

Chelate complexes with boron as lithium salts for lithium battery electrolytes

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Abstract

The electrolytic conductivity and charge–discharge characteristics of lithium electrodes are examined in propylene carbonate (PC)- and ethylene carbonate (EC)-based binary solvent electrolytes containing lithium bis[1,2-benzenediolato(2-)-O,O']borate (LBBB), lithium bis[2,3-naphthalenediolato(2-)-O,O']borate (LBNB) and lithium bis[2,2'-biphenyldiolato(2-)-O,O']borate (LBBPB). The LBBPB exhibits high thermal and electrochemical stability compared with LBBB and LBNB. Conductivities in PC-THF and EC-THF binary solvent electrolytes at X_{THF} (mole fraction of tetrahydrofuran, THF) = 0.5 containing 0.5 M LBBB and LBNB are nearly equal to that in 0.5 M LiCF₃SO₃ electrolyte as a typical lithium battery electrolyte. The conductivity in 0.3 M LBBPB/PC-DME (DME: 1,2-dimethoxyethane) electrolyte is fairly low compared with that in other electrolytes. The energy density with the LBNB electrolyte is higher than that with LBBB or LBBPB electrolyte. In general, lithium cycling efficiencies in THF-based LBBB and LBNB electrolytes become higher than those in DME-based electrolytes. The 0.5 M LBNB/PC-THF electrolyte is a moderately rechargeable lithium battery electrolyte. The 0.3 M LBBPB/PC-DME equimolar solvent electrolyte displays the highest cycling efficiency, viz., > 70%, at a high range of cycle number. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lithium batteries; Electrolytic conductivity; Lithium cycling efficiency; Organic electrolytes; Organoborates

1. Introduction

Many workers have attempted to develop improved electrolytes for lithium batteries with high energy density and good rechargeability as power sources for many portable instruments and electric vehicles. Recently, Barthel et al. [1–5] reported new complexes with boron as lithium salts for lithium battery electrolytes, such as lithium bis[1,2-benzenediolato(2-)-O,O']borate (LBBB), lithium bis[2,3-naphthalenediolato(2-)-O,O']borate (LBNB) and lithium bis[2,2'-biphenyldiolato(2-)-O,O']borate (LBBPB), see Fig. 1. The molecular modelling of these organoborates, shown in Fig. 1, was carried out using CS ChemOffice Chem3D Pro software (CambridgeSoft) on a PC-9821 (NEC). These complexes are noted to be very good electrolytes for lithium batteries because they are non-toxic

and are thermally, chemically and electrochemically stable lithium salts. In previous papers [6,7], we reported the thermal characteristics of LBBB and LBNB and the electrolytic behaviour in propylene carbonate (PC)-1,2-dimethoxyethane (DME), ethylene carbonate (EC)-DME, PC-tetrahydrofuran (THF) and EC-THF binary solvent electrolytes containing LBBB and LBNB.

The purpose of the present study is to elucidate the electrolytic behaviour and charge–discharge characteristics of lithium electrodes in PC and EC-based binary solvent electrolytes containing LBBB and LBNB in comparison with those in LBBPB/PC-DME electrolyte.

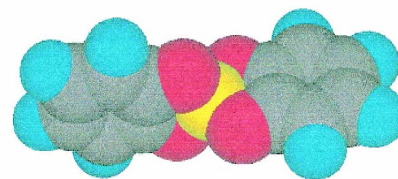
2. Experimental

2.1. Materials

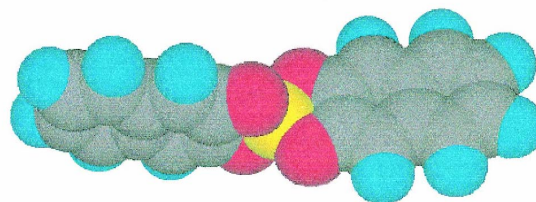
The LBBPB raw salt was obtained easily by cooling to room temperature after addition of a 2,2'-dihydroxybi-

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Lithium bis[1,2-benzenediolato(2-)-O,O']borate (LBBB)



Lithium bis[2,3-naphthalenediolato(2-)-O,O']borate (LBNB)



