



Short communication

Studies on the influence of tris(pentafluorophenyl)borane on the properties of ethylene carbonate, dimethyl carbonate and poly(ethylene oxide) dimethyl ether lithium trifluoromethanesulfonate electrolytes

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ABSTRACT

In this paper we present our studies on the properties of battery electrolyte based on EC/DMC (ethylene carbonate/dimethyl carbonate, w/w ratio 2:5) and PEODME (poly(ethylene oxide) dimethyl ether) ($M_w = 500$) doped with LiCF_3SO_3 –lithium trifluoromethanesulfonate (LiTf) and modified with TPFPB (tris(pentafluorophenyl)borane) as a potential anion trapping agent. We were particularly interested how this compound behaves in different solvents, e.g. battery mixture EC/DMC and model polymeric matrix PEODME. We also verified stability of the proposed solutions by means of DSC and FTIR, determined influence on conductivity and lithium transference numbers by impedance spectroscopy, and finally attempted to define mechanism of influence of boron addition on different systems.

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1. Introduction

One of the major goals of the modern electrolytes is the enhancement of the cation transport properties producing the so-called single ion conductors. Several approaches have been employed to produce material which, with a transference number of one, would avoid the development of concentration gradients resulting in voltage drop during discharge. Among many of the strategies towards single ion conductors, one of the very obvious and logical is simply to immobilize the anion. Lonergan et al. [1] reported the paper on cryptands addition to the polyelectrolytes and from this time complexing agents have met an increased interest [2–5]. Unfortunately, application of this idea at lithium batteries electrolytes and other devices [6] appeared extremely difficult mainly due to low conductivity as well as mechanical properties.

The idea that electron-deficient boron would complex the anion has been started and elaborated by McBreen who synthesized series of neutral boron compounds as anion receptors [7]. These kind of materials also displayed high electrochemical stability up to 5 V [8]. This concept was further enhanced by attaching electron-withdrawing groups and synthesis of the boron compounds with lower molecular weight [4].

Numerous different compounds have been synthesized and tested recently [9–12]. Among them series of fluorinated 1,3,2-

benzodioxaborole and 1,3,2-dioxaborolane [13] and a new family of borinate compounds (B bonded with one oxygen and two carbon atoms), which were found to have excellent electrochemical stability [14].

Large group of fluorinated derivatives of phenylboronic acid [15] showed superior conductivity properties in comparison with the pure electrolytes containing LiCl or LiF salts.

However, in our opinion, there is still lack of information and description of details of the mechanism of complexation in such composite systems with more sophisticated salts.

We already analyzed properties of triphenylborane (Ph_3B) [16] in polymer electrolyte system and we observed the increase of lithium transference number. This effect was followed by changes in infrared and Raman spectra confirming complex formation [16,17].

Some novel bororganic compounds have also been tested in our group in order to verify their stability and application as anion trapping agents [18].

Tris(pentafluorophenyl)borane (TPFPB) has been previously studied as an anion receptor in systems consisting of polyethylene oxide (PEO) [19] and 1,2-dimethoxyethane [4,20–22]. In all these cases lithium-ion transference number increased with increasing TFPFB content due to the restriction of anion conduction by the interaction between anion and anion receptor. We particularly would intend to follow and compare the idea proposed by Park and co-workers [23] in similar solvent systems but we also extend our studies to polyether based system. Moreover, Park used LiClO_4 which is known as an explo-

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sive material, so we decided to use lithium triflate as a safer one.

Consequently in this paper we decided to explore the effect of commercially available anhydrous tris(pentafluorophenyl)borane (TPFPB) as a component of LiCF_3SO_3 electrolyte. The complex formation ability in the presence of lithium salt was tested in various organic solvents, e.g. in ethylene carbonate/dimethyl carbonate (EC/DMC) mixture of solvents and model polymer polyethylene oxide dimethyl ether (PEODME) matrix. Such systems were never described before in the literature.

