

# Lithium ion conduction in ionic liquid-based gel polymer electrolyte

Minato Egashira\*, Hirotaka Todo, Nobuko Yoshimoto, Masayuki Morita

*Graduate School of Science and Engineering, Yamaguchi University, Tokiwadai, Ube, Yamaguchi 755-8611, Japan*

Received 3 July 2007; received in revised form 4 October 2007; accepted 19 October 2007

Available online 26 October 2007

## Abstract

The conduction mechanism of gel electrolyte system consisting of poly(ethylene oxide) branched poly(methyl methacrylate) (PEO-PMA) matrix and ionic liquid containing lithium salt has been investigated. The kinetics of ion conduction and the mobility of lithium ion are different by the kind of ionic liquid; 1-ethyl-3-methyl imidazolium bis(trifluoromethane sulfone)imide (EMITFSI) or hexyltrimethylammonium bis(trifluoromethane sulfone)imide (HTMATFSI). Lithium ion exhibits a significant contribution for ion conduction in the gel electrolyte containing HTMATFSI. In contrast, the mobility of lithium ion is not obvious in the gel electrolyte containing EMITFSI. Such difference is considered to originate from the difference in ‘miscibility’ of polymer component in ionic liquid.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Gel electrolyte; Ionic liquid; Lithium ion conduction

## 1. Introduction

The application of ionic liquid to electrolyte component of lithium battery has been an attractive issue for the improvement of cell safety [1]. Unfortunately, one of the most versatile ionic liquids, 1-ethyl-3-methyl imidazolium (EMI)-based ones, are not adequate for such usage due to their low cathodic stability [2]. Therefore, much attempt has been made to find novel ionic liquid with good compatibility toward negative electrode [3–6], or to apply additives to stabilize the electrolyte/negative electrode interface [2,7–11]. In some studies cells containing ionic liquid-based electrolyte displayed good charge–discharge properties except for rate capability.

In order to be used as electrolyte solvent, several problems for ionic liquid, its high viscosity, the mobility of lithium ion in ionic liquid electrolyte, etc., are still remained. The viscosity of ionic liquids themselves is markedly higher than that of conventional organic solvents. For example, the viscosity of EMI salt of bis(trifluoromethane sulfone)imide (TFSI), one of the least viscous ionic liquids, is as high as 30 cP around room temperature [12]. The dissolution of lithium salt into ionic liquid increases further the viscosity and decreases the conduc-

tivity, which implies that lithium salt forms contact ion pairs in ionic liquid solution [13]. Therefore, it seems a good idea that ionic liquid is utilized as a liquid component in a gel polymer electrolyte system instead of organic solvent electrolyte. Ionic liquids are expected to provide a similar plasticizing effect to conventional organic solvent electrolyte at as a low temperature as room temperature regardless of their viscosities.

For gel polymer electrolyte systems containing organic solvent electrolyte used in lithium batteries, such matrices as co-polymer of vinylidene difluoride and hexafluoropropylene (PVdF-HFP), which exhibits low ability to coordinate to lithium ion, are generally used because of organic solvent can dissociate lithium salt sufficiently. On the other hand, polymer matrix can be selected to contribute to the dissociation of lithium salt for gel electrolyte systems containing ionic liquids, exhibiting themselves low ability to dissociate a lithium salt. In this case ionic liquid in the gel system play the role in plasticizer, and a medium for a short range conduction of lithium ion. This concept is expected to be helpful for the design of an ionic liquid-based gel electrolyte system providing good performance.

Indeed, there have been many studies on the preparation of gel electrolyte systems containing ionic liquid. Noda and Watanabe proposed the conceptual name “*ionic gel*” to the products. In case that the application is limited to lithium battery electrolyte, many candidates have already been proposed [14]. Nakagawa et al. prepared gel electrolyte system consisting of poly(ethylene

\* Corresponding author. Tel.: +81 836 85 9212; fax: +81 836 85 9201.  
E-mail address: [minato@yamaguchi-u.ac.jp](mailto:minato@yamaguchi-u.ac.jp) (M. Egashira).

oxide) (PEO) as polymer matrix and  $\text{LiBF}_4/\text{EMIBF}_4$  ionic liquid solution, and applied the gel electrolyte with  $\text{LiTiO}_2/\text{LiCoO}_2$  model cell [15]. Shin et al. have energetically investigated to utilize a gel electrolyte system containing pyridinium ionic liquid [16–18]. The authors have proposed the gel electrolyte system containing ionic liquid and polymethacrylate having ethylene oxide side chain as matrix, where magnesium ion conducts [19,20]. In contrast, the optimization of the material selection, composition and structure of the gel electrolyte for good conduction of lithium ion are not sufficient over these studies, expect for some special cases such as polyanion system [21,22] and the system containing so called ‘lithium ionic liquid’ [23]. In order to design a high-performance ionic liquid–gel electrolyte, or to select polymer matrix with which ionic liquid show a good ion-conduction property, it is necessary to know the influence of the interaction mode between ionic liquid and polymer matrix on ion (in particular lithium ion) conduction behavior.

