



A pentafluorophenylboron oxalate additive in non-aqueous electrolytes for lithium batteries

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ARTICLE INFO

Article history:

Received 18 September 2009

Received in revised form 8 October 2009

Accepted 10 October 2009

Available online 5 November 2009

Keywords:

Pentafluorophenylboron oxalate

Boron-based anion receptors

Solid electrolyte interphase

Propylene carbonate

Lithium fluoride

Lithium oxide

Lithium peroxide

Non-aqueous electrolyte

ABSTRACT

A novel compound named pentafluorophenylboron oxalate (PFPBO) has been synthesized. PFPBO has a unique molecular structure containing a boron atom center with electron deficiency and an oxalate group. It is found that when PFPBO is used as additive, the solubility of lithium fluoride (LiF) or lithium oxide (Li₂O, Li₂O₂) in propylene carbonate (PC) and dimethyl carbonate (DMC) solvents can be increased dramatically. The new electrolytes show high ionic conductivity, high lithium ion transference number and good compatibility with LiMn₂O₄ cathode and MCMB anode. PFPBO was synthesized with the designed structure to act as a bi-functional additive: boron-based anion receptor (BBAR) additive and stable solid electrolyte interphase (SEI) formation additive in PC-based electrolytes. The results show it does possess these two desired functionalities.

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1. Introduction

LiPF₆ based carbonate solutions are widely used as non-aqueous electrolytes in lithium batteries for many years. The success of LiPF₆ based electrolyte is due to the combination of a series of well-balanced properties with some concomitant compromises and restrictions [1]. The instability of LiPF₆ toward ambient moisture, and high temperature, as well as its low lithium ion transference number are some examples of problems associated. Many other lithium salts have been tested to replace LiPF₆ [1–5]. One approach developed at Brookhaven National Lab. (BNL) is using boron-based anion receptors (BBARs) to complex anions and increase the solubility of lithium fluoride and lithium oxides. BBARs have boron-based Lewis acid centers and can promote the dissolution of lithium salts in carbonate solvents, even some insoluble compounds, such as LiF [6–11], Li₂O and Li₂O₂ [11,12]. The electrolytes based on BBARs show high lithium ion transference numbers (0.6–0.8) [10–12]. This type of anion receptors have also been used in Li-(CF)_x battery to promote discharge [13] and enhance the dual-ion intercalation of lithium–fluoride into graphite [14]. In addition, 0.1 M tris(pentafluorophenyl) borane (TPFPB) can be used as additive to stabilize the LiPF₆ salt [15–18]. Recently, Chen and

Amine [19] reported that 2-(pentafluorophenyl)-tetrafluoro-1,3,2-benzodioxaborole was used as a bi-functional electrolyte additive in lithium-ion batteries to serve as both redox shuttle and anion receptor at the same time.

Our previous investigations indicate that the compatibility of TFPFB-LiF/Li₂O/Li₂O₂-PC/DMC electrolytes with graphitized mesocarbon microbead (MCMB) is not satisfied due to the lack of capability to form stable SEI film on MCMB anode to serve as a barrier to block the co-intercalation of PC. It was found that lithium bis (oxalato) borate (LiBOB) is a quite effective additive for the above electrolytes in forming a stable SEI film on MCMB [11]. In light of this finding, we designed a new boron-based compound with both BBAR and LiBOB function groups. In this communication, we report the synthesis of pentafluorophenylboron oxalate (PFPBO), a new boron-based bi-functional additive, and the characterization relating to transport properties and electrochemical performances of the electrolytes.

2. Experimental

PFPBO was synthesized by one-step reaction: a mixture of 0.05 M of pentafluorophenylboronic acid (purchased from Alfa Aesar, Word Hill, Massachusetts) and 0.05 M of oxalic acid dihydrate in 80 mL of benzene was refluxed for about 4–5 h and the nascent water was collected in a Dean–Stark trap. After cooling, the solid

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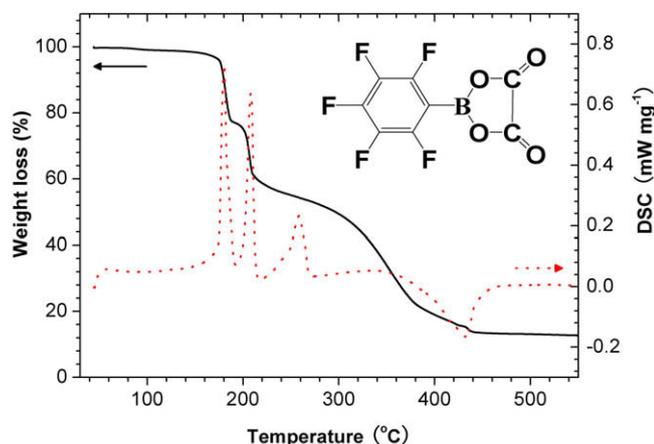


Fig. 1. TG-DSC curve for PFPBO compound.

