



Short communication

New electrolytes for lithium ion batteries using LiF salt and boron based anion receptors

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ABSTRACT

The thermal and electrochemical stability, as well as compatibility with various bench mark cathode and anode materials of two new lithium fluoride salt (LiF) based electrolytes have been studied. These two new electrolytes are formed by using boron-based anion receptors, tris(pentafluorophenyl) borane (TPFPB), or tris(2H-hexafluoroisopropyl) borate (THFPB) as additives, which were designed and synthesized at Brookhaven National Laboratory (BNL), to dissolve the LiF salt in carbonate solvents. The transference number of Li⁺ for these electrolytes is as high as 0.7 and the room-temperature conductivity is around $2 \times 10^{-3} \text{ S cm}^{-1}$. The electrolytes containing propylene carbonate (PC) show superior low-temperature conductivity properties. The electrochemical window is approaching 5.0 V. It was also found that the new electrolytes work well with LiCoO₂ or LiMn₂O₄ cathodes. However, when PC containing electrolytes were used, PC co-intercalation is still a problem for graphite anodes. The formation of a stable solid electrolyte interface layer on the surface of anode in this type of electrolyte needs to be studied further.

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1. Introduction

Most non-aqueous lithium battery electrolyte solvents are Lewis bases that interact with cations, causing a high degree of ion pairing and the formation of triplets and higher aggregates. This decreases the lithium ion transference and results in polarization losses in batteries. Another problem with lithium battery electrolytes is decomposition of the salt. This is particularly true for LiPF₆, which is unstable at elevated temperatures and sensitive with trace amount of water [1–3]. The decomposition reaction produces PF₅ and HF that promotes ring opening and polymerization of ethylene carbonate in addition to corrosion of the cathode [3,4]. In searching the new chemistry of lithium-ion batteries with higher energy density, non-LiPF₆ electrolytes with higher lithium ion transference number, higher electrochemical stability and wider operating temperature are desired. In order to increase the transference of lithium ions, one new approach has been developed at BNL by using boron based anion receptors to complex anions. Several families of neutral anion complexing agents have been synthesized by Lee et al., each based on boron based Lewis acid centers [5–9]. It was found that the complexing agents have the ability to promote the dissolution of LiF [6–9], which is normally insoluble in organic

solvents. These type of anion receptors have also been used in a Li-(CF)_x battery to promote discharge [10] and enhance the dual-ion intercalation of lithium-fluoride into graphite [11]. In addition, the addition of 0.1 M tris(pentafluorophenyl) borane (TPFPB) can stabilize the LiPF₆ salt [12]. The capacity retention of Li/LiMn₂O₄ can be significantly improved when cycled at 55 °C when TPFPB is used as an additive in the electrolyte [12–15]. Recently, 2-(pentafluorophenyl)-tetrafluoro-1,3,2-benzodioxaborole, another boron compound, was used as a bifunctional electrolyte additive for lithium-ion batteries, which acts as both the redox shuttle and the anion receptor as reported by Chen and Amine [16]. The potential of using LiF and boron additives based electrolytes in high voltage lithium-ion batteries is very attractive. However, in order to be used in lithium batteries, the compatibility of these electrolytes with bench mark cathode and anode materials has to be studied first. So far, not much work has been reported yet. This is the main goal of this study. Here we report our preliminary results on the conductivity, the lithium ion transference number and the electrochemical behaviors of these new electrolytes using tris(pentafluorophenyl) borane (TPFPB) or THFPB as anion receptor, LiF as lithium salt and PC, EC and DMC carbonates as solvents. As can be seen in the discussion part, although the combination of conductivity and Li ion transference number are rather good, the wider electrochemical stability window are quite promising, many problems, especially on the compatibility with carbon anodes and the formation of stable SEI layer, remain to be studied and answered before these new electrolyte can make their way to the real batteries. These problems

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are being studied intensively in our Laboratories and hopefully new results will be reported soon.

