



Conductivity of libob-based electrolyte for lithium-ion batteries

Fadhel Azeez^a, Peter S. Fedkiw^{b,*}

^a Chemical Engineering Department, Kuwait University, PO Box 5969, Safat 13060, Kuwait

^b Department of Chemical & Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695-7905, USA

ARTICLE INFO

Article history:

Received 20 May 2010

Received in revised form 4 June 2010

Accepted 9 June 2010

Available online 15 June 2010

Keywords:

Li-ion batteries

LiBOB

Conductivity

Viscosity

Ester solvents

ABSTRACT

This work reports the use of mixtures of γ -butyrolactone (GBL) and ethyl acetate (EA), with and without ethylene carbonate (EC), as solvents for lithium bis(oxalato)borate (LiBOB) salt as potential electrolytes for Li-ion cells. The effects of salt concentration, ethylene carbonate (EC) content, and temperature on the conductivity and viscosity of the mixture are reported. Results indicate that the best electrolyte for high-temperature application is that which contains 1 kmol m^{-3} LiBOB in GBL + EA + EC of composition 1:1:0.1 (wt). For low-temperature applications, the best electrolyte is that which contains 0.7 kmol m^{-3} LiBOB in GBL + EA + EC of composition 1:1:0 (wt). The product of conductivity with viscosity was essentially independent of temperature but was dependent on solvent composition showing that at fixed salt concentration, the viscosity is the major criteria affecting electrolyte conductivity rather than dielectric constant.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Li-ion batteries are used in many applications such as portable electronics, cellular phones and laptop computers. In addition, there is interest in using Li-ion batteries in electric vehicles (EVs) and hybrid electric vehicles (HEVs) due to their high-energy and -power density compared to alternatives such as Ni–Cd and Ni–MH [1].

Currently, the state-of-art electrolyte for a Li-ion battery is composed of lithium hexafluorophosphate (LiPF_6) salt dissolved in a mixture of ethylene carbonate (EC) and linear esters such as dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC). Lithium hexafluorophosphate has been used as the salt in Li-ion batteries for more than a decade because of its unique balance of properties such as good ionic conductivity and ability to passivate an aluminum current collector. However, LiPF_6 is thermally unstable and it decomposes into undesired products such as LiF and PF_5 that can trigger detrimental reactions on the electrode surfaces [2,3]. In addition, LiPF_6 and PF_5 react with trace of water to form HF [4]:



* Corresponding author at: Department of Chemical and Biomolecular Engineering, North Carolina State University, 911 Partners Way, Box 7905, Raleigh, NC 27615, USA. Tel.: +1 919 515 3572; fax: +1 919 515 3456.

E-mail address: fedkiw@eos.ncsu.edu (P.S. Fedkiw).

The LiF deposits on the electrode surface and results in high-interfacial impedance and is an impediment for Li^+ insertion and deinsertion processes, which lead to cell capacity fade [5]. Also, HF causes dissolution and migration of the cathode's transition metals which leads to structural changes and capacity fade [6,7].

Efforts have been devoted to develop lithium salts for commercial lithium-ion cells. For that purpose many salts have been examined including lithium perchlorate (LiClO_4), lithium arsenate (LiAsF_6), lithium tetrafluoroborate (LiBF_4), lithium triflate (LiCF_3SO_3), and lithium bis(trifluoromethane sulfone)imide ($\text{LiN}(\text{SO}_2\text{CF}_3)_2$). However, each salt has its own challenges that prevent it from being used in commercial Li-ion batteries. For example, LiClO_4 and LiAsF_6 cannot be used because of explosion risks of ClO_4^- [8] and toxicity of AsF_6^- and its degradation products [9–12], respectively. The main challenge with LiBF_4 is its low conductivity, although it was observed recently that electrolytes with LiBF_4 have good performance at low temperature [13–16]. Lithium triflate has two shortcomings. First, it has poor ion conductivity in nonaqueous solvents, which is attributed to the low-dissociation constant of LiCF_3SO_3 in solvents with a low-dielectric constant [12,17] and the moderate ion mobility of CF_3SO_3^- as compared to other salts anions [18]. The second problem with using LiCF_3SO_3 is the aluminum current-collector corrosion that occurs with it [19], which is also a problem with $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ [19].

LiBOB, which was independently disclosed by Lischka et al. [20] in Germany (1999) and Angell and co-workers [21] in the USA (2001), has attracted attention as a promising candidate for Li-ion batteries [22–26]. The LiBOB salt has many advantages such as high thermal stability (up to 575 K), ability to passivate aluminum, and ability to form a solid electrolyte interface (SEI) on graphite even in the absence of EC [27,28], which is a major sol-

vent component due to its ability to form the SEI. On the other hand, EC is believed to be at least partially responsible for the low-temperature limit of Li-ion batteries [29]. Although LiBOB has many advantages, it also has disadvantages when used with linear carbonate co-solvents that are used to lower viscosity. The problems of using LiBOB with linear carbonate solvents come from LiBOB essentially being insoluble in these solvents [30] and, consequently, practical solvents must be EC- or PC-rich. However, high-EC or -PC content in an electrolyte increases its viscosity, which renders the electrolyte with poor low-temperature performance and rate capability. There is a need to find a proper solvent mixture that is tailored for LiBOB to give high conductivity and good solubility for the salt. Previous work on conductivity of LiBOB dissolved in a mixture of carbonate solvents as a function of temperature, salt concentration, and solvent composition was reported by Ding et al. [31]. In this work, we used mixtures of γ -butyrolactone (GBL), ethyl acetate (EA), and ethylene carbonate (EC) to dissolve LiBOB and studied the conductivity and viscosity of the electrolyte. The effects of salt concentration, solvent composition, and temperature on conductivity and viscosity are reported here. The cycling performance of lithium-ion cells using our electrolyte is going to be reported in future.

