



Short communication

LBDOB, a new lithium salt with benzenediolato and oxalato complexes of boron for lithium battery electrolytes

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ABSTRACT

A new unsymmetrical lithium salt containing $C_6H_4O_2^{2-}$ [dianion of 1,2-benzenediol] and $C_2O_4^{2-}$ [dianion of oxalic acid], lithium [1,2-benzenediolato(2-)-O,O' oxalato]borate (LBDOB), is synthesized and characterized. The thermal characteristics of it, lithium bis[1,2-benzenediolato(2-)-O,O']borate (LBBB) and lithium bis(oxalato)borate (LiBOB) are examined by thermogravimetric (TG) analysis. The thermal decomposition in Ar begins at 250, 256, and 302 °C for LBBB, LBDOB, and LBOB, respectively. The order of the stability toward oxidation of these organoborates is LBOB > LBDOB > LBBB, which is in the same order of the thermal stability. The cyclic voltammetry study shows that the LBDOB solution in PC is stable up to 3.7 V vs. Li⁺/Li. They are soluble in common organic solvents. Ionic dissociation properties of LBDOB and its derivatives are examined by conductivity measurements in PC, PC + DME, EC + DME, PC + THF, EC + THF (molar ratio 1:1) solutions. The conductivity values of the 0.10 mol m⁻³ LBDOB electrolyte in PC, PC + DME, EC + DME, PC + THF, EC + THF solutions are higher than those of LBBB, but lower than those of LBOB electrolytes.

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1. Introduction

Many researchers have attempted to develop improved electrolytes for lithium batteries with high energy density and long cycle life [1–4] as power sources for portable electronic instruments and electric vehicles in order to protect the environment and natural resources. Barthel et al. reported a new class of wide electrochemical windows and thermally stable lithium salts [5,6] with a chelate-type boron-containing anion, such as lithium bis[1,2-benzenediolato(2-)-O,O']borate (LBBB) [7], lithium bis[2,3-naphthalene-diolato(2-)-O,O']borate (LBNB) [8,9], lithium bis[2,2-biphenyldiolato(2-)-O,O']borate (LBBPB) [10], and lithium bis[salicylato(2-)]borate (LBSB) [10]. Xu et al. also reported lithium bis(oxalato)borate (LBOB) and lithium (malonato oxalato)borate (LMOB) as an advanced electrolyte for Li-ion battery [11,12]. The common feature of these anions is that extensive charge delocalization is present in them because they are composed of strongly electron withdrawing substituents. Thus, the lithium salts of these anions yield sufficiently high ionic conductivity in solutions, which exhibit wide electrochemical stability windows and good thermal stability.

According to our previous studies [13–19], the pronounced charge delocalization anions, $C_6H_4O_2^{2-}$ [dianion of 1,2-benzenediol] and $C_2O_4^{2-}$ [dianion of oxalic acid], were chosen as the unsymmetrical chelators to coordinate with boron to form lithium salt in this study to further our understanding the relationship between property and structure of these lithium salts. A new lithium salt, lithium [1,2-benzenediolato(2-)-O,O' oxalato]borate (LBDOB), as shown in Fig. 1, was synthesized. Its thermal and electrochemical stabilities, conductivities in some solvent mixtures were studied and compared with those in the LBBB and LBOB electrolytes.

2. Experimental

LBDOB was synthesized according to reaction (1). Specifically, 0.1 mol 1,2-benzenediol, 0.1 mol oxalic acid, 0.1 mol boric acid, and 120 ml toluene were transferred into a flask fitted with stirrer and water separator. After heating to 60 °C under purified argon, first of all approximately 0.01 mol of Li₂CO₃ were added using a solids dosing bulb. Within half an hour, no significant formation of gas could be established. Thereupon, 0.45 ml of H₂O was added with a syringe. The reaction now began immediately, with strong formation of gas. Within 5 min, the remaining amount of Li₂CO₃ (in total 0.05 mol) was added. The gas was thereby formed. The reaction mixture was then heated to boiling point and refluxed for 4 h. After 4 h of refluxing, no more water precipitated. After cooling

