

Short communication

New lithium salts with croconato-complexes of boron for lithium battery electrolytes

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Abstract

A new lithium salt containing $C_5O_5^{2-}$, lithium bis[croconato]borate (LBCB), and its novel derivative, lithium [croconato salicylato]borate (LCSB) were synthesized and characterized. The thermal characteristics of them and lithium bis[salicylato(2-)]-borate (LBSB) were examined by thermogravimetric analysis (TG). The thermal decomposition in Ar begins at 250, 328, and 350 °C for LBCB, LCSB, and LBSB, respectively. The order of the stability toward oxidation of these organoborates is LBCB > LCSB > LBSB, which differs from the thermal stability. The cyclic voltammetry study shows that the LiCB and LCSB solutions in PC are stable up to 5.5 and 4.8 V versus Li^+/Li , respectively. They are moderately soluble in common organic solvents, being 0.14, 0.16, and 1.4 mol dm^{-3} at 20 °C in EC + DME (molar ratio 1:1) for LBCB, LCSB, and LBSB, respectively. Ionic dissociation properties of LBCB and its derivatives were 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 dm^{-3} LBCB electrolyte in PC, PC + DME, EC + DME, PC + THF, EC + THF solutions are higher than those of LCSB and LBSB electrolytes. It means that LBCB has the higher dissociation ability in those solutions.

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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 electrochemically 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 (LiBOB) as an advanced electrolyte for Li-ion battery [11]. 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 theoretical studies [12–16], the strongly electron-withdrawing anion, $C_5O_5^{2-}$ [dianion of croconic acid (4,5-dihydroxycyclopent-4-ene-1,2,3-trione)], was chosen as the chelator to coordinate with boron to form lithium salt in this study. Two new lithium salts containing $C_5O_5^{2-}$, lithium bis[croconato]borate (LBCB) and its novel derivative, lithium [croconato salicylato]borate (LCSB), as shown in Fig. 1, were synthesized. Their thermal and electrochemical stabilities, conductivities in some solvent mixtures were studied and compared with those in the LBSB electrolyte.

2. Experimental

LBCB was synthesized according to reaction (1). Specifically, 0.02 mol croconic acid, 0.01 mol lithium hydroxide, 0.01 mol boric acid, and 25 ml distilled water were transferred

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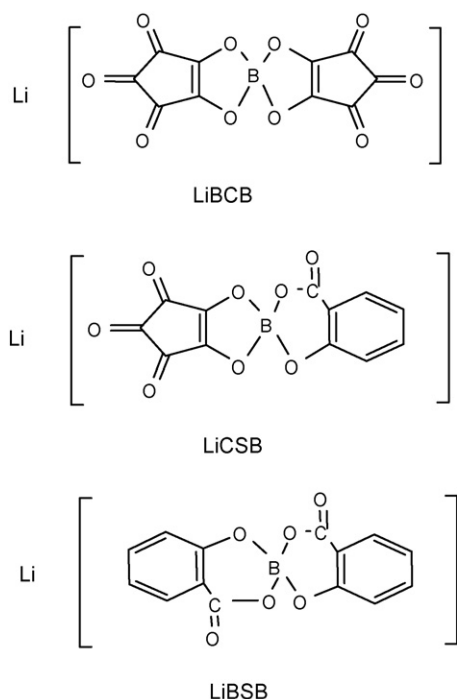
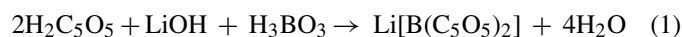


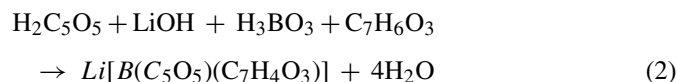
Fig. 1. Structures of LBCB, LCSB, and LBSB.

into a flask fitted with a reflux condenser. The heterogeneous mixture was heated up to boiling under purified argon, until a homogeneous solution was obtained. The solution was refluxed for 24 h. After removing 15 ml water from the solution and cooling down to room temperature, a straw yellow precipitate was observed. Then the mixture was stored in a refrigerator at 2 °C for 12 h. After filtration, a solid was obtained. It was purified by multi-time recrystallizations by dissolving into acetonitrile (AN) and drying in vacuo at 80 °C for 24 h followed by 120 °C for 48 h. The purity of the compound was examined by inductively coupled plasma (ICP) analysis for Li and B contents, which were measured as Li 2.29% and B 3.67%. These data were close to the calculated values Li 2.35% and B 3.69% for LBCB. The ¹³C NMR spectra of the prepared solid in dimethyl sulfoxide (DMSO-d₆) gave two signals at chemical shifts of 158.627 and 160.760 ppm.



