



Short communication

Studies on the enhancement of solid electrolyte interphase formation on graphitized anodes in LiX-carbonate based electrolytes using Lewis acid additives for lithium-ion batteries

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ABSTRACT

The new electrolyte systems utilizing one type of Lewis acids, the boron based anion receptors (BBARs) with LiF, Li₂O, or Li₂O₂ in carbonate solutions have been developed and reported by us. These systems open up a new approach in developing non-aqueous electrolytes with higher operating voltage and less moisture sensitivity for lithium-ion batteries. However, the formation of a stable solid electrolyte interphase (SEI) layer on the graphitized anodes is a serious problem needs to be solved for these new electrolyte systems, especially when propylene carbonate (PC) is used as a co-solvent. Using lithium bis(oxalato)borate (LiBOB) as an additives, the SEI layer formation on mesophase carbon microbeads (MCMB) anode is significantly enhanced in these new electrolytes containing boron-based anion receptors, such as tris(pentafluorophenyl) borane, and lithium salt such as LiF, or lithium oxides such as Li₂O or Li₂O₂ in PC and dimethyl carbonate (DMC) solvents. The cells using these electrolytes and MCMB anodes cycled very well and the PC co-intercalation was suppressed. Fourier transform infrared spectroscopy (FTIR) studies show that one of the electrochemical decomposition products of LiBOB, lithium carbonate (Li₂CO₃), plays a quite important role in the stabilizing SEI layer formation.

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1. Introduction

Most of the commercial non-aqueous electrolytes for rechargeable lithium batteries have a high degree of ion pairing, triplets and higher aggregates which decreases the lithium ion transference and results in polarization losses in batteries [1]. In order to increase the transference number of lithium ions, Lewis acid type compounds have been developed at BNL for last decade as additives to complex anions and free the lithium cations in the electrolytes [2–8]. Among these Lewis acid compounds, the boron based anion receptors (BBARs) are the most promising and some of them showed the ability to promote the dissolution of LiF in organic solvents [3,6]. Recently, it was reported that one type of these BBARs, tris(pentafluorophenyl) borane (TPFPB) is able to promote the dissolution of Li₂O and Li₂O₂ in organic carbonate solvents at room temperature [9]. The transference numbers for lithium ions of the new electrolytes containing BBAR and Li₂O or Li₂O₂ are as high as 0.6–0.8 [9], similar to the values in the BBAR–LiF system [10]. These values are more than two times higher than the 0.2–0.3

values for the conventional LiPF₆ based electrolytes. In addition, these new electrolytes show high oxidation stability up to 5.0 V vs Li/Li⁺ and good compatibility with bench-marked cathodes, i.e., LiCoO₂, LiMn₂O₄ and LiFePO₄. These findings open a new approach for designing and developing new electrolytes for high operating voltage and low moisture sensitivity electrolytes to replace the widely used LiPF₆ based electrolytes.

However, our recent studies show that the new BBAR–LiX carbonate electrolytes have poor compatibility with graphite anodes and suffer from the lack of stable SEI layer formation [9,10]. It was found that when graphitized mesophase carbon microbeads (MCMB) were used as the anode material, the coulomb efficiency was only 50% in 0.6 M TPFPB–0.6 M LiF–ethylene carbonate (EC)–dimethyl carbonate (DMC) (1:1 in v/v) electrolyte. Severe PC co-intercalation in 0.6 M TPFPB–0.6 M LiF–PC–DMC (1:1 in v/v) electrolyte was observed [10]. These results show that the formation of stable SEI layer on the graphitized anode materials is a serious problem and the studies on this subject will not only be helpful in the development of these new electrolytes, but also be valuable in improving the properties of other conventional electrolytes as well.

It has been reported that the addition of LiBOB is an effective way to form a stable SEI film on graphitized carbon anodes, which can suppress the PC co-intercalation [11–16]. In this paper, the effects

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of using LiBOB as an additive in the TPFPPB–LiX–PC–DMC electrolyte systems for SEI formation enhancement are reported.

