Short communication

A new lithium salt with dihydroxybenzene and lithium tetrafluoroborate for lithium battery electrolytes

Zhao-Ming Xue [a,*], Bin-Bin Sun [a], Wei Zhou [a], Chun-Hua Chen [b]

[a] Department of Chemistry, Anhui University, Hefei, Anhui 230039, PR China
[b] Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, PR China

ARTICLE INFO

ABSTRACT

A new unsymmetrical lithium salt containing F^-, $C_6H_4O_2{}^{2-}$ [dianion of 1,2-benzenediol], lithium difluoro(1,2-benzene-diolato(2-)-o,o′)borate (LDFBDB) is synthesized and characterized. Its thermal decomposition in nitrogen begins at $170\,^\circ C$. The cyclic voltammetry study shows that the LDFBDB solution in propylene carbonate (PC) is stable up to 3.7 V versus Li^+/Li. It is soluble in common organic solvents. The ionic dissociation properties of LDFBDB are examined by conductivity measurements in PC, PC+ ethyl methyl carbonate (EMC), PC+dimethyl ether (DME), PC+ethylene carbonate (EC)+EMC solutions. The conductivity values of the $0.564\,mol\,dm^{-3}$ LDFBDB electrolyte in PC+DME solution is $3.90\,mS\,cm^{-1}$. All these properties of the new lithium salt including the thermal characteristics, electrochemical stabilities, solubilities, ionic dissociation properties are studied and compared with those of its derivatives, lithium difluoro(3-fluoro-1,2-benzene-diolato(2-)-o,o′)borate (FLDFBDB), lithium [3-fluoro-1,2-benzenediolato(2-)-o,o′ oxalato]borate (FLBDOB), and lithium bis(oxalate)borate (LBOB).

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

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 in order to protect the environment and natural resources [1–3]. Barthel et al. reported a new class of electrochemically and thermally stable lithium salts with a chelate-type boron-containing anion [4,5], such as lithium bis[1,2-benzenediolato(2-)-O,O]borate (LBBB) [6]. Xu et al. also reported lithium bis(oxalate) 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 the formation of solid electrolyte interphase (SEI) layer and support Li-ion battery operating stably at high temperatures, and (4) the ability to enhance 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 $C_6H_4O_2{}^{2-}$ [dianion of 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(1,2-benzene-diolato(2-)-o,o′)borate (LDFBDB), as shown in Fig. 1, is synthesized. Its thermal and electrochemical stabilities, conductivities in some solvent mixtures are studied and compared with those in the FLDFBDB, FLBDOB and LBOB electrolytes.

2. Experimental and computational methods

DFBDB was synthesized according to reaction (1):