In the present study, the authors prepared a series of gel electrolyte containing two kinds of ionic liquid having different cations, and poly(methacrylate) having partially cross-linked ethylene oxide branches (PEO-PMA). The ionic conductivity and lithium ion mobility are compared in terms of the difference in ionic liquid component and the length of ethylene oxide unit in PEO-PMA matrix. The influence of the interaction among components (lithium ion, ionic liquid, and polymer matrix) on the lithium ion conduction is to be revealed for the optimum design of gel electrolyte system.

## 2. Experimental

In the present study, two kinds of ionic liquids, EMITFSI and hexyltrimethylammonium bis(trifluoromethane sulfone)imide (HTMATFSI), were applied. EMITFSI with high purity was supplied by Nippon Synthetic Chemical Co., Japan. HTMATFSI was prepared by an ion-exchange reaction between HTMABr (Fluka) and LiTFSI (Fluka) in water. The resulting precipitate was collected, washed by water, and dried under vacuum. LiTFSI (Fluka) was dissolved into EMITFSI or HTMATFSI as the content of LiTFSI was to be 20 mol% to prepare LiTFSI/ionic liquid solution.

Ionic liquid/PEO-PMA gel electrolyte was prepared by in situ photopolymerization process as described precisely [19,24]. The precursor of polymer matrix used here was the mixture of poly(ethyleneglycol) monomethacrylate (PEM; Shin-Nakamura Industry Co., Japan) and poly(ethyleneglycol) dimethacrylate (PED; Shin-Nakamura Industry Co., Japan) with the PEM:PED molar ratio of 3:1. Resulting polymer matrix has a cross-linked structure of poly(ethylene oxide) (PEO) branches as shown in Fig. 1. In the present study, two kinds of PEO-PMA matrix having different PEO chain length  $n=4$  and 9, were applied. In all cases the gravimetric ratio of liquid component: PEO-PMA was 7:3. The gel electrolytes are denoted by the existence of lithium salt, cation of ionic liquid, and EO chain length of PEO-PMA matrix: for example, the gel electrolytes containing LiTFSI, consisting of EMITFSI and PEO-PMA with  $n=9$  is denoted as Li-EMI(9), while the gel electrolyte with similar component without LiTFSI is denoted as EMI(9). The prepara-

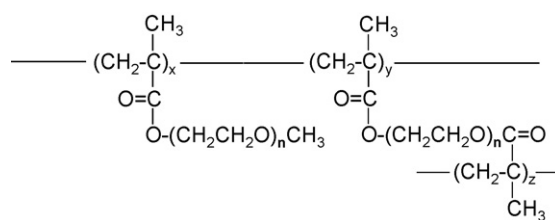


Fig. 1. Structural formula of PEO-PMA matrix.

tion procedure above was carried out in a glove box filled with argon. The thermal behavior of a gel membrane was analyzed using a differential scanning calorimeter (DSC; TA-50WS, Shimadzu Co., Japan). Each sample for DSC analyses in a sealed aluminum pan was first cooled to 173 K ( $-100\text{ }^\circ\text{C}$ ), then heated to 373 K ( $100\text{ }^\circ\text{C}$ ), under the rate of  $10\text{ K min}^{-1}$ .

A hermetically sealed cell consisting of cylindrical stainless-steel (SS) electrodes and a hollow Teflon body was used for electrochemical measurements. For conductivity measurement, the cell was assembled with gel electrolyte membrane after cut into a disk with 13 mm in diameter and SS electrodes. The cell was placed in a sealed transfer vessel and the cell temperature was controlled by a temperature chamber (SU240, Espec Co., Japan). The conductivity measurement was carried out by an alternative-current (ac) method using a frequency response analyzer (Solartron 1260/1286). In each measurement, a  $Z'$  value for the frequency where  $-Z''$  was smallest was picked up as an electrolyte resistance  $R_O$  at prescribed temperature. A conductivity value was calculated from  $R_O$  and the dimension of the disk of gel membrane. The lithium ion transport number of a gel membrane was estimated by ac impedance measurements using the similar sealed cell with lithium foils at both electrolyte/electrode interfaces. The measurement conditions were as follows; at  $55\text{ }^\circ\text{C}$ , 10 mV bias, and the frequency region of  $10^6$  to  $10^{-1}$  Hz. The mobility of lithium ion in gel electrolyte was also estimated by measuring the temperature dependence of relaxation in  $^7\text{Li}$  NMR (JNM-CMX, JEOL Co., Japan). The sample temperature was varied between  $-40$  to  $60\text{ }^\circ\text{C}$ , and the spin-lattice relaxation temperature  $T_1$  was measured at each temperature using a pulse technique.