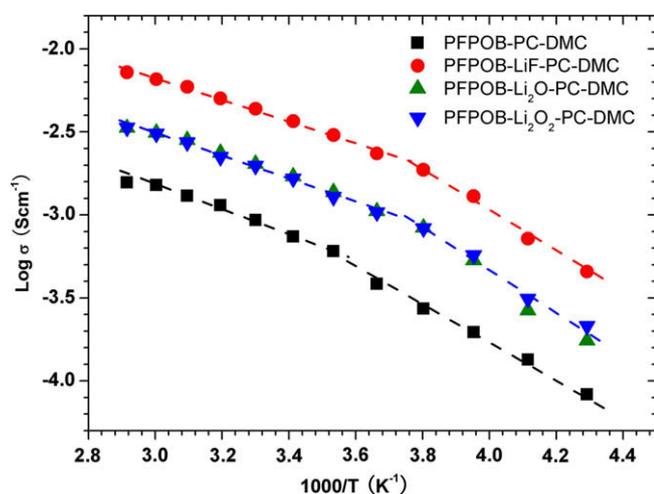


Fig. 2. Temperature-dependent conductivities of different electrolytes.

product was collected by filtration. The solid product was treated with ether solvent. After filtering out the insoluble solid (which is boroxin), the ether solution was concentrated by evaporation of ether. Then 20 mL of benzene was added to the residue. After leaving the benzene solution in the refrigerator for 12 h, crystals of the product were isolated. The crystals were further filtered out and further washed using benzene. The boiling point is 248–250 °C, and the yield is 52%. ^{13}C NMR (400 MHz, $\text{DMSO}-d_6$) result was: δ 116.6 (C_1), 138.1 (C_3 , C_5), 140.9 (C_4), 148.2 (C_2 , C_6), 161.2 ($\text{C}=\text{O}$), (ppm).

Anhydrous LiF, Li_2O and Li_2O_2 were purchased from Aldrich. PFPBO, LiF, Li_2O and Li_2O_2 were dried under vacuum at 100 °C for

12 h before use. PC and DMC (Battery grade, Shanghai Topsol, $\text{H}_2\text{O} < 5$ ppm) were dried further through 4 Å size molecular sieves in an argon-filled glove box. The electrolytes were prepared by dissolving PFPBO and LiF or Li_2O or Li_2O_2 in PC and DMC mixed solvents. Five electrolytes were prepared: 0.5 M PFPBO–0.5 M LiF in PC/DMC (1:1, v/v), 0.5 M PFPBO–0.25 M Li_2O PC/DMC (1:1, v/v) and 0.5 M PFPBO–0.25 M Li_2O_2 PC/DMC (1:1, v/v). 1 M LiPF_6 , PC/DMC (1:1, v/v) with 5 wt% or 10 wt% PFPBO. Among them, LiF was dissolved completely, but Li_2O and Li_2O_2 were dissolved partially. The saturated solutions were used for this study.

The thermal stability of PFPBO was investigated by a NETSCH STA 449C. Conductivity measurements were performed using a Nova-control impedance analyzer in the frequency range from 1 Hz to 10 MHz. A testing cell with two Pt electrodes was used for the conductivity measurements. The cell constant was determined using a standard 0.01 M KCl aqueous solution before each measurement. The lithium ion transference number was obtained by combining ac impedance and dc polarization measurement using the same Li/electrolyte/Li cell [11,12].

Commercial products of LiMn_2O_4 (Wuxi Jewel, China) and graphite (MCMB28, Osaka Gas, Japan) were used as cathode and anode respectively. The electrodes were composed of 90 wt% active material, 5 wt% acetylene black and 5 wt% poly(vinylidene fluoride) (PVDF) (KynarFlex 2801, Atochem). Aluminum foil and copper foil were used as current collectors for cathode and anode respectively. The battery was a Swaglock-type two-electrode cell using a lithium foil as anode and a Celgard 2300 as separator. Charge–discharge test was carried out on a Land battery test system at room temperature.

3. Results and discussion

Fig. 1 shows the chemical structure of PFPBO and its TG-DSC curve. The DSC curve shows three exothermic peaks at 180, 208 and 258 °C and one endothermic peak at 432 °C. The TG curve shows four weight losses. It can be seen that PFPBO is stable up to 180 °C. The weight loss is 87.2% after heating over 500 °C, closed to a theoretical weight loss of 86.8% when B_2O_3 becomes the final product.