γ -Butyrolactone (GBL) is chosen as a co-solvent because it has a reasonably high-dielectric constant (~ 39), a relatively moderate viscosity (~ 1.7 mPa s at 298 K), a similar structure to EC, and good solubility for LiBOB [32–34]. In addition, it was reported that GBL can improve the low-temperature performance of a LiBOB-based electrolyte [35–37]. Ethyl acetate is chosen because it has a low-melting point (~ 189 K), which will increase the liquid range of the electrolyte. In addition, the low viscosity (~ 0.5 mPa s at 298 K) of EA will improve conductivity. Also, it has been reported that EA enhances the low-temperature performance of Li-ion cells because of improved solution transport properties [38–41].

2. Experimental

Ethylene carbonate, ethyl acetate, and γ -butyrolactone are obtained from Aldrich and dried over 0.4 nm molecular sieves (Fisher Scientific) for at least 1 week. Lithium bis(oxalato)borate is obtained from Chemetall and used as is.

The water content of solvents is measured to be below 20 ppm using a Mitsubishi CA-06/VA-06 Karl–Fisher titrator. The water content of the electrolyte solution is calculated as approximately 70 ppm from the measured water content in the salt and solvents.

2.1. Conductivity measurements

Conductivity is measured using EG&G Princeton Applied Research PowerSine software to control an EG&G Model 273 potentiostat and EG&G Model 5210 lock-in amplifier in the frequency range 100 kHz to 100 mHz. The cell constants are found using a KCl standard solution ($1409 \mu\text{S cm}^{-1}$ at 298 K) (Fisher Scientific) prior to and after each measurement.

The conductivity cell consists of a glass cell containing two blocking platinum wire electrodes (0.64-mm diameter, Fisher Scientific), a thermocouple opening, an O-ring seal, and glass vial. The conductivity cell has a diameter of ~ 1.5 cm and height of 5 cm. The design of the cell is described by Riley [42], and a schematic of the conductivity cell is shown in Fig. 1.

Temperature is controlled by putting the conductivity cells inside wells in an insulated aluminum block with an internal-coolant circuit connected to a temperature-controlled circulating water bath (Isotope 1016P Fisher Scientific). Conductivities are measured over the temperature range of 271–333 K (lower temperatures than 271 K was not examined because of the instrument

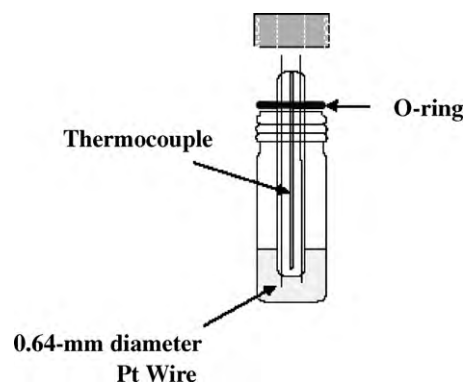


Fig. 1. Conductivity cell.

limitation) and the temperature of each sample is measured using a T-type thermocouple (Omega) placed in a sealed glass compartment fully submerged in the sample. The data acquisition system consists of a National Instruments Field point Module (FP 1000) connected to two National Instruments 8-channel thermocouple modules (FP-TC-120).

Two methods are used to calculate the resistance of the electrolyte Z_{RE} from the electrochemical impedance spectroscopy (EIS) data: From the intercept on a Nyquist plot of Z with the real impedance axis at high frequency; and use of a program (ZSimpWin from EG&G Princeton Applied Research) to calculate equivalent-circuit parameters, as shown in Fig. 2. The first method is used in this study with the second method periodically used to verify the results. There is a small difference in the resistance between two methods ($<2\%$).

For each electrolyte sample, the conductivity in five separate cells is measured with the reported value representing the average. The electrolyte conductivity is obtained from the cell constant and measured resistance using Eq. (4):

$$\sigma_i = \frac{\sigma_{\text{KCl}} \times Z_{\text{RE,KCl}}}{Z_{\text{RE},i}} \quad (4)$$

where σ_{KCl} is the conductivity of KCl the standard, $Z_{\text{RE,KCl}}$ is the measured intercept of the real impedance axis for the KCl standard [ohm], and $Z_{\text{RE},i}$ is the measured intercept of the real impedance axis for sample i [ohm].

2.2. Viscosity measurement

Rheological measurements are conducted using a TA AR2000 stress rheometer over a temperature range of 283–298 K. The liquid viscosities are determined using conical concentric cylinders. The inner radius of the outer stator cylinder is 15 mm; the outer radius of the inner rotor is 14 cm; and the cylinder immersed height is 42 mm. Typically, the liquid sample volume is 19.6 cm^3 .

Liquid viscosities are measured by a steady-state flow mode. Typical Newtonian behavior is observed for the liquid sample: vis-

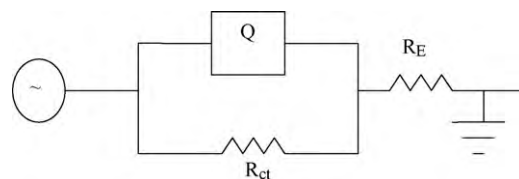


Fig. 2. Equivalent circuit used for electrolyte resistance calculation, where R_E is bulk electrolyte resistance, R_{ct} is charge transfer resistance, and Q is a constant phase element.