2. Experimental

TPFPB was synthesized as described in our previous work [3]. LiF, Li₂O and Li₂O₂ were purchased from Aldrich. LiBOB was purchased from Shanghai Topsol. TPFPPB was dried under vacuum at 80 °C for 12 h and lithium salts were dried under vacuum at 100 °C for 12 h before use. PC and DMC (Battery grade, Shanghai Topsol, H₂O < 5 ppm) were dried further through 4 Å size molecular sieves in an argon-filled glove box. Six electrolytes were prepared: 0.6 M TPFPPB and 0.6 M LiF in PC/DMC (1:1 in volume) solution (Named as TPL01); 0.4 M TPFPPB and 0.2 M Li₂O in PC/DMC (1:1 in volume) solution (Named as TPL02); 0.4 M TPFPPB and 0.2 M Li₂O₂ in PC/DMC (1:1 in volume) solution (Named as TPL03). The above electrolytes with addition of 0.05 M LiBOB were named as B-TPL01, B-TPL02 and B-TPL03, respectively. Graphitized anode material (MCMB, Osaka Gas, Japan) was obtained as a commercial product and was used as it is.

The test electrodes were prepared using 92 wt% MCMB, 3 wt% acetylene black and 5 wt% poly(vinylidene fluoride) (PVDF) (KynarFlex 2801, Atochem). Copper foil was used as the current collector for the test electrode. The battery was a Swaglock-type two-electrode half-cell using lithium foil as the counter electrode and Celgard 2325 as the separator. Charge–discharge tests were carried out on a Land battery testing system.

Infrared spectra were collected by a Bruker EQUINOX55 FT-IR spectrometer in the range of 4000–400 cm⁻¹. The resolution was set to 4 cm⁻¹. The sample preparations for FTIR were similar as our previous procedures [17].

3. Results and discussion

Fig. 1 shows the charge–discharge curves of Li/MCMB cells using TPL01 (Fig. 1a) and B-TPL01 (Fig. 1b) electrolytes in a voltage range of 0–3 V. A short voltage plateau at 1.6 V and a long voltage plateau at 0.8 V can be seen in Fig. 1a for TPL01 electrolyte. They are assigned to the decomposition of the TPFPPB and PC co-intercalation respectively [10]. Without any additive, the cell using TPL01 could not cycle at all. After adding 0.05 M LiBOB, the cell cycled well and achieved an initial coulomb efficiency of 89.5% and a reversible capacity of 308 mAhg⁻¹. This is clear evidence for the stability of

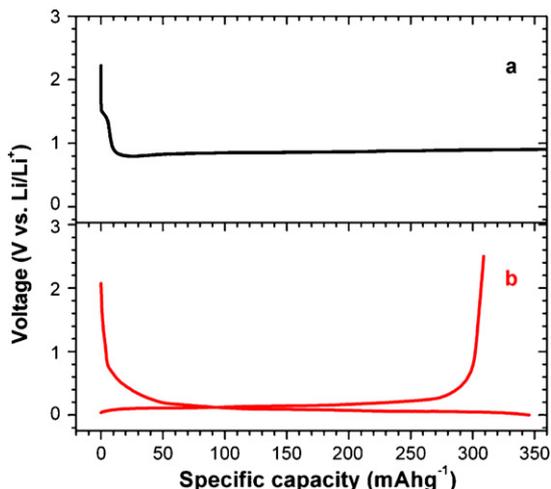


Fig. 1. Charge–discharge curves for Li/MCMB cells using electrolytes of (a) TPL01 and (b) B-TPL01.

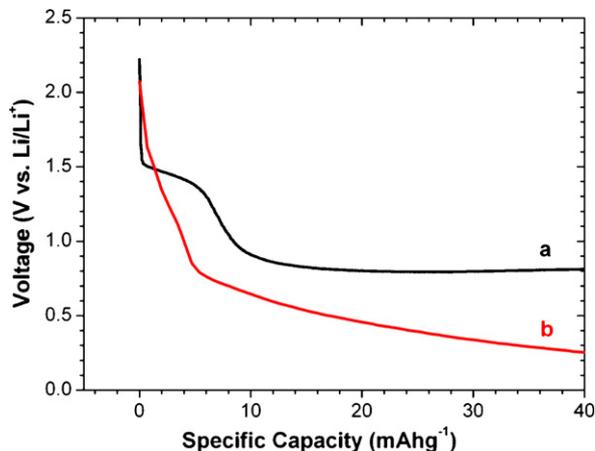


Fig. 2. The exploded plot of the early stage of first discharge curves in Fig. 1: (a) TPL01 and (b) B-TPL01.

the SEI film on the MCMB anode in the first cycle. A similar phenomenon has been observed in other LiBOB–PC systems [11,13].