LCSB was synthesized according to reaction (2) and purified in a similar procedure for LBCB. Specifically, 0.01 mol croconic acid, 0.01 mol lithium hydroxide, 0.01 mol boric acid, 0.01 mol salicylic acid and 20 ml distilled water were transferred into a flask fitted with a reflux condenser. After dissolution and distillation, a white precipitate was obtained and separated. It was purified subsequently by recrystallization and drying. The purity of the compound was confirmed by ICP for Li and B contents as Li 2.33% and B 3.69%. These data are close to the calculated values, i.e., Li 2.38% and B 3.74%. Its NMR spectra in dimethyl sulfoxide (DMSO-d₆) gave following signals: ¹³C NMR 164.38, 159.59, 158.76, 136.01, 135.24, 129.83, 119.37, 118.59, 115.91 ppm; ¹H NMR: 7.77–7.79 ppm (m, 1H),

7.42–7.46 ppm (m, 1H), 6.73–6.93 ppm (m, 2H).



LBSB was obtained by the direct reaction of lithium hydroxide, boric acid, and the bidentate ligand salicylic acid in water. The procedures of synthesis LBSB were described previously [6]. The purity of the compound was confirmed by ICP for Li and B contents as Li 2.27% and B 3.57%. These data were close to the calculated values of Li 2.41% and B 3.79%.

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] and [8].

Thermogravimetric (TG) analysis of the lithium organoborates was carried out with Perkin-Elmer Pyres-1 DMDA-V 1 model, using a sample of about 10 mg. The NMR spectra were measured with DMX-500. 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 (stainless steel plate 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).

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, 328, and 350 °C for LBCB, LCSB, and LBSB, respectively. Therefore, among the three salts LBSB exhibits the highest thermal stability while LBCB shows the lowest. This means that a croconic compound, such as LBCB

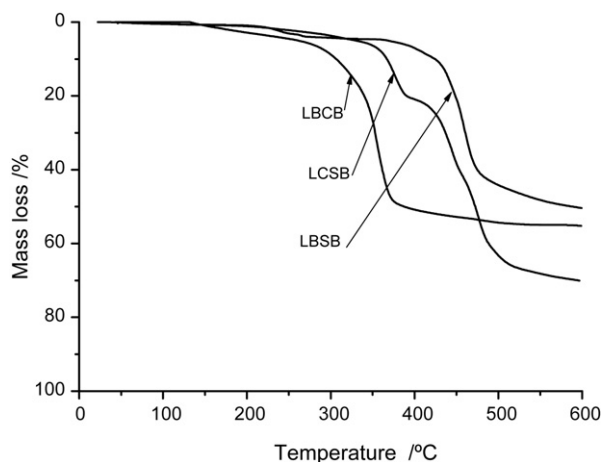


Fig. 2. TG curves of lithium organoborates at a heating rate of 10 °C min⁻¹ in Ar. α-Alumina was used as a reference.

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
LBCB	0.10	1.31	0.12	1.90	0.14	2.40	0.11	2.14	0.10	1.63
LSCB	0.13	1.95	0.15	2.72	0.16	2.89	0.14	2.55	0.13	2.53
LBSB	1.0	2.53	1.34	4.27	1.41	5.08	1.05	2.67	0.87	3.60

decomposes easily on heating at comparatively lower temperature in spite of having a heavier molecule. Furthermore, it seems that the thermal stability depends on the higher conjugate energies of the chelate-type anion with boron [17].

3.2. Solubility

Similar to LBSB, LBCB and LCSB are stable in organic electrolyte solutions but it may decompose by hydrolysis, yielding beginning reactants. Unfortunately, they are not very soluble. They are only moderately soluble, e.g., in EC + DME (1:1), 0.14 and 0.16 mol dm⁻³ at 20 °C for LBCB and LCSB (Table 1), respectively.

3.3. Conductivity

Figs. 3 and 4 show the temperature dependence of ionic conductivity of LBCB and LCSB solutions in different 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 mol dm⁻³ solution of LBCB in PC shows a conductivity of 1.32×10^{-3} S cm⁻¹ at 25 °C. The room temperature conductivity of 0.10 mol dm⁻³ LCSB–PC solution is 1.09×10^{-3} S cm⁻¹. The solutions of 0.10 mol dm⁻³ LBCB in EC–DME and in PC–DME have room temperature conductivity of as high as 1.41 and 1.37×10^{-3} S cm⁻¹, respectively, indicating that the ions in LBCB and LCSB solutions are highly mobile. As can be seen in Fig. 3, the conductivity of the 0.10 mol dm⁻³ LBCB and 0.10 mol dm⁻³ LCSB electrolyte solutions in EC–DME, which have higher molecular weight and

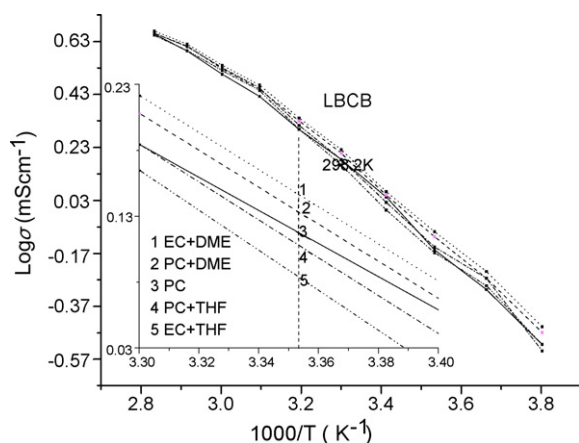


Fig. 3. Temperature-dependence of ionic conductivities of LBCB solutions in different solvents.