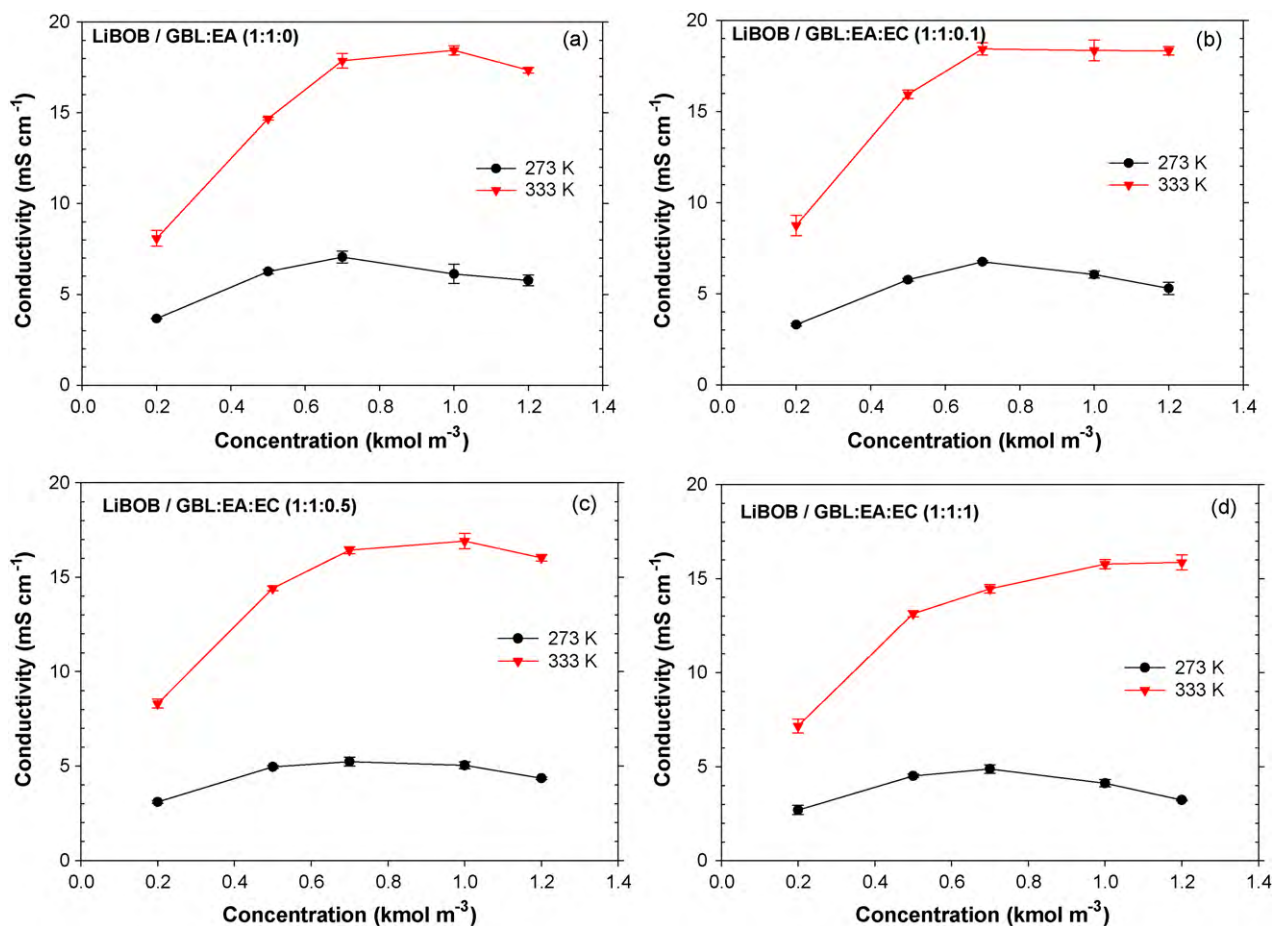


Fig. 3. Concentration dependence of conductivity for electrolytes containing LiBOB in GBL:EA:EC of (a) 1:1:0, (b) 1:1:0.1, (c) 1:1:0.5, and (d) 1:1:1 (wt) composition at 273 and 333 K.

cosity does not vary with shear stress or shear rate; viscosity is constant with time of shearing; and stress in fluid immediately falls to zero when shear is stopped.

3. Result and discussion

3.1. Salt concentration effect on conductivity and viscosity

As evident in Fig. 3, conductivity increases with salt concentration at low-salt concentrations, which is attributable to the number of free ions increasing with salt concentration. After achieving a maximum conductivity, an increase in salt concentration results in higher ion aggregation and higher viscosity of the solution, which reduces the free-ion number and the ionic mobility, respectively. It is a universal phenomenon for liquid electrolytes to have a maximum in conductivity at a certain salt concentration, and it has been reported for many electrolytes of lithium salts [43–47].