## 3. Results and discussion

Fig. 2 shows the DSC profiles for heating scan of gel electrolytes consisting of PEO-PMA with  $n=9$  (a) and  $n=4$  (b). In all cases an endothermic peak is observed around  $-60\text{ }^\circ\text{C}$ , which is assigned to the glass transition of PEO-PMA matrix [25]. The onset temperature of this peak shows a significant shift depending on both polymer matrix, ionic liquid component and the existence of LiTFSI. In particular, the ionic liquid used provides the strongest influence to the onset temperature: the gel electrolytes containing EMITFSI and HTMATFSI show the onset temperature around  $-70$  and  $-58\text{ }^\circ\text{C}$ , respectively. While the effect of the existence of LiTFSI appears to be rather small, the behavior of the onset temperature deviation on coexisting LiTFSI is dependent on the type of ionic liquid. The gel electrolytes containing EMITFSI show similar onset temperature

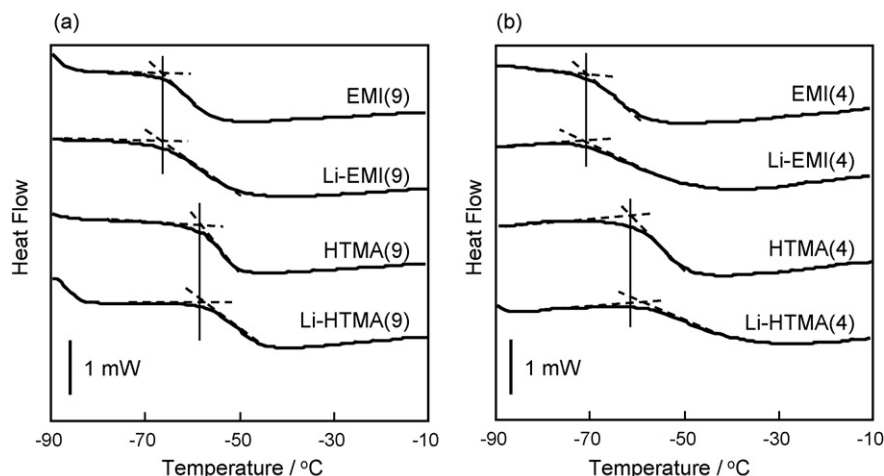


Fig. 2. DSC profiles of ionic liquid/PEO-PMA gel electrolytes on heating. Heating rate:  $10^{\circ}\text{C min}^{-1}$  (a) PEO-PMA matrix with  $n=9$ , (b) PEO-PMA matrix with  $n=4$ .

regardless of coexisting LiTFSI. In contrast, the coexisting of LiTFSI provides a higher shift of the onset temperature in the case of the gel electrolytes containing HTMATFSI.

Fig. 3a shows the Arrhenius plots of the conductivity of gel electrolytes containing EMI(9), Li-EMI(9), HTMA(9), and Li-HTMA(9) with various liquid components. The Arrhenius plots for the conductivity of liquid components with the same scale are shown in Fig. 3b. While the conductivity values of gel electrolytes are onefold lower than those of liquid components, Li-EMI(9) still exhibits the conductivity of ca.  $2.3 \times 10^{-4} \text{ S cm}^{-1}$ . Moreover, the conductivity behavior under the coexistence of LiTFSI is particularly different between the liquid and the gel systems. For the liquid system, the conductivity significantly decreases over the temperature range plotted when LiTFSI is dissolved into both ionic liquids. In contrast, the amount of conductivity decrease when coexisting LiTFSI is rather small in the gel electrolyte systems regardless of the type of ionic liquid. The authors previously confirmed that the polymer matrix used in the present study, PEO-PMA, can dissociate magnesium salt [20]. Also in a LiTFSI/ionic liquid/PEO-PMA gel electrolyte system, PEO-PMA polymer matrix is considered to contribute to accelerate the dissociation of LiTFSI by solvating with lithium ion. In such a gel electrolyte system, ionic liquid must play a main role with conductance. Under such assumption, the conductivity behavior shown here is reasonable.

Fig. 3a exhibits another interesting feature for the comparison of the conductivity of gel electrolytes containing different type of ionic liquid. The slope of the Arrhenius plot for Li-EMI(9) appears to be similar to that for EMI(9). In contrast, the feature of Arrhenius plot Li-HTMA(9) is obviously different from that for HTMA(9). While the Arrhenius plot for HTMA(9) shows a linear relationship, the one for Li-HTMA(9) shows a slight convex relationship, suggesting an increase of activation energy for conductance at lower temperature. The apparent activation energies ( $E_a$ ) for conductance, as relative indicators for the slopes of the Arrhenius plots, are estimated as 30, 34, 35, 52  $\text{kJ mol}^{-1}$  for EMI(9), Li-EMI(9), HTMA(9), and Li-HTMA(9), respectively.