We also attempt to explain the mechanism of the salt–receptor complex formation in solvents with different chemical structure. Our results confirm the strong correlation between structural properties of solvent and bororganic compound and the ability of anion complexation in different electrolytes.

2. Experimental

2.1. Sample preparation

All anhydrous ethylene carbonate (EC, Aldrich), dimethyl carbonate (DMC, Aldrich) and tris(pentafluorophenyl)borane ($(\text{C}_6\text{F}_5)_3\text{B}$, TPFPB, Aldrich) were used as received in argon filled dry-box atmosphere.

Polyethylene oxide dimethyl ether (PEODME, $M_w = 500$, Aldrich) was dried under high vacuum (10^{-6} Torr) at 80°C for 60 h. LiCF_3SO_3 (LiTf) was dried under vacuum at 80°C for 60 h prior to the dissolution in the polyether. After drying procedure, still under vacuum, the polymer was transferred to an argon filled dry-box (moisture content lower than 2 ppm), where LiTf was dissolved in the polymer using a magnetic stirrer. The salt concentrations were equal to 0.2 and 1 mol kg^{-1} of solvents. Samples were prepared either by direct dissolution of the salt in the polyether or carbonate mixture, or dilution of higher concentrated samples. Samples were heated at 50°C to facilitate the dissolution process. TPFPB concentrations were equal to 0.04, 0.06, 0.1 and 0.2 M. Set of different mixtures: TPFPB (0.1 M) in CH_2Cl_2 ; TPFPB (0.2 M) in 0.2 M LiCF_3SO_3 EC/DMC and TPFPB (0.06 and 0.04 M, 0.1 M, respectively) have been prepared using same procedures as described before for spectroscopic studies [16,18].

2.2. Impedance spectroscopy with blocking electrodes

Ionic conductivity was measured using the electrochemical impedance spectroscopy (EIS) in the temperature range from 20 to 70°C . Electrolyte samples were sandwiched between stainless steel blocking electrodes and placed in a cryostat–thermostat system. A cylindrical cell between electrodes of 13 mm diameter was used for measurements, with electrolyte layer thickness of between 170 and 180 μm (measured each time with 1 μm precision). All impedance measurements were carried out on a computer-interfaced Bio-Logic VMP3 multichannel potentiostat within frequency range from 500 kHz to 100 mHz with 10 mV a.c. (alternating current) signal. All conductivity data were averaged over three samples and every point is an average of three measurements.

2.3. Transference numbers

Transference numbers (t_+) were calculated using d.c. polarization method combined with a.c. impedance method introduced by Bruce and Vincent [24,25]. Impedance spectroscopy measurements were performed on VMP3 multichannel potentiostat with a.c. signal of 10 mV in 500 kHz to 100 mHz range. Impedance spectra were analyzed with Equivalent-circuit 4.55 application by Bernard A. Boukamp. Chronoamperometry measurements were executed also on Bio-Logic VMP3 multichannel potentiostat. Polarization with

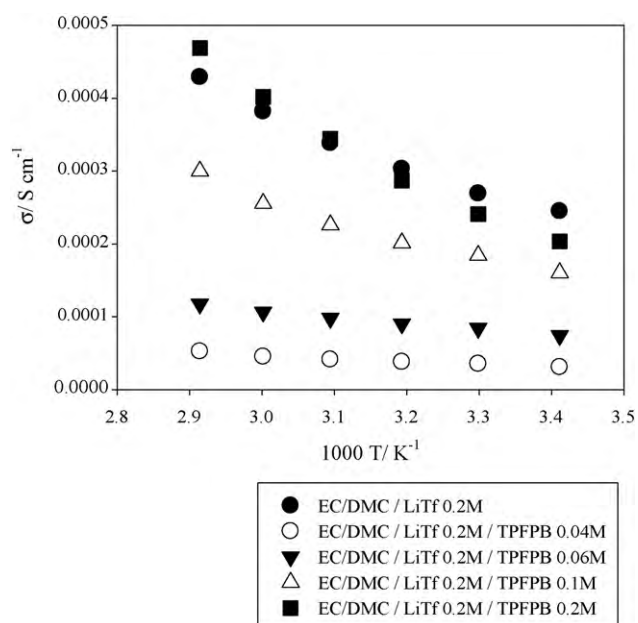


Fig. 1. Ionic conductivity vs. reciprocal temperature for EC/DMC LiTf TPFB electrolyte. Unmodified system was used as a reference.