The concentration at the maximum in conductivity was $\sim 0.7 \text{ kmol m}^{-3}$ LiBOB at 273 K for all solvent compositions studied. At 333 K the system with GBL:EA:EC at 1:1:0 shows a broad maximum around 1.0 kmol m^{-3} LiBOB. The salt concentration at the maximum in conductivity increases with EC content. For the system with solvent composition of 1:1:0.1 (GBL:EA:EC), the maximum in conductivity occurs between 0.7 kmol m^{-3} and 1.2 kmol m^{-3} LiBOB. The system with GBL:EA:EC at 1:1:0.5 has the maximum conductivity around 1.0 kmol m^{-3} LiBOB, and finally for the system with solvent composition of 1:1:1, there is no maximum in the studied range of salt concentration. As seen in Eq. (5), the

required distance q for ion-pair formation decreases as temperature increases [48]:

$$q = \frac{|z_i z_j|}{8\pi\epsilon_0\epsilon_k T} e^2 \quad (5)$$

A decrease in q means that more salt can be dissolved without ion pairing, which will shift the maximum conductivity to a higher salt concentration than the same electrolyte at lower temperature. At high temperature (333 K), the maximum conductivity occurs at higher salt concentration as the EC content increases because of the higher dielectric constant of the solvent mixture. The maximum conductivity at 273 K occurs around 0.7 kmol m^{-3} LiBOB irrespective of EC content. Although addition of EC increases the solvent dielectric constant, the high viscosity of EC decreases conductivity; that is, at low temperature the viscosity effect appears to dominate over the dielectric constant effect.

The molar conductivity Λ is shown as a function of salt concentration in Fig. 4. The molar conductivity decreases with increase of salt concentration because of the two negative factors (viscosity and ion association). That is, as the salt concentration increases, the viscosity and ion association increases. A viscosity increase will lower ion mobility and an ion association increase will lower the number density of free ions, both which will lower conductivity.

The relation between the viscosity and the salt concentration is shown in Fig. 5 for GBL:EA:EC of 1:1:0.1. As the salt concentration increases so does the viscosity because of the increasing intermolecular force between ions and molecules. This trend is typical for other solvent compositions.

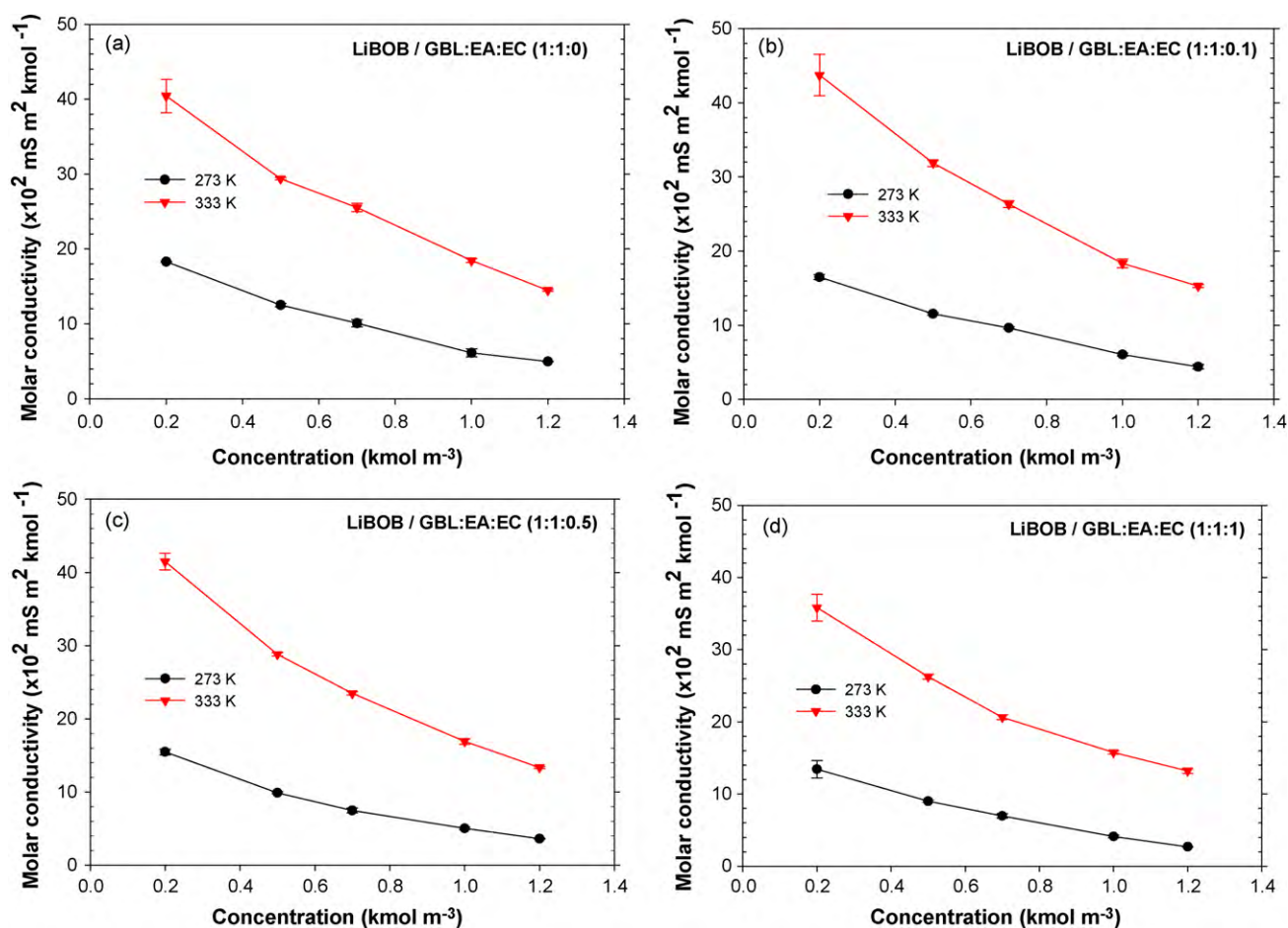


Fig. 4. Concentration dependence of molar conductivity for electrolytes containing LiBOB in GBL:EA:EC of (a) 1:1:0, (b) 1:1:0.1, (c) 1:1:0.5, and (d) 1:1:1 (wt) compositions at 273 and 333 K.