Fig. 4 shows the Arrhenius plots for the gel electrolytes containing PEO-PMA ( $n=4$ ) matrix. The feature of the Arrhenius plot, *i.e.*, the tendency of the change of the slope of Arrhenius plot by the coexistence of LiTFSI, is basically similar to that for the gel electrolytes containing PEO-PMA ( $n=9$ ). However, in this case, particularly for the gel electrolyte with EMITFSI, the coexistence of LiTFSI significantly decreases the conductivity. The conductivity drop from EMI(4) to Li-EMI(4) is a reflect of the lower dissociation property of this polymer matrix than that with longer EO chains. In the case that the polymer matrix is changed from PEO-PMA ( $n=9$ ) to that of  $n=4$ , the slope for the gel electrolyte with HTMATFSI increases by the coexistence of LiTFSI. The apparent activation energies ( $E_a$ ) for conductance are estimated as 30, 32, 35, 57  $\text{kJ mol}^{-1}$  for EMI(4), Li-EMI(4), HTMA(4), and Li-HTMA(4), respectively. The apparent  $E_a$  values, as relative indicators for the slopes of the Arrhenius plots, are close to those for the gel electrolytes with EO chains of  $n=9$  in EMITFSI but different at some extent in HTMATFSI.

In order to estimate the mobility of lithium in the gel electrolytes, the spin-lattice relaxation time  $T_1$  for lithium ion was measured at various temperatures. The measured  $T_1^{-1}$  values, an indication of the relaxation rate, of the gel electrolytes with each ionic liquid component are plotted as a function of inverse temperature in Fig. 5. All gel electrolytes provide similar convexes except for the Li-HTMA(4). These convexes are typical Bloembergen–Purcell–Pound (BPP) behavior found for polymer and gel electrolyte systems conducting lithium ion [26,27]. Both gel electrolytes containing EMITFSI exhibit a similar maximum temperature of  $T_1^{-1}$  around  $20^{\circ}\text{C}$ . In contrast, Li-HTMA(9) exhibits a maximum around  $40^{\circ}\text{C}$  while Li-HTMA(4) shows no peak at measured temperature range. The mobility of lithium in these electrolyte systems are indicated by the peak temperature of  $T_1^{-1}$  [27]. Therefore, the results in Fig. 5 indicate that the mobility of lithium is similar regardless the length of EO unit in the gel electrolytes containing EMITFSI, while Li-HTMA(9) exhibits higher lithium mobility than Li-HTMA(4). The gel electrolytes containing EMITFSI appear to have higher mobility of lithium than those containing

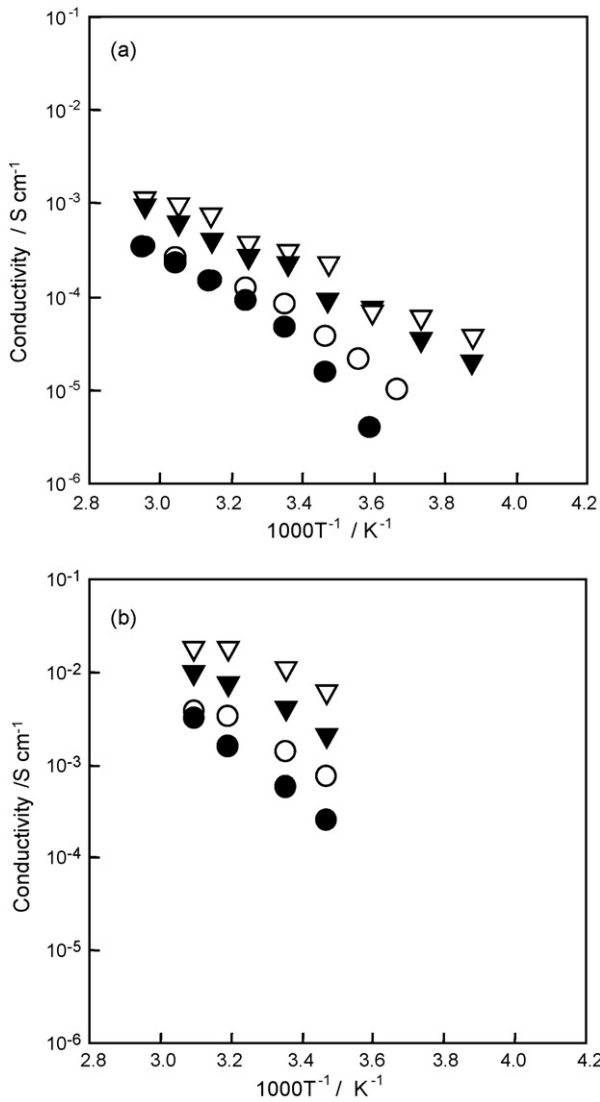


Fig. 3. (a) Arrhenius plots for the conductivity of ionic liquid/PEO-PMA gel electrolytes. ( $\nabla$ ) EMI(9), ( $\blacktriangledown$ ) Li-EMI(9), ( $\circ$ ) HTMA(9), ( $\bullet$ ) Li-HTMA(9); (b) Arrhenius plots for the conductivity of ionic liquids and their LiTFSI Solutions. ( $\nabla$ ) EMITFSI, ( $\blacktriangledown$ ) LiTFSI/EMITFSI, ( $\circ$ ) HTMATFSI, ( $\bullet$ ) LiTFSI/HTMATFSI.

HTMATFSI due to the lower peak temperature of EMI-based gel electrolyte than those in HTMATFSI.

