



Short communication

A new lithium salt with 3-fluoro-1,2-benzenediolato and lithium tetrafluoroborate for lithium battery electrolytes

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ABSTRACT

A new unsymmetrical lithium salt containing F^- , $C_6H_3O_2F^{2-}$ [dianion of 3-fluoro-1,2-benzenediol], lithium difluoro(3-fluoro-1,2-benzene-diolato(2-)-o,o')borate (FLDFBDB) is synthesized and characterized. The thermal characteristics of it, and its derivatives, lithium bis[3-fluoro-1,2-benzenediolato(2-)-o,o']borate (FLBBB), and lithium fluoroborate ($LiBF_4$) are examined by thermogravimetric analysis (TG). The thermal decomposition in air begins at 256 °C, 185 °C, and 162 °C for FLBBB, FLDFBDB and $LiBF_4$, respectively. The order of the stability toward the oxidation of these organoborates is $LiBF_4 > FLDFBDB > FLBBB$. The cyclic voltammetry study shows that the FLDFBDB solution in propylene carbonate (PC) is stable up to 3.9 V vs. Li^+/Li . It is soluble in common organic solvents. Ionic dissociation properties of FLDFBDB and its derivatives are examined by conductivity measurements in PC, PC + ethyl methyl carbonate (EMC), PC + dimethyl ether (DME), PC + ethylene carbonate (EC) + DME, PC + EC + EMC solutions. The conductivity values of the 0.10 mol dm^{-3} FLDFBDB electrolyte in these solutions are higher than those of FLBBB, but lower than those of $LiBF_4$ 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 [1–3] 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 [4,5] with a chelate-type boron-containing anion, such as lithium bis[3-fluoro-1,2-benzenediolato(2-)-O,O]borate (FLBBB) [6]. Xu et al. also reported lithium bis(oxalato) borate (LBOB) and lithium [malonato oxalato]borate (LMOB) as advanced electrolytes for Li-ion battery [7,8]. Recently, a novel lithium salt, lithium oxalyldifluoroborate (LODFB) [9], has drawn intensive attention because of its significant merit such as (1) the ability to support metallic lithium cycling reversibly on the surface of copper anode current collector, (2) the ability to passivate aluminum cathode current collector at high potentials, (3) the ability to participate in formation of the SEI and support Li-ion battery operating stably at high temperatures, and (4) the ability to increase battery safety protection and overcharge tolerance [9–12]. 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.

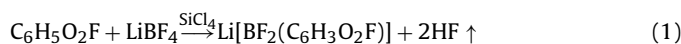
Based on our previous theoretical studies [13–18], anions with pronounced charge delocalization, F^- and $C_6H_3O_2F^{2-}$ [dianion of 3-fluoro-1,2-benzenediol], are chosen as the unsymmetrical chelators to coordinate with boron to form lithium salt in this study to further our understanding on the relationship between the property and structure of these lithium salts. A new lithium salt, lithium difluoro(3-fluoro-1,2-benzene-diolato(2-)-o,o')borate (FLDFBDB), 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 FLBBB and $LiBF_4$ electrolytes.

To understand the properties of this new lithium salt at a quantum chemistry level, the density functional theory (DFT) B3LYP method was chosen. We will address the relationship between molecular structures and properties regarding the FDFBDB⁻, FLBBB⁻, and BF_4^- anions and their lithium salts.

2. Experimental and computational methods

2.1. Synthesis

FLDFBDB was synthesized according to reaction (1):