Fig. 6 shows the product of conductivity and viscosity as a function of temperature for the solvent compositions studied. The product is nearly temperature independent, although there is a slight increase at the lowest temperature shown. At fixed temperature, increasing values of the product $\sigma\eta$ indicate increasing salt dissociation [47]. Fig. 6 shows that the highest $\sigma\eta$ value is for GBL:EA:EC of 1:1:1 and the smallest value is for solvent composition

of 1:1:0. The increase of the $\sigma\eta$ product with EC content is due to the increase of the mixture's dielectric constant [49], leading to an increase of ion disassociation. Although it is reasonable to expect that the solvent composition of 1:1:1 (GBL:EA:EC) should produce the highest ion disassociation, its conductivity is the lowest (Fig. 3) because of the high viscosity of EC. In Figs. 3 and 6, we deduce that viscosity is the dominate factor in our electrolyte.

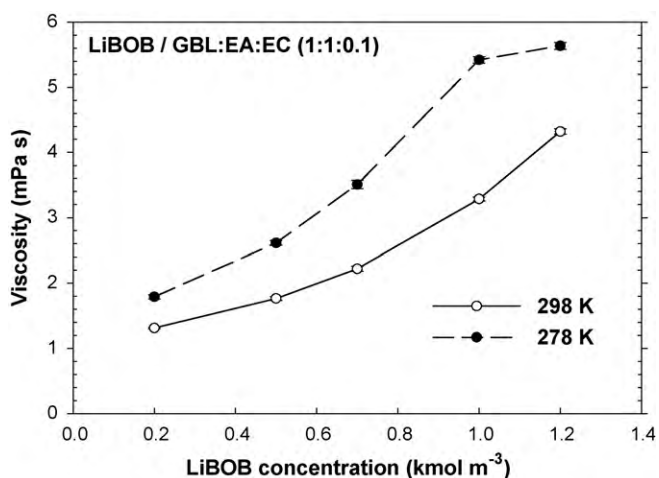


Fig. 5. Concentration dependence of viscosity for electrolytes containing LiBOB in GBL:EA:EC composition of 1:1:0.1 (wt) at 278 and 298 K.

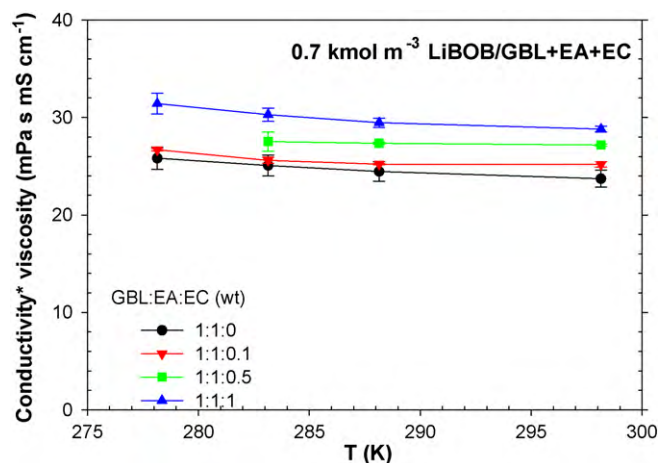


Fig. 6. Product of viscosity and conductivity for 0.7 kmol m^{-3} LiBOB dissolved in GBL:EA:EC as a function of temperature for various solvent compositions.

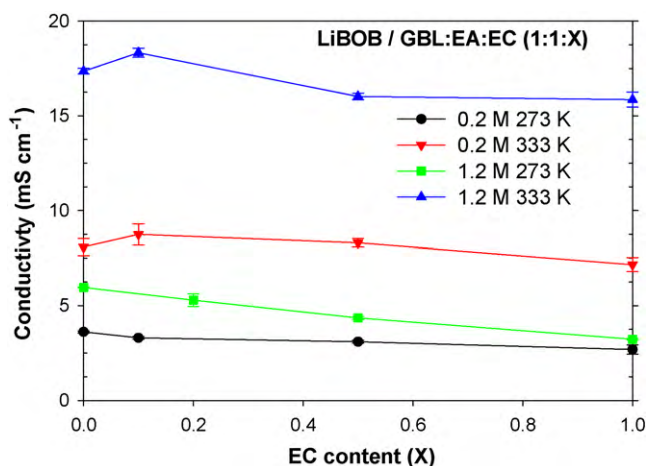


Fig. 7. Dependence of conductivity on EC content for 0.2 and 1.2 kmol m⁻³ LiBOB dissolved in GBL:EA:EC at 273 and 333 K.

3.2. EC content effect on conductivity and viscosity

At fixed temperature and salt concentration, the solvent viscosity and dielectric constant change with solvent composition [49], which affects the conductivity of the electrolyte through its dependence on viscosity and dielectric constant; however, the temperature and salt concentration influence the degree of the effect. For example, at 0.2 kmol m⁻³ LiBOB and 273 K (Fig. 7), the conductivity decreases as EC content increases. The conductivity decrease is due to the dominant role of viscosity over dielectric constant at low temperature. In comparison at 333 K, initially the conductivity slightly increases with EC content and reaches a maximum at 1:1:0.1 (GBL:EA:EC); at higher EC content it decreases. The initial increase of conductivity with EC content occurs because the number of free ions increases upon addition of the high-dielectric constant EC ($\epsilon \sim 89.6$). At the same time, however, the solution viscosity increases because of the high viscosity of EC (Fig. 8). At the combination condition of low-EC content, low-salt concentration, and high temperature, the effect of free ions dominates over the viscosity effect. However, as the EC content increases the viscosity effect dominates.

