An Investigation of Gel Polymer Electrolytes Plasticized with Imidazolium Ionic Liquid

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Gel polymer electrolytes were developed by adding room temperature ionic liquid 1-butyl-3-methylimidazolium *bis*(trifluoromethyl-sulfonyl)imide in poly(glycidyl methacrylate) matrix with 30 wt. % of lithium *bis*(trifluoromethylsulfonyl)imide salt. The physical properties of the transparent and non-volatile membranes were investigated. The interactions between polymer, ionic liquid and salt were studied using Fourier transformation infra-red. Besides, the thermal properties were investigated using differential scanning calorimetry, whereas the ionic conductivity of the membranes was looked into using electrochemical impedance spectroscopy. The results showed insignificant interactions between oxygen atoms in polymer backbone and ionic dopants. Nevertheless, it was observed that a decrease in the temperature for glass transition led to an increase in the conductivity of ionic up to 2.66×10^{-6} S cm^{-1} and a decrease in the activation energy for PGMA-30 wt. % of LiTFSI-BmimTFSI mixtures in the membrane.

Keywords: Gel polymer electrolytes, Ionic conductivity, 1-Butyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide, Ionic liquids.

INTRODUCTION

Gel polymer electrolytes are potential candidates to be used as electrolyte membranes in lithium batteries due to its high ionic conductivity and they possess both solid and liquid properties[1]. Their mechanism of conductivity is almost similar to liquid electrolyte, but gels are safer and have a more stable and flexible form. Usually, they are prepared by dissolving polymer, salt and some additive as plasticizer to obtain flexible, light weighed and highly ionic conductive membranes[2,3]. Electrolyte rich plasticizers provide a pathway for ionic conductivity to occur[4]. Nevertheless, the use of plasticizers, such as ethylene carbonate, propylene carbonate, dimethyl carbonate and diethyl carbonate, leads to some problems like flammable and volatile and therefore, limit their safety and their use in lithium batteries. Besides, they are also reactive to lithium metal surface[5]. Thus, to overcome this problem, ionic liquids that are chemically stable and non-volatile are used to replace the plasticizers in the preparation of gel polymer electrolytes.

The combination of lithium salt and ionic liquid in gel polymer electrolytes can provide high energy density, higher storage capacity and specific energy of lithium ion batteries[6]. Ionic liquids are attractive additives in the recent gel polymer electrolytes compared to conventional plasticizers because they are tuneable systems and possess wide electrochemical window[7]. *Bis*(rifluoromethylsulfonyl)imide anion, abbreviated

as TFSI$^-$, which has highly delocalized negative charge that can reduce its local interaction with cations and has high thermal resistance was used in this study[8]. On the other hand, 1-butyl-3-methylimidazolium cation, abbreviated as Bmim$^+$, was used in combination with *Bis*(trifluoromethylsulfonyl)-imide anion as the acidity of C-2 proton attached to the imidazolium ring would enhance salt dissociation[9].

On the other hand, glycidyl methacrylate based polymers are less toxic to both monomer and polymer, have high chemical resistance, high mechanical properties and also good surface resistivity[10,11]. In addition, the oxygen atoms in poly(glycidyl methacrylate) structure can act as active site for lithium ions to coordinate. According to Isken *et al.*[12], lithium ions can form complexes with oxygen atoms, either in the main chain or in the polymer chain segments and therefore, can be transported through segmental motions. Furthermore, poly(glycidyl methacrylate) was used as polymer host to hold liquid electrolytes and to avoid risk of leakage. Besides, some previous studies have reported that the ionic conductivities of methacrylate based polymer as host and the use of ionic liquids in polymer electrolytes can achieve up to 2.80×10^{-6} S cm^{-1} and 1.20×10^{-3} S cm^{-1}, respectively[7,10,13-16].