$$C_6H_6O_2 + LiBF_4 \xrightarrow{SiCl_4} Li[BF_2(C_6H_4O_2)] + 2HF \uparrow \qquad (1)$$
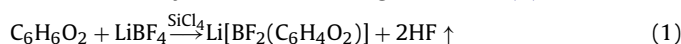
Specifically, in an argon-filled glove box, 0.02 mol $LiBF_4$, 0.02 mol o-dihydroxybenzene and 20 mL dimethyl carbonate (DMC) solvent were placed in a flask. $SiCl_4$ (reaction aid) was added drop-wise to the solution at room temperature with stirring. During the addition of $SiCl_4$, a gas was generated violently. With this, the undissolved o-dihydroxybenzene was dissolved, and the reaction proceeded. After the addition of silicon tetrachloride, stirring was continued for 8 h. It was judged that the reaction had terminated when the genera-
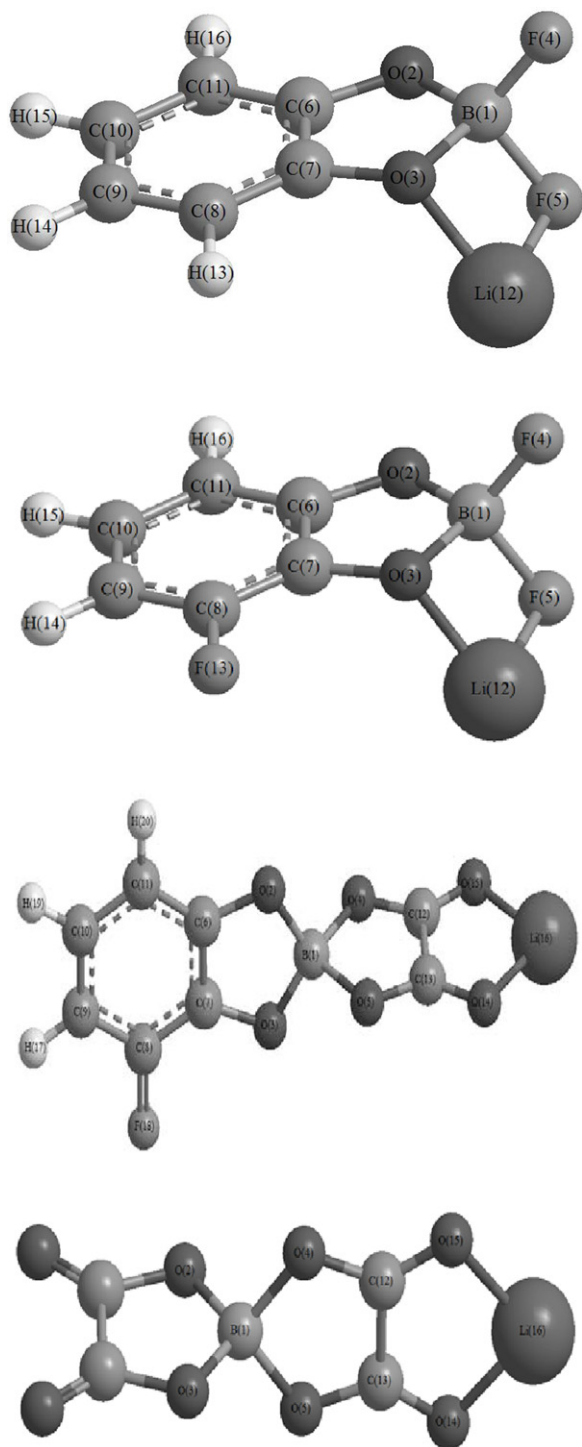
Fig. 1. Structures of LDFBDB, FLDFBDB, FLBDOB and LBOB.

tion of the gas 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 removed from the resulting reaction liquid at 50 °C under a reduced pressure of 133 Pa, thereby obtaining 2.09 g of a white solid as a 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 o-dihydroxybenzene 90%. The purity of the compound was examined by inductively coupled plasma (ICP, Poasma—Spec) analysis for Li and B contents. The ^{1}H NMR and

^{13}C NMR spectroscopy (DMX-500, Bruker) of the prepared solid in dimethyl sulfoxide (DMSO-d6) was also performed.

Meanwhile, LBOB, FLBDOB and FLDFBDB were synthesized with the procedures described previously [7,18,19]. 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 FLDFBDB, LDFBDB, FLBDOB and LBOB 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 4.91×10^{-4} cm^2 as working electrode, and Li plate 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 ppm), and oxygen (<1 ppm) contents.

The local minima of the complexes have been fully optimized by analytic gradient techniques. The computational methods were described previously [18,19].