The mobility of lithium species in the gel electrolytes was estimated also by an ac impedance measurement using Li/gel electrolyte/Li symmetrical cell. Fig. 6a and b shows Nyquist plots for the cell consisting of Li-EMI(a) and LiHTMA(b) gel electrolytes. For Li-EMIs, a spike without any semicircle is observed in each Nyquist diagram regardless the kind of matrix. Such a feature is typical for the blocking electrode/electrolyte interface. It should be noted that the diagram for Li-EMIs is deformed even after 1 day storage of cell to provide a semicircle feature. The deformation of the diagram in Li-EMIs may be due to the decomposition of a certain gel electrolyte component, likely the ionic liquid. In contrast, the interface between lithium electrode and the gel electrolyte provides a multiple semicircle feature after an inductive portion around high fre-

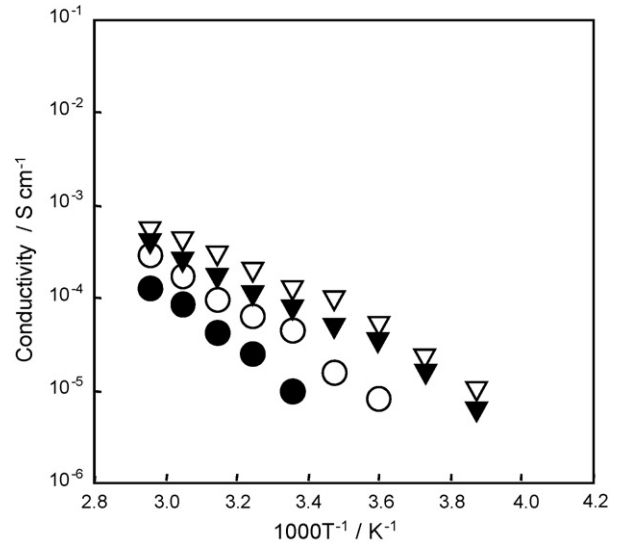


Fig. 4. Arrhenius plots for the conductivity of liquid/PEO-PMA gel electrolytes. ( $\nabla$ ) EMI(4), ( $\blacktriangledown$ ) Li-EMI(4), ( $\circ$ ) HTMA(4), ( $\bullet$ ) Li-HTMA(4).

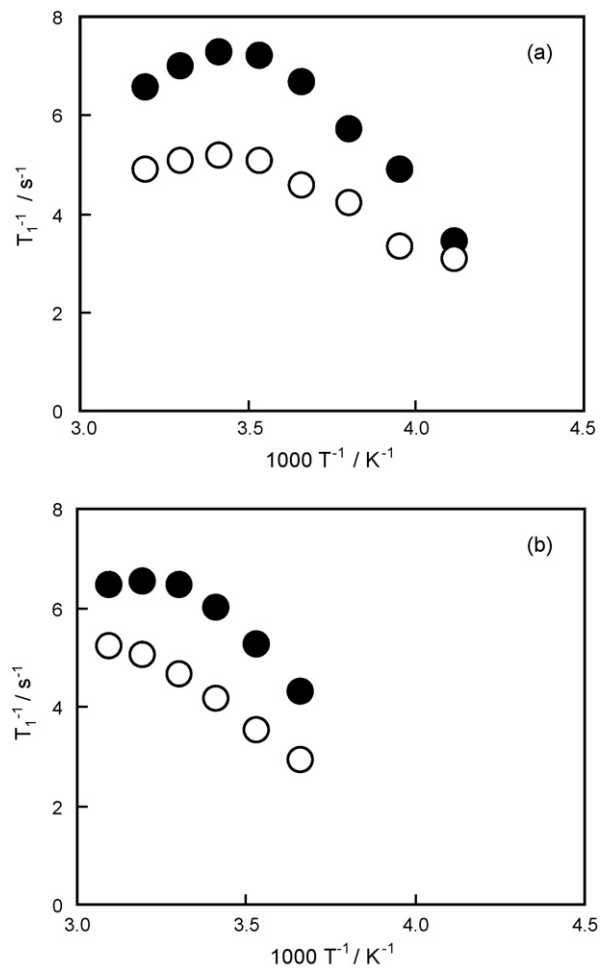


Fig. 5. Temperature dependence of  ${}^7\text{Li}$  spin-lattice relaxation rate  $T_1^{-1}$  in ionic liquid/PEO-PMA gel electrolytes. (a) Containing EMITFSI, ( $\bullet$ ) Li-EMI(9), ( $\circ$ ) Li-EMI(4); (b) containing HTMATFSI, ( $\bullet$ ) Li-HTMA(9), ( $\circ$ ) Li-HTMA(4).