20 mV potential difference took place on each sample until current reached steady state.

Polarization method, where $t_+ = I_s/I_0$ (I_0 initial current; I_s steady-state current) is working well in assumption of ideal conditions. Under real conditions current flow is affected by passive layer forming, so the adequate correction for resistance changes is needed. For the $\text{Li}/\text{Li}^+\text{X}^-/\text{Li}$ cell type, Bruce and co-workers introduced the following correction:

$$t_+ = \frac{I_s(\Delta V - R_0 I_0)}{I_0(\Delta V - R_s I_s)}$$

where ΔV is d.c. (direct current) voltage applied; R_0 the initial passive layer resistance; R_s the steady-state passive layer resistance; I_0 the initial current and I_s is the steady-state current.

Impedance spectroscopy measurements were taken just before d.c. polarization and just after it reached steady state. The lithium cation transference numbers of the samples were measured at room temperature. Every concentration of each salt was measured on three samples to show reproducibility of data.

2.4. DSC

DSC experiments were carried out on TA Q-200 apparatus in -100 to 60°C range with the heating rate of 5°C min^{-1} . Mass of the sample was ~ 3 mg.

2.5. FTIR

Infrared absorption spectra were recorded on a computer-interfaced Perkin-Elmer 2000 FTIR system with a wavenumber resolution of 1 cm^{-1} . FTIR studies were performed at 25°C for sample in a form of a thin film sandwiched between two NaCl plates (high salt concentration) or placed in a cuvette with NaCl windows and a 0.1 mm Teflon spacer.

3. Results and discussion

Figs. 1 and 2 present conductivity data for systems using EC/DMC and PEODME based solutions with and without addition of bororganic compound vs. reciprocal temperatures.

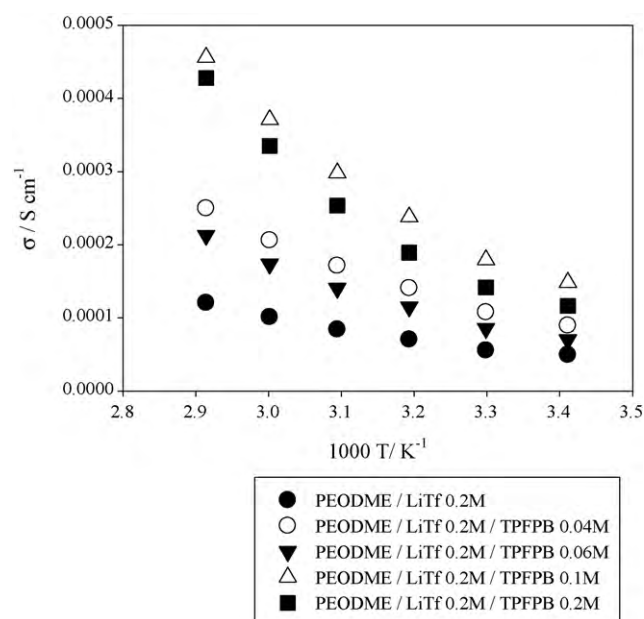


Fig. 2. Conductivity data as a function of reciprocal temperature for PEODME-LiTF system with and without bororganic additive.

Fig. 1 depicts ionic conductivity plots for EC/DMC system containing 0.2 M solution of lithium triflate salt with various amounts of tris(pentafluorophenyl)borane. Fig. 2 presents the same plots for PEODME-LiTF.

It can be clearly observed, that the addition of bororganic compound results in the huge – almost one order of magnitude decrease in the ionic conductivity for the solution with the lowest TPFPB concentration. For higher amount of the bororganic compound in the system, the conductivity increases gradually, but never exceeds the values obtained for unmodified system.