Lithium bis[2,2'-biphenyldiolato(2-)-O,O']borate (LBBPB)

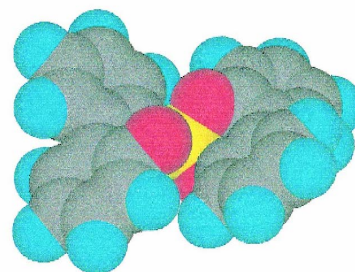
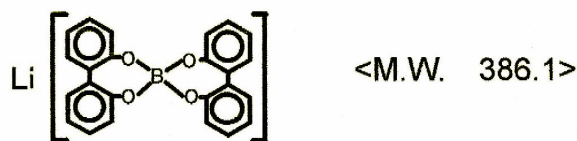


Fig. 1. Structures of LBBB, LBNB and LBBPB.

phenyl and boric acid (mol ratio 2:1) mixture in methanol at 60°C to a lithium hydroxide monohydrate–methanol solution dispersed at 60°C. This synthetic process is different from that of Barthel et al. [4] which started with tetramethanolatoborate. The raw lithium salt was recrystallized several times from DME until the solution of the salt in DME became clear, and then the recrystallized salt was dried in vacuo for 12 h at 120°C. The yield was about 50%. The purity and structure were confirmed by elemental and ICP analyses for B and Li (found: C, 71.10; H, 4.36; O, 19.98; B, 2.74; Li, 1.82 wt.%; calculated for $\text{LiBC}_{24}\text{H}_{16}\text{O}_4$: C, 74.65; H, 4.18; O, 16.57; B, 2.80; Li, 1.80 wt.%) and C–H COSY NMR. The preparation and purification of LBBB and LBNB have been described elsewhere [1,3]. Commercial THF and DME were purified by refluxing over night with LiAlH_4 , followed by fractional distillation [8]. These solvents were dehydrated using purified molecular sieves (4 Å) before preparation of the solutions. The solvents, such as PC and EC (Mitsubishi

Chem.), were used as received (battery-grade). Commercial reagent grade lithium salts including LiClO_4 , LiPF_6 , LiBF_4 and LiCF_3SO_3 , were dried in vacuo for 24 h at

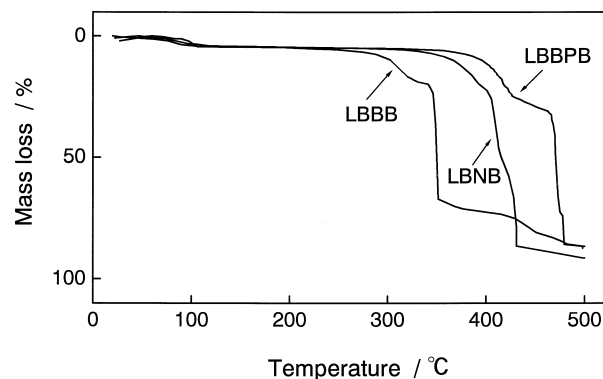


Fig. 2. TG curve of LBBB, LBNB and LBBPB at a heating rate of 1°C min⁻¹ in air. α -Alumina was used as a reference.

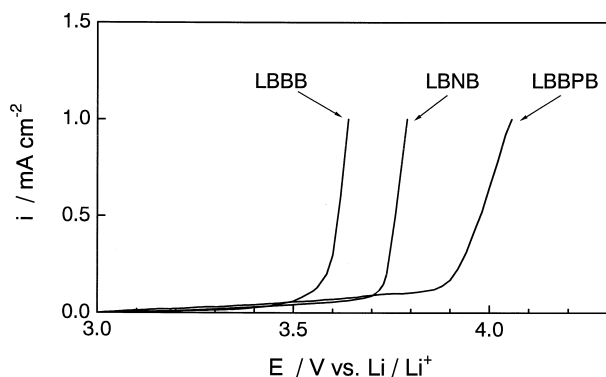


Fig. 3. i - E curves in PC solutions containing 0.1 M LBBB, LBNB or LBBPB using a platinum working electrode at a scan rate of 10 mV s^{-1} at 25°C .