Similarly, salt concentration also affects the dependence of conductivity on solvent composition. For example, at 333 K and 0.2 kmol m⁻³ LiBOB (Fig. 7), conductivity increases with EC content up to a GBL:EA:EC composition of 1:1:0.1 but decreases at higher EC

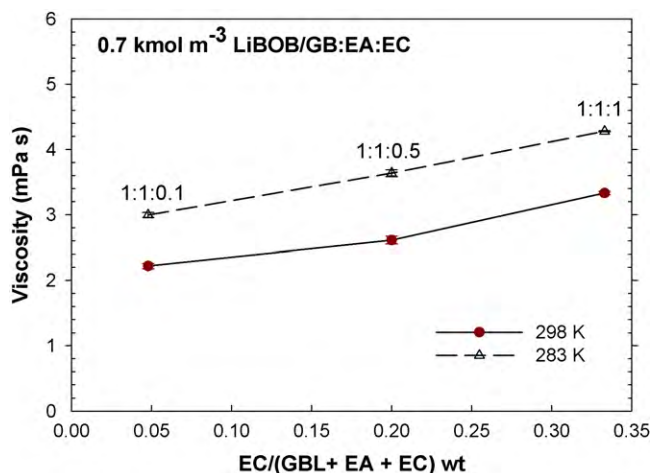


Fig. 8. Dependence of viscosity on EC content in 0.7 kmol m⁻³ LiBOB in GBL:EA:EC at 283 and 298 K.

content. For 1.2 kmol m⁻³ LiBOB at 333 K (Fig. 7), the conductivity increases with increasing EC content up to a solvent composition of 1:1:0.1 but decreases more slowly at higher EC content. At low-salt concentration, the positive effect of EC is effective only for low-EC content since a low-salt concentration does not require a high-dielectric solvent to disassociate the salt. This is because the distance between ions in the electrolyte is already large, which reduces the effect of dielectric constant on ion disassociation. So, as the EC content increases, its effect on ion disassociation will not be significant; however, the viscosity increases with EC content (Fig. 8) and reaches a value where the viscosity effect is more important than the free-ion effect. In the case of high-salt concentration (1.2 kmol m⁻³), the conductivity initially increases with EC content until it reaches the point where conductivity decreases because the viscosity effect becomes dominant over the number density of free ions; however, as the EC content continues to increase, the number of free ions effect opposes the effect of viscosity so the two effects counter one another and conductivity levels off at high-salt concentration. For low temperature, the viscosity effect of EC is always more important than the effect of free ions generated by adding more EC.

3.3. Temperature effect on conductivity

At a given salt concentration and solvent composition, the conductivity of LiBOB-containing electrolytes increases with temperature, as shown in Fig. 9. As the temperature increases, the viscosity and dielectric constant decrease. In the studied temperature range, the effect of viscosity outweighs the effect of dielectric constant. Although the dielectric constant increases with a decrease in temperature, at low temperature ion conductivity is predominately determined by electrolyte viscosity. As the salt concentration increases, the drop in conductivity with decreasing temperature increases since the increasing salt concentration contributes to a higher viscosity. High viscosity resulted from high-salt concentration and low-temperature causes more rapid decrease in conductivity compared to the low-salt concentration electrolytes as seen in Fig. 9. Solvent composition also has an influence on the temperature dependence of ion conductivity. In Fig. 9, we see that the rate of change of conductivity with temperature increases as the EC content increases.

4. Summary

The trends observed in conductivity of LiBOB in GBL:EA:EC solvent mixtures with changing salt concentration, solvent composition, and temperature can be interpreted in terms of the variation in dielectric constant and viscosity with these same variables. Since these factors and their effect on ion conductivity are not unique to the LiBOB/GBL+EA+EC system, these trends provide general guidance how ion conductivities of other electrolyte systems with similar solvent compositions would change with these same variables, and they should constitute a useful database for the understanding of more complex systems, such as quaternary mixtures.

The electrolyte conductivity depends on the solvent composition (GBL:EA:EC ratio), LiBOB concentration, and temperature. For example, the best electrolyte for high-temperature application is that which contains 1 kmol m⁻³ LiBOB in GBL+EA+EC of composition 1:1:0.1. For low-temperature applications, the best electrolyte is that which contains 0.7 kmol m⁻³ LiBOB in GBL+EA+EC of composition 1:1:0. In terms of conductivity, the co-solvent EC is not recommended at low temperature because its high viscosity and melting point affects the ion mobility and decreases conductivity.