EXPERIMENTAL

Glycidyl methacrylate (GMA), 2,2-dimethoxy-2-phenyl-acetophenone (DMPP), lithium *bis*(trifluoromethyl-sulfonyl)-

imide) (LiTFSI) and 1-butyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide were purchased from Aldrich. Ethanol (95 % purity) was obtained from systerm, while tetrahydrofuran was purchased from J.T. Baker. All chemicals were used without further purification, except for 1-butyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide that was purified prior to use[17].

Preparation of samples: Poly(glycidyl methacrylate) was prepared by exposing an appropriate amount of glycidyl methacrylate and 2,2-dimethoxy-2-phenylacetophenone solution under UV lamp (Rs. Ltd) for 18 min according to the method reported previously[10,18]. The resulted poly(glycidyl methacrylate) had molecular weight of 42 500 g/mol was then washed with ethanol to dissolve unreacted monomer. Poly-(glycidyl methacrylate) was used to prepare solid polymer electrolyte PGMA-LiTFSI at 30 wt. % of LiTFSI (F0) by solution casting technique as a blank. Both PGMA and LiTFSI were dissolved in tetrahydrofuran and stirred until a homogenous solution was obtained. As for gel polymer electrolyte, 1-butyl-3-methylimidazolium *bis*(trifluoromethyl-sulfonyl)imide was added to the PGMA-30 wt. % of LiTFSI-tetrahydrofuran solution at 10 wt. % (F1), 20 wt. % (F2), 30 wt. % (F3), 40 wt. % (F4), 50 wt. % (F5) and 60 wt. % (F6) of the polymer, stirred until a homogenous solution was obtained and was casted into a Teflon mould. Tetrahydrofuran was then dried at room temperature and in vacuum oven for further drying.

Fourier transformation infra-red analysis was carried out using Perkin Elmer Spectrum with frequency ranging from 4000-650 cm⁻¹. Glass transition temperature was measured using Mettler Toledo differential scanning calorimeter under nitrogen with a scanning rate of 10 °C/min. Ionic conductivity was measured by HIOKI 3532-50 LCR HiTESTER. The polymer film was sandwiched between stainless steel electrodes with frequency range of 50-5 MHz at ambient temperature. The ionic conductivity was calculated using the equation of $\sigma = [t/(A.R_b)]$, where t is thickness of the film, A is the surface area and R_b is the bulk resistivity calculated from cole-cole plot.

RESULTS AND DISCUSSION

Fourier transformation infra-red spectroscopy was used to determine the interactions between polymer, salt and ionic liquid. Fig. 1 shows the Fourier transformation infrared spectrum for F0, F1, F2, F3, F4, F5, F6 and ionic liquid from region of 3000 to 650 cm⁻¹. In this research, only some of the functional groups presented in poly(glycidyl methacrylate) were focused, which were C=O, COC ether and epoxy, respectively. This was to confirm if the interactions occurred at oxygen atoms in the functional groups. As for F0, the absorption of carbonyl for poly(glycidyl methacrylate) was at wavenumber 1724 cm⁻¹, 1254 cm⁻¹ for weak epoxy ring stretching band (breathing mode), two strong ring deformation bands for epoxy ring, which was at 905 cm⁻¹ (asymmetric) and 846 cm⁻¹ (symmetric) for both COC ether and epoxy, respectively. The band at 1147 cm⁻¹ for unsymmetrical stretch of ether. As for F1 until F6, the wavenumber of carbonyl moved to 1726 cm⁻¹, similar to weak epoxy ring stretching band wavenumber, as it increased to 1257 cm⁻¹. Furthermore, the wavenumbers at 905 and 846 cm⁻¹ moved to 906 and 848 cm⁻¹. In case of ionic liquid