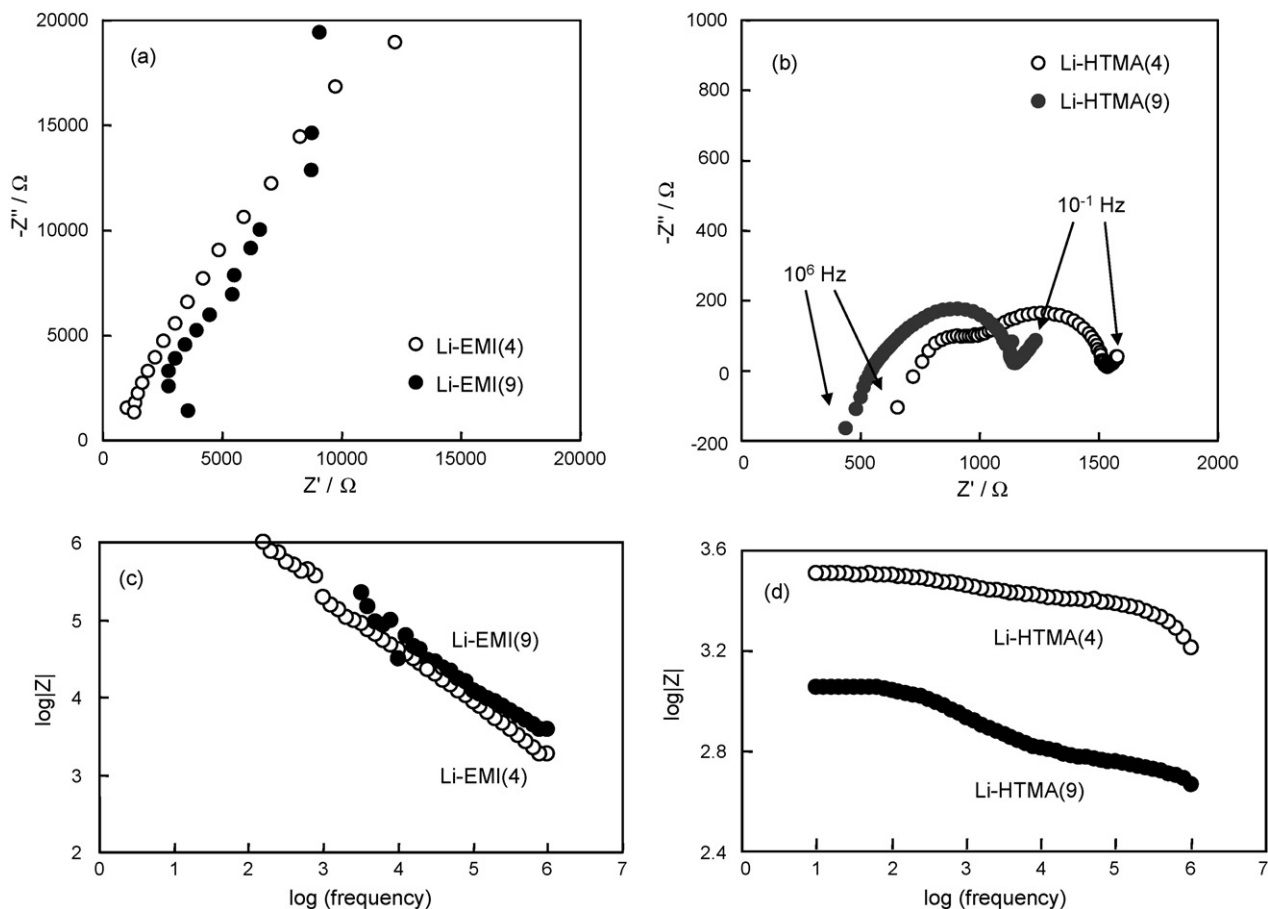


Fig. 6. Impedance diagrams for Li/gel electrolyte/Li cells. Temperature: 55 °C. (a) Nyquist plots of the cell containing the Li-EMI gel electrolytes. (b) Nyquist plots of the cell containing the Li-HTMA gel electrolytes. (c) Bode plots of the cell containing the Li-EMI gel electrolytes. (d) Bode plots of the cell containing the Li-HTMA gel electrolytes.

quency limit. The inductive portion around  $10^6$  Hz may be due to the electron-conductive part of the cell assembly. The width of semicircle region on the  $Z'$  axis is around 700–800  $\Omega$  for both Li-HTMA(4) and Li-HTMA(9). And also in both cases, a very small line at as a low frequency as  $10^{-1}$  Hz attributed to Warburg impedance is obtained. These features are typical in a limited diffusion field frequently observable for lithium electrode/lithium-ion conductive polymer electrolytes [28]. Fig. 6c and d shows the corresponding Bode plots of Li-EMIs and Li-HTMAs, respectively. Li-EMIs also clearly show the different frequency dependences of impedance from those of Li-HTMAs. Such a difference in the impedance diagrams suggests that the electrochemically active lithium ion conducts only in the gel electrolytes Li-HTMAs. This finding is somewhat contradict from the results of the temperature dependence of NMR relaxation time, which indicates the higher mobility of lithium in the gel electrolyte based on EMI than that based on HTMA. Here the authors intend that NMR methods do not distinguish the migration in an electric field with the diffusion as a neutral species. The motion observed in Li-EMIs by  $^7\text{Li}$  NMR is therefore suggested to be the diffusion as an electrochemically inactive species, namely an ion pair. This may be the reason why the minimum temperatures of  $T_1$  in the  $^7\text{Li}$  NMR relaxation measurements for the Li-EMIs are similar regardless