For the system with PEODME based electrolyte the receptor addition enhances the conductivity for all electrolytes studied. Conductivity increases with the TPFPB content up to 0.1 M. For the highest amount of TPFPB, 0.2 M, we observed a slight drop in conductivity.

Table 1 summarizes the lithium transference numbers. In the case of electrolytes based on EC/DMC we found an increase in the transference numbers upon addition of the anion trapping additive. In PEODME, however, we do not observe any significant enhancement of the transference number values. In contrast, there is a slight decrease of the transference number for electrolytes with higher TPFPB content.

The difference in the trends observed for EC/DMC and PEODME based systems is a consequence of several factors. Firstly, as it was shown in our previous papers, anion receptors interact with all of the electrolyte components, i.e. both solvents and salts [26]. Depending on the donor properties of anions and solvents, the complex formation either with an anion or with solvent may be preferred. Glymes and PEODME are characterized by higher donor numbers (DN) (of order 20–25) values than carbonates, such

Table 1
Lithium transference numbers measured for systems based on EC/DMC and PEODME. Salt concentration was equal to 0.2 M/kg solvent.

TPFB concentration/M kg ⁻¹	EC/DMC LiTF	PEODME/LiTF
0	0.77	0.70
0.04	0.94	0.75
0.06	0.88	0.67
0.1	0.98	0.67
0.2	0.98	0.60

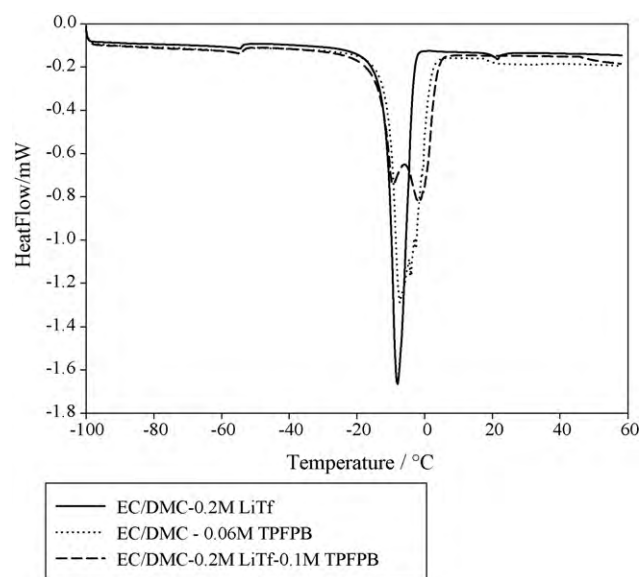


Fig. 3. DSC curves for EC/DMC with 0.2 M salt, EC/DMC and 0.06 M TPFPB and EC/DMC 0.2 M of salt and 0.1 M TPFPB.

as EC or DMC (16.4 and 15.1, respectively) [27,28], therefore it can be expected that glymes also strongly interact with receptor molecules. On the other hand, in EC/DMC based systems, simultaneous effect of increase of the transference numbers and initial decrease in conductivity, for low TPFPB/salt ratio points on the preferred complexation of an anion. It has to be noted that receptor may be able to interact both with charged free anions and with neutral ion pairs. The complexation of free anions would result in the decrease in conductivity, and that was actually observed for the low TPFPB content. With rise in the receptor/salt ratio, increases the possibility of interactions with ionic pairs, leading to an increase in conductivity due to the better dissociation of the salt.

Fig. 3 presents the comparison of DSC curves for EC/DMC and 0.2 M of salt, EC/DMC with 0.06 M of TPFPB, and finally for EC/DMC with 0.2 M LiTF and 0.1 M TPFPB samples. All thermograms show huge endothermic peak around -8°C . Intensity and shape of this peak changes in the TPFPB containing systems and a second peak close to 0°C appears in the curve for composite electrolyte. Besides the spectroscopic evidence the appearance of this new signal can originate from complex formation. However, even addition of a small amount of anion complexing agent influences the position of the melting EC/DMC signal. That suggests interactions also between solvents and bororganic compound itself in addition to the postulated interactions with an anion, which also confirms previously reported spectroscopic evidence for the complexation.