PFPBO can also promote dissolution of LiF, Li_2O and Li_2O_2 in carbonate solvents, similarly as TFPFB [10–12]. Fig. 2 and Table 1 show the conductivities of these electrolytes at a temperature range from –40 to 70 °C. The 0.5 M PFPBO–0.5 M LiF-PC/DMC (1:1) electrolyte shows the highest conductivities, comparable to the TFPFB-based electrolytes. The Li-ion transference numbers are comparable with TFPFB series, but much higher than that of LiPF_6 or LiClO_4 or LiBF_4 based electrolytes [10–12]. The results of high conductivities and Li-ion transference numbers indicate strong interaction between PFPBO and F or O anions, due to the strong electron withdrawing effect of the fluorinated phenyl in PFPBO, as we had explained for other BBARs compounds.

The charge and discharge behaviors of LiMn_2O_4 cathode and MCMB anode in PFPBO-PC-based electrolytes were studied. It can

Table 1

Conductivity comparison of various electrolytes at several temperatures and lithium ion transference number measurement at 25 °C.

Electrolytes	Conductivity (mS cm^{-1})			t_{Li^+} (25 °C)	E_a (kJ mol^{-1})	
	–30 °C	30 °C	60 °C		Low	High
0.5 M PFPBO–PC/DMC	0.1	0.9	1.5	–	20.8	13.3
0.5 M PFPBO–0.5 M LiF PC/DMC	0.7	4.4	6.6	0.58	19.9	11.2
0.5 M PFPBO–0.25 M Li_2O PC/DMC	0.3	2.0	3.1	0.83	22.1	11.2
0.5 M PFPBO–0.25 M Li_2O_2 PC/DMC	0.3	2.0	3.1	0.78	19.6	12.1
0.6 M TFPFB–0.6 M LiF PC/DMC [12]	0.8	4.3	6.1	0.71	13.6	13.6
0.4 M TFPFB–0.2 M Li_2O PC/DMC [13]	0.3	1.7	2.8	0.78	14.1	6.0
0.4 M TFPFB–0.2 M Li_2O_2 PC/DMC [13]	0.4	2.1	3.2	0.74	13.7	5.9