2. Experimental

Tris(pentafluorophenyl) borane (TPFPB) and tris(2H-hexafluoroisopropyl) borate (THFPB) were synthesized as described in our previous work [6]. LiF was purchased from Aldrich. Both TFPFB and LiF were dried under vacuum at 80 °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. Four electrolytes were prepared: 0.6 M LiF and 0.6 M TFPFB in PC/DMC (1:1, v/v) solution (named as TPL01); 0.6 M LiF and 0.6 M TFPFB in EC/DMC (1:1, v/v) solution (named as TPL02); 0.6 M LiF and 0.6 M THFPB in PC/DMC (1:1) solution (named as THL01) and 0.6 M LiF and 0.6 M THFPB in EC/DMC (1:1, v/v) solution (named as THL02). Commercial electrolytes (1 M LiPF₆ in EC/DMC (1:1), 1 M LiClO₄ in PC–DMC (1:1), 1 M LiBF₄ in PC/DMC (1:1), battery grade, Shanghai Topsol, H₂O < 5 ppm) were used directly for comparison. Conductivity measurements were performed using a Hewlett–Packard 4192A impedance analyzer in the frequency range from 5 Hz to 1 MHz. Cells with Pt electrodes were used for the conductivity measurements. The cell constant was determined using a standard 0.01 M KCl aqueous solution in for every sample measured. The lithium ion transference number was obtained by combining AC impedance and DC polarization measurements using the same Li/electrolyte/Li cell. Electrochemical windows were studied by cyclic voltammogram technique using a three-electrode cell with a titanium foil or Cu foil as working electrode, one lithium metal foil as counter electrode and another lithium metal foil as reference electrode. The scanning rate was 0.25 mV s⁻¹ and the measurement was performed at room temperature.

LiMn₂O₄ (Wuxi Jewel, China), LiCoO₂ (Japan Chemicals; battery grade) and graphite (MCMB, Osaka Gas, Japan) were obtained as commercial products and was used as is. The electrodes for battery testing were prepared using 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 the 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 an Arbin battery test system.

The thermal stability of the electrolytes and anion receptors were determined using differential scanning calorimetry (DSC) analysis method by a NETSCH STA 449C. About 20 mg sample was sealed in an aluminum crucible in the glove box. A pinhole was punched on the crucible before DSC measurement. The crucible was first cooled down to -70 °C and then heated to 150 °C at a heating rate of 5 °C min⁻¹ for electrolytes and heated from 30 to 500 °C for TFPFB and THFPB additives.

3. Results and discussion

Fig. 1 shows the TGA–DSC curves of the THFPB and TFPFB at a heating rate of 5 °C min⁻¹. It can be seen that the melting and boiling points are 40 and 127 °C for THFPB and in the range of 123–131 and 223–260 °C for TFPFB, respectively.

LiF has negligible solubility in PC/DMC solvent and the impedance measurement of the 0.6 M LiF–PC–DMC (1:1, v/v) solution was too low to be measured using the Hewlett–Packard 4192A impedance analyzer (conductivity < 10⁻⁷ S cm⁻¹). After adding 0.6 M TFPFB or THFPB anion receptor, the solubility of LiF in PC/DMC is increased significantly. This increased solubility and conductivity has been reported previously using 1,2-dimethoxyethane (DME)

