Ionic Conductivity Studies on Magnesium-Based Cellulose Acetate Polymer Gel Electrolytes

Aniza Omar[a,1], Siti Zafirah Zainal Abidin[b,d], Ainnur Sherene Kamisan[a], Siti Irma Yuana Saaid[c], Ab Malik