB significantly reduces this small plateau, (2) voltage of this plateau is consistent with that of oxalate reduction and (3) traditional Karl-Fisher titration is not suitable for the determination of water content in LiBOB-containing solutions due to the presence of the reductive oxalate impurities.

Differential capacities of the first cycle of Li-ion cells with the electrolyte added by 2 and 5 mol% of LiBOB, respectively, are plotted in Fig. 4, the inset of which distinctly shows irreversible capacity of the plateau at 1.8–2.0 V increases with the content of LiBOB. There are many small satellite irreversible peaks at around 3.1 V for the cell containing 2 mol% of LiBOB. These peaks, which are identified to correspond to those at ~0.54 V in Li/graphite cell as shown in inset of Fig. 1b, completely vanished as the content of LiBOB was increased to 5 mol%. This observation suggests that 5 mol% of LiBOB would be necessary for the improvement of SEI formation in Li-ion cells using a LiNiO₂-based cathode and 1.0 m LiBF₄ 1:1:3 PC/EC/EMC electrolyte.

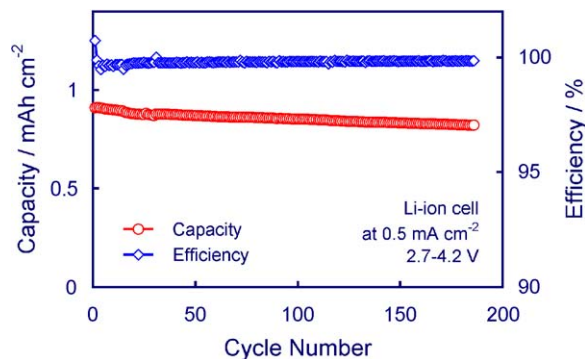


Fig. 5. Discharge capacities and cycling efficiencies of the graphite/LiNiO₂ cell with 1.0 m (0.98LiBF₄-0.02LiBOB) 1:1:3 PC/EC/EMC electrolyte.

After two forming cycles, the cell was cycled at room temperature and low temperature, respectively. Fig. 5 shows cycling performance at room temperature of the Li-ion cell with the electrolyte containing 2 mol% of LiBOB, in which the cell has very good capacity retention and excellent cycling efficiency against progressive cycling. It is estimated from the figure that the cell retained as high as 90% of the initial capacity after 180 cycles at room temperature.

Voltage-capacity curves for discharge of the Li-ion cell at various low temperatures are compared in Fig. 6, in which the capacities were normalized as “relative capacity”. We see that both operating voltage and discharge capacity of the cell decreased with lowering the temperature. Decrease of the operating voltage at low temperatures is attributed to the electric polarization caused by an increase of the cell resistance (including electrolyte, electrodes and SEI) and by a slow-down of the cell electrochemical reaction. It is estimated from Fig. 6 that relative capacity of the cell was 0.63 at -40 °C and 0.83 at -30 °C, respectively. These values are very close to those (0.71 at -40 °C, and 0.86 at -30 °C) observed from the same cell except for addition of 1 wt% vinylene carbonate (VC) instead of LiBOB [4]. The results above indicate that addition of small amount of LiBOB can effectively improve cycling performance of graphite in LiBF₄-PC based elec-

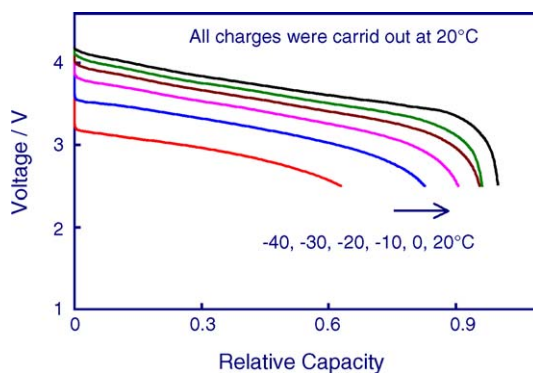


Fig. 6. Cycling performance of the graphite/LiNiO₂ cell with 1.0 m (0.98LiBF₄-0.02LiBOB) 1:1:3 PC/EC/EMC electrolyte at low temperatures.

trolites with negligible adverse effect on the low temperature performance.

4. Conclusions

In conclusion, addition of small amount of LiBOB is very effective in improving SEI formation on graphite in LiBF₄-PC based electrolytes. Due to extreme sensitivity of LiBOB to the impurities, its amount required for the optimized improvement strongly depends on the purity of salt, solvents and electrode materials. Although 1 mol% of LiBOB is sufficient to improve SEI formation on graphite in lithium half cells, a little higher amount of LiBOB is necessary for LiNiO₂-based Li-ion cells, probably due to the presence of impurities such as Li₂CO₃ on the surface of the cathode. LiBOB has a negligibly adverse effect on the low temperature performance of Li-ion cells as its concentration is at the level of electrolyte additives.

Acknowledgement

Receipt of electrode sheets from Saft America is gratefully acknowledged.

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