spectra, peaks at 3158 cm⁻¹, 2880, 1178, 1133 and 1052 cm⁻¹ were the peaks of CH stretching, asymmetric stretching of CH₃, CF stretching, OSO symmetric stretch and strong SO stretch, respectively. Besides, it was observed that all the electrolyte films (F1-F6) contained both peaks related to polymer and ionic liquids although at different intensity due to the different amount used. Nonetheless, there was insignificant change or shift of wavenumber for those functional groups and it was assumed that the electrolytes did not interact with the oxygen atoms at polymer chain in this system, but were dispersed between the polymer networks. This is because, only significant interactions induce changes in the vibrational modes of atoms or molecules in the electrolyte polymer[4]. In fact, a similar case was observed by Singh *et al.*[14], when ionic liquid of 1-ethyl-3-methylimidazolium thiocyanate was used[19].
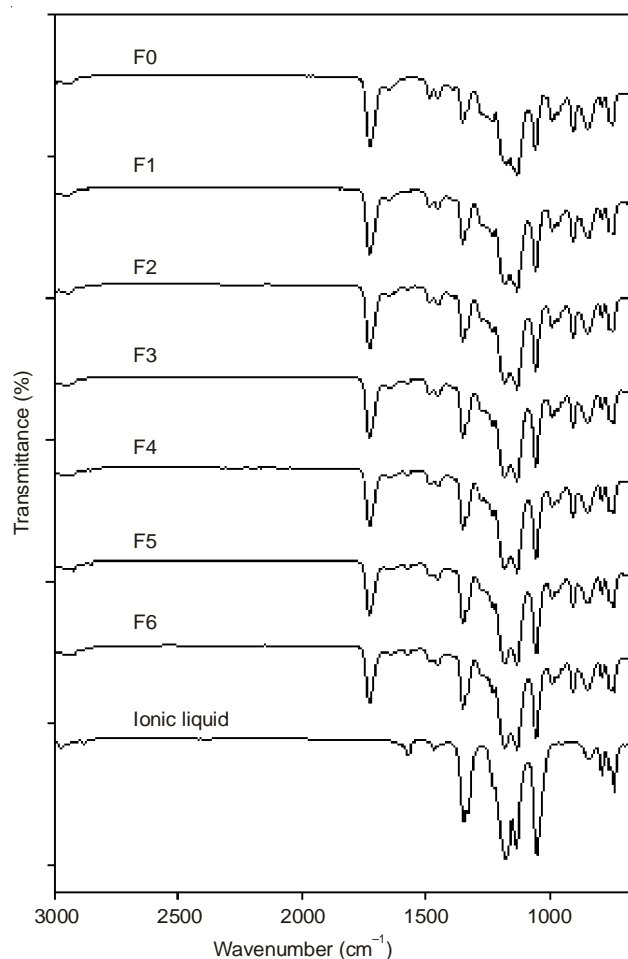

Fig. 1. Fourier transform infrared spectra of F0, F1, F2, F3, F4, F5, F6 and ionic liquid

On the other hand, glass transition temperature explains the changing nature of the properties from glass to amorphous upon heating a polymer that involves the movement and the rearrangement of chains[20]. Table-1 lists the glass transitions, T_g of F0 to F6. The T_g value was found to decrease in gel polymer electrolytes when the amount of ionic liquid was increased. This showed that ionic liquid plasticized the system and promoted fast relaxation in polymer chains[6]. According to Ramesh *et al.*[21], ionic liquid weakens the dipole-dipole interactions and disrupts the molecular arrangement of polymer matrix[21].

Hence, the segmental motion and the flexibility of polymer chain are increased and therefore, the T_g value is decreased.

In addition, it was found that ionic conductivity for F0 was 3.69×10^{-8} S cm^{-1}. The ambient temperature for ionic conductivity of PGMA-30 wt. % of LiTFSI-BmimTFSI was increased up to 2.66×10^{-6} S cm^{-1} for F5 electrolyte, which was the maximum ionic conductivity for this system due to the increase of charge carrier carried by Bmim$^+$ and TFSI^{-} [14]. The other factor that increased the ionic conductivity of this electrolyte had been the enhancement of salt decomposition by oxygen atoms attached to the TFSI$^-$ anions and this increased the number of charge carriers[4,22]. Besides, further doping of the ionic liquid decreased the value of ionic conductivity to 2.43×10^{-6} S cm^{-1} and this was caused by the limited ionic mobility due to the saturated system that occurred at very high amount of ionic species.