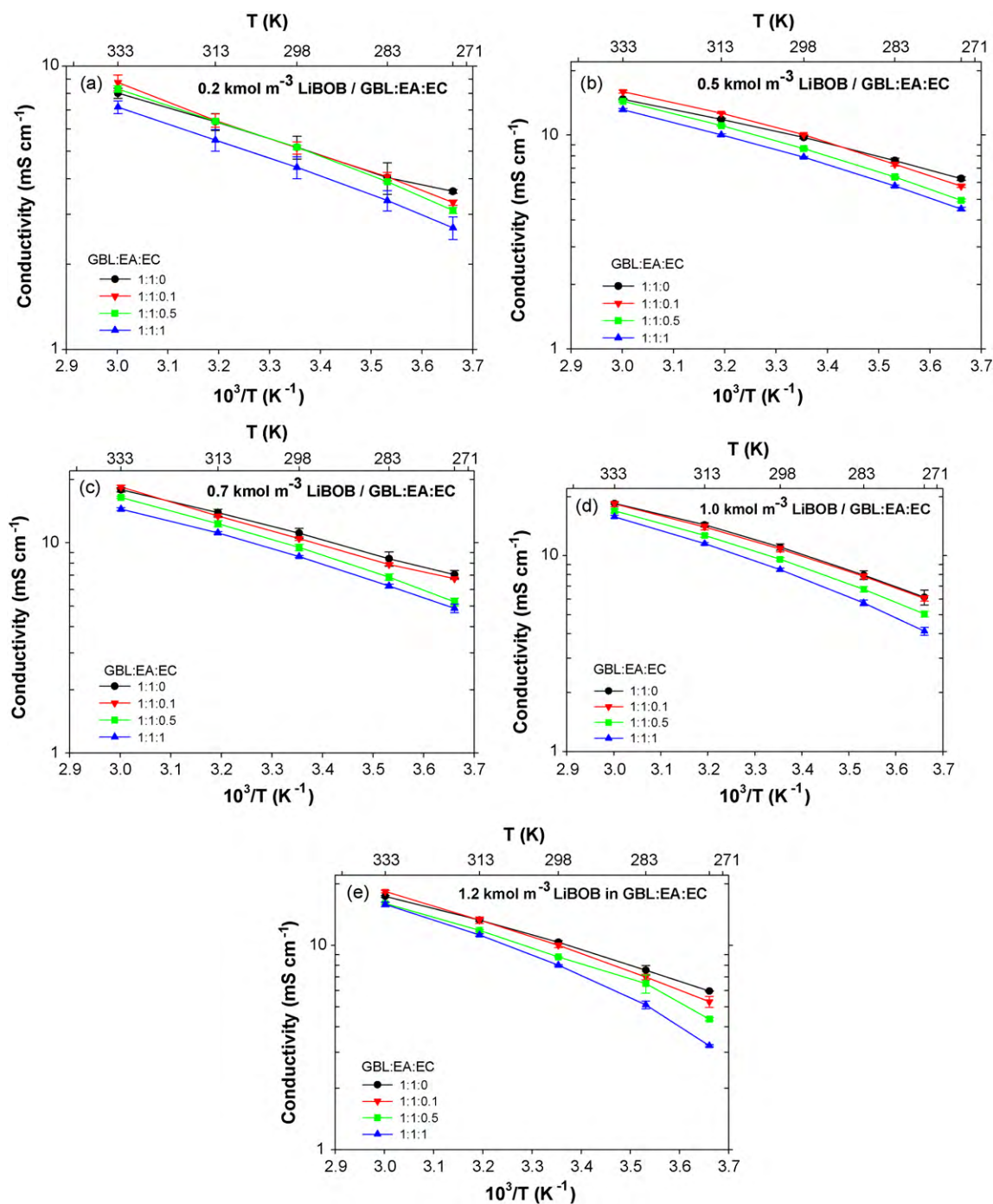


Fig. 9. Temperature dependence of conductivity for (a) 0.2 kmol m^{-3} , (b) 0.5 kmol m^{-3} , (c) 0.7 kmol m^{-3} , (d) 1.0 kmol m^{-3} , and (e) 1.2 kmol m^{-3} LIBOB in a GBL:EA:EC solvent mixture of varying EC content.

Acknowledgments

The authors gratefully acknowledge funding from Kuwait University, the BATT program, U.S. Department of Energy, and the DOE Office of FreedomCar. The authors express their gratitude toward Professor Saad Khan (NCSSU) for use of his lab's rheometer and Dr. Yangxing Li for help in measuring viscosity.

References

- [1] J.M. Tarascon, M. Armand, *Nature (London)* 414 (2001) 395.
- [2] S.E. Sloop, J.K. Pugh, S. Wang, J.B. Kerr, K. Kinoshita, *Electrochem. Solid-State Lett.* 4 (2001) A42.
- [3] E. Zinigrad, L. Larush-Asraf, J.S. Gnanaraj, M. Sprecher, D. Aurbach, *Thermochim. Acta* 438 (2005) 184.
- [4] A.M. Andersson, K. Edstrom, *J. Electrochem. Soc.* 148 (2001) A1100.
- [5] D. Aurbach, K. Gamolsky, B. Markovsky, G. Salitra, Y. Gofer, *J. Electrochem. Soc.* 147 (2000) 1322.
- [6] A.D. Pasquier, A. Blyr, P. Courjal, G. Armatucci, B. Gerand, J.M. Tarascon, *J. Electrochem. Soc.* 146 (1999) 428.
- [7] K. Amine, J. Liu, S. Kang, I. Belharouak, Y. Hyung, D. Vissers, G. Henriksen, *J. Power Sources* 129 (2004) 14.
- [8] R. Jasinski, S. Carroll, *J. Electrochem. Soc.* 117 (1970) 218.
- [9] K.M. Abraham, J.L. Goldman, D.L. Natwig, *J. Electrochem. Soc.* 129 (1982) 2404.
- [10] C. Nanjundiah, J.L. Goldman, L.A. Dorney, V.R. Koch, *J. Electrochem. Soc.* 135 (1988) 2914.
- [11] V.R. Koch, *J. Electrochem. Soc.* 126 (1979) 181.
- [12] A. Webber, *J. Electrochem. Soc.* 138 (1991) 2586.
- [13] S.S. Zhang, K. Xu, T.R. Jow, *J. Electrochem. Soc.* 149 (2002) A586.