70°C . The commercial reagent grade $\text{LiBPh}_4 \cdot 3\text{DME}$ (Ph: phenyl) was used as received.

2.2. Apparatus and measurements

The conductivities of the electrolytes were measured using a conductometer (Toa Electronics, Model CM-60S) with a cell (Model CGT-511B). The decomposition voltages (i - E curves) in electrolytes using a three-electrode system (Ni plate working, Li plate counter and Li foil references electrodes) were measured at a scan rate of 10 mV s^{-1} by means of a potentiostat (Hokuto Denko, Model HA-501) equipped with a potential sweep unit (Model HB-104). The lithium cycling efficiency (charge-discharge coulombic efficiency of the lithium electrode) was estimated by means of a 6-channel charge-discharge unit (Hokuto Denko, Model HJ-101SM6) by a galvanostatic plating-stripping method which was reported by Koch and Brummer [9]. Preparation of the electrolyte solutions and the cell assembly were carried out in an argon-filled dry box. A prototype Li/ V_2O_5 (Toshiba Battery) cell (Hohsen) with a glass filter (Advantec Toyo GA-100) as a

separator was used for the measurement of the energy density at a cut-off potential of $2.5 \text{ V vs. Li/Li}^+$ and at a current density of 1.0 mA cm^{-2} . Thermogravimetric (TG) analyses of lithium organoborates were carried out with equipment from Seiko Instruments.

3. Results and discussion

3.1. Thermal stability

The TG curves of LBBB, LBNB and LBBPB are shown in Fig. 2. The LBBPB exhibits a high thermal stability compared with that of LBBB and LBNB. In these organoborates, the start of decomposition occurred at 250 [6], 320 [6] and 370°C for LBBB, LBNB and LBBPB, respectively. The order of the decomposition temperature is in fair agreement with that of the conjugate energies of benzene, naphthalene and biphenyl. In other words, the thermal stability of organoborates closely depends on the conjugate energies in the aromatic ring systems.

3.2. Decomposition voltage (i - E curve)

The decomposition voltages (i - E curves) in PC solutions containing 0.1 M LBBB, LBNB or LBBPB are given in Fig. 3. The data show that LBBPB has a high stability for oxidation in these organoborates. The order of the stability is $\text{LBBPB} > \text{LBNB} > \text{LBBB}$, which is the same as that of the thermal stability in Fig. 2. Accordingly, LBBPB with high thermal and electrochemical stability is a favorable lithium battery electrolyte.

3.3. Conductivity

The variation in specific conductivity in PC-THF solutions containing 0.5 M electrolytes at 25°C is shown in

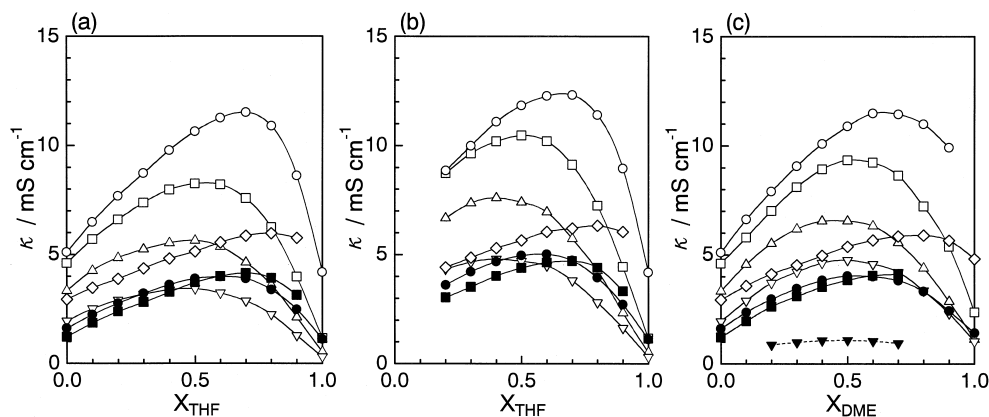


Fig. 4. Variation in specific conductivity (κ) in (a) PC-THF, (b) EC-THF, and (c) PC-DME solutions containing 0.5 M electrolytes at 25°C . X_{THF} and X_{DME} denote the mole fraction of THF and DME. Concentration of LBBPB/PC-DME electrolyte is 0.3 M, (●) LBBB, (■) LBNB, (▼) LBBPB, (○) LiPF_6 , (□) LiClO_4 , (△) LiBF_4 , (▽) LiCF_3SO_3 , (◇) LiBPh_4 .