The early part of the discharge curves in the high voltage region is plotted in Fig. 2. The 1.6 V voltage plateau reflecting the TPFPPB reduction can be seen clearly in the curve “a” of Fig. 2 for the TPL01 electrolyte without the additive. In contrast, this plateau around 1.4–1.7 V in the curve “b” of Fig. 2 is significantly suppressed when LiBOB was used in B-TPL01. It is known that the SEI formation originated by LiBOB occurs in the range of 1.6–1.8 V vs Li/Li⁺ [12,16]. It is natural to assume that the decomposition of LiBOB occurs first, forms a stable SEI film, and reduces the TPFPPB decomposition.

In order to study the SEI formation mechanism of LiBOB, FTIR spectra were collected on MCMB electrodes after discharge to a certain capacity for the electrolytes with and without LiBOB additive. Fig. 3 shows the FTIR spectra of the electrode discharged to 1000 mAhg⁻¹ in the TPL01 electrolyte (curve “a”) and the electrode discharged to 0 V in B-TPL01 electrolyte (curve “b”). The most noticeable difference between spectrum a and b in Fig. 3 is the relative intensity variation of the bands at 1506, 1443 and 862 cm⁻¹, all related to lithium carbonate, Li₂CO₃ [18]. It is quite clear that the addition of LiBOB promotes the formation of Li₂CO₃. FTIR spectrum of lithium oxalate reported by Zhuang et al. [13] shows the two strongest bands at 1640 and 1320 cm⁻¹. Larush-Asraf et al. also observed weak bands at 1423, 774, 517 and 443 cm⁻¹ for lithium oxalate [16]. As shown in Fig. 3, although the existence of lithium oxalate can not be excluded, the characteristic bands related to

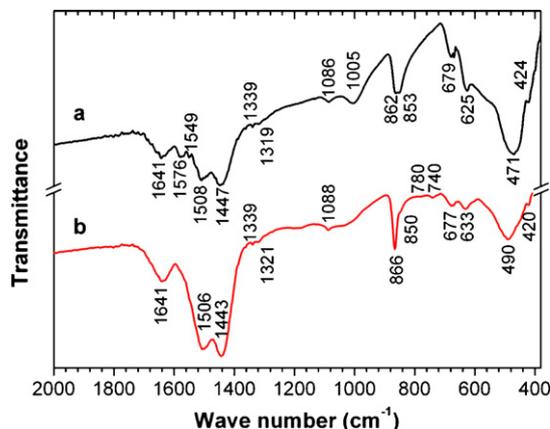


Fig. 3. FTIR spectra of the MCMB electrodes: (a) discharged to 1000 mAhg⁻¹ in TPL01 electrolyte; (b) discharged to 0 V in B-TPL01 electrolyte.