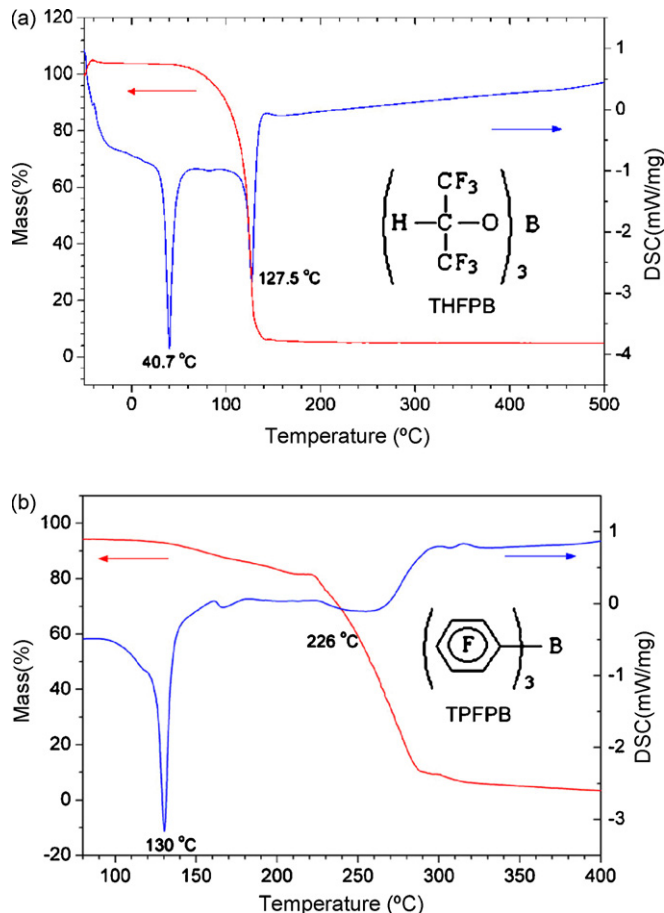


Fig. 1. TG–DSC curves for THFPB (a) and TFPFB (b).

as solvent for TFPFB [6] or EC–DMC (1:2) as solvent for THFPB [8]. Fig. 2 shows the conductivities of different electrolytes in a relative wide temperature range (-40 to +80 °C). It can be seen clearly that PC-based electrolytes show nearly linear Arrhenius response in the whole temperature range while EC-based electrolytes show two slopes due to the liquid–solid phase transition below 0 °C. The activation energies for different electrolytes are listed in Table 1. It can be seen that 0.6 M LiF–0.6 M TFPFB–PC:DMC

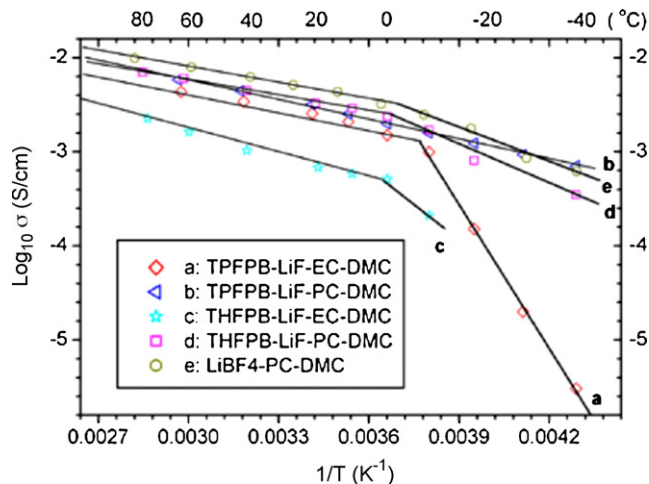


Fig. 2. Temperature-dependent conductivities of different electrolytes.

Table 1
E_a comparison of different electrolytes in high and low temperature ranges

Number	Electrolyte	E _a (kJ mol ⁻¹)	
		High temperature	Low temperature
a	0.6 M TFPFB–0.6 M LiF–EC:DMC (1:1)	12.4	98.9
b	0.6 M TFPFB–0.6 M LiF–PC:DMC (1:1)	13.6	13.6
c	0.6 M THFPB–0.6 M LiF–EC:DMC (1:1)	15.6	52.9
d	0.6 M THFPB–0.6 M LiF–PC:DMC (1:1)	10.7	26.0
e	1 M LiBF ₄ –PC–DMC (1:1)	11.1	23.8
f	1 M LiPF ₆ , EC–DMC (1:1)	9.6	69 ^a
g	1 M LiClO ₄ , PC–DMC (1:1)	12.6	21.7

^a –30 to 0 °C, frozen below –30 °C.