- [14] N. Takami, T. Ohsaki, H. Hasebe, M. Yamamoto, *J. Electrochem. Soc.* 149 (2002) A9.
- [15] S.S. Zhang, K. Xu, T.R. Jow, *Electrochem. Commun.* 4 (2002) 928.
- [16] S.S. Zhang, K. Xu, T.R. Jow, *J. Solid State Electrochem.* 7 (2003) 147.
- [17] F. Croce, A. D'Aprano, C. Nanjundiah, V.R. Koch, C. Walker, M. Salomon, *J. Electrochem. Soc.* 143 (1996) 154.
- [18] M. Ue, *J. Electrochem. Soc.* 141 (1994) 3336.
- [19] L.J. Krause, W. Lamanna, J. Summerfield, M. Engle, G. Korba, R. Loch, R. Atanasoski, *J. Power Sources* 68 (1997) 320.
- [20] U. Lischka, U. Wietelmann, M. Wegner, German Patent DE 19829030 C1, 1999, doi:10.1149/1.1701584.
- [21] W. Xu, C.A. Angell, *Electrochem. Solid-State Lett.* 4 (2001) E1.
- [22] S.S. Zhang, *J. Power Sources* 162 (2006) 1379.
- [23] K. Xu, S.S. Zhang, U. Lee, J.L. Allen, T.R. Jow, *J. Power Sources* 146 (2005) 79.
- [24] W. Xu, C.A. Angell, *Solid State Ionics* 147 (2002) 295.
- [25] B.T. Yu, W.H. Qiu, F.S. Li, G.X. Xu, *Electrochem. Solid-State Lett.* 9 (2006) A1.
- [26] K. Xu, S. Zhang, B.A. Poese, T.R. Jow, *Electrochem. Solid-State Lett.* 5 (2002) A259.
- [27] J.S. Gnanaraj, M.D. Levi, Y. Gofer, D. Aurbach, M. Schmidt, *J. Electrochem. Soc.* 150 (2003) A445.
- [28] K. Xu, *Chem. Rev.* 104 (10) (2004) 4303.
- [29] K. Xu, *J. Electrochem. Soc.* 155 (2008) A733.
- [30] M. Salomon, E. Plichta, *J. Electrochim. Acta* 30 (1985) 113.
- [31] M.S. Ding, K. Xu, T.R. Jow, *J. Electrochem. Soc.* 152 (2005) A132.
- [32] A. Chagnes, B. Carre, P. Willmann, D. Lemordant, *J. Power Sources* 109 (2002) 203.
- [33] T. Fukushima, Y. Matsuda, H. Hashimoto, R. Arakawa, *J. Power Sources* 110 (2002) 34.
- [34] A. Chagnes, B. Carre, P. Willmann, R. Dedryvere, D. Gonbeau, D. Lemordant, *J. Electrochem. Soc.* 150 (2003) A1255.
- [35] T.R. Jow, K. Xu, M.S. Ding, S.S. Zhang, J.L. Allen, K. Amine, *J. Electrochem. Soc.* 151 (2004) A1702.
- [36] K. Sawai, T. Ohzuku, *J. Electrochem. Soc.* 150 (2003) A674.
- [37] M.C. Smart, B.V. Ratnakumar, S. Surampudi, *J. Electrochem. Soc.* 149 (2002) A361.
- [38] S. Herreyre, O. Huchet, S. Barusseau, F. Pertont, J.M. Bodet, Ph. Biensan, *J. Power Sources* 97/98 (2001) 576.
- [39] J. Vetter, P. Novak, *J. Power Sources* 119/121 (2003) 338.
- [40] M. Riley, P.S. Fedkiw, S.A. Khan, *J. Electrochem. Soc.* 149 (2002) A667.
- [41] A. Cisak, L. Werblan, *High-energy Non-aqueous Batteries*, Ellis Horwood, New York, 1993 (chapter 7).
- [42] M. W. Riley, *Hectorite-based nanocomposite electrolytes for lithium-ion batteries*, PhD Thesis, North Carolina State University, 2002.
- [43] Y. Choquette, G. Brisard, M. Parent, D. Brouillette, G. Perron, J.E. Desnoyers, M. Armand, D. Gravel, N. Slougui, *J. Electrochem. Soc.* 145 (1998) 3500.
- [44] J. Barthel, R. Buestrich, E. Carl, H.J. Gores, *J. Electrochem. Soc.* 143 (1996) 3565.
- [45] J. Barthel, H.J. Gores, G. Schmeer, B. Bunsenges, *Phys. Chem.* 83 (1979) 911.
- [46] B.E. Conway, *Electrochemical Super capacitors-Scientific Fundamentals and Technological Applications*, Kluwer Academic/Plenum Publishers, New York, 1999 (chapter 13).
- [47] I. Geoffroy, P. Willmann, K. Mesfae, B. Carré, D. Lemordant, *Electrochim. Acta* 45 (2000) 2019.
- [48] J.O.'M Bockris, A.K.N. Reddy, *Modern Electrochemistry*, vol. 2, 2nd ed., Plenum Press, New York, 2000.
- [49] F. Azeez, *Transport properties of lithium bis(oxalate)borate-based electrolyte for lithium-ion cells*, Master Thesis, North Carolina State University, 2005.