A Raman spectroscopy investigation of the interactions of LiBOB with γ-BL as electrolyte for advanced lithium batteries

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ABSTRACT

LiBOB (lithium bis(oxalato)-borate) based electrolytes for high power Li-ion batteries are prepared by dissolving different concentrations of LiBOB into two different types of liquid solvents, γ-Butyrolactone (γ-BL) and propylene carbonate (PC). The ionic conductivity, solubility, and viscosity of the as-prepared electrolytes are characterized and compared. Raman spectroscopic and ^{13}C nuclear magnetic resonance spectroscopy (NMR) are employed to investigate the fundamental solvation interactions of the LiBOB with the two types of solvents. The results indicate that lithium cation tends to coordinate with the carbonyl functional group of γ-BL. In contrast, it exists mainly through ion-pairing in PC solvent. By fitting the Raman spectra, the solvation numbers for both electrolytes are calculated and compared, which would further help understand the observed difference in ionic conductivity shown by these two electrolytes.

1. Introduction

There have been numerous studies of lithium salts used as electrolyte solute in lithium-ion batteries [1–4], such as LiAsF$_6$, LiClO$_4$, and LiF. Lithium bis(oxalato)-borate (LiBOB) salt has recently been developed as a alternative candidate for lithium-based batteries [5]. However, Xu [6] suggests that LiBOB is much less soluble or conductive in organic carbonate-based solvents that are usually used for the electrolyte solvents compared to other traditionally investigated lithium salts such as LiPF$_6$. The author thus attempts a thorough search of solvents such as γ-Butyrolactone (γ-BL), propylene carbonate (PC), ethylmethyl carbonate (EMC), and dimethyl carbonate (DMC) [6] and finds out the γ-Butyrolactone (γ-BL) is the best liquid solvent for LiBOB in terms of the ionic conductivity and electrochemical stability. The physical properties of the two different solvents γ-BL and PC and the solubility of LiBOB in these two electrolytes are listed in Table 1. It indicates that although both solvents have similar physical properties, there is a striking difference in the solubility of LiBOB. Huang et al. [7] further showed that the LiBOB in γ-BL indicates an excellent electrochemical compatibility with LiFePO$_4$ and the LiBOB–γ-BL electrolyte used in Li/LiFePO$_4$ half cell performs much better than LiPF$_6$–γ-BL. Efforts have also been made to further improve the conductivity of the LiBOB based electrolyte by adding additives [8]. However, the fun-

damental understanding of the chemical interactions of LiBOB with the solvents has been rather limited so far.

It has been believed that the ionic conductivity is dominantly determined by viscosity and ion-association of the lithium salts in the different types of the solvents, which essentially reflects the interactions of the salts and liquid solvents [6,9]. Therefore, it will be necessary for an investigation on the chemical interactions of the LiBOB with the liquid solvents in order to further optimize the electrochemical properties of this novel electrolyte. Here, we have reported a Raman spectroscopy and NMR investigations on the chemical interactions of solvating and ion-paring of LiBOB dissolved in γ-BL. A comparison with the solution of LiBOB in PC is also conducted.

2. Experiments

LiBOB was prepared and purified in the lab as described in the previous publication [10]. γ-Butyrolactone (γ-BL) and propylene carbonate (PC), anhydrous, 99.9+%(Gold Buck Co.), were used as received. The salt was added into the solvent slowly in a glove box filled with argon as protecting atmosphere. Concentration of the solution was expressed by molar per kilogram of solvent. LiFePO$_4$ (0.5 cm^2) was used as positive electrode as mentioned in the prior paper [11]. Lithium foil (2 cm^2) was used as anode electrode. The separator used in the T-type cell was Celgard 2400 microporous membrane. The cells were assembled and sealed in the glove box. The cycling and rate discharge performance were tested on LAND CT2001C tester (Wuhan, China). The cut-off voltage was 2.6–4.25 V.

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Table 1
Physical properties of γ-BL and PC.