of the matrix. It should be noted that a ‘native film’ which is considered to exist on lithium foil before use, may affect the charge transfer process on Li/the gel electrolyte interfaces. The net transfer rate of lithium ion across the Li-EMI, where the mobility of  $\text{Li}^+$  is small, is considered to become negligibly low also due to the interrupt by a native film, while the influence of such interrupt by a native film appears to be small in case of the Li-HTMA, where the mobility of  $\text{Li}^+$  is rather large. The authors also made an effort to measure the lithium ion transport number ( $t_{\text{Li}^+}$ ) of the Li-HTMA gel electrolytes using a direct current polarization. The resulting  $t_{\text{Li}^+}$  values were ranged within 0.10–0.16 regardless of the type of polymer matrix, while the lack of thorough reproducibility for the  $t_{\text{Li}^+}$  measurements prevented us from discussing the effect of polymer matrix to the  $t_{\text{Li}^+}$  values.

All the results above indicate that the conduction behavior of a PEO-PMA/LiTFSI/ionic liquid gel electrolyte system is varied with the type of ionic liquid component. When HTMATFSI is contained in the gel electrolyte system, both the coexistence of lithium salt and the selection of polymer component, with different dissociation mode of LiTFSI, contributes to the conduction behavior and lithium mobility in the gel electrolyte. In contrast, the conduction behavior of the EMITFSI-containing gel electrolytes appears to be independent from such factors.

As reflected in the conductivity for the gel electrolytes with or without LiTFSI, in both cases lithium ion is considered to be dissociated by EO chain. The dissociated lithium ion surely contributes to the conduction on some extent in the HTMATFSI-containing gel electrolytes at some extent. In contrast, lithium ion appears to be inactive as conductive species in the EMITFSI-containing systems. One interpretation for such behavior is as described below. In the gel electrolyte system containing EMITFSI, a lithium ion is suggested to be solvated strongly with ethylene oxide chains and ‘fixed’ in polymer matrix. On the other hand, a dissociated lithium ion acts as a charge carrier, perhaps through HTMATFSI. The expected schematic images for the ion conduction in the gel electrolyte systems containing EMITFSI and HTMATFSI are illustrated in Fig. 7. The difference of the motion of a lithium ion in these two systems may originate from the difference of the interaction between ionic liquid and polymer matrix. The authors previously revealed that the miscibility of organic carbonates in EMITFSI and HTMATFSI: in HTMATFSI small amount of carbonate is miscible more uniformly than in EMITFSI [13]. Also in the case of polymer component, the ‘miscibility’ of PEO-PMA polymer in these two types of ionic liquid appears to be different. In the gel electrolyte containing EMITFSI, ionic liquid component may be somewhat isolated from polymer matrix containing dissociated lithium ion. Therefore, the migration of the lithium ion through EMITFSI phase appears less probable than that through HTMATFSI, which is well ‘miscible’ with poly(ethylene oxide) matrix.

From the results shown above, HTMATFSI appears to be preferable for the component of gel electrolyte system compared with EMITFSI. However, the good property of EMITFSI as a plasticizer, which provides higher absolute mobility of lithium, is still attractive. Therefore, such investigation will be required as the finding of adequate polymer matrix having moderate interaction mode toward EMI-based ionic liquids for realization of novel ionic liquid-based gel electrolyte system with applicable properties.

#### 4. Conclusion

The mobility of lithium ion in the gel electrolyte consisting of ionic liquid and poly(ethylene oxide)-based polymer matrix is markedly influenced by the selection of ionic liquid. Quaternary ammonium-based ionic liquid appears to be more compatible than imidazolium-based ones for this purpose, due to preferable interaction between ionic liquid and polymer matrix, which enables the facile conduction of lithium ion in ionic liquid phase. The optimization of the composition of gel electrolyte should be based on such an interaction mode.

#### Acknowledgements

A part of the present study has been financially supported by CREST of JST (Japan Science and Technology Agency). A part of the present study has been financially supported by Electric Technology Research Foundation of Chugoku. The sample of EMITFSI was kindly provided by the Nippon Synthetic Chemical Industry Co., Ltd.