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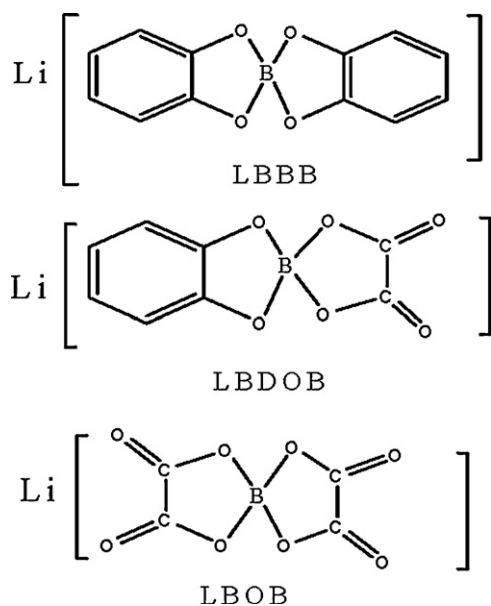
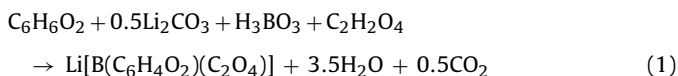
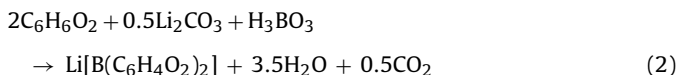


Fig. 1. Structures of LBBB, LBDOD and LBOB.

down to room temperature, a white precipitate was observed. After filtration, a solid was obtained. It was purified by multi-time recrystallizations by dissolving into THF and drying in vacuo at 60 °C for 4 h followed by 90 °C for 4 h. After drying in vacuo, the product was translated into glove box. The yield for the purified salt was up to 82%. The purity of the compound was examined by inductively coupled plasma (ICP) analysis for Li and B contents, which were measured as Li 3.25% and B 5.06%. These data were close to the calculated values Li 3.38% and B 4.52% for LBDOD. The ^{13}C NMR spectra of the prepared solid in dimethyl sulfoxide (DMSO- d_6) gave four signals at chemical shifts of 158.60, 152.01, 117.76, 108.07 ppm. ^1H NMR: 6.4 ppm



LBBB [7] was synthesized according to reaction (2) and purified in a similar procedure for LBDOD. Specifically, 0.2 mol 1,2-benzenediol, 0.1 mol boric acid, and 120 ml toluene were transferred into a flask fitted with stirrer and water separator. After heating to 60 °C under purified argon, first of all approximately 0.01 mol of Li_2CO_3 was added using a solids dosing bulb. Within half an hour, no significant formation of gas could be established. Thereupon, 0.45 ml of H_2O were added with a syringe. The reaction now began immediately, with strong formation of gas. Within 5 min, the remaining amount of Li_2CO_3 (in total 0.05 mol) was added. The gas was thereby formed. The reaction mixture was then heated to boiling point and refluxed for 4 h. After 4 h of refluxing, no more water precipitated. After cooling down to room temperature, a white precipitate was observed. After filtration, a solid was obtained. It was purified by multi-time recrystallizations by dissolving into THF and drying in vacuo at 60 °C for 4 h followed by 90 °C for 4 h. The purity of the compound was examined by ICP analysis for Li and B contents, which were measured as Li 2.97% and B 4.62%. These data were close to the calculated values Li 3.18% and B 4.66% for LBBB. Its NMR spectra in dimethyl sulfoxide (DMSO- d_6): gave following signals: ^{13}C NMR 151.6, 117.3, 107.6 ppm; ^1H NMR: 6.5 ppm.



LBOB was obtained by the direct reaction of lithium carbonate, boric acid, and the bidentate ligand oxalic acid in toluene. The procedures of synthesis LBOB were described previously [11]. The purity of the compound was confirmed by ICP for Li and B contents as Li 3.58% and B 5.58%. These data were close to the calculated values of Li 3.87% and B 5.48%. Its NMR spectra in dimethyl sulfoxide (DMSO- d_6) gave following signals: ^{13}C NMR 161.8 ppm.

The purification procedures for propylene carbonate (PC), ethylene carbonate (EC), 1,2-dimethoxyethane (DME), acetonitrile (AN), and tetrahydrofuran (THF), as well as the electrochemical equipment for electrochemical studies, are given in Refs. [7,8].

Thermogravimetric (TG) analysis of the lithium organoborates was carried out with PerkinElmer Pyres-1 DMDA-V 1 model, using a sample of about 10 mg. The NMR spectra were measured with AV-400 (Bruker, 9.40T, 400.13 MHz ^1H NMR). Inductively coupled plasma (ICP) emission spectrometry for both Li and B (model Poasma-Spec). The decomposition voltages (i - E curves) of the electrolytes using a three-electrode system (platinum wire, surface area $4.91 \times 10^{-4} \text{ cm}^2$, working Li plate counter, and Li plate reference electrodes) were measured at a scan rate of 9 mV s^{-1} . Preparation of the electrolyte solutions and the cell assembly were carried out in a glove box (Labmaster 130, MBRAUN) at low water (<1 ppm), and oxygen (<1 ppm) contents.