3. Results and discussion

3.1. The composition and structure of LDFBDB

The ICP analysis of the synthesized solid contains Li 4.26% and B 6.33%. These data are close to the calculated values Li 4.24% and B 6.60% for LDFBDB, meaning that a pure LDFBDB product has been successfully obtained. ^{13}C NMR spectrum of this product gives three signals at chemical shifts of 152.00 (C6/C7), 117.77 (C9/C10), 108.08 (C8/C11) ppm while its ^{1}H NMR spectrum shows two signals at 6.41 (H14/H15) and 6.61 (H13/H16) ppm. It can be concluded from the ICP and the NMR spectra that pure crystallization product LDFBDB (shown in Fig. 1) has 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 302, 262, 185, and 170 °C for LBOB, FLBDOB, FLDFBDB, and LDFBDB, respectively. Therefore, among the four salts LDFBDB exhibits the lowest thermal stability. It seems that the thermal stability depends on the higher conjugate energies of the chelate-type anion with boron [20]. The higher degree the conjugation has, the smaller the energy difference between HOMO and LOMO. Obviously, the phenyl group has higher degree of conjugation than oxalato group.

According to our previous theoretical researches [19], we have also chosen to calculate the chemical reactivity index, the hardness (η) of these anions in HF. The calculated hardness (η) is 3.66, 3.79, 4.08, 6.54 for DFBDB$^-$, FDFBDB$^-$, and FBDOB$^-$, BOB$^-$, respectively. According to the HSAB principle, the hard acid Li$^+$ prefers to coordinate with the hardest base BOB$^-$, meaning that the most thermally stable lithium salt in the five salts is L$^+$BOB$^-$.

3.3. Solubility

Similar to LBOB, FLBDOB and FLDFBDB, LDFBDB 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 0.518 mol dm^{-3} at 25 °C for LDFBDB (Table 1). As can be seen in Table 1, the solubility of LDFBDB salt is the greatest among the four lithium salts in PC solutions.
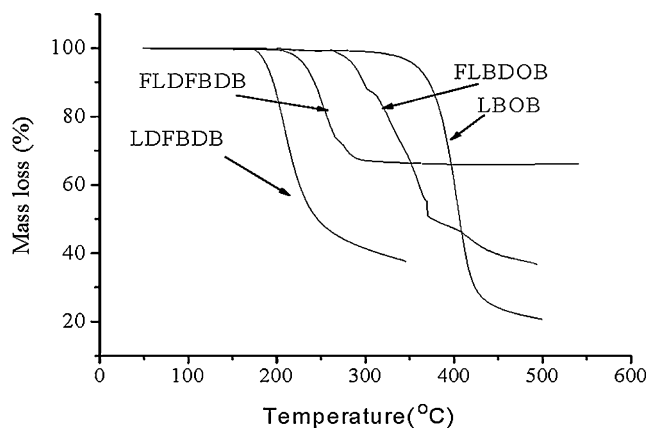
Fig. 2. TG curves of lithium organoborates at a beating rate of $10\,^\circ C\,min^{-1}$ in N_1 α-Alumna was used as a reference.

Table 1
Solubility $(S/mol\,dm^{-3})$ and corresponding conductivity $(\sigma/mS\,cm^{-1})$ of lithium salts in PC solutions at $25\,^\circ C$.

	FLBDOB	LBOB	FLDFBDB	LDFBDB
S(m, PC, 298.2k)	0.275	0.362	0.443	0.518
$\sigma/mS\,cm^{-1}$	5.60	6.76	1.88	1.18

3.4. Conductivity

Fig. 3 shows the temperature dependence of ionic conductivity of $0.10\,mol\,dm^{-3}$ LDFBDB in PC solvent. We also include data for solutions in the mixed solvents of PC+DME, PC+EMC and PC+EC+EMC (mass ratio 1:1 and 1:1:1). A $0.10\,mol\,dm^{-3}$ solution of LDFBDB in PC shows a conductivity of $0.414\,mS\,cm^{-1}$ at $25\,^\circ C$. The solutions of $0.10\,mol\,dm^{-3}$ LDFBDB in PC–DME and in PC–EMC have a room temperature conductivity of as high as 2.17 and $1.12\,mS\,cm^{-1}$, respectively, indicating that the ions in LDF-BDB solutions are highly disassociated. As can be seen in Fig. 3, the conductivity of the $0.10\,mol\,dm^{-3}$ LDFBDB electrolyte solution in PC–DME is greater than those in the other solvents. Apparently, LDFBDB is highly dissociating in PC–DME mixture.

