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A DFT study of electronic structures, energies, and molecular properties of lithium bis[croconato]borate and its derivatives

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Abstract

Theoretical studies on electrolyte salts, lithium bis[croconato(2-)]borate (LBCB) and its derivatives, lithium [croconato(2-) salicylato(2-)]borate (LCSB), and bis[salicylato(2-)]borate (LBSB) are carried out using density functional theory (DFT) method and B3LYP theory level for the first time. Bidentate structures involving two oxygen atoms are preferred. Based on these conformations, a linear correlation was observed between the highest occupied molecular orbital (HOMO) energies and the limiting oxidation potentials measured by linear sweep voltammetry, which supports experimental results that strongly electron-withdrawing substituent anions are more resistant against oxidation than their organic counterparts. The correlations were also observed between ionic conductivity and binding energy, solubility and theoretical set of parameters of anion, thermal stability and the hardness (η). Wave function analyses have been performed by natural bond orbital (NBO) method to further investigate the cation–anion interactions.

Keywords: DFT; Lithium salts; Borate; Electronic structures; Energies; Molecular properties

1. Introduction

Many researchers have attempted to develop improved electrolytes for lithium batteries with high energy density and good rechargeability [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-naphtha-lene-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]. Recently, Xu and Angell reported an advanced electrolyte of Li-ion battery, lithium bis(oxalate)borate (LiBOB) [11]. The common feature of these anions is an extensive charge delocalization in their anions caused by strongly electron-withdrawing substituents. Due to this particular feature, the lithium salts of these anions yield sufficiently high ionic conductivity solutions, and exhibit wide electrochemical stability windows and high thermal stability.

The focus on the development of the novel lithium salts has been placed on seeking proper anions for coordination with lithium cation to obtain desired species with appropriate chemical and electrochemical property. This is usually time-consuming and sometimes even clueless. To save both time and resources and to provide a guideline to experimental studies, a theoretical treatment on predicting the structure and (electro) chemical characteristics is undoubtedly necessary and important. Because the anion–cation interaction within the lithium salts plays an important role in determining to the solubility, ionic conductivity, electrochemical windows and thermal stability [12–14], a thorough computational investigation on the electronic structures, energies, and orbitals of this B-containing lithium salts would be desirable to better our understanding their properties at a quantum chemistry level.

According to our previous theoretical researches [15–19], the strongly electron-withdrawing anion, $C_5O_5{}^{2-}$[dianion of croconic acid (4,5-dihydroxycyclopent-4-ene-1,2,3-trione)], was

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chosen as the chelator to coordinate with boron to form new lithium salts, lithium bis[croconato]borate (LBCB) and its novel derivative, lithium [croconato salicylato]borate (LCSB), which yield high ionic conductivity solutions, and exhibit wide electrochemical stability windows and high thermal stability [20].

In this study, to further our understanding the properties of these new lithium salts at a quantum chemistry level, the density functional theory (DFT) B3LYP method [21,22] was chosen because it accounts better for electron correlation energies and greatly reduces the calculation expenses with rather reliable description of both geometries and energy of targeted molecules. We will address the following issues regarding the BCB^-, CSB^- and BSB^- anions and their lithium salts: (a) the conformational characteristics of the three anions, (b) molecular structures and the electronic distributions of the stable Li^+BCB^-, Li^+CSB^- and Li^+BSB^- ions pairs, (c) the nature of the bonding corresponding to each local energy minimum by estimating electrostatic and charge transfer contributions to the binding energy, and (d) the relationship between molecular structures and properties.

2. Calculation and experimental methods

The local minima of the sextuple 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(d,p) level for full geometry optimization. Nature population analysis (NPA) and natural bond orbital (NBO) [23] analysis were performed at the same level using NBO program to obtain quantitative analysis of cation–anion interactions between NBOs of the complexes.

Single-point energy calculations at higher level basis set (B3LYP/6-311++G (3df, 3pd)//B3LYP/6-31+G(d,p)) were also performed to obtain more accurate binding energies, which were defined as $E_{\text{bind}} = E_{\text{metalcomplex}} - (E_{\text{cation-free}} + E_{\text{anion-free}})$. 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 [24].

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 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)

Table 1
Optimized geometries of the free anions, their lithium ion pairs[a,b]

	Anion			Ion pair		
	BSB^-	CSB^-	BCB^-	LBSB	LCSB	LBCB
r(B1–O2)		1.533	1.498		1.544	1.566
r(B1–O3)		1.530	1.498		1.636	1.524
r(B1–O4)	1.483	1.445		1.520	1.409	
r(B1–O5)	1.463	1.443		1.433	1.406	
r(O2–C18)		1.314	1.323		1.293	1.282
r(O3–C14)		1.314	1.323		1.271	1.301
r(O4–C7)	1.330	1.341		1.323	1.365	
r(O5–C8)	1.336	1.342		1.345	1.361	
r(O6–C7)	1.226	1.220		1.250	1.211	
r(C8–C9)	1.409	1.406		1.403	1.399	
r(C8–C13)	1.412	1.409		1.416	1.406	
r(C14–C15)		1.457	1.458		1.484	1.427
r(C14–C18)		1.390	1.384		1.425	1.416
r(Li–O_a)				1.873	1.867	1.880
r(Li–O_b)				1.873	1.909	1.926
α(O_a–Li–O_b)				140.7	94.0	92.9
α(O2–B1–O3)		102.6	104.6		108.3	101.4
α(O2–B1–O4)		109.6			110.2	111.0
α(O4–B1–O5)	112.5	115.3		111.3	119.2	107.8
d(O3–B1–O2–C18)		0.2	0.0		1.5	0.0
d(O5–B1–O4–C7)	24.5	2.1		50.5	10.2	
d(O2– B1–O4–C7)		121.9			139.4	
d(C8–C9–C10–C11)	0.2	0.0		0.6	0.0	
dC15–C14–C18–C17)		0.0	0.0		0.0	0.0

[a] Bond lengths in Å, bond angles and dihedral angles in degrees.

[b] Optimized with the DFT method at B3LYP/6-31++G(2df,2p) level.