3. Results and discussion

3.1. Thermal stability

Fig. 2 shows the TG curves of the lithium organoborates in argon atmosphere. It can be seen that the salt decomposition starts to occur at 250, 256, and 302 °C for LBBB, LBDOD, and LBOB, respectively. Therefore, among the three salts LBOB exhibits the highest thermal stability while LBBB shows the lowest. This means that the benzenediolato compound such as LBBB decomposes easily on heating at comparatively lower temperature. Furthermore, it seems that the thermal stability depends on the higher conjugate energies of the chelate-type anion with boron [20].

3.2. Solubility

Similar to LBOB and LBBB, LBDOD is stable in organic electrolyte solutions, but it may decompose by hydrolysis, yielding beginning products. It is moderately soluble in EC + THF (1:1), 0.36 mol m^{-3} at 25 °C for LBDOD (Table 1).

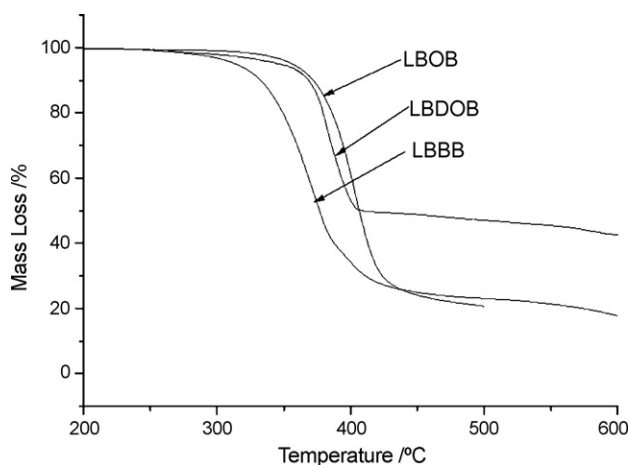


Fig. 2. TG curves of lithium organoborates at a heating rate of $10^\circ\text{C min}^{-1}$ in Ar α -alumina was used as a reference.

Table 1
Solubility ($S/\text{mold m}^{-3}$) and corresponding conductivity ($\sigma/\text{mS cm}^{-1}$) of lithium salts in PC, PC- and EC-based equimolar binary solutions at 25 °C.

	PC		PC+DME		EC+DME		PC+THF		EC+THF	
	S	σ	S	σ	S	σ	S	σ	S	σ
LBBB	0.218	5.27	0.290	5.99	0.178	4.81	0.305	5.87	0.358	6.35
LDBOB	0.274	5.36	0.302	6.21	0.201	4.96	0.318	5.98	0.360	6.53
LBOB	0.362	6.76	0.349	7.79	0.352	6.37	0.358	7.30	0.362	8.05

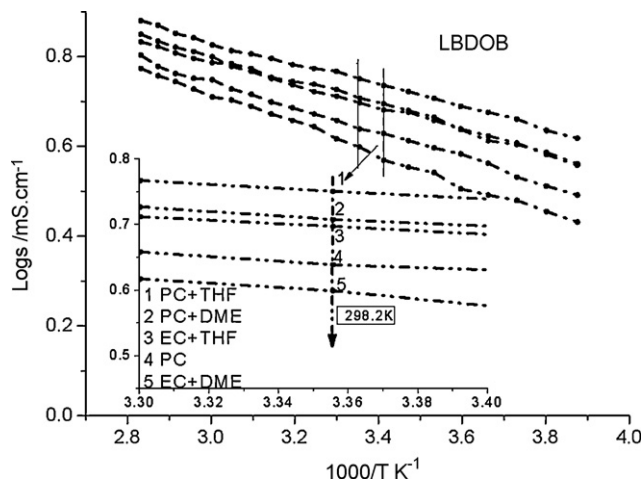


Fig. 3. Temperature dependence of ionic conductivity of LDBOB solution in different solvents (inset shows only in a narrow range of temperature ($1000/T$) from 3.3 to 3.4 for clarity).