Our previous studies [16–18] on systems containing various bororganic receptors, such as Ph_3B , tris(pentafluorophenyl) borane and pentafluorophenylboronic acid esters revealed changes in infrared and Raman modes of these compounds, indicate formation of complexes, not only with anion, but also with solvent molecules. We have shown in our former paper [18], that tris(pentafluorophenyl)borane remains stable in the presence of various species with strong donor properties.

Fig. 4 presents the comparison of the spectral range the of ring stretching vibrations in FTIR spectra of tris(pentafluorophenyl) borane in CH_2Cl_2 and in EC/DMC solutions with various additive/salt molar ratio. The slight shift of the peak maximum, from 1521 to 1519 cm^{-1} , indicates the complex formation in the EC/DMC solution. However, there is no significant change in the position and shape of the peak between the solutions with different salt content and additive/salt ratio, which points on the competition

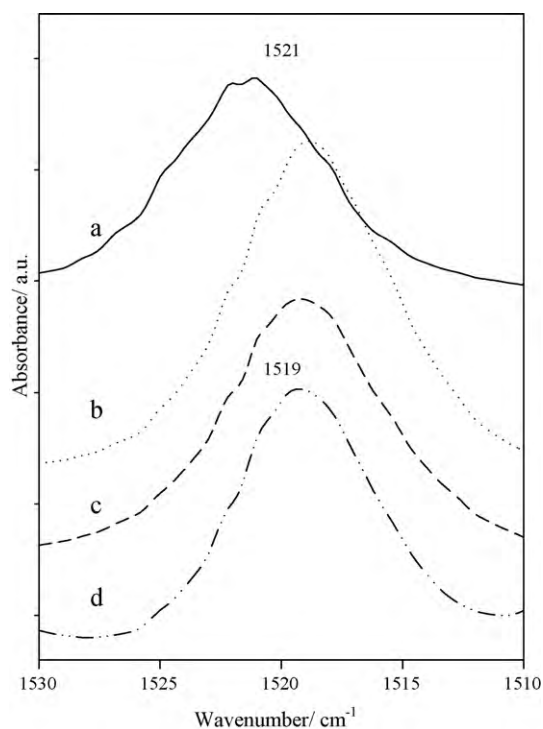


Fig. 4. FTIR spectra of TPFPB solutions in CH_2Cl_2 (1a, 0.1 M), in 0.2 M LiCF_3SO_3 in EC/DMC (2a, 0.2 M TPFPB) and in 1 M LiCF_3SO_3 in EC/DMC (1c and 1d, 0.06 and 0.04 M TPFPB, respectively).

of anions and solvent molecules in formation of the complex with receptor.

Fig. 5 shows $\nu_s\text{SO}_3$ spectral range of triflate anion in FTIR spectra of LiCF_3SO_3 /TPFPB/EC/DMC solutions with low (0.2 M) salt concentration. The position of the maximum, at 1040 cm^{-1} , is typical for anion pair [29], but the increase in TPFPB/salt ratio is followed by a slight increase in the intensity of the shoulder at 1033 cm^{-1} , attributed to free anions. This effect indicates the possibility of the formation of ionic pair–receptor complex, resulting in better salt dissociation.

A confirmation of the presence of such complex can be concluded on the basis of the B–C bending modes, assigned *per analogiam* to BPh_3 [30]. Fig. 6 shows comparison of the similar set of spectra, but in the spectral range of the BC_3 bending vibrations.