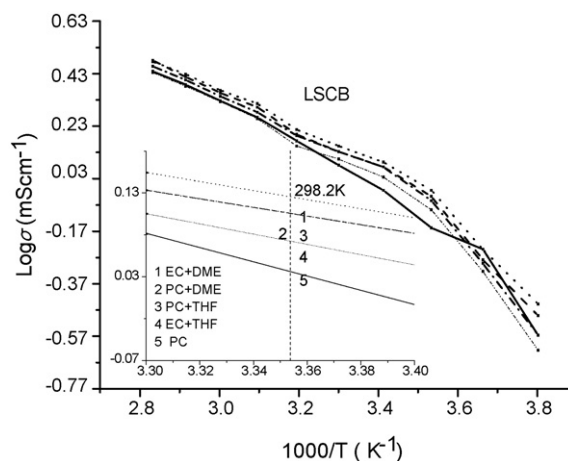


Fig. 4. Temperature-dependence of ionic conductivities of LCSB solutions in different solvents.

larger anions, is greater than those in the other solvents. Apparently, LBCB and LCSB are highly dissociating in EC–DME mixture.

Table 2 compares the conductivities of 0.10 mol dm⁻³ LBCB solutions in different solvents with those of LCSB and LBSB. It is seen that LBCB solutions with the same concentration show conductivities higher than those of LCSB and LBSB 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 in the vicinity of 1 mS cm⁻¹ (Table 1).

3.4. Electrochemical stability

The electrochemical stabilities of LBCB, LCSB, and LBSB solutions in PC on stainless steel electrodes are shown in Fig. 5. The electrochemical oxidation potentials can be obtained as ca. 5.5 and 5.0 V versus Li⁺/Li for the 0.1 mol dm⁻³ solutions of LBCB and LCSB in PC. These are significantly higher than the

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	EC+THF
LBCB	1.317	1.369	1.411	1.292	1.224
LCSB	1.088	1.275	1.335	1.224	1.182
LBSB	0.858	0.952	0.977	0.926	0.867

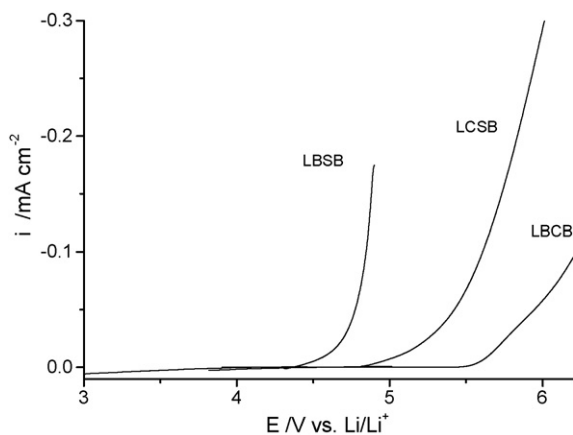


Fig. 5. i - E curves in PC saturated solutions using a stainless steel working electrode at a scan rate of 9 mV s^{-1} at 25°C .

oxidation potential for LBSB-PC solution (4.3 V) [17]. Thus, the order of the oxidation stability in these organoborates is $\text{LCB} > \text{LCSB} > \text{LBSB}$, which is in a reverse order of the thermal stability in Fig. 2.

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 with 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 energies are found to be -6.844 , -6.044 , and $-5.637 \text{ eV mol}^{-1}$ for LCB, LCSB, and LBSB, respectively. Obviously, the two sets of data (E_{ox} and E_{HOMO}) are strongly correlated ($R = 0.996$).

4. Conclusions

Two new lithium salts, one with symmetric chelatorborate anion based on two same chelators, one with asymmetric chelatorborate anion based on two different chelators, have been synthesized. The salts, LCB and LCSB, are thermally stable but moderately soluble, lower than 0.5 M, in many of the common organic solvents used in batteries. Nevertheless, the solutions are highly conductive and electrochemically stable.

The conductivities of LCB and LCSB solutions are higher than those of LBSB solutions. Their electrochemical oxidation potentials are much higher than those of LBSB in the common organic solvents used in batteries. Therefore, LCB and LCSB are promising to replace some lithium salts in current lithium-ion 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., croconato-) would lower the HOMO energy, and improve the electrochemical stability of the electrolyte.

Acknowledgments

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