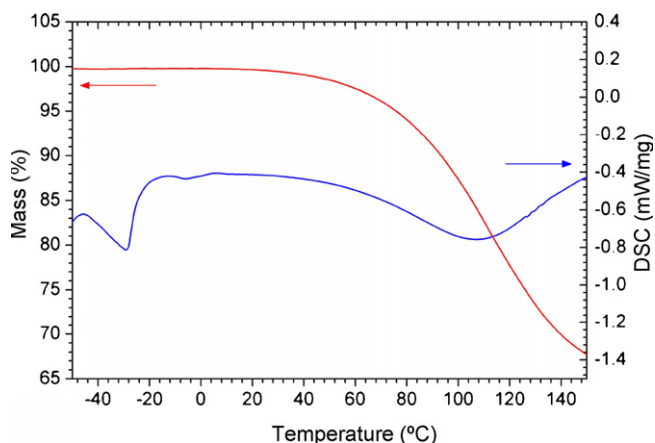


Fig. 3. TG–DSC curves for 0.6 M TFPFB–0.6 M LiF–PC:DMC (1:1) electrolyte.

(1:1) (TPO1) shows the lowest activation energy, especially in the low temperature range. A DSC curve of TPO1 is shown in Fig. 3 with a melting point starting at –45 °C, which is responsible for the high conductivity of this electrolyte at low temperature. Conductivity comparisons of different electrolytes at several temperatures are listed in Table 2. It can be seen that the 0.6 M LiF–0.6 M TFPFB–PC:DMC (1:1) electrolyte has excellent conductivity at room temperature and impressive conductivity at temperature as low as –40 °C. This is comparable with data for commercial electrolytes, as shown in Table 2.

The Li ion transference numbers were measured by combining AC impedance and DC polarization on the same cell containing same sample using two lithium foils as non-blocking electrodes. Firstly, AC impedance was measured to obtain a total resistance R_{total} . Then a constant DC voltage V_{DC} (50–200 mV) was applied on the same cell. After polarization, a stable current I_{DC} was obtained. The DC resistance $R_{\text{DC}} = V_{\text{DC}}/I_{\text{DC}}$. The Li ion transference number $t_{\text{Li}^+} = R_{\text{total}}/R_{\text{DC}}$ can be calculated (the same cell constant is cancelled out through the calculation). This simplified evaluation of the transfer number is valid presuming that the I_{DC} is caused by

Table 2
Conductivity comparison of different electrolytes at several temperatures

Number	Electrolyte	Conductivity (mS cm ⁻¹)				
		–40 °C	–20 °C	0 °C	20 °C	60 °C
a	0.6 M TFPFB–0.6 M LiF–EC:DMC (1:1)	0.003	0.15	1.5	2.6	4.4
b	0.6 M TFPFB–0.6 M LiF–PC:DMC (1:1)	0.71	1.2	2.0	3.2	5.8
c	0.6 M THFPB–0.6 M LiF–EC:DMC (1:1)	<1e–4	<1e–4	0.51	0.68	1.6
d	0.6 M THFPB–0.6 M LiF–PC:DMC (1:1)	0.34	0.80	2.4	3.3	6.0
e	1 M LiBF ₄ –PC–DMC (1:1)	0.62	1.8	3.2	4.9	7.9
f	1 M LiPF ₆ , EC–DMC (1:1)	<1e–4	0.58	5.9	8.8	14.8
g	1 M LiClO ₄ , PC–DMC (1:1)	0.3	1.0	2.4	3.9	8.0