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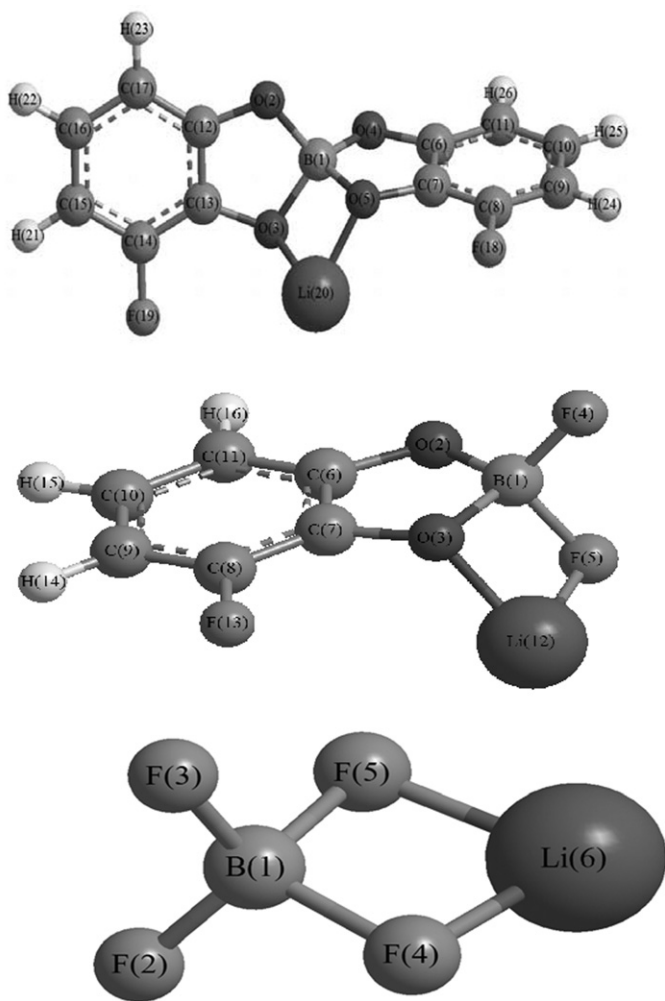


Fig. 1. Structures of FLBBB FLDFBDB and LiBF_4 .

Specifically, in an argon-filled glove box, 0.02 mol LiBF_4 , 0.02 mol 3-fluoro-1,2-benzenediol and 20 mL dimethyl carbonate (DMC) solvent were placed in a flask. SiCl_4 was added drop-wise to the solution which was then stirred overnight under purified nitrogen. The completion of the reaction was judged by making sure that gas generation stopped completely. Then, the solution was refluxed for 2 h at 50°C under purified nitrogen until it becomes transparent. After that, the solvent DMC was evaporated on a rotary evaporator to obtain a solid product. It was purified by multi-time recrystallizations by dissolving into acetonitrile (AN) and drying in vacuum at 60°C for 2 h followed by 120°C for 48 h. Then, the product was transferred into the glove box. The yield for the purified salt was up to 86.5%. The purity of the compound was examined by inductively coupled plasma (ICP, Poasma–Spec) analysis for Li and B contents. The ^1H NMR and ^{13}C NMR spectroscopy (DMX-500, Bruker) of the prepared solid in dimethyl sulfoxide (DMSO-d_6) was also performed.

Meanwhile, FLBBB and LiBF_4 were synthesized with the procedures described previously [6,19]. The purification procedures for propylene carbonate (PC), ethylene carbonate (EC), 1,2-dimethoxyethane (DME), ethyl methyl carbonate (EMC), were the same as given in Barthel et al.'s paper [6].

Thermogravimetric analyses (TGA) of the FLBBB, FLDFBDB, LiBF_4 were carried out with Perkin-Elmer Pyres-1 DMDA-V1 model, using a sample of about 10 mg. The decomposition voltages (i - E curves) of the electrolytes using a three-electrode system (platinum wire with a surface area of $4.91 \times 10^{-4} \text{ cm}^2$ as working electrode, and Li plate

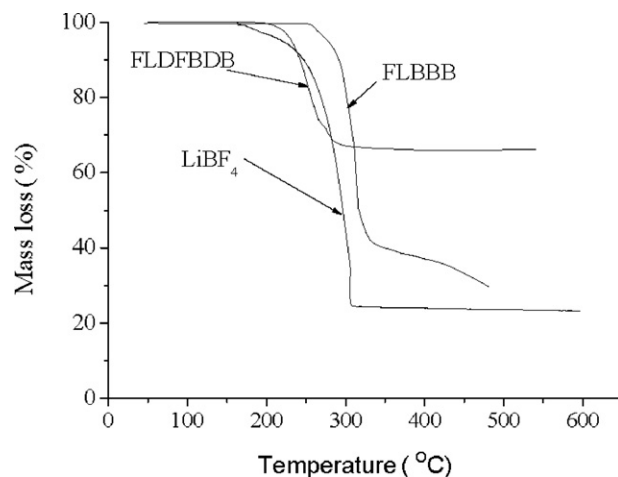


Fig. 2. TG curves of lithium organoborates as a heating rate of 10°Cmin^{-1} in N_2 α -alumina was used as a reference.

as both counter and reference electrodes) were measured at a scan rate of 9 mV s^{-1} . The preparation of the electrolyte solutions and the cell assembly were carried out in a glove box (Labmaster 130, MBRAUN) at low water ($<1 \text{ ppm}$), and oxygen ($<1 \text{ ppm}$) contents.