Fig. 4a. It is difficult to dissolve 0.5 M LBBPB in a PC-THF mixture. The conductivities in these electrolytes gradually increases with the addition of the THF through a certain mole fraction of THF (X_{THF}). In the high range of X_{THF} , these conductivities gradually decreased with increasing THF concentration. This behaviour of the conductivity, which is dependent on the variation in viscosity and dielectric constant of the PC-THF mixture (bulk), is similar to that in the EC-THF mixture, as shown in Fig. 4b. The conductivity in LBBB and LBNB electrolytes at $X_{\text{THF}} = 0.5$ in Fig. 4a and b is nearly equal to that in LiCF_3SO_3 electrolyte as a typical lithium battery electrolyte. In addition, the difference in the conductivity of LBBB and LBNB electrolytes is very small, although the viscosity in LBNB electrolyte, which has a large molecular weight and anion, is considerably higher than that in LBBB electrolyte, as shown in Fig. 5. This means that the ionic dissociation of LBNB by high charge delocalization because of two naphthalene diols in the BNB^- ion becomes larger in these mixtures. The specific conductivities in PC-DME solutions containing 0.5 M electrolytes at 25°C are given in Fig. 4c. The electrolyte of more than 0.3 M LBBPB was insoluble in the PC-DMC system. Furthermore, the dissolution concentration of LBBPB is less than 0.3 M in EC-DME, PC-THF and EC-THF systems. The variation in the electrolytic conductivities, except for LBBPB in PC-DME solutions, is similar to those in PC-THF solutions in Fig. 4a. In Fig. 4c, the conductivity in 0.3 M LBBPB/PC-DME electrolyte is found to be fairly low compared with that in other electrolytes.

3.4. Discharge capacity

The discharge curves for a $\text{Li}/\text{V}_2\text{O}_5$ prototype cell in PC-DME equimolar binary solutions containing 0.5 M electrolytes, except for LBBPB (0.3 M) at 25°C, are shown in Fig. 6. The LBBB and LBNB electrolytes show moderate discharge capacities compared with those in LiPF_6 and

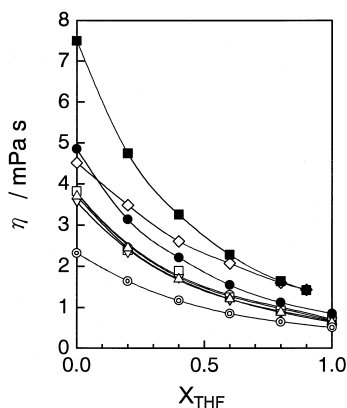


Fig. 5. Variation in viscosity (η) in PC-THF solutions containing 0.5 M electrolytes at 25°C. X_{THF} denotes mole fraction of THF. (●) LBBB, (■) LBNB, (○) LiPF_6 , (□) LiClO_4 , (△) LiBF_4 , (▽) LiCF_3SO_3 , (◇) LiBPh_4 , (small circle within a circle) solvent.

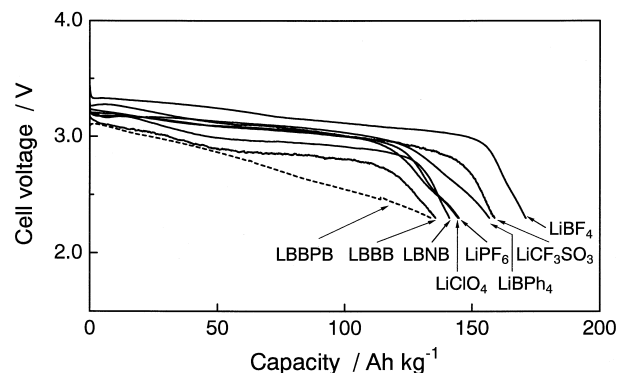


Fig. 6. Discharge curves for $\text{Li}/\text{V}_2\text{O}_5$ prototype cell in PC-DME equimolar binary solutions containing 0.5 M electrolytes at 25°C. Concentration of LBBPB/PC-DME electrolyte is 0.3 M.