Table 2 compares the conductivities of $0.10\,mol\,dm^{-3}$ LDFBDB solutions in different solvents with those of LBOB, FLBDOB and FLDFBDB. It seems that LDFBDB solutions with the same concentration show the lowest conductivities.

According to our previous theoretical researches [19], the 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 electrical conductivity. Ue and Mori analyzed the contribution of the number of ions and the ion mobility to the electric conductivity for a
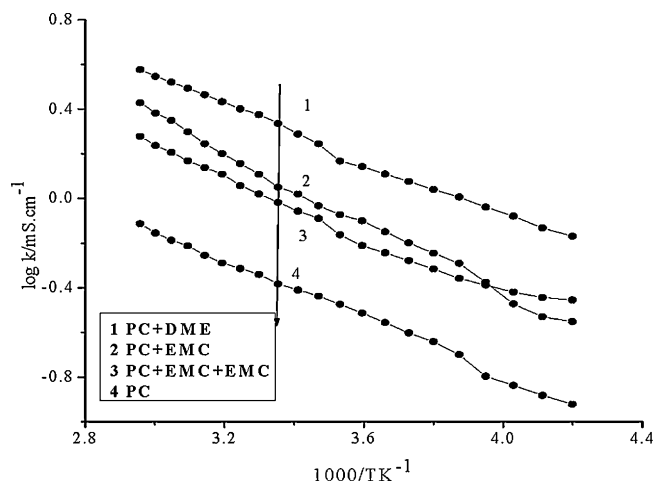

Fig. 3. Temperature dependence of ionic conductivities of LDFBDB solutions $(0.10\,mol\,dm^{-1})$ in different solvents.

variety of Li-ion nonaqueous electrolytes [21]. 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 electrical conductivity of a cell, and hence in the overall battery performance.

As generally recognized, the weaker the coordination is, the easier the separation of an ion-pair. With the increase in the number of C_2O_4 and the decrease in the number of F, the calculated order of binding energies is $E_{bind}(LDFBDB) > E_{bind}(FLDFBDB) > E_{bind}(FLBDOB) > E_{bind}(LBOB)$ (Table 2). Meanwhile, the Li–O bond length gradually becomes longer with this sequence, e.g. 1.836, 1.837, 1.882 and 1.894 Å. Therefore, the BOB^- is the weakest anion of the four salts and L^+BOB^- would be disassociated more than the other three salts at the same concentration of electrolyte solutions. Compared with the calculated data, the experimental conductivity (Table 2) increases with the Li–O bond length, and decreases with E_{bind}.

As we mentioned above, the common feature of these anions is that extensive charge delocalization is present in them because they are composed of strongly electron-withdrawing substituents. There is only a single negative charge distributed across these anions. The stronger the electron-withdrawing, the more extensive the charge delocalization. So the LBOB is the lithium salt with the weakest coordination. Its solutions in molecular solvents are extremely conductive.

On the other hand, for the saturated solutions of each lithium salt in the solvent of PC+DME, which concentrations are $0.518\,mol\,dm^{-3}$ for LDFBDB, $0.443\,mol\,dm^{-3}$ for LFDFBDB, $0.362\,mol\,dm^{-3}$ for LBOB and $0.275\,mol\,dm^{-3}$ for FLBDOB, they all

Table 2
Total, binding energies of the free anions, their lithium ion pairs at B3LYP/6-311++G(3df,3pd)//B3LYP/6-31++G(2df,2p) level.[a]