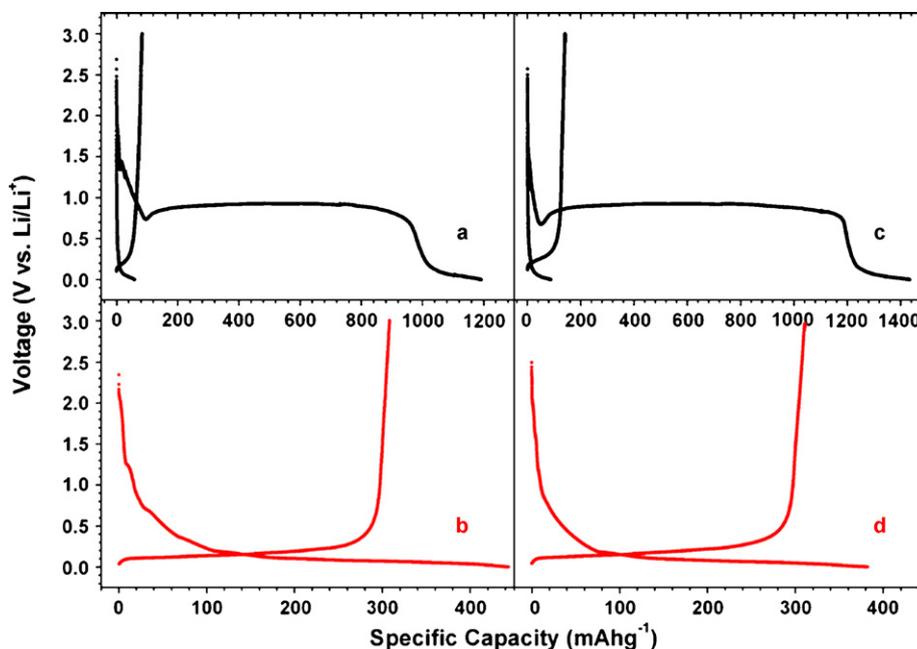


Fig. 4. Charge–discharge curves for Li/MCMB cells at room temperature, with: (a) TPL02; (b) B-TPL02; (c) TPL03; (d) B-TPL03 as the electrolytes. The cells were cycled between 0 and 3 V at 0.2 C.

lithium oxalate appear in both spectra and their relative intensities are quite similar. The peak at 1090 cm^{-1} is assigned to a $>\text{B-O}$ functional group [19] or ROCO_2Li [20]. The bands at 1576 , 1549 and 1005 cm^{-1} in the spectrum *a* are weak or disappear in the spectrum *b*. The band at 471 cm^{-1} in the spectrum *a* shifts to 490 cm^{-1} in the spectrum *b* becomes broader. The new bands may originate from the decomposition products from TPFPB, but further studies are needed to confirm it. These results indicate that the addition of LiBOB does have strong influences on the SEI formation on MCMB in TPFPB–LiF–PC–DMC electrolytes.

As suggested by Aurbach et al. [20] and later calculations by Vollmer et al. [21], when PC concentration in the electrolyte is increased, the decomposition tends to form a much less protective and passivating ROCO_2Li species. Therefore, the key issue for a good SEI formation additive to prevent PC co-intercalation into graphite is the ability to form a more protective and passivating layer, such as Li_2CO_3 . Obviously, the addition of LiBOB does provide this type of functionality. The detailed LiBOB decomposition mechanism in these new electrolytes needs to be explored further to develop an in depth understanding of these systems.

Recently, we have reported two new electrolytes, $0.2\text{ M Li}_2\text{O}$ and 0.4 M TPFPB in PC–DMC (TPL02) and $0.2\text{ M Li}_2\text{O}_2$ and 0.4 M TPFPB in PC–DMC (TPL03). They show a very high lithium ion transference number, reasonable ionic conductivity and good compatibility with LiMn_2O_4 cathode [9]. The discharge curves of the MCMB anode in these two electrolytes with and without LiBOB are shown in Fig. 4. Without LiBOB in the electrolyte, the cells show a long plateau for PC decomposition. Surprisingly, different from the other new PC-based electrolytes using LiF salt and TPFPB, the PC decomposition in these electrolytes using Li_2O or Li_2O_2 oxides with TPFPB stopped after discharging over 1000 mAhg^{-1} . It was found that both cells could be charged back, regardless of the less than 100 mAhg^{-1} reversible capacity. This means that the TPFPB– $\text{Li}_2\text{O}/\text{Li}_2\text{O}_2$ combination could form a better SEI film than that of TPFPB–LiF combination. After 0.05 M LiBOB was added in the electrolytes, the cells can be discharged to 0 V suppressing the plateau of PC co-intercalation, similar as Fig. 1. The coulomb efficiency was 69.5%

and the reversible capacity was 308 mAhg^{-1} for the B-TPL02 electrolyte in the first cycle. The corresponding values for the B-TPL03 electrolyte are 81.3% and 310 mAhg^{-1} respectively. These results show that the lithium oxides also have some good SEI formation functionality, although much smaller effects than the LiBOB.

4. Conclusion

The TPFPB–LiX–PC–DMC electrolytes (LiX: LiF, Li_2O , Li_2O_2) show very poor compatibility with graphitized MCMB anodes in rechargeable lithium batteries, due to the lack of good SEI formation and PC co-intercalation (for PC based systems). Adding LiBOB promotes the formation of Li_2CO_3 , which is the key component for the formation of a good SEI layer with better protective and passivating functions. A good SEI film can effectively reduce the decomposition of TPFPB and PC in these electrolytes and prevent the PC co-intercalation into the graphite. The detailed mechanisms on LiBOB and TPFPB decomposition and the accurate identification of the SEI components will be further investigated using other techniques, such as XPS and TG–DSC–MS.

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