LiClO_4 electrolytes, which are typical lithium battery electrolytes. The dependence of discharge capacity on the intercalation (electrodics) of Li^+ ions in the cathode is influenced by many factors, such as the characteristics of the electrode active materials, the type of electrolyte and solvent (selective ion solvation), the conductivity and the viscosity of the electrolyte, etc. Accordingly, the lower discharge capacities in organoborate electrolytes, especially in LBBPB electrolyte, seem to be appreciably influenced by the conductivity (Fig. 4c) in these electrolytes. The energy density of the $\text{Li}/\text{V}_2\text{O}_5$ prototype cell for V_2O_5 (cathode) in various electrolytes obtained from the discharge curves at a cut-off voltage of 2.5 V vs. Li/Li^+ are shown in Table 1. The energy density in LBNB electrolyte is higher than that in LBBB and LBBPB electrolytes. In addition, it is found that the LBNB electrolyte shows a moderate energy density compared with that for a common lithium battery electrolyte.

3.5. Lithium cycling efficiency

The lithium cycling efficiencies in PC-THF and PC-DME equimolar binary solutions at 25°C are shown in

Table 1

Energy density of various electrolyte solutions for $\text{Li}/\text{V}_2\text{O}_5$ prototype cell at 25°C

	mol dm ⁻³	Specific energy (W h kg ⁻¹)				
		PC	PC-DME	EC-DME	PC-THF	EC-THF
LBBPB	0.3	310				
LBBB	1.0	30	290	370	190	350
LBNB	0.5	30	410	460	280	400
LiClO_4	1.0	300	510	540	500	510
LiPF_6	1.0	340	510	510	490	500
LiBF_4	1.0	250	510	530	480	510
LiCF_3SO_3	1.0	220	510	500	470	460
LiBPh_4	0.5	230	450	470	410	420

Cut-off voltage: 2.5 V vs. Li/Li^+ .

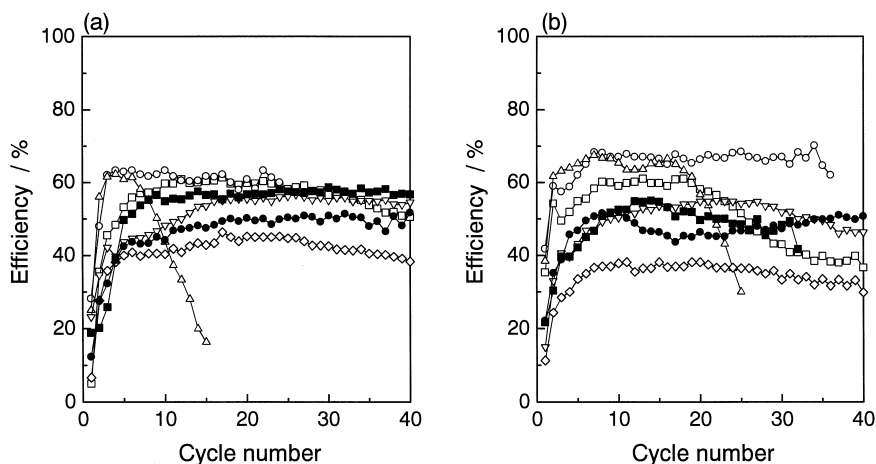


Fig. 7. Variation in lithium cycling efficiency in PC-THF (a) and PC-DME (b) equimolar binary solutions at 25°C. Concentration of electrolytes, except LBNB and LiBPh₄ (0.5 M), is 1.0 M. $i_p = i_s = 1.27 \text{ mA cm}^{-2}$, $Q_p = 0.38 \text{ C cm}^{-2}$. (●) LBBB, (■) LBNB, (○) LiPF₆, (□) LiClO₄, (△) LiBF₄, (▽) LiCF₃SO₃, (◇) LiBPh₄.