TABLE-1
IONIC CONDUCTIVITY AND GLASS TRANSITION
TEMPERATURE (T_g) FOR THE INVESTIGATED FILMS

bmimTFSI (wt. %)	Label	T_g (°C)	Conductivity (S cm^{-1})
0	F0	28	3.69×10^{-8}
10	F1	22	1.04×10^{-7}
20	F2	20	1.58×10^{-7}
30	F3	4	9.57×10^{-7}
40	F4	-6	1.21×10^{-6}
50	F5	-20	2.66×10^{-6}
60	F6	-22	2.43×10^{-6}

Fig. 2 shows the temperature dependency of the ionic conductivity for the electrolytes film with 0 wt. % of BmimTFSI doping concentration. The observation from Arrhenius plot for the concentration of salt and BmimTFSI was slightly deviated from the Arrhenius equation, but it was found to obey the Vogel-Tamman-Fulcher equation:

$$\sigma = A/T^m \exp [(-E_a/(T-T_o)] \qquad (1)$$

where σ is ionic conductivity, A is a pre-exponential factor, E_a is activation energy for the charge transport within SPEs, T_o is 30 K-50 K less than glass transition temperature value of SPE, T is evaluated ionic conductivity temperature and m is a factor which is ½[23,24]. The T_o value was used as 50 K less than the experimental T_g value of SPEs, which was the best fit for eqn. 1 to the experimental data. The constant A revealed the number of charge carriers in the gel polymer electrolytes system[4]. The regression values that were close to unity by using VTF in eqn. 1 showed that ionic conduction for F0 was based on segmental motion of polymer matrix.

Meanwhile, Fig. 3 shows the temperature dependency of the ionic conductivity for the electrolytes film with 30, 50 and 60 wt. % of doping concentrations of BmimTFSI, which adhered to the Arrhenius equation of:

$$\sigma = \sigma_o \exp (-E_a/kT) \qquad (2)$$

where σ is the ionic conductivity, σ_o is pre-exponential factor, E_a is the activation energy, k is Boltzmann constant and T is the temperature. This plot portrayed a linear relationship between conductivity and temperature with pre-exponential factor, σ_o 4.57×10^{-5}, 1.28×10^{-3} and 4.39×10^{-5} S cm^{-1} for F3, F5 and F6, respectively. The activation energy, E_a was
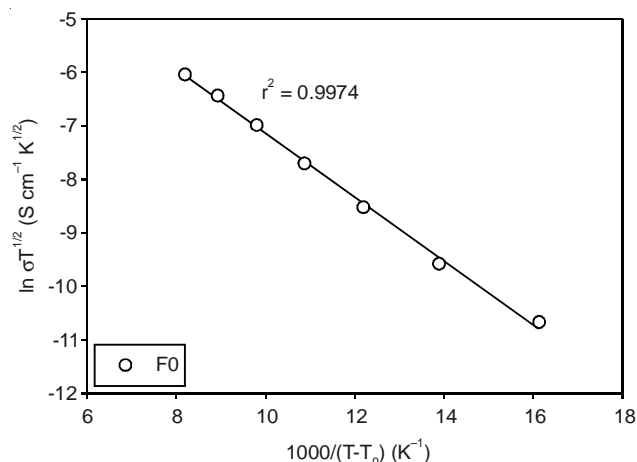

Fig. 2. Vogel-Tamman-Fulcher plot of ionic conductivity as a function of temperature for F0

determined by fitting it in the Arrhenius equation and the results are reported in Table-2.