Table 3
Transfer number measurement on electrolytes

Number	Electrolyte	t_{Li^+}	t_{x^-}
a	0.6 M TFPFB–0.6 M LiF–EC:DMC (1:1)	0.65	0.35
b	0.6 M TFPFB–0.6 M LiF–PC:DMC (1:1)	0.71	0.29
c	0.6 M THFPB–0.6 M LiF–EC:DMC (1:1)	0.58	0.42
d	0.6 M THFPB–0.6 M LiF–PC:DMC (1:1)	0.46	0.54
e	1 M LiBF ₄ –PC–DMC (1:1)	0.29	0.71
f	1 M LiPF ₆ , EC–DMC (1:1)	0.21	0.79
g	1 M LiClO ₄ , PC–DMC (1:1)	0.34	0.66

the transport of lithium ions only and the interphase resistance (SEI film) is negligible and the electrolyte is stable during polarization. The results are listed in Table 3. It can be seen that the Li ion transference number for every LiF–B-based electrolyte is at least 100% higher than that of LiPF₆ or LiClO₄ or LiBF₄ based electrolytes. TFPFB series show higher values than THFPB series, indicating a stronger electron withdrawing effect by the fluorinated phenyl ring. The higher Li ion transference number can improve effective Li ion conductivity (defined as total conductivity multiplies the Li ion transference number). The 1.8×10^{-3} S cm⁻¹ effective Li-ion conductivity of TPO1 (2.6×10^{-3} S cm⁻¹, $t_{\text{Li}^+} = 0.71$) at 20 °C is comparable to the 1.8×10^{-3} S cm⁻¹ value of 1.0 M LiPF₆ in EC–DMC (8.8×10^{-3} S cm⁻¹, $t_{\text{Li}^+} = 0.21$). The potential advantage in reducing the polarization and improving the rate capability due to the higher Li ion transference number will be further studied. At this stage, we are not sure if F⁻ anions are free or coordinated tightly with the anion receptors (TFPFB or THFPB) to form large anions.

The electrochemical window of TPO1 was investigated in a wide potential range of 0–5.1 V versus Li/Li⁺ using a Ti foil as working electrode. The results are shown in Fig. 4a. The CV curve in Fig. 4a shows that that TPO1 electrolyte is stable up to 5.0 V. This is comparable to the standard electrolyte of 1 M LiPF₆ in EC–DMC (1:1) [17]. The cyclic voltammogram of Cu foil as working electrode in a voltage range of 0–3.5 V versus Li/Li⁺ is shown in Fig. 4b. In both Fig. 4a and b, there is an irreversible reduction reaction below 2.0 V. The reduction current does not decrease in the second cycle. This type of reaction is assigned to the decomposition of electrolytes as observed in most of other nonaqueous electrolytes. However, when a stable SEI is formed, the reduction current is decreased to almost zero in the second cycle. In viewing the high reduction current in the second cycle in Fig. 4a and b, we believe no stable SEI is formed on Cu or Ti electrodes when TPO1 is used as electrolyte to prevent the further electrolyte decomposition in the second cycle.

The charge–discharge curves of Li/LiCoO₂ cells with THLO1 or TPO1 electrolyte in a voltage range of 2.5–4.3 V are shown in Fig. 5. The Coulomb efficiencies on the first cycle are 74 and 73%, respectively. The reversible capacities are 145 and 155 mAh g⁻¹, which are similar to the published values of LiCoO₂ cathode using conventional LiPF₆ based electrolytes. The low initial Coulomb efficiencies could be caused by the oxidation decomposition of the electrolyte, which may be related to the surface properties of the cathode or superior solubility of lithium salts. The charge–discharge curves of