3.3. Conductivity

Fig. 3 shows the temperature dependence of ionic conductivity of LDBOB solution in PC solvent. We also include data for solutions in the mixed solvents of PC+DME, EC+DME, PC+THF and EC+THF (molar ratio 1:1). A 0.10 mold m^{-3} solution of LDBOB in PC shows a conductivity of $4.35 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C. The solutions of 0.10 mold m^{-3} LDBOB in PC+THF and in PC+DME have room temperature conductivity of as high as 5.63 and $5.10 \times 10^{-3} \text{ S cm}^{-1}$, respectively, indicating that the ions in LDBOB solutions are highly mobile. As can be seen from Fig. 3, the conductivity of the 0.10 mold m^{-3} LDBOB electrolyte solution in PC+THF is greater than those in the other solvents. Apparently, LDBOB is highly dissociating in PC–THF mixture.

Table 2 compares the conductivities of 0.10 mold m^{-3} LDBOB solutions in different solvents with those of LBBB, and LBOB. It is seen that LDBOB solutions with the same concentration show conductivities higher than those of LBBB, but lower than LBOB solutions. On the other hand, for the saturated solutions of each lithium salt in the solvents of PC, PC+DME, EC+DME, PC+THF and EC+THF (molar ratio 1:1), they all have a quite high conductivity of more than 5.0 mS cm^{-1} (Table 1).

Table 2
Specific conductivities in different solvents containing 0.10 mold m^{-3} lithium organoborates at 25 °C.

Organoborate	PC	Specific conductivity (mS cm^{-1})			
		PC+DME (1:1)	EC+DME (1:1)	PC+THF (1:1)	EC+THF (1:1)
LBBB	4.24	4.96	3.82	5.45	4.88
LDBOB	4.35	5.10	3.97	5.63	4.98
LBOB	5.56	6.79	5.37	7.05	6.30

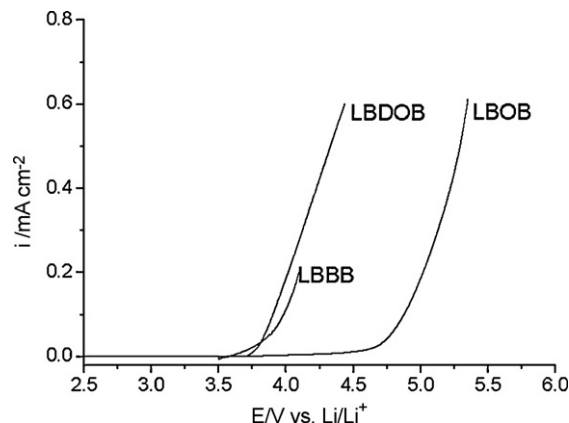


Fig. 4. i - E curves in PC saturated solutions using a platinum wire working electrode at a scan rate of 9 mV s^{-1} at 25 °C.

3.4. Electrochemical stability

The electrochemical stabilities of LBBB, LDBOB and LBOB solutions in PC on stainless steel electrodes are shown in Fig. 4. The electrochemical oxidation potential can be obtained as ca. 3.7 V vs. Li^+/Li for the 0.1 mold m^{-3} solutions of LDBOB in PC. This is higher than the oxidation potential for LBBB–PC solution (3.6 V) [7]. Thus, the order of the oxidation stability in these organoborates is $\text{LBOB} > \text{LDBOB} > \text{LBBB}$, which is in the same order of the thermal stability in Fig. 2.

Several studies of anion oxidation potentials were recently updated and extended by Xue and Chen [13]. They performed two types of calculations on the anions, obtaining HOMO energies from *ab initio* Hartree–Fock calculations and adiabatic ionization potential (I_p) from hybrid density functional B3LYP calculations. They have found that E_{ox} can be correlated with HOMO energies and with I_p . Similarly, in this study, the HOMO energies of different orthoborate anions can be calculated using Hartree–Fock/6-311++G(3df,3pd) methods. The HOMO energies are found to be -4.32 , -4.86 , and $-8.75 \text{ eV mol}^{-1}$ for LBBB, LDBOB and LBOB, respectively. Obviously, the two sets of data (E_{ox} and E_{HOMO}) are strongly correlated ($R=0.9999$).

4. Conclusions

A new lithium salt with asymmetric chelatorate anion based on two different chelators, has been synthesized. The salt, LDBOB, is thermally stable and soluble in many of the common organic solvents used in batteries. The solutions are highly conductive stable. The conductivities of LDBOB solutions are higher than those of LBBB solutions and nearly the same as those of LBOB. Its electrochemical oxidation potential is in some sort higher than those of LBBB in the common organic solvents used in batteries. A strong correlation between the HOMO energy and the electrochemical stability is established. This proves that an extensive charge delocalization, in their anions, caused by strongly electron withdrawing anion (e.g., oxalato) would lower the HOMO energy, and improve the electrochemical stability of the electrolyte.

Acknowledgments

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