2.2. Computation

The local minima of the complexes have been fully optimized by analytic gradient techniques. The method used was the density functional theory (DFT) with Becke's three parameters (B3) exchange functional along with the Lee–Yang–Parr (LYP) non-local correlation functional (B3LYP). All of the complexes were treated with DFT method at B3LYP/6-31++G(2df,2p) level for full geometry optimization. Nature population analysis (NPA) and natural bond orbital (NBO) [20] analysis were performed at B3LYP/6-311++G(3df,3pd) level using NBO program to obtain quantitative analysis of cation–anion interactions between NBOs of the complexes.

Single-point energy calculations were performed to obtain more accurate energies at higher level basis set (B3LYP/6-311++G(3df,3pd)//B3LYP/6-31++G(2df,2p)). The HF method at the same level computation was performed for comparing with DFT at some cases. All of the HF, DFT and NBO calculations were performed using the Gaussian 03 program package [21].

3. Results and discussion

3.1. The composition and structure of FLDFBDB

The ICP analysis of the synthesized solid contains Li 3.86% and B 5.85%. These data are close to the calculated values Li 3.82% and B 5.95% for FLDFBDB, meaning that a pure FLDFBDB product has been successfully obtained. ^{13}C NMR spectrum of this product (not shown here) gives six signals at chemical shifts of 153.84 (C6), 148.20 (C8), 133.77 (C7), 118.81 (C10), 111.94 (C11), 106.96 (C9) ppm while its ^1H NMR spectrum shows three signals at 6.10 (H14), 6.40 (H15) and 6.58 (H16) ppm. It can be concluded from the ICP and the NMR spectra that fairly pure crystallization product (shown in Fig. 1) have been obtained in this work.

3.2. Thermal stability

Fig. 2 shows the TG curves of the lithium organoborates in N_2 . It can be seen that the salt decomposition starts to occur at 256, 185, and 162°C for FLBBB, FLDFBDB, and LiBF_4 , respectively. Therefore,

Table 1
Solubility (S , mol dm⁻³) and corresponding conductivity (σ , mS cm⁻¹) of lithium salts in PC solution at 25 °C.

	FBBB ⁻	FDLBDB ⁻	BF ₄ ⁻
S (m, PC, 298.2k)	0.210	0.443	1.010
$\log(S)$	-0.678	-0.354	0.004
π^* /(a.u.)	1.220	5.214	0.000
μ /Debye	181.586	99.243	23.775
σ /mS cm ⁻¹	2.02	1.88	3.70

among the three salts FLDFBDB exhibits a thermal stability higher than that of LiBF₄, but lower than that of FLBBB. Furthermore, it seems that the thermal stability depends on the higher conjugate energies of the chelate-type anion with boron [22].

3.3. Solubility

Similar to LiBF₄ and FLBBB, FLDFBDB is stable in organic electrolyte solutions but it may be decomposed by hydrolysis in aqueous solutions and converted back to their beginning reactants. They are moderately soluble in PC with a solubility of 0.443 mol dm⁻³ at 25 °C for FLDFBDB (Table 1).

As can be seen in Table 1, the solubility of LiBF₄ salt is greater than others in PC solutions. According to our previous theoretical researches [13] we have also chosen to calculate a theoretical set of parameters of TLSE (Theoretical Linear Solvation Energy Relationships), developed by Cramer [23] and co-workers, and correlated them with the solubility of a lithium salt.