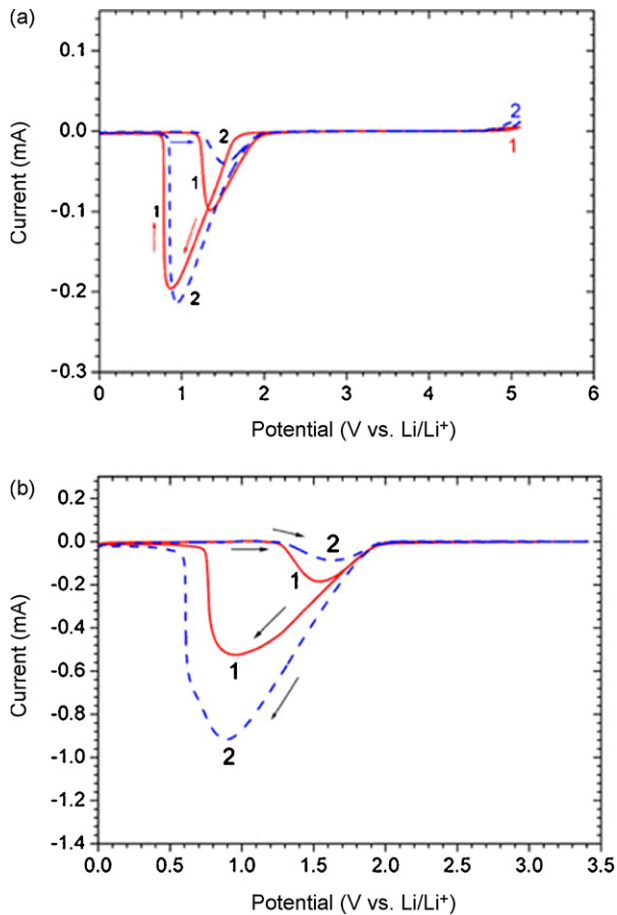


Fig. 4. Cyclic voltammogram of 0.6 M LiF and 0.6 M TPFPB in PC/DMC (1:1, v/v) using a three-electrode cell in the first two cycles. (a) Working electrode: Ti foil, counter electrode and reference electrode: Li foils. (b) Working electrode: Cu foil, counter electrode and reference electrode: lithium foils, cutoff voltages: (a) 0–5.1 V vs. Li/Li⁺, (b) 0–3.5 V vs. Li/Li⁺. Scan rate: 0.25 mV s⁻¹. (Solid line) the first scan, marked as 1; (dash line) the second scan, marked as 2. First scans started from open circuit voltage to high potential for (a) and from open circuit voltage to 0 V for (b).

a Li/LiMn₂O₄ using TPL01 is plotted in Fig. 6. The LiMn₂O₄ used in this study is a surface coated material. It shows an improved initial Coulomb efficiency of 90% and a reversible capacity of 103 mAh g⁻¹. The improvement of the initial Coulomb efficiency using the surface coated cathode indicates that the compatibility of this series of electrolytes with cathode materials can be improved by surface modification of the cathode.

The discharge curves of Li/MCMB cells with THL01 or TPL01 electrolyte are shown in Fig. 7. It can be seen that there are two voltage plateaus, a high voltage plateau at 1.8 V and a low voltage plateau at 0.8 V. The low voltage plateau may be caused by PC co-intercalation, a common phenomenon occurring in PC-containing electrolytes. In order to clarify the origin of the 0.8 V plateau in Fig. 7, comparative measurements were carried out on a similar half cell using LiF/TPFPB in EC/DMC electrolyte. The results are plotted in Fig. 8. It can be seen clearly that the 0.8 V plateau has completely disappeared, indicating that the origin of this plateau is the co-intercalation of the PC. Unlike LiBOB [18–20], TFPBPB combined with LiF does not form an effective solid electrolyte interface (SEI) to prevent the co-intercalation of PC molecules into graphite, which cause exfoliation of graphite. This observation is consistent with the cyclic voltammogram results in Fig. 4. It implies that the reduction–decomposition reactions in these two electrolytes are quite different compared with conventional electrolytes. The low