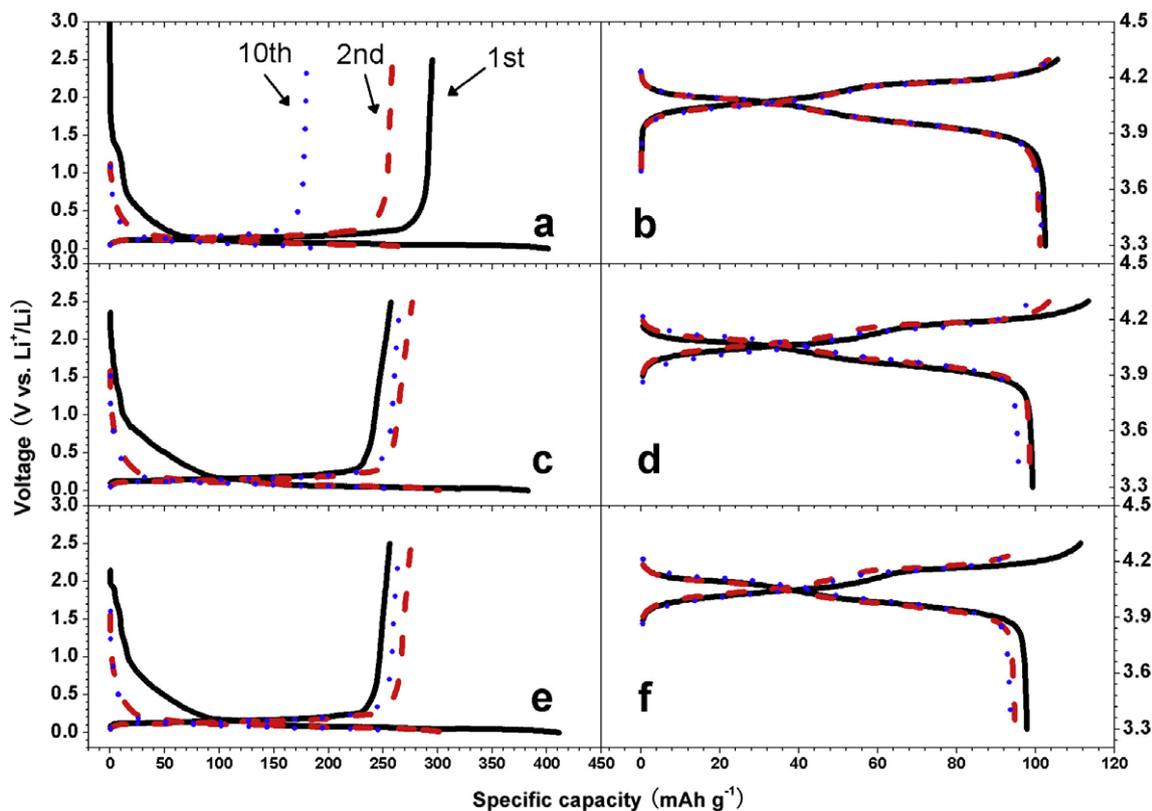


Fig. 3. Charging and discharging behaviors of LiMn_2O_4 cathode and MCMB anode in PFPBO-based electrolyte. (a) MCMB anode in 0.5 M PFPBO and 0.5 M LiF in PC/DMC (1:1), (b) LiMn_2O_4 cathode in 0.5 M PFPBO and 0.5 M LiF in PC/DMC (1:1), (c) MCMB anode in 0.5 M PFPBO and 0.25 M Li_2O in PC/DMC (1:1), (d) LiMn_2O_4 cathode in 0.5 M PFPBO and 0.25 M Li_2O in PC/DMC (1:1), (e) MCMB anode in 0.5 M PFPBO and 0.25 M Li_2O_2 in PC/DMC (1:1), (f) LiMn_2O_4 cathode in 0.5 M PFPBO and 0.25 M Li_2O_2 in PC/DMC (1:1). All tests were performed at 25 °C at 0.1 C rate.

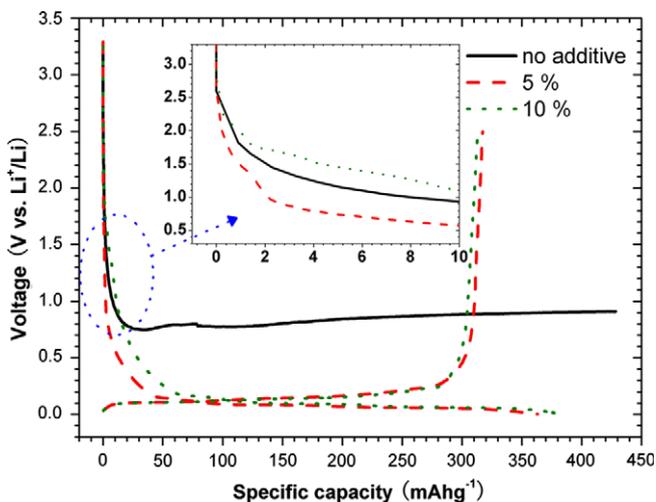


Fig. 4. The first discharge curves of MCMB anode in the electrolytes of 1 M LiPF_6 -PC/DMC (1:1) (1) without additive, (2) adding 5 wt% PFPBO, (3) adding 10 wt% PFPBO.

be seen in Fig. 3 that these electrolytes show good compatibility with surface coated LiMn_2O_4 cathode. MCMB anode can operate properly in these PC-based electrolytes, which were not possible for TFPFB-PC-based electrolyte without LiBOB additive [10,11]. As expected, the oxalate group in PFPBO acts as an effective additive to form stable SEI film on MCMB anode in PC-based electrolyte, similar as adding LiBOB in TFPFB-PC-based electrolytes [11].

The function of PFPBO as the SEI film promoter can be seen more clearly when small amount of PFPBO was added into 1 M LiPF_6 -PC/DMC (1:1 in v/v) electrolyte. As shown in Fig. 4, MCMB anode can be discharged properly after adding 5% or 10% PFPBO.

These results indicate that the electrolyte containing PFPBO combined with LiF or Li_2O or Li_2O_2 in PC/DMC solvents can form an effective SEI film to prevent PC co-intercalation and similar effect can be obtained with only 5% concentration PFPBO in LiPF_6 based electrolytes. It is found by further FTIR investigation that C=O rich compounds of Li_2CO_3 or $\text{Li}_2\text{C}_2\text{O}_4$ products appear in discharged MCMB anodes after adding PFPBO, similar as the LiBOB anion reduction decomposition mechanism [11]. This might be a key point in forming the stable SEI film in PC-based electrolytes.

4. Conclusion

A new compound pentafluorophenylboron oxalate (PFPBO) is synthesized. It can promote the dissolution of LiF, Li_2O or Li_2O_2 in non-aqueous solvents due to anion receptor effect. The PFPBO-based electrolytes show high ionic conductivity and lithium ion transference number. PFPBO is also effective as additive to form a stable SEI film on MCMB anode in PC-based electrolyte, due to the existence of oxalate structure in PFPBO. This bi-functional additive has potential to be used in Li-ion batteries or Li-air batteries.

Acknowledgements

The work at Institute of Physics, Chinese Academy of Science was supported by Nature Scientific Foundation of China (50672122, 50730005), “863” project (2006AA03Z346) and “973”

project (2007CB936501) of China. The work at BNL was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the US Department of Energy under Contract Number DEAC02-98CH10886.

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