Sekhar et al.[25] suggested that the value of E_a is due to the energy that is required to provide effective conductive condition for the transportation of the ions. The conductivity of films for F3, F5 and F6 increased with an increase in temperature and reached the highest value of 5.52×10^{-4} S cm^{-1} at 100 °C for F5. The increase of conductivity in the films with temperature was due to the decrease in viscosity of ionic liquid in the electrolyte system, which reduced the E_a value and improved the mobility of the ions[21]. From Table-2, the E_a of integrated polymer electrolytes system had been in the order of F3 > F5 > F6 and it was higher than E_a for F0. The E_a for F0 was lower than the E_a reported before for polymer matrix of PMMA-PVC[22] and this may be caused by the limited electronegative oxygen atoms in PGMA backbone compared to chloride atoms in PVC, resulting less effective complexes between polymer and lithium ion. The reason for higher value of E_a in the integrated system was due to attraction that might have occurred between lithium ions and TFSI$^-$ anions that formed stable ion triplets or aggregates[26]. Hence, the increase of ionic conductivity was contributed by the mobility of ion triplets. Meanwhile, as for integrated electrolytes system, the conduction mechanisms were based on hopping of lithium
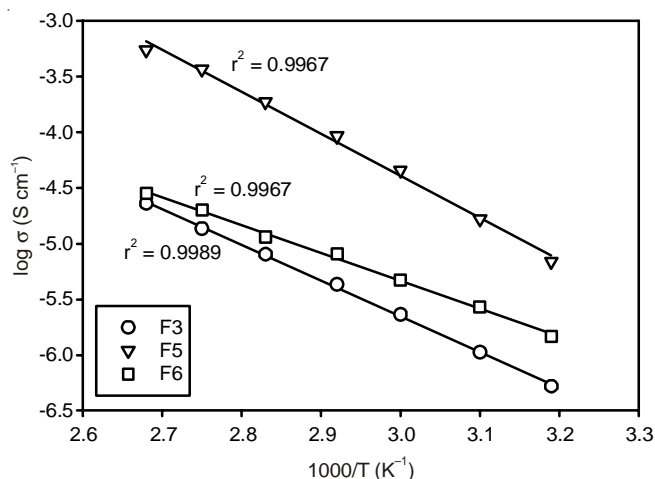

Fig. 3. Arrhenius plot of ionic conductivity as a function of temperature for F3, F5 and F6

TABLE-2
ACTIVATION ENERGY AND PRE-EXPONENTIAL
FACTOR FOR THE INVESTIGATED FILMS

Label	E_a (kJ/mol)	A/σ_o (S cm^{-1})	Equation
F0	5.2102	1.75×10^{-1}	VTF
F3	70.8964	4.57×10^{-5}	Arrhenius
F5	69.3922	1.28×10^{-3}	Arrhenius
F6	47.3550	4.39×10^{-5}	Arrhenius

ions theory, which was present by obeying the Arrhenius equation. The neighbouring ions in adjacent sites occupied the vacant site to provide conductive conditions[21].

Conclusion

This study found that there was no significant interaction between ionic liquid and oxygen atoms in polymer chains. The temperature of glass transition also decreased with the increase of BmimTFSI doping and was followed by the increase in ambient temperature of ionic conductivity. The highest ambient temperature for ionic conductivity was 2.66×10^{-6} S cm^{-1}. The integrated electrolyte system obeyed the Arrhenius theory and it represented the mechanisms of ion hopping that occurred for conductive condition. Besides, the ionic liquids acted as charge carrier and plasticizer in the studied integrated electrolytes system and therefore, increased the value of ionic conductivity.