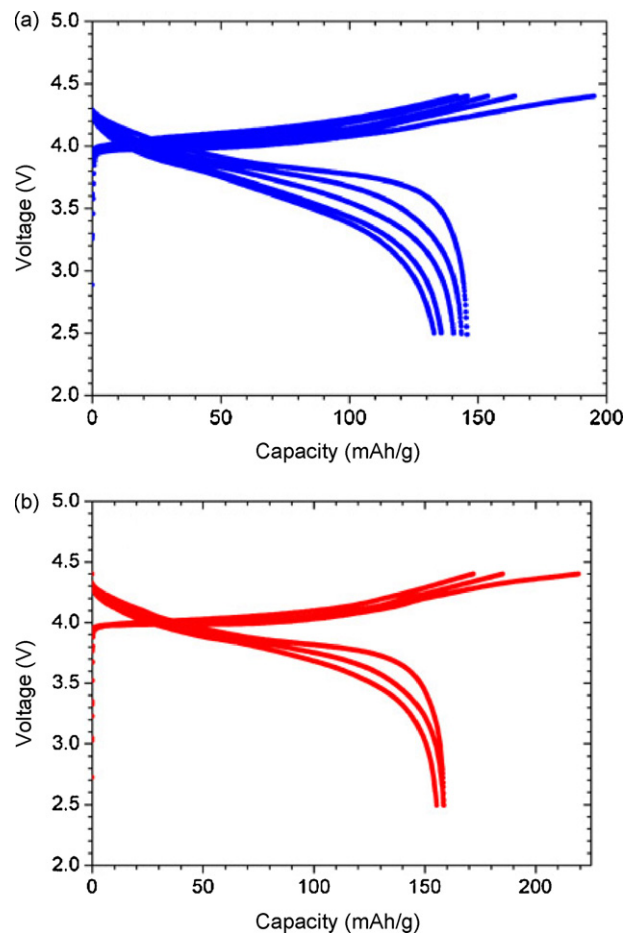


Fig. 5. Charge–discharge curves for the Li/LiCoO₂ cells at room temperature, with (a) 0.6 M THFPB and 0.6 M LiF in PC/DMC (1:1, v/v) and (b) 0.6 M TFPBPB and 0.6 M LiF in PC/DMC (1:1, v/v) as the electrolytes. The cells were cycled between 2.5 and 4.4 V at 0.2 C.

initial Coulomb efficiency and low capacity might also be due to the lack of stable SEI layer formation. Whether a stable SEI layer can be formed on the MCMB or other anode surface in these new LiF based electrolytes is a very important issue. New LiF based electrolytes using various combinations of solvents and additional additives are being tested for MCMB anodes, as well as for Li₄Ti₅O₁₂ type anodes

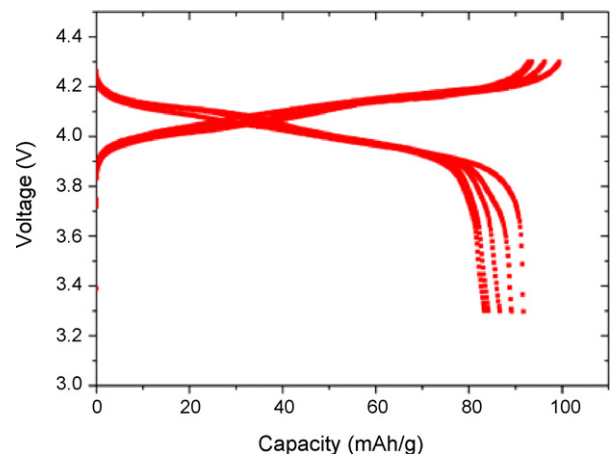


Fig. 6. Charge–discharge curves for Li/LiMn₂O₄ cells with composite electrolytes containing 0.6 M TFPBPB and 0.6 M LiF in PC/DMC (1:1, v/v) between 3.3 and 4.3 V at 25 °C at 0.06 C rate.