#### References

- [1] P.G. Balakrishnan, R. Ramesh, T. Prem Kumar, J. Power Sources 155 (2006) 401.
- [2] J. Fuller, R.T. Carlin, R.A. Osteryoung, J. Electrochem. Soc. 144 (1997) 3881.
- [3] D.R. MacFarlane, P. Meakin, J. Sun, N. Amini, M. Forsyth, J. Phys. Chem. B 103 (1999) 4164.
- [4] P.C. Howlett, D.R. MacFarlane, A.F. Hollenkamp, Electrochem. Solid State Lett. 7 (2004) A97.
- [5] H. Sakaebe, H. Matsumoto, Electrochem. Commun. 5 (2003) 594.
- [6] T. Sato, T. Matsuo, S. Marukane, K. Takagi, J. Power Sources 138 (2004) 253.
- [7] N. Koura, K. Iizuka, Y. Idemoto, K. Ui, Electrochemistry 67 (1999) 706.
- [8] Y. Katayama, M. Yukumoto, T. Miura, Electrochem. Solid State Lett. 6 (2003) A96.
- [9] M. Egashira, T. Kiyabu, I. Watanabe, S. Okada, J. Yamaki, Electrochemistry 71 (2003) 1114.
- [10] M. Egashira, M. Nakagawa, I. Watanabe, S. Okada, J. Yamaki, J. Power Sources 146 (2005) 685.
- [11] M. Egashira, M. Tanaka-Nakagawa, I. Watanabe, S. Okada, J. Yamaki, J. Power Sources 160 (2006) 1387.
- [12] P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, Inorg. Chem. 35 (1996) 1168.
- [13] M. Egashira, H. Shimomura, N. Yoshimoto, M. Morita, J. Yamaki, Electrochemistry 73 (2005) 585.
- [14] A. Noda, M. Watanabe, Electrochim. Acta 45 (2000) 1265.
- [15] H. Nakagawa, S. Izuchi, K. Kuwana, T. Nukuda, Y. Aihara, J. Electrochem. Soc. 150 (2003) A695.

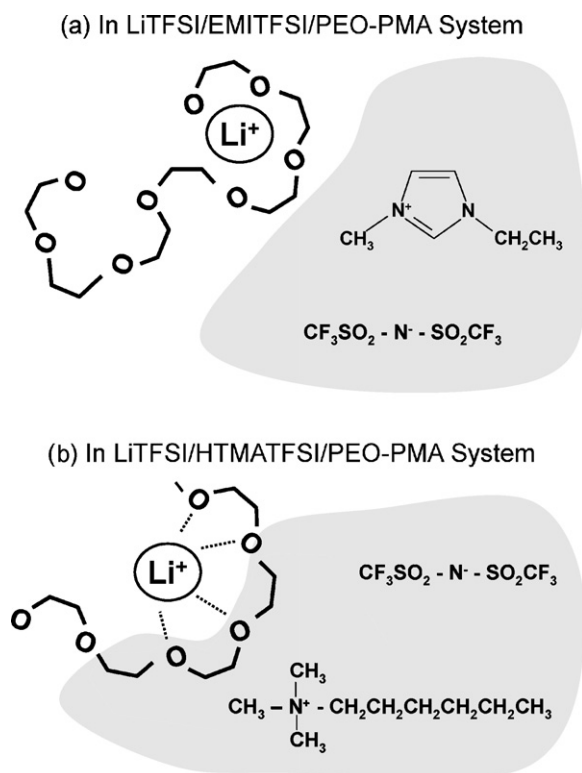


Fig. 7. Schematic model for lithium ion conduction in ionic liquid/PEO-PMA gel electrolyte system.

- [16] J.-H. Shin, W.A. Henderson, S. Passerini, *Electrochem. Commun.* 5 (2003) 1016.
- [17] J.-H. Shin, W.A. Henderson, C. Tizzani, S. Passerini, S.-S. Jeong, K.-W. Kim, *J. Electrochem. Soc.* 153 (2006) A1649.
- [18] J.-H. Shin, W.A. Henderson, S. Scaccia, P. Paolo Prosini, S. Passerini, *J. Power Sources* 156 (2006) 560.
- [19] N. Yoshimoto, T. Shirai, M. Morita, *Electrochim. Acta* 50 (2005) 3866.
- [20] M. Morita, T. Shirai, M. Egashira, N. Yoshimoto, *Electrochemistry* 73 (2005) 579.
- [21] J. Sun, D.R. MacFarlane, M. Forsyth, *Solid State Ionics* 147 (2002) 333.
- [22] T. Sato, S. Marukane, T. Narutomi, T. Akao, *J. Power Sources* 164 (2007) 390.
- [23] H. Shobukawa, H. Tokuda, Md. Abu Bin Hasan Susan, M. Watanabe, *Electrochim. Acta* 50 (2005) 3872.
- [24] M. Morita, T. Fukumasa, M. Motoda, H. Tsutsumi, Y. Matsuda, T. Takahashi, H. Ashitaka, *J. Electrochem. Soc.* 137 (1990) 3401.
- [25] M. Morita, F. Araki, K. Kashiwamura, N. Yoshimoto, M. Ishikawa, *Electrochim. Acta* 45 (2004) 1335.
- [26] S.H. Chung, K.R. Jeffrey, J.R. Stevens, *J. Chem. Phys.* 94 (1991) 1803.
- [27] L.V.S. Lopes, G.O. Machado, A. Pawlicka, J.P. Donoso, *Electrochim. Acta* 50 (2005) 3978.
- [28] M. Watanabe, N. Ogata, in: J.R. MacCallum, C.A. Vincent (Eds.), *Polymer Electrolyte Reviews*, vol. 1, Elsevier, 1987, p. 39.