The equation [23] has been applied to the three anions (FBBB⁻, FDLBDB⁻, and BF₄⁻). With B3LYP/6-311++G(3df,3pd)//B3LYP/6-31++G(2df,2p)-derived descriptors (Table 1). We obtain a result that the solubility, S , of a lithium salt to be most sensitive to anion polarizability π^* (Fig. 3). The regression is of

$$\log(S) = 0.0956 - 0.0043\pi^* \quad (R = 0.9985, \quad SD = 0.0260)$$

3.4. Conductivity

Fig. 4 shows the temperature dependence of ionic conductivity of 0.10 mol dm⁻³ FLDFBDB in PC solvent. We also include data for solutions in the mixed solvents of PC+DME, PC+EMC, PC+EC+EMC and PC+EC+DME (mass ratio 1:1 and 1:1:1). A 0.10 mol dm⁻³ solution of FLDFBDB in PC shows a conductivity of 1.06 mS cm⁻¹ at 25 °C. The solutions of 0.10 mol dm⁻³ FLDFBDB in PC-DME and in PC-EC-DME have room temperature conductivity of as high as 3.46 and 3.42 mS cm⁻¹, respectively, indicating

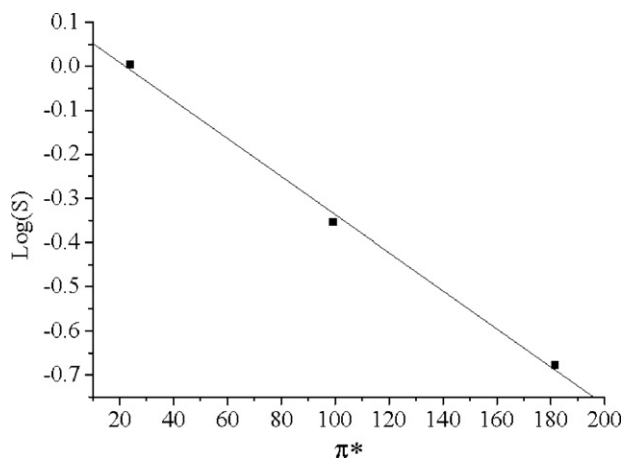


Fig. 3. The relation between solubility $\log(S)$ and anion polarizability (π^*) of lithium salts.

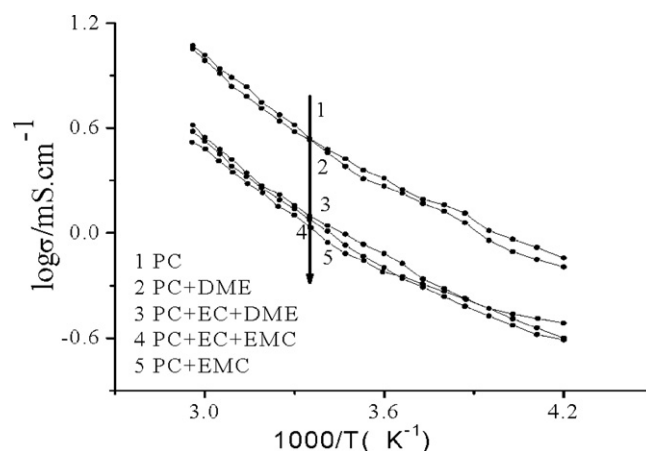


Fig. 4. Temperature dependence of ionic conductivities of FLDFBDB solution (0.10 mol dm⁻³) in different solvents.

that the ions in FLDFBDB solutions are highly dissociated. As can be seen in Fig. 4, the conductivity of the 0.10 mol dm⁻³ FLDFBDB electrolyte solution in PC-DME is greater than those in the other solvents. Apparently, FLDFBDB is highly dissociating in PC-DME mixture.

Table 2 compares the conductivities of 0.10 mol dm⁻³ FLDFBDB solutions in different solvents with those of LiBF₄ and FLBBB. It is clear that FLDFBDB solutions with the same concentration show conductivities higher than those of FLBBB solutions, but lower than those of LiBF₄. On the other hand, for the saturated solutions of each lithium salt in the solvent of PC, which concentrations are 0.443 mol dm⁻³ for FLDFBDB 0.210 mol dm⁻³ for FLBBB and 1.01 mol dm⁻³ for LiBF₄, they all have a quite high conductivity, 2.02, 1.88, and 3.70 mS cm⁻¹ for FLBBB, FLDFBDB and LiBF₄, respectively.

The dissociation 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. Ue and Mori analyzed the contribution of the number of ions and the ion mobility to the electric conductivity for a variety of Li-ion nonaqueous electrolytes [24]. They found that the contribution from the number of free ions is generally larger than that from the ion mobility. Thus, the number of ions available plays a major role in determining the electric conductivity of a cell, and hence in the overall battery performance.