REFERENCES

1. J.Y. Song, Y.Y. Wang and C.C. Wan, *J. Power Sources*, **77**, 183 (1999).
2. Y. Wang, J. Travas-Sejdic and R. Steiner, *Solid State Ion.*, **148**, 335 (2002).
3. M. Imperiyka, A. Ahmad, S.A. Hanifah, N.S. Mohamed and M.Y.A. Rahman, *Int. J. Hydrogen Energy*, **39**, 3018 (2014).
4. T. Uma, T. Mahalingam and U. Stimming, *Mater. Chem. Phys.*, **90**, 239 (2005).
5. J.H. Shin, W.A. Henderson and S. Passerini, *J. Electrochem. Soc.*, **152**, A978 (2005).
6. M.J. Park, I. Choi, J. Hong and O. Kim, *J. Appl. Polym. Sci.*, **129**, 2363 (2013).
7. A.S. Fisher, M.B. Khalid, M. Widstrom and P. Kofinas, *J. Power Sources*, **196**, 9767 (2011).
8. N. Madria, T.A. Arunkumar, N.G. Nair, A. Vadapalli, Y.W. Huang, S.C. Jones and V.P. Reddy, *J. Power Sources*, **234**, 277 (2013).
9. D.R. Macfarlane, M. Forsyth, P.C. Howlett, J.M. Pringle, J. Sun, G. Annat, W. Neil and E. Izgorodina, *Acc. Chem. Res.*, **40**, 1165 (2007).
10. M. Imperiyka, A. Ahmad, S.A. Hanifah and M.Y.A. Rahman, *Int. J. Electrochem. Sci.*, **8**, 10932 (2013).
11. S.F. Mohammad, N. Zainal, S. Ibrahim and N.S. Mohamed, *Int. J. Electrochem. Sci.*, **8**, 6145 (2013).
12. P. Isken, M. Winter, S. Passerini and A. Lex-Balducci, *J. Power Sources*, **225**, 157 (2013).
13. L.C. Rodrigues, P.C. Barbosa, M.M. Silva and M.J. Smith, *Electrochim. Acta*, **53**, 1427 (2007).
14. P.K. Singh, K.W. Kim and H.W. Rhee, *Synth. Met.*, **159**, 1538 (2009).
15. P.K. Singh, K.W. Kim, R.K. Nagarale and H.W. Rhee, *J. Phys. D Appl. Phys.*, **42**, 125101 (2009).
16. P.K. Singh, N.A. Jadhav, S.K. Mishra, U.P. Singh and B. Bhattacharya, *Ionics*, **16**, 645 (2010).
17. K.R. Seddon, A. Stark and M.J. Torres, *Pure Appl. Chem.*, **72**, 2275 (2000).
18. S.A. Hanifah, N. Hamzah and L.Y. Heng, *Sains Malaysia*, **42**, 487 (2013).
19. P.K. Singh, B. Bhattacharya, R.K. Nagarale, K.W. Kim and H.W. Rhee, *Synth. Met.*, **160**, 139 (2010).
20. C.B. Roth and J.R. Dutcher, *J. Electroanal. Chem.*, **584**, 13 (2005).
21. S. Ramesh, C.W. Liew and K. Ramesh, *J. Non-Cryst. Solids*, **357**, 2132 (2011).
22. J. Sun, D.R. Macfarlane and M. Forsyth, *Electrochim. Acta*, **40**, 2301 (1995).
23. II Olsen and R. Koksbang, *The Electrochem. Soc. Proc.*, **94-98**, 421 (1995).
24. I. Albinsson, B.E. Mellander and J.R. Stevens, *J. Chem. Phys.*, **96**, 681 (1992).
25. P.C. Sekhar, P.N. Kumar, U. Sasikala, V.V.R.N. Rao and A.K. Sharma, *Eng. Sci. Technol. Int. J.*, **2**, 908 (2012).
26. J.K. Kim, D.H. Lim, J. Scheers, J. Pitawala, S. Wilken, P. Johansson, J.H. Ahn, A. Matic and P. Jacobsson, *J. Korean Electrochem. Soc.*, **14**, 92 (2011).