	Total energy (au)	Binding energies $(kJ\,mol^{-1})$	Conductivity $(0.1\,mol\,dm^{-3}, 298.2k, mS\,cm^{-1})$			
			PC	PC+DME	PC+EC+EMC	PC+EMC
LDFBDB	−614.041127	−587.5	0.414	2.167	0.960	1.124
DFBDB⁻	−606.532456					
FLDFBDB	−713.312314	−579.1	1.06	3.46	1.18	1.24
FDFBDB⁻	−705.806818					
FLBDOB	−2338772.8	−552.4	4.58	5.94	–	–
FBDOB⁻	−2319093.8					
LBOB	−787.167699	−527.87	5.56	6.79	–	–
BOB⁻	−779.681725					

[a] E_{Li+} = −7.284918 (au), total energy of lithium cation is calculated at the same level.
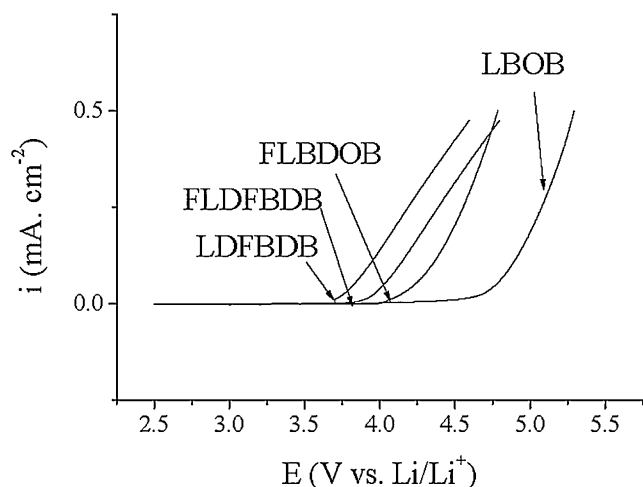
Fig. 4. i–E curves in PC saturated solutions using a platinum wire working electrode at a scan rate of $9\,mV\,s^{-1}$ at $20\,°C$.
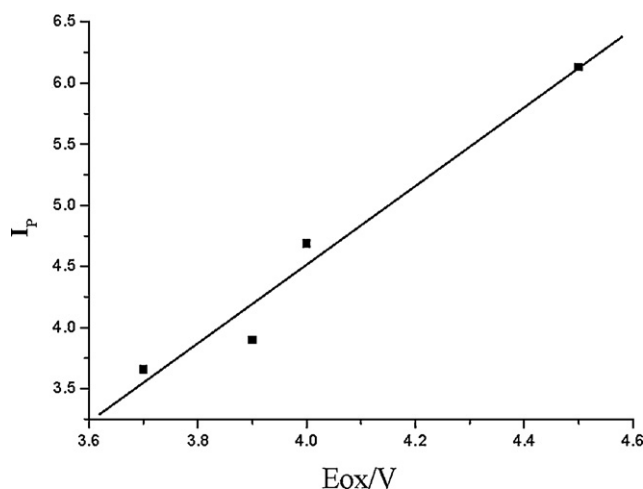

Fig. 5. Relation between E_{ox} and I_p of anions at DFT B3LYP/6-311++G(3df,3pd) level.

have a quite high conductivity, 1.18, 1.88, 6.76, and $5.60\,mS\,cm^{-1}$ for LDFBDB, LFDFBDB, LBOB, and FLBDOB, respectively.

3.5. Electrochemical stability

The electrochemical stabilities of LBOB, FLBDOB, FLDFBDB and LDFBDB solutions in PC on platinum wire electrode are shown in Fig. 4. The electrochemical oxidation potential can be obtained as ca. 3.7 V vs. Li^+/Li for the $0.1\,mol\,dm^{-3}$ solution of LDFBDB in PC. The order of the oxidation stability in these organoborates is LBOB (4.5 V) > FLBDOB (4.0 V) > FLDFBDB (3.9 V) > LDFBDB (3.7 V).

Several studies of anion oxidation potentials were recently updated and extended by Xue et al. [22]. They have found that E_{ox} can be correlated with adiabatic ionization potential (I_p). The I_p is found to be 6.13, 4.69, 3.90 and 3.66 eV for BOB$^-$, FBDOB$^-$, FDFBDB$^-$ and DFBDB$^-$, respectively. Obviously, the two sets of data (E_{ox} and I_p) are strongly correlated, as shown in Fig. 5 ($R = 0.982$).

4. Conclusions

A new lithium salt, lithium difluoro(1,2-benzene-diolato(2-)-o,o′)borate (LDFBDB), with asymmetric chelatoborate anion, has been synthesized. The salt, LDFBDB, is thermally stable and soluble in many of the common organic solvents used in batteries. The solutions are highly conductive and stable. The conductivity and electrochemical oxidation potential of LDFBDB solutions are slightly lower than those of its derivative in the common organic solvents used in batteries. But it may be used a successful replacement for some lithium salts in low-voltage lithium-ion 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 a strong electron withdrawing anion (e.g. dianion of 1,2-benzenediol) would raise the adiabatic ionization potential I_p, and improve the electrochemical stability of the electrolyte.

References

[1] N. Nanbu, K. Tsuchiya, T. Shibazaki, Y. Sasaki, Electrochem. Solid-State Lett. 5 (9) (2002) A202.
[2] M. Handa, M. Suzuki, J. Suzuki, H. Kanematsu, Y. Sasaki, Electrochem. Solid-State Lett. 2 (2) (1999) 60.
[3] X.M. Wang, E. Yasukawa, S. Kasuya, J. Electrochem. Soc. 147 (7) (2000) 2421.
[4] J. Barthel, A. Schmid, H.J. Gores, J. Electrochem. Soc. 147 (1) (2000) 21.
[5] J. Barthel, R. Buestrich, H.J. Gores, M. Schmidt, M. Wühr, J. Electrochem. Soc. 144 (1997) 3866.
[6] J. Barthel, M. Wühr, R. Buestrich, H.J. Gores, J. Electrochem. Soc. 142 (8) (1995) 2527.
[7] W. Xu, C.A. Angell, Electrochem. Solid-State Lett. 4 (1) (2001) E1.
[8] W. Xu, A.J. Shusterman, R. Marzke, C.A. Angell, J. Electrochem. Soc. 151 (4) (2004) A632.
[9] S.S. Zhang, Electrochem. Commun. 8 (2006) 1423.
[10] K. Xu, S.S. Zhang, B.A. Poese, T.R. Jow, Electrochem. Solid-State Lett. 5 (2002) A259.
[11] K. Xu, S.S. Zhang, T.R. Jow, Electrochem. Solid-State Lett. 6 (2003) A117.
[12] G.V. Zhuang, K. Xu, T.R. Jow, P.N.J. Ross, Electrochem. Solid-State Lett. 7 (2004) A224.
[13] Z.M. Xue, C.H. Chen, Electrochim. Acta 49 (2004) 5167.
[14] Z.M. Xue, C.H. Chen, Prog. Chem. 17 (3) (2005) 399 (Chinese).
[15] Z.M. Xue, B. Liu, C.H. Chen, Electrochim. Acta 51 (2006) 4554.
[16] Z.M. Xue, J.J. Cheng, C.H. Chen, J. Mol. Struct.: Theochem. 763 (2006) 181.
[17] Z.M. Xue, C.H. Chen, Mol. Simul. 32 (2006) 401.
[18] Z.M. Xue, C.Q. Ji, W. Zhou, C.H. Chen, J. Power Sources 195 (2010) 853.
[19] Z.M. Xue, B.H. Zhao, C.H. Chen, J. Power Source (2011), doi:10.1016/j.jpowsour.2011.04.011.
[20] Y. Sasaki, M. Handa, K. Kurashima, T. Tonuma, K. Usamib, J. Electrochem. Soc. 1489 (2001) A999.
[21] M. Ue, S. Mori, J. Electrochem. Soc. 141 (1994) 3336.
[22] Z.M. Xue, W. Zhou, J. Ding, C.H. Chen, Electrochim. Acta 55 (2010) 5342.