As generally recognized, the weaker the coordinating, the easier the separating of an ion-pair is. Natural bond orbital (NBO) analysis is carried out to further our understanding of orbital interactions and charge delocalization. Of particular interests are the interactions between O(F) (bounded with lithium cation) lone pairs and antibonding orbitals of lithium cation lone pair. The magnitudes of the interactions are shown in Table 3. With the increase of the number of F, it is interesting to notice that the calculated order of main orbital interaction energies (E_{int}) is $E_{\text{int}}(\text{FLBBB}) > E_{\text{int}}(\text{FLDFBDB}) > E_{\text{int}}(\text{LiBF}_4)$, although E_{int} only accounts for part of E_{bind} . In fact, E_{int} may be roughly attributed to the covalency contributions to binding. Thus, the electron transfer from anion (BF₄⁻, FDLBDB⁻, FBBB⁻) to Li⁺ becomes lesser according to NPA and the effective cation charge becomes larger (+0.9619, +0.96825 and +0.97247 e for FLBBB, FLDFBDB and LiBF₄, respectively). Therefore, BF₄⁻ is the weakest anion of the three salts and Li⁺BF₄⁻ would be dissociated more than the other two salts at the same concentration of electrolyte solutions. Compared with the calculated data, the experimental conductivity (Table 2) increases with the effective cation charge, and decreases with E_{int} and the extent of electron transfer from anion to cation.

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+EMC (1:1)	PC+DME (1:1)	PC+EC+DME (1:1:1)	PC+EC+EMC (1:1:1)
FLBBB	0.96	1.04	1.77	1.94	1.12
FLDFBDB	1.06	1.24	3.46	3.42	1.18
LBF ₄	2.96	4.26	4.42	4.00	4.00

3.5. Electrochemical stability

The electrochemical stabilities of FLBBB, FLDFBDB, and LiBF₄ solutions in PC on platinum wire electrode are shown in Fig. 5. The electrochemical oxidation potential can be obtained as ca. 3.9 V vs. Li⁺/Li for the 0.1 mol dm⁻³ solution of FLDFBDB in PC. This is higher than the oxidation potential for FLBBB–PC solution (3.7 V) [6]. The order of the oxidation stability in these organoborates is LiBF₄ > FLDFBDB > FLBBB.

Several studies of anion oxidation potentials were recently updated and extended by Xue et al. [25]. They have found that E_{ox} can be correlated with adiabatic ionization potential (I_p).

To further examine this experimental result, the ionization potentials were also calculated by *ab initio* density functional theory. This method usually gives higher accuracy in energy calculations, where the relative accuracies of various different model chemistries were considered by their performances on the G2 molecule sets [26]. The structural optimization of the anion was carried out by B3LYP/6-31++G(2df,2p) followed by the energy calculations on higher basis sets, 6-311++G(3df,3pd). The adiabatic ionization potential I_p was calculated from the energy difference ΔE between the total energy of the anion E_{anion} and that of the neutral radical $E_{radical}$ generated by one-electron oxidation. The structure and energy of the neutral radical was calculated by the same methods. Zero-point energies (ZPE) were also calculated by frequency analysis using B3LYP/6-31++G(2df,2p). The ionization potentials were calculated from the following equation

$$I_p = \Delta E - \Delta ZPE$$

The results are summarized in Table 4 and Fig. 6. Fig. 6 shows good correlation between I_p and E_{ox} , completely confirming the experimental result: $E_{ox}(FBBB^{-1}) < E_{ox}(FDFBDB^{-1}) < E_{ox}(BF_4^{-1})$. The regression result is

$$E_{ox} = 2.90597 + 0.22089 \times I_p \quad (R = 0.99684, \quad SD = 0.09153)$$

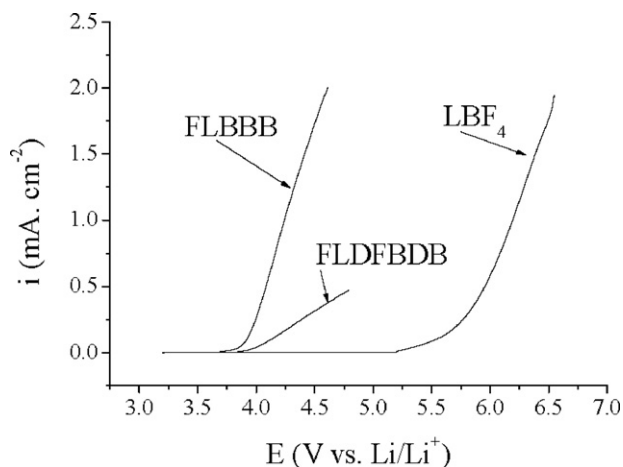


Fig. 5. i - E curves in PC saturated solution using platinum wire working electrode at a scan rate of 9 mV s⁻¹ at 20 °C.