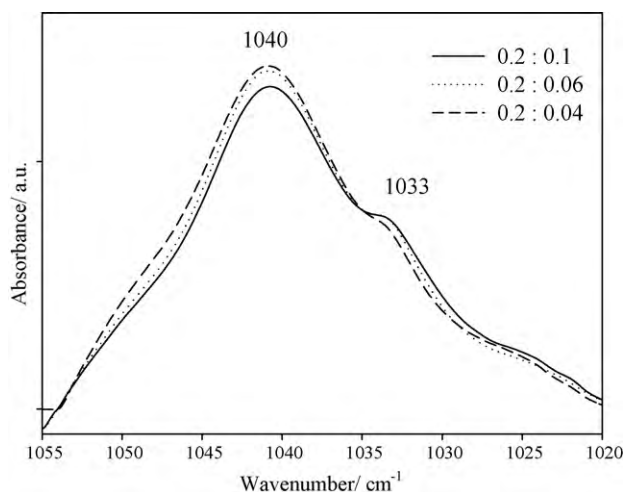


Fig. 5. FTIR spectra of TPFPB solutions in 0.2 M LiCF_3SO_3 in EC/DMC with TPFPB concentration equal to 0.04, 0.06 and 0.1 M, respectively.

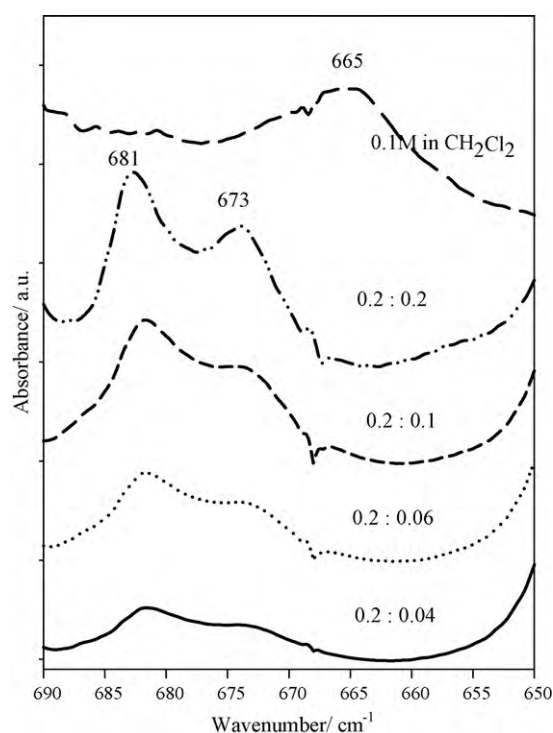


Fig. 6. FTIR spectra of TPFPB solutions in CH_2Cl_2 (0.1 M) and in 0.2 M LiCF_3SO_3 in EC/DMC with TPFPB concentration equal to 0.04, 0.06, 0.1 and 0.2 M, respectively.

It is seen, that the single peak at 665 cm^{-1} , present in spectrum of the TPFPB/ CH_2Cl_2 solution, is shifted and split into two bands, with maxima at 681 and 673 cm^{-1} in solutions of the electrolytes, which indicates on coordination by TPFPB either anions, or solvents. Similar changes in the positions of bands attributed to B–C bending and ring stretching vibrations we observed in previously studied electrolytes doped with BPh_3 [17].

4. Conclusions

Performed research showed differences in conductivity followed by large increase in lithium transference numbers for EC/DMC solutions. These two facts were expected and desired. IR spectroscopy results confirmed that addition of bororganic compound to EC/DMC solutions provides reduction of number of ion pairs in exchange to free ions.

For PEODME solutions an increase in conductivity is followed by almost not changed (slightly decreasing) lithium transference numbers. Such behavior suggests that bororganic additive is more readily combined with solvent than with anion.

TPFPB shows good compatibility and stability with EC/DMC and PEODME based electrolytes and we did not find any signs of decomposition neither of the TPFPB itself nor the signs of degradation of the electrolytes.

In our general opinion, anion trapping agents when used in electrolytic system (polymer and conventional) should be considered as a tailored material for specific salt and matrix or solvent. Usefulness of commonly applied receptors might be wider for simple anions but might fail for salts with more complicated structure.

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