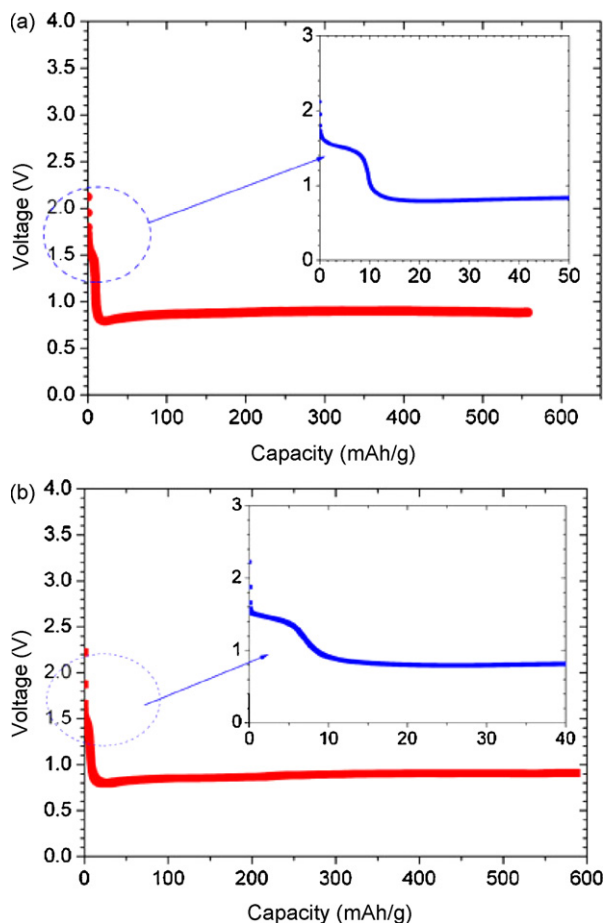


Fig. 7. Charge–discharge curves for Li/MCMB cells with composite electrolytes containing: (a) 0.6 M THFPB and 0.6 M LiF in PC/DMC (1:1, v/v); (b) 0.6 M TPFPB and 0.6 M LiF in PC/DMC (1:1, v/v) at 25 °C.

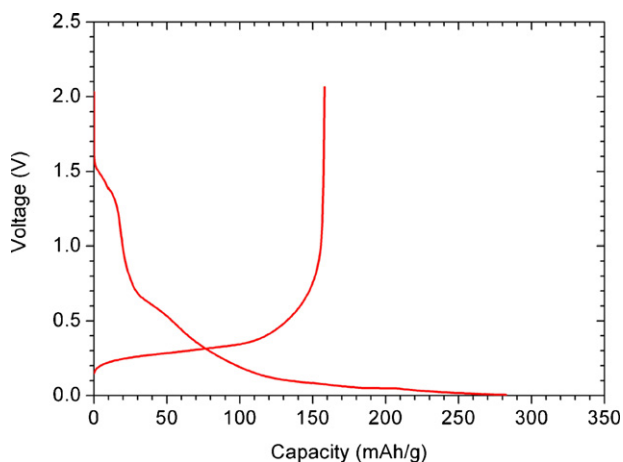


Fig. 8. Charge–discharge curves for Li/MCMB cells with an electrolyte containing 0.6 M TPFPB and 0.6 M LiF in EC/DMC (1:1, v/v) at the first cycle at 25 °C.

in our Laboratory. The results on the improvement of the anode compatibility with the new LiF based electrolytes will be published later.

The water content in our reference electrolytes of 1 M LiPF₆, EC–DMC (1:1) and 1 M LiClO₄, PC:DMC (1:1) are less than 5 ppm tested by Karl Fisher method. The exact water content of TPL01, TPL02, THL01, and THL02 was not measured, due to the limited

amount of samples. However, since the LiF based electrolytes were prepared under the similar conditions for the reference electrolyte, the water level should be comparable. Therefore, the incompatibility of the new electrolyte with graphite anode is caused by the electrolyte, not the water content. This will be clarified further in our later publications.

4. Conclusion

LiF can be dissolved with rather high concentration in carbonate based solvent systems after adding anion receptors as additives. These electrolytes show very good conductivity at low temperatures when PC is used as part of the solvents. The Li ion transference number is much higher than conventional electrolytes, indicating high effective lithium ion conductivity. An electrochemical stability window as high as 5.0 V was obtained for one of the electrolytes (TLP01), showing a good potential in the application of lithium-ion batteries operating at high voltage and low temperature. These new type of electrolytes are compatible with LiCoO₂ and LiMn₂O₄ bench mark cathode materials. However, these electrolytes still have problems in forming stable SEI layers when working with MCMB anode materials. The approaches on how to form stable SEI layers at the anode surface needs to be further studied and the composition of the electrolyte needs to be varied to improve the compatibility with MCMB anode materials.

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