Table 3
NBO energetic analysis for FLBBB, FLDFBDB, and LBF₄ at B3LYP/6-311++G(3df,3pd) level^a (energies in kJ mol⁻¹).

	FLBBB	FLDFBDB	LBF ₄
$n^1 o_1 \rightarrow n^* M$	21.02	17.72	/
$n^2 o_1 \rightarrow n^* M$	6.86	4.47	/
$n^1 F_2 \rightarrow n^* M$	21.02	12.79	11.08
$n^2 F_2 \rightarrow n^* M$	6.86	2.28	10.24
$n^3 F_2 \rightarrow n^* M$	/	8.61	11.08
$n^4 F_2 \rightarrow n^* M$	/	2.28	10.24
E_{int}	55.76	48.15	42.64

^a nO and nF refer to the p lone pairs of the oxygen and fluorine atoms; n*_M refers to the antibonding orbital of lone pair of the lithium cation.

Table 4
Limiting oxidation potentials, ionization potential calculations using DFT methods at 6-311++G(3df,3pd) level.

Anion	FBBB ⁻	FDFBDB ⁻	BF ₄ ⁻
$E_{radical}$ (a.u.)	-986.759655	-705.652788	-424.318151
E_{anion} (a.u.)	-986.904556	-705.806818	-424.705408
ΔE (kJ mol ⁻¹)	380.43754	404.40573	1016.74316
$ZPE_{radical}$ (kJ mol ⁻¹)	422.96276	233.17851	22.85498
ZPE_{anion} (kJ mol ⁻¹)	428.74936	232.35673	36.38417
ΔZPE (kJ mol ⁻¹)	5.7866	-0.8218	13.5292
I_p (eV)	3.88	4.20	10.40
E_{ox} (V vs. Li ⁺ /Li)	3.7	3.9	5.2

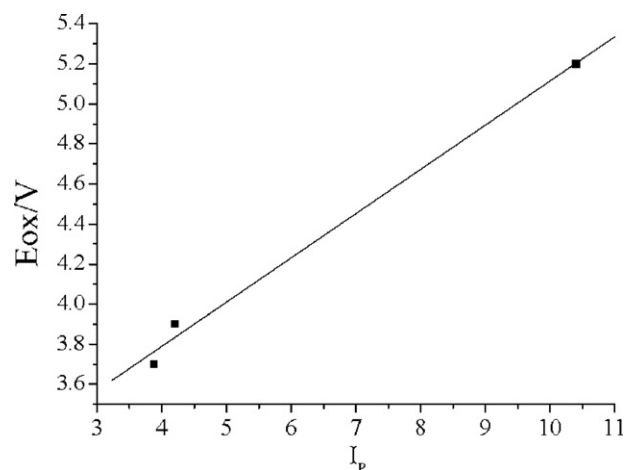


Fig. 6. Relation between E_{ox} and I_p of anions at DFT, B3LYP/6-311++G(3df,3pd) level.

4. Conclusions

A new lithium salt, lithium difluoro(3-fluoro-1,2-benzene-diolato(2-)-o,o')borate (FLDFBDB), with asymmetric chelatorborate anion, has been synthesized. The salt, FLDFBDB, is thermally stable and soluble in many of the common organic solvents used in batteries. The solutions are highly conductive and stable. The conductivities of FLDFBDB solutions are higher than those of FLBBB solutions. Its electrochemical oxidation potential is higher than that of FLBBB in the common organic solvents used in batteries. A strong correlation between the adiabatic ionization potential

and the electrochemical stability is established. This proves that an extensive charge delocalization, in their anions, caused by strongly electron withdrawing anions (e.g. F^- and dianion of 3-fluoro-1,2-benzenediol) would raise the adiabatic ionization potential I_p , and improve the electrochemical stability of the electrolyte.

Acknowledgments

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