Fig. 7a and b, respectively. The efficiencies in THF-based LBBB and LBNB electrolytes are generally higher than those in DME-based electrolytes. In addition, a decrease in the efficiencies in THF-based LBBB and LBNB electrolytes is hardly observed in spite of the increase in cycle number compared with that for other electrolytes. In Fig. 7a, the efficiency of the LBNB electrolyte with lower conductivity in Fig. 4a at a higher cycle number is nearly equal to that in LiPF₆ and LiClO₄ electrolytes, which are important salts for lithium secondary batteries. The lithium cycling efficiencies in PC-DME equimolar binary solutions containing 0.3 M electrolytes as a common concentration at 25°C are presented in Fig. 8. The LBBPB electrolyte displays the highest cycling efficiency, viz., more than 70%, at a higher range of cycle number. By comparing the cycling efficiencies in Fig. 8 and the conductivities in 0.3 M electrolytes in Fig. 9, it is found that

the cycling efficiency is not dependent on the conductivity in the electrolytes. This means that the lithium cycling efficiency, i.e., the charge–discharge process, depends on the morphology and chemical composition of the passivating films on the electrode due to the reduction of reactive impurities and electrolytes. In addition, it is in Fig. 7b Fig. 8 that the lithium cycling efficiency is almost independent of the electrolyte concentration.

One of the reasons for the difference in the cycling efficiency due to electrolyte concentration seems to be related to the thickness of the passivating film formed on the electrode.

In conclusion, the 0.5 M LBNB/PC-THF electrolyte is a moderate electrolyte for rechargeable lithium batteries, in comparison with 1.0 M LiPF₆ and LiClO₄ electrolytes. The 0.3 M LBBPB/PC-DME electrolyte shows the highest lithium cycling efficiency of more than 70% at a higher range of cycle number.

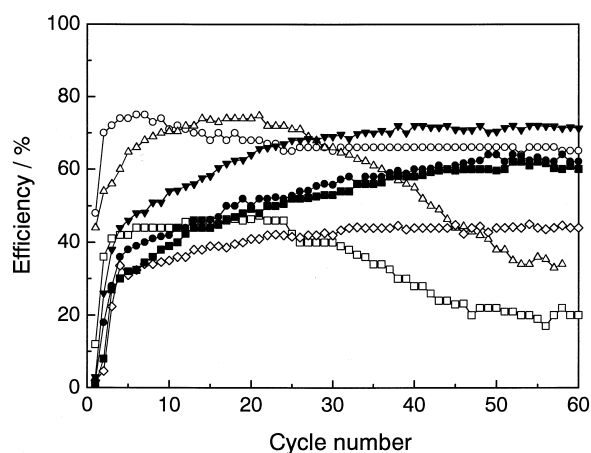


Fig. 8. Variation in lithium cycling efficiency in PC-DME equimolar binary solutions containing 0.3 M electrolytes at 25°C. $i_p = i_s = 0.1 \text{ mA cm}^{-2}$, $Q_p = 10 \text{ mC cm}^{-2}$. (●) LBBB, (■) LBNB, (▼) LBBPB, (○) LiPF₆, (□) LiClO₄, (△) LiBF₄, (◇) LiBPh₄.

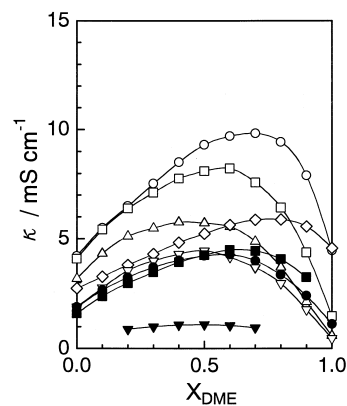


Fig. 9. Variation in specific conductivity (κ) in PC-DME solutions containing 0.3 M electrolytes at 25°C. X_{DME} denotes mole fraction of DME. (●) LBBB, (■) LBNB, (▼) LBBPB, (○) LiPF₆, (□) LiClO₄, (△) LiBF₄, (▽) LiCF₃SO₃, (◇) LiBPh₄.

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