	Melting point (°C)	Boiling point (°C)	Flash point (°C)	Solubility of LiBOB (mol kg^{-1})	Dielectric constant
γ-BL	−43.5	204	98.3	2.31	39
PC	−49	242	128	0.83	66

Viscosities were measured by DV-II+ viscometer produced by Brookfield Engineering Laboratories. Ionic conductivities were measured by Rex DDST-308A conductivity meter. FT-Raman spectra were excited at 633 nm, using JY HR800 equipment with a He–Ne laser. Solution preparation and spectra scanning were both carried out at the room temperature. The magnetic resonance studies of the nuclei ^{13}C were performed on an INSTRUM av600 spectrometer. ^{13}C NMR spectra were obtained by using a 5 mm tube. Solvation shifts ($\Delta\delta$) are estimated by Eq. (1), where δs and δo represent the chemical shifts of electrolyte with salt and without salt, respectively:

$$\Delta\delta = \delta s - \delta o \qquad (1)$$

3. Results and discussion

3.1. Characterizations of LiBOB/γ-BL and LiBOB/PC electrolytes

Conductivity and viscosity are very important physical properties for electrolytes. The relationship between them is expressed by the Stokes–Einstein–Lorenz formalism [12]:

$$\lambda_i = \frac{Z_i F^2}{6\pi\eta r_i} \qquad (2)$$

where λ_i is the equivalent conductivity, F is the Faraday constant and η is the viscosity of the electrolyte. It can be indicated from Eq. (2) that the conductivity is inversely proportional to the viscosity. The measured viscosity and conductivity of the two electrolytes with the similar concentration (0.8 mol L^{-1} (0.71 mol kg^{-1}) LiBOB/γ-BL and 0.8 mol L^{-1} (0.67 mol kg^{-1}) LiBOB/PC) are listed in Table 2. It can be observed that with γ-BL as the solvent, the LiBOB based electrolyte shows higher conductivity than the one dissolved in PC solvent and higher viscosity is correlated with a lower conductivity.

On further investigation on the electrochemical compatibility with the electrodes, the cycle performances of Li/0.8 mol L^{-1} LiBOB–γ-BL/LiFePO$_4$ and Li/0.8 mol L^{-1} LiBOB–PC/LiFePO$_4$ half cells are tested at room temperature and the results are shown in Fig. 1. In the first 5 cycles, discharge capacities of both electrolytes increase. The discharge capacities of LiBOB–γ-BL reach 153 mAh g^{-1} and remain around 150 mAh g^{-1} with little fading during the rest 40 cycles. In contrast, the discharge capacities of the LiBOB–PC electrolyte only retains around 138 mAh g^{-1}. Fig. 2 shows the 8th charge–discharge curves of LiBOB–γ-BL and LiBOB–PC at room temperature. It can be observed that LiBOB–γ-BL shows a smaller polarizing voltage at 0.09 V than LiBOB–PC. Consequently, as observed in Fig. 3, the rate discharged capacities of LiBOB–γ-BL exhibit higher capacity even at very high discharging rate of 2 C, and the decline of the capacity is much slower compared to LiBOB–PC as the rate increases.

Clearly, from above results, these two electrolytes show a striking difference in the ionic conducting ability, viscosity and

Table 2
Conductivities and viscosities for LiBOB in γ-BL and PC solutions (20 °C).

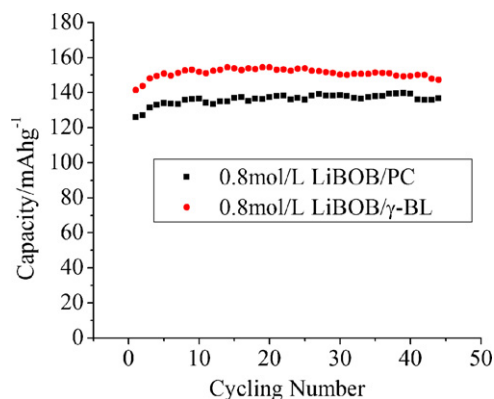| Electrolytes	Conductivity (mS cm^{-1})	Viscosity (mPa s)
0.8 M LiBOB/γ-BL	6.74	4.48
0.8 M LiBOB/PC	3.35	9.25

Fig. 1. Cycle performances of 0.8 mol L^{-1} LiBOB–γ-BL and 0.8 mol L^{-1} LiBOB–PC.
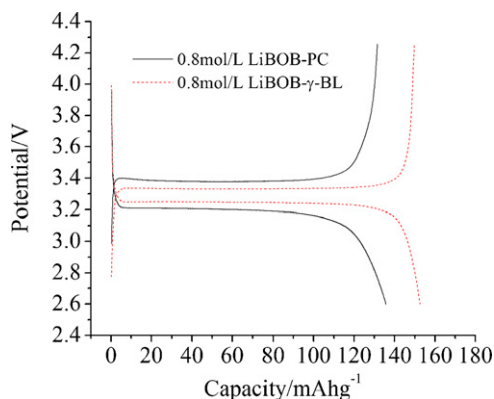

Fig. 2. The 8th charge–discharge curves of LiBOB–γ-BL and LiBOB–PC at room temperature.

electrochemical compatibility with the cathode electrodes. According to Ding and Richard Jow [9], there are several important factors that have a significant influence on the conductivity and viscosity of the electrolyte. One of them is the performance of Li$^+$ in the solutions, such as solvating and ion-paring. Therefore, Raman spectroscopy and NMR have been employed attempting to eluci-
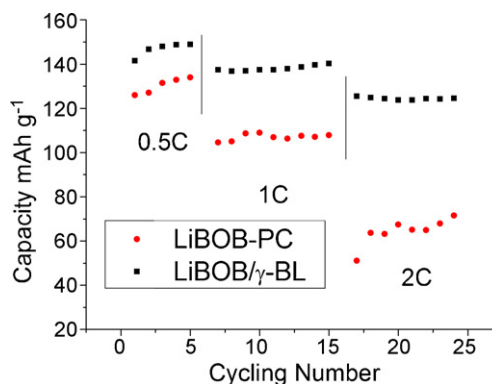

Fig. 3. Rate discharged capacities of 0.8 mol L^{-1} LiBOB–γ-BL and 0.8 mol L^{-1} LiBOB–PC.
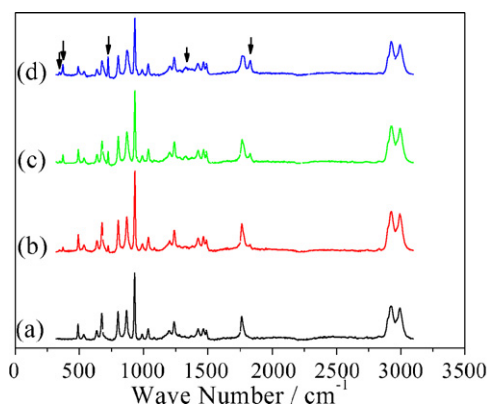
Fig. 4. Raman spectra of pure γ-BL and different concentrations of LiBOB in γ-BL: (a) pure γ-BL, (b) 0.18 mol kg^{-1}, (c) 0.89 mol kg^{-1} and (d) 1.78 mol kg^{-1}. The bands of BOB$^-$ are marked by arrows.

date the fundamental interactions of LiBOB with these two different solvents.

3.2. Raman Spectroscopy and NMR investigations on desolation of LiBOB in γ-BL solution

Raman spectra of pure γ-BL and different concentrations of LiBOB in γ-BL are presented in Fig. 4. The observed frequencies and assignments for γ-BL are listed in Table 3. The bands of BOB$^-$ occurring at 345 cm^{-1}, 371 cm^{-1}, 725 cm^{-1}, 1326 cm^{-1}, 1830 cm^{-1} are marked with arrows in Fig. 4(d). It can be seen from Fig. 4 that the addition of LiBOB has no influence on the frequency and shape of Raman spectra of γ-BL except the bands at 675 cm^{-1} and 1765 cm^{-1}. These two bands are assigned to the C–C symmetric stretching mode and the C=O stretching vibration [13], respectively. The intensity of peak at 689 cm^{-1} increases as the concentration of solute increases, which may be due to librational motions of γ-BL molecules binding to lithium cation. And a shoulder at 1780 cm^{-1} also increases with the increase of concentration of solute, which is probably to be considered as the C=O stretching vibration of γ-BL solved with lithium cation.

Table 3
Frequencies (cm^{-1}) and assignments, for Butyrolactone [13].

Observed frequencies (cm^{-1})	Calculated frequencies (cm^{-1})	Assignment
2995	2981.3	υ(CH$_2$) asym
2924	2931	υ(CH$_2$) sym
1765	1772.9	υ(C=O),
1489	11,484.3	s
1464	1467.7	s
1425	1454.4	s
1372	1375.3	υ(c′–o);w
1276	1274.6	W
1237	1254.2	T
1196	1233.3	T
1080	1076.5	R
1035	1030.2	R
988	977.4	R
928	920.8	υ(c–c′) υ(c–c)
868	879.6	υ(c–c)
800	836.0	υ(c–c)
673	682.2	υ(c–c)
635	631.8	υ(c–c)
532	527.0	δ (C=O),
489	490.5	χ(C=O), ring bond torsions

Note: υ: stretch; S, W, T, R: CH$_2$ scissor, wag, twist, rock; δ, χ: in-plane and out-of-plane deformation; c′: carbonyl carbon.
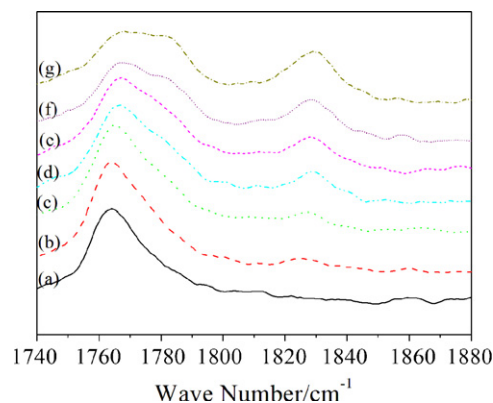

Fig. 5. Raman spectra for pure γ-BL and different concentrations of LiBOB in γ-BL in the region of 1740–1880 cm^{-1}: (a) pure γ-BL, (b) 0.18 mol kg^{-1}, (c) 0.36 mol kg^{-1}, (d) 0.71 mol kg^{-1}, (e) 0.89 mol kg^{-1}, (f) 1.33 mol kg^{-1} and (g) 1.78 mol kg^{-1}.

To investigate in detail how the Raman spectra in the C=O (of γ-BL) stretching vibration region change as the concentration of LiBOB increases, Raman spectra in the region of 1740–1880 cm^{-1} for pure γ-BL (a) and LiBOB/γ-BL solutions ((b)–(f)) are presented in Fig. 5. A new band at ca. 1783 cm^{-1} which is quite weak in Fig. 5(b)–(e), however, is obvious in Fig. 5(f) and (g). This peak tends to grow up with increasing of LiBOB concentration. Fig. 5 indicates that two kinds of γ-BL coexist in the electrolyte solution. One kind, from the bulk solvent, described as "free", results in the 1765 cm^{-1} band. The other one solvates the lithium cation and gives rise to the 1783 cm^{-1} band. So the lithium cation probably binds through the carbonyl functional group of γ-BL. However, from Fig. 4, it is noticed that both carbonyl functional group of γ-BL at 1765 cm^{-1} and the band at 675 cm^{-1} have been affected dramatically. As Holomb et al. [13] reported, the carbonyl functional group of BOB$^-$ also contributes to the intensities of the peak at 1780 cm^{-1}. Therefore, it is hard to conclude that the lithium cation is solved with the solvent molecules through the atom O in carbonyl group. In order to confirm the solvating atom with lithium cation, NMR technique is required to supply more evidence.

The chemical shifts of carbon atoms in the γ-BL molecule can indicate how the molecules interact with lithium cation in the solutions. If a certain atom of the solvent molecule solvates with Li$^+$, the electron density around the solvated atom will decrease dramatically leading to the chemical shifts of the neighbor atoms moving to the low field, the value of shifts becoming large in number. In order to distinguish carbon atoms from one another in the molecule γ-BL, we have numbered them as shown in Fig. 6. The figure also gives out the chemical shifts of different carbons. The unmarked one is chloroform.
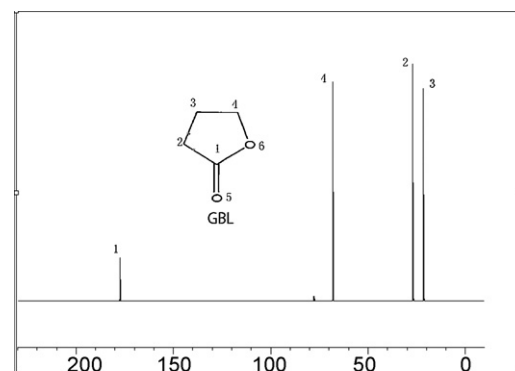

Fig. 6. ^{13}C NMR spectra of the pure γ-BL, the chemical shifts of different carbons are ordered in number and the unmarked one is chloroform.
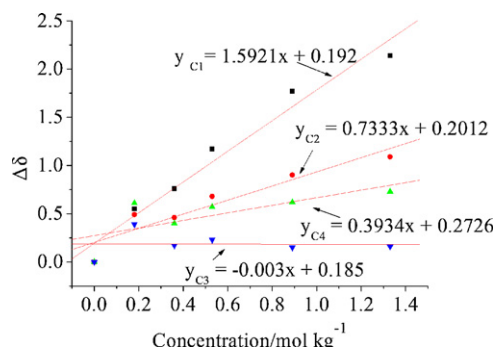
Fig. 7. Dependence of the relative ^{13}C NMR chemical shift ($\Delta\delta$) of γ-BL on the molality of the solutions.

Fig. 7 illustrates the dependence of the relative ^{13}C NMR chemical shift ($\Delta\delta$) of γ-BL on the molality of the solutions. When the concentration of LiBOB increases from 0 to 1.5 mol kg^{-1}, the chemical shifts of C1, C4, C2 increase linearly, except for C3, which is quite stable. The slopes of the former three lines are 1.5921, 0.7333, and 0.3934, respectively, with the ratio of 1:0.46:0.25. The lithium cation should bind through carbonyl functional group of γ-BL because the chemical shift of carbon atom in C=O has been affected most strongly with the increase of the salt concentration. C4 is nearer to O6 than C2, C3, which means that the electron density of C4 can be affected more easily by solvating with lithium cation, thus making its chemical shift more sensitive to the concentration.

Based on Raman and NMR studies, it can be concluded that the lithium cation interacts strongly with the carbonyl functional group of γ-BL molecule in solution LiBOB/γ-BL. The solved lithium cation by C=O leads to the variation of Raman band at 675 cm^{-1}. Besides the solvating effect, according to Holomb et al. [13], carbonyl functional group of BOB$^-$ also contributes to the different intensities of the peak at 1780 cm^{-1}.

In order to calculate solvation number of lithium cation from the measured Raman intensities of different salt concentrations, a standard intensity is required. Deng and Irish [14] have given an internal standard: it should ideally be sufficient soluble in the solvent should not have Raman bands that interfere with the bands being measured, and should not compete by complexation. We find that the band of γ-BL at 1035 cm^{-1} is satisfactory. It remains a single, symmetrical band profile on the addition of LiBOB.

Raman spectra in the 650–710 cm^{-1} region of pure γ-BL (a) and LiBOB/γ-BL solutions ((b)–(f)) are presented in Fig. 8, which illustrates how the Raman spectra in the C=C stretching vibration
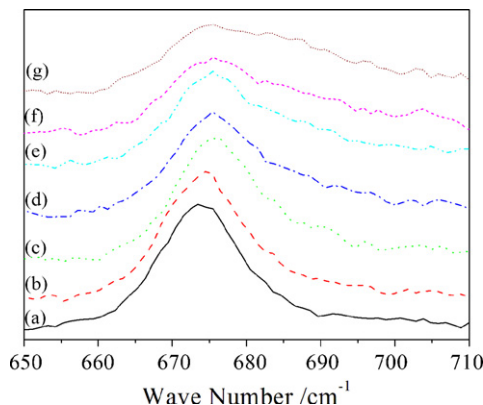

Fig. 8. Raman spectra in the 650–710 cm^{-1} region of pure γ-BL (a) and LiBOB/γ-BL solutions, the concentrations are (b) 0.18 mol kg^{-1}, (c) 0.36 mol kg^{-1}, (d) 0.71 mol kg^{-1}, (e) 0.89 mol kg^{-1}, (f) 1.33 mol kg^{-1} and (g) 1.78 mol kg^{-1}, respectively.

Fig. 9. Application of BNDFT to the spectrum of pure γ-BL (a) and LiBOB/γ-BL solutions in the 650–710 region. The concentrations are (b) 0.18 mol kg^{-1}, (c) 0.36 mol kg^{-1}, (d) 0.71 mol kg^{-1}, (e) 0.89 mol kg^{-1}, (f) 1.33 mol kg^{-1} and (g) 1.78 mol kg^{-1}, respectively.
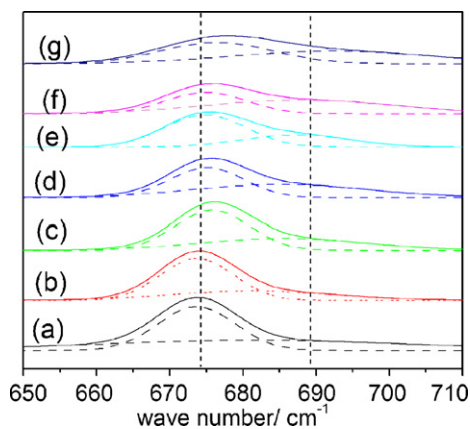
region of γ-BL change as the concentration of LiBOB increases. As the concentration of LiBOB increases from 0.18 to 1.78 mol kg^{-1}, a new band at 689 cm^{-1} increases in intensity at the expense of the 675 cm^{-1} band. Fig. 9 displays the results of applying the BNDFT program to the spectrum of LiBOB/γ-BL solutions with the concentration from 0 to 1.78 mol kg^{-1}. The two bands occurring at 675 cm^{-1} and 689 cm^{-1} are clearly portrayed. Based on the above discussion, the band at 689 cm^{-1} is ascribed to the combination of the γ-BL molecules with lithium cation. And the band at 675 cm^{-1} is supposed to be the "free" γ-BL molecules in solution. Fig. 10 shows the relative intensities I_{689}/I_{1035}, I_{675}/I_{1035}, and $I_{total}/I_{1035} = (I_{689} + I_{675})/I_{1035}$ depending on the concentration of LiBOB. The intensity of the band at 689 cm^{-1} increases at the sacrifice of that at 675 cm^{-1} as the concentration of LiBOB increases. The total intensity, $(I_{689} + I_{675})/I_{1035}$, remains almost constant over a quite wide concentration range.

With the method of Deng and Irish [14], we define the relative integrated intensity of free spices as I_f and the concentration as C_f, so do for bound species as I_b and C_b. The total intensity and total concentration are defined as $I_t = I_f + I_b$ and C_t (a constant value of 11.6 mol kg^{-1}), respectively. Assume that $I_f = J_f C_f$ and $I_b = J_b C_b$, where J_f and J_b are the molar scattering coefficients for the two species. So we can get:

$$I_f = J_f C_f \quad I_b = J_b C_b \quad C_t = C_f + C_b \tag{3}$$

$$I_t = I_f + I_b = J_f C_f + J_b C_b \tag{4}$$

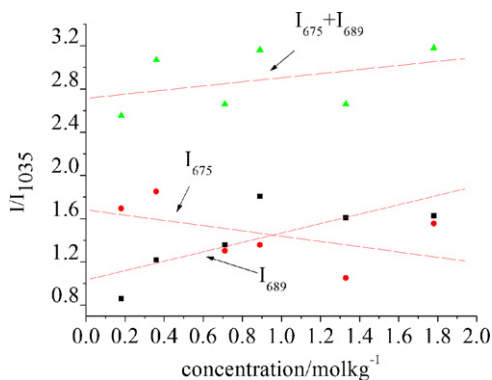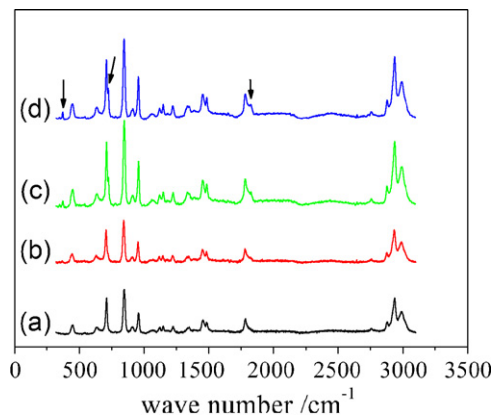$$I_t = \left(1 - \frac{J_f}{J_b}\right) I_b + J_f C_t \tag{5}$$

Fig. 10. Relative intensities of bands and the sum versus the concentration of solute.

Table 4
Composition, relative integrated intensities, and solvation number of lithium.

LiBOB (mol kg^{-1})	I_b	I_t	n
0.18	0.859	2.553	12.9
0.36	1.219	3.070	9.2
0.71	1.358	2.660	5.2
0.89	1.807	3.163	5.5
1.33	1.610	2.661	3.3
1.78	1.623	3.181	2.5

Fig. 11. Raman spectra of the solution LiBOB/PC: (a) pure PC, (b) 0.27 mol kg^{-1}, (c) 0.5 mol kg^{-1} and (d) 0.67 mol kg^{-1}.

The linear equation is $I_t = 0.49I_b + 2.19$, when I_t is plotted versus I_b, with a correlation coefficient of 0.59. We calculate the solvation number of lithium cation using Eq. (6):

$$n = \frac{C_b}{C_{Li}} = \frac{I_b}{C_{Li}J_b} \tag{6}$$

The value is listed in Table 4 for each concentrations of LiBOB. As the concentration of solute increases from 0.18 to 1.78 mol kg^{-1}, the solvation number declines from 12.9 to 2.5, meaning that in the solution LiBOB/γ-BL, Li$^+$ mainly solvates with solvent molecules (the salvation number of 12.9, which conflicts with conventional concept of primary solvation shell, means that Raman intensity analysis might cover all the affected solvent molecules, including those in secondary salvation shell). This decline of solvation number is due to two reasons. Firstly, it is caused by the lack of available solvent molecules as the concentration of LiBOB increases. Secondly, according to the reduction of positive charge in the lithium cation neutralized by the BOB$^-$ anion group, the neutralization displacing more solvent molecules from within the solvating shell into the free space. In addition, in solutions with high concentrations of salt, there must be some ion-pairing.

3.3. Raman spectroscopy of lithium cation solved in LiBOB/PC solutions

Fig. 11 shows the Raman spectra of LiBOB/PC solutions with different salt concentrations. The peaks which are marked by the arrows associate to the bands of BOB$^-$ [13]. There is little change of frequency or shape as the concentration of LiBOB increasing from 0 to 0.67 mol kg^{-1}, except for the bands belonging to BOB$^-$ group. Thus, we may deduce that the bulk lithium cations exist in

Table 5
The binding energies and total energies of Li$^+$-BOB$^-$ and Li$^+$-PC.

	Binding energy (eV)	Total energy (eV)
Li$^+$-BOB$^-$	−80.45	−21,417.43
Li$^+$-PC	−56.04	−10,588.76

the form of [Li$^+$ (BOB)$^-$], and only the minority interact with PC molecule, which are so seldom that they cannot be identified by Raman spectra.

The binding energies and total energies of Li$^+$-BOB$^-$ group and Li$^+$-PC group are calculated (Table 5). From the calculation results, it can be concluded that the group Li$^+$-BOB$^-$ is much more stable than the group Li$^+$-PC, thus leading to the fact that lithium cation exists mainly in the form of [Li$^+$ (BOB)$^-$], instead of solvating with solvent molecules in LiBOB/PC solutions. Furthermore, BOB$^-$ can bind with more than one lithium cation, thereby forming an extended structure and increasing the viscosity of the electrolytes.

As discussed above, in the solvent γ-BL, lithium cation mainly solvates with solvent molecules, in contrast to ion-paring with BOB$^-$ in PC. The solvation effect in γ-BL accelerates the dissociation of LiBOB, promoting the salt's solubility in the solvent. That is why more LiBOB salts solute in γ-BL than in PC.

4. Conclusion

From the analysis of Raman and NMR spectra, lithium cations perform differently in different solvents such as γ-BL and PC. Lithium cation tends to coordinate with the carbonyl functional group of γ-BL and the solvation number for the lithium cation varies with the LiBOB concentrations. The lithium cation in PC solvent exists mainly in the form of [Li$^+$ (BOB)$^-$] through ion-pairing instead of solvating with the solvent molecules as it shows in γ-BL solvent. These performances of lithium cations in different solvents lead to the diversity of solubility, conductivity and viscosity of electrolytes. The LiBOB–γ-BL electrolyte with higher conductivity and lower viscosity shows better cycle and rate performances than LiBOB–PC.

References

[1] D.E. Irish, Z. Deng, M. Odziemkowski, J. Power Sources 54 (1995) 28–33.
[2] D. Battisti, G.A. Nazri, B. Klassen, R. Aroca, J. Phys. Chem. 97 (1993) 5826–5830.
[3] X.P. Xuan, J.J. Wang, J.M. Tang, G.R. Qu, J.S. Lu, Spectrochim. Acta Part A 56 (2000) 2131–2139.
[4] L.F. Li, H.S. Lee, H. Li, X.Q. Yang, K.W. Nam, W.S. Yoon, J. McBreen, X.J. Huang, J. Power Sources 184 (2008) 517–521.
[5] M.S. Ding, K. Xu, T. Richard Jow, J. Electrochem. Soc. 152 (2005) A132–A140.
[6] K. Xu, J. Electrochem. Soc. 155 (2008) A733–A738.
[7] J.Y. Huang, X.J. Liu, X.L. Kang, Z.X. Yu, T.T. Xu, W.H. Qiu, J. Power Sources 189 (2009) 458–461.
[8] H.G. Schweiger, M. Multerer, M. Schweizer-Berberich, H.J. Gores, Int. J. Electrochem. Sci. 3 (2008) 427–443.
[9] M.S. Ding, T. Richard Jow, J. Electrochem. Soc. 151 (2004) A2007–A2015.
[10] B.T. Yu, W.H. Qiu, F.S. Li, G.X. Xu, Electrochem. Solid-State Lett. 9 (2006) A1–A4.
[11] S. Wang, W.H. Qiu, Y.L. Guan, B.T. Yu, H.L. Zhao, W. Liu, Electrochim. Acta 52 (2007) 4907–4910.
[12] R.Z. Lorenz, Phys. Chem. 37 (1910) 252.
[13] R. Holomb, W. Xu, H. Markusson, P. Johansson, P. Jacobsson, J. Phys. Chem. A 110 (2006) 11467–11472.
[14] Z. Deng, D.D. Irish, Can. J. Chem. 69 (1991) 1766–1773.