Short communication

A new lithium salt with 3-fluoro-1,2-benzenediolato and oxalato complexes of boron for lithium battery electrolytes

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ABSTRACT

A new unsymmetrical lithium salt, lithium [3-fluoro-1,2-benzenediolato(2-)-o,o′ oxalato]borate (FLB-DOB), is synthesized and characterized. The thermal characteristics of FLBDOB and its counterparts lithium bis[3-fluoro-1,2-benzenediolato(2-)-o,o]borate (FLBBB) and lithium bis[oxalate]borate (LBOB) are examined and compared by thermogravimetric analysis (TG). The thermal decomposition of these salts in air is found to begin at 302, 262 and 256 °C for LBOB, FLBDOB and FLBBB, respectively. The order of the stability toward oxidation of these organoborates is LBOB > FLBDOB > FLBBB, which is in the same order of the thermal stability. The cyclic voltammetry study shows that the FLBDOB solution in PC is stable up to 4.0 V versus Li$^+$/Li. It is soluble in common organic solvents such as propylene carbonate (PC), ethylene carbonate (EC), 1,2-dimethoxyethane (DME), and tetrahydrofuran (THF). Ionic dissociation properties of FLBDOB and the counterparts in PC, PC + THF, PC + DME, EC + DME, EC + THF (molar ratio 1:1) solutions are also examined by conductivity measurements. The conductivity values of the 0.10 mol dm^{-3} FLBDOB electrolyte in PC, PC + THF, PC + DME, EC + DME, EC + THF solutions are higher than those of FLBBB, but lower than those of LBOB electrolytes.

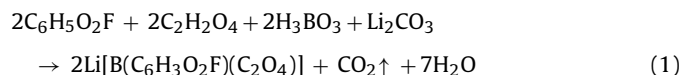© 2010 Published by Elsevier B.V.

1. Introduction

In order to protect the environment and natural resources, many researchers have attempted to develop improved electrolytes for lithium batteries with high energy density and long cycle life as power sources for portable electronic instruments and electric vehicles [1–3]. Barthel et al. reported a new class of electrochemically and thermally stable lithium salts with a chelate-type boron-containing anion, such as lithium bis[1,2-benzenediolato(2-)-o,o]borate (LBBB), and lithium bis[3-fluoro-1,2-benzene-diolato(2-)-o,oo′]borate (FLBBB) [4–7]. Xu et al. also reported lithium bis(oxalate)borate (LBOB) and lithium [malonato oxalato]borate (LMOB) as advanced electrolytes for Li-ion battery [8,9]. The common feature of these anions is that extensive charge delocalization is present in them because they are composed of strongly electron-withdrawing substituents. Because there is only a single negative charge distributed across them, these anions are very weakly coordinating. In consequence, their solutions in molecular solvents are extremely conductive [9]. Extensive charge delocalization also lowers the highest occupied molecular orbital (HOMO) [7]. Thus, the lithium salts of these anions give rise to wide electrochemical stability windows.

According to our previous theoretical studies [10–15], the pronounced charge delocalization anions, $C_2O_4{}^{2-}$ [dianion of oxalic acid] and $C_6H_3O_2F^{2-}$ [dianion of 3-fluoro-1,2-benzenediol], were chosen as the unsymmetrical chelators to coordinate with boron to form a lithium salt in this study to further our understanding on the relationship between property and structure of these lithium salts. This new lithium salt, lithium [(3-fluoro-1,2-benzenediolato(2-)-o,o′ oxalato)]borate (FLBDOB), as shown in Fig. 1, was first synthesized. Its thermal and electrochemical stabilities, conductivities in some solvent mixtures were studied and compared with those in the FLBBB and LBOB electrolytes.

2. Experimental

FLBDOB was synthesized according to reaction (1).

$$2C_6H_5O_2F + 2C_2H_2O_4 + 2H_3BO_3 + Li_2CO_3$$
$$\rightarrow 2Li[B(C_6H_3O_2F)(C_2O_4)] + CO_2\uparrow + 7H_2O \qquad (1)$$

Specifically, 0.02 mol oxalic acid, 0.02 mol 3-fluoro-1,2-benzenediol, 0.01 mol lithium carbonate, 0.02 mol boric acid, and 15 ml distilled water were placed in a flask with a stirrer and water separator and the system was flushed with high-purity nitrogen. Then the heterogeneous mixture was slowly heated to 60 °C under purified nitrogen. After an hour, no significant gas evolution was observed anymore. Thereupon, 20 ml toluene was added into the
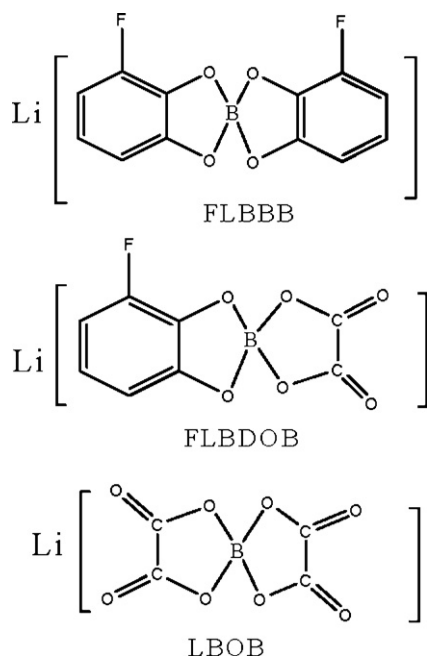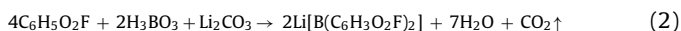
Fig. 1. Structures of FLBBB, FLBDOB and LBOB.

system. The mixture in the flask was then slowly heated to the boiling point of toluene (111 °C) to obtain a clear brown solution. After removing 16.2 ml water from the solution within 20 h and cooling down to room temperature, a straw brown precipitate was obtained by filtration. It was purified with several times of recrystallization process by dissolving it into acetonitrile (AN) and drying in vacuum at 80 °C for 24 h followed by 120 °C for 48 h. Then the product was transferred into an argon-filled glove box. The yield for the purified salt was up to 89%. The composition of the compound was determined by inductively coupled plasma (ICP) analysis, which gave that Li and B contents are Li 3.01% and B 4.71%, respectively. These data were close to the calculated values Li 3.02% and B 4.74% for FLBDOB. The ^{13}C NMR spectra of the prepared solid in dimethyl sulfoxide (DMSO-d6) gave seven signals at chemical shifts of 172.54, 161.75, 160.71, 158.60, 118.74, 111.88, 106.944 ppm while ^{1}H NMR analysis gave chemical shifts of 6.25, 6.60, 7.00, 7.05, 7.08, 7.20 ppm.

FLBBB was synthesized according to reaction (2) [7].

$$4C_6H_5O_2F + 2H_3BO_3 + Li_2CO_3 \rightarrow 2Li[B(C_6H_3O_2F)_2] + 7H_2O + CO_2\uparrow \quad (2)$$

Specifically, 0.04 mol 3-fluoro-1,2-benzenediol, 0.01 mol lithium carbonate, 0.02 mol boric acid, and 15 ml distilled water were placed in a flask with a stirrer and water separator and flushed with high-purity nitrogen. The heterogeneous mixture was slowly heated to 60 °C under purified nitrogen. After an hour, no significant gas evolution was observed anymore. Thereupon, 20 ml toluene was added into the system. The reaction mixture was then slowly heated to the boiling point of toluene (111 °C) to obtain a clear brown solution. After removing 16.2 ml water from the solution within 20 h and cooling down to room temperature, a straw brown precipitate was obtained by filtration. It was purified with several times of recrystallization process by dissolving it into acetonitrile (AN) and drying in vacuum at 80 °C for 24 h followed by 120 °C for 48 h. Then the product was transferred into an argon-filled glove box. The yield for the purified salt was up to 87%. The composition of the compound was determined by inductively coupled plasma (ICP) analysis, which gave that Li and B contents are Li 2.60% and B 4.03%, respectively. These data were close to the calculated values Li 2.59% and B 4.07% for FLBDOB. The ^{13}C NMR spectra of the prepared solid in dimethyl sulfoxide (DMSO-d6) gave

seven signals at chemical shifts of 154.39, 145.70, 137.63, 117.49, 106.23, 105.02 ppm while ^{1}H NMR analysis gave chemical shifts of 6.39, 6.41, 6.43, 6.45, 6.47, 6.49, 6.51, 6.53, and 6.55 ppm [7].

LBOB was obtained by the direct reaction of lithium carbonate, boric acid, and oxalic acid in toluene [8]. The procedures of synthesis LBOB were described previously [16]. The composition of the compound was analyzed by ICP that gave the Li and B contents are Li 3.60% and B 5.56%, respectively. These data were close to the calculated values of Li 3.58% and B 5.58%. Its ^{13}C NMR spectrum in dimethyl sulfoxide (DMSO-d6) gave a signal at the chemical shift of 161.8 ppm.

$$4C_2H_2O_4 + 2H_3BO_3 + 4Li_2CO_3 \rightarrow 2Li[B(C_2O_4)_2] + CO_2\uparrow + 7H_2O$$

$$(3)$$
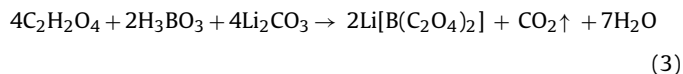
The purification procedures for propylene carbonate (PC), ethylene carbonate (EC), 1,2-dimethoxyethane (DME), acetonitrile (AN), and tetrahydrofuran (THF), as well as the electrochemical equipment for electrochemical studies, are given in our previous papers [7,8].

Thermogravimetric (TG) analyses of the LBOB, FLBDOB, FLBBB were carried out with Perkin-Elmer Pyres-1 DMDA-V1 model, using a sample of about 10 mg. The NMR analyses were conducted with the instrument AV-400 (Bruker, 9.40T, 400.13 MHz, ^{1}H NMR), while the inductively coupled plasma (ICP) emission spectrometry for both Li and B was performed on the instrument with model Poasma—Spec. The decomposition voltages (*i–E* curves) of the electrolytes using a three-electrode system (with platinum wire, surface area 4.91×10^{-4} cm^2, as the working electrode while Li sheets as the counter and reference electrodes) were measured at a scan rate of 9 mV s^{-1} on an Electrochemical Workstation CHI 660. Note that the preparation of the electrolyte solutions and the cell assembly were all 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 air. It can be seen that the salt decomposition starts to occur at 302, 262, and 256 °C for LBOB, FLBDOB and FLBBB, respectively. Therefore, among the three salts LBOB exhibits the highest thermal stability while FLBBB shows the lowest. This means that the 3-fluoro-1,2-benzenediolato compound such as FLBBB decomposes easily on heating at a comparatively low temperature, which seems to be
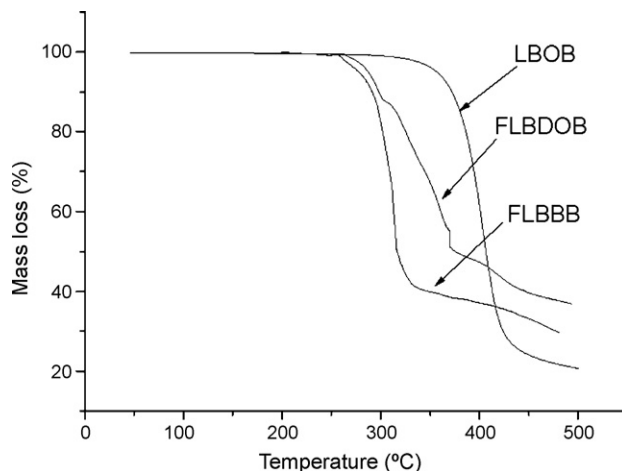

Fig. 2. TG curves of lithium organoborates at a heating rate of 10 °C min^{-1} in air. α-Alumina was used as a reference.

Table 1
Solubility (S, mol dm^{-3}) and corresponding conductivity (σ, 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
FLBBB	0.210	5.41	0.283	6.43	0.379	5.92	0.234	6.20	0.496	7.02
FLBDOB	0.275	5.60	0.284	6.55	0.388	6.00	0.248	6.34	0.506	7.68
LBOB	0.362	6.76	0.349	7.79	0.352	6.37	0.358	7.30	0.362	8.05

related to the higher conjugate energy of its chelate-type anion with boron [17]. The higher the conjugation, the smaller the energy difference between HOMO and LOMO. These energy gaps allow one to calculate a chemical reactivity index, the hardness (η) of these anions. Indeed, by applying Koopmans' theorem, Pearson showed that for closed-shell molecules 2η is equal to the gap between the HOMO and LUMO, i.e., $\eta = (E_{LUMO} - E_{HOMO})/2$. The LBOB hold the biggest η. According to the HSAB (Hard and Soft Acids and Bases) principle, the hard acid Li$^+$ prefers to coordinate with hardest base BOB$^-$, meaning that the most thermo stable lithium salt in the three salts is LBOB.

3.2. Solubility

Similar to LBOB, FLBDOB and FLBBB are stable in organic electrolyte solutions but it may be decomposed by hydrolysis in aqueous solutions and converted back to their beginning reactants as shown in reactions (1) and (2). They are moderately soluble in EC + THF (1:1) with a solubility of 0.5062 mol dm^{-3} at 25 °C for FLBDOB (Table 1).

As can be seen in Table 1, the solubilities of the lithium salts in EC – based are greater than those in PC – based equimolar binary solutions. The results could be explained by the "like dissolves like" principle. All the three anions of lithium salts, FBBB$^-$, FBDOB$^-$, and BOB$^-$, have small total dipole movement. Compared with PC, the EC hold the smaller total dipole movement. So the three lithium salts show the higher solubilities in EC than those in PC.

3.3. Conductivity

Fig. 3 shows the temperature dependence of ionic conductivity of 0.10 mol dm^{-3} FLBDOB in PC solvent. We also include the measurement results for the solutions in the mixed solvents of PC + THF, PC + DME, EC + DME, and EC + THF (molar ratio 1:1). The
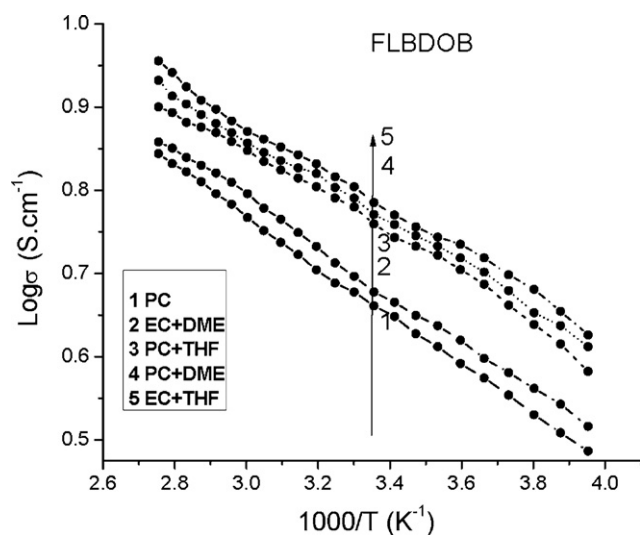
Fig. 3. Temperature dependence of ionic conductivities of FLBDOB solutions (0.10 mol dm^{-3}) in different solvents.

disassociation of a lithium salt in the electrolyte solution is one of the key elements affecting Li-ion battery performance. It determines the number of free ions in an electrolyte, and thus the electric conductivity. A 0.10 mol dm^{-3} solution of FLBDOB in PC shows a conductivity of 4.64×10^{-3} S cm^{-1} at 25 °C. The solutions of 0.10 mol dm^{-3} FLBDOB in PC–DME and in PC–THF have a room temperature conductivity of as high as 5.94 and 5.85×10^{-3} S cm^{-1}, respectively, indicating that the ions in FLBDOB solutions are highly disassociated. As can be seen in Fig. 3, the conductivity of the 0.10 mol dm^{-3} FLBDOB electrolyte solution in EC–THF is greater than those in the other solvents. Hence it can be concluded that FLBDOB is highly dissociating in the EC–THF mixed solvent.

In Table 2, the conductivities of 0.10 mol dm^{-3} FLBDOB solutions in different solvents with those of LBOB and FLBBB are compared. It seems that FLBDOB solutions with the same concentration show conductivities higher than those of FLBBB solutions, but lower than those of LBOB. On the other hand, for the saturated solutions of each lithium salt in the solvents of PC, PC + THF, PC + DME, EC + DME, and EC + THF (molar ratio 1:1), which concentrations are 0.50 mol dm^{-3} for FLBBB and FLBDOB but only 0.36 mol dm^{-3} for LBOB, they all have a quite high conductivity of more than 5.0 mS cm^{-1} (Table 1).

3.4. Electrochemical stability

The electrochemical stabilities of LBOB, FLBDOB, and FLBBB solutions in PC on platinum wire electrode are evaluated by their cyclic voltammograms as shown in Fig. 4. The electrochemical oxidation potential can be obtained as ca. 4.0 V vs. Li$^+$/Li for the 0.1 mol dm^{-3} solution of FLBDOB in PC. This is significantly higher than the oxidation potential for FLBBB–PC solution (3.7 V) [7]. Thus, the order of the oxidation stability in these organoborates is LBOB > FLBDOB > FLBBB, as shown in Fig. 2.

Electrochemical reactions can be achieved by a direct electron transfer at a certain potential. If electrons are transferred from the HOMO of a compound, a correlation is expected between the E_{HOMO} and the oxidation potential E_{ox}, because the negatives of the orbital energies in the ground state are equal to the ionization potentials according to Koopman's theorem. Several studies of anion oxidation potentials were recently updated and extended by Xue et al. [12]. 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 I_p. Similarly, in this study, the HOMO energies of different organoborate anions can be calculated using Hartree-Fock/6-311++G(3df,3pd) methods. The HOMO ener-

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

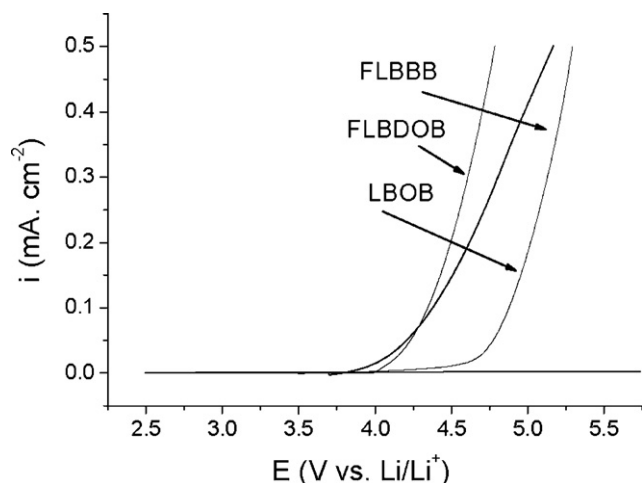| Organoborate	Specific conductivity (mS cm^{-1})				
	PC	PC + DME (1:1)	EC + DME (1:1)	PC + THF (1:1)	EC + THF (1:1)
FLBBB	4.43	5.73	4.58	5.64	5.85
FLBDOB	4.58	5.94	4.76	5.85	6.00
LBOB	5.56	6.79	5.37	7.05	6.30

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 $20\,°C$.

gies (E_{HOMO}) are found to be -8.75, -5.18, and $-4.74\,eV\,mol^{-1}$ for LBOB, FLBDOB, and FLBBB, respectively. The electrochemical oxidation potential (E_{ox}) are found to be 4.5, 4.0 and 3.7 V vs. Li$^+$/Li for LBOB, FLBDOB, and FLBBB, respectively. Obviously, the two sets of data (E_{ox} and E_{HOMO}) are strongly correlated ($R = 0.96$) so that they give the above measured order of oxidation stability.

4. Conclusions

A new lithium salt, lithium [3-fluoro-1,2-benzenediolato (2-)-o,o′ oxalato]borate (FLBDOB), with asymmetric chelatoborate anion based on two different chelators has been synthesized and characterized. It is found to be thermally stable and soluble in many of the common organic solvents used in lithium batteries. The solutions are highly conductive with a conductivity of up to $6.0\,mS\,cm^{-1}$ at room temperature. The conductivities of FLBDOB solutions are higher than those of FLBBB solutions. Its electrochemical oxidation potential is much higher than that of FLBBB 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 affect the HOMO energies, and the distribution of negative charge. With the result that charge delocalization affects the electrochemical stability and electric conductivity of the electrolyte. The conjugate energy would affect the gaps between the HOMO and LUMO energies, and thus affect the thermal stability of the lithium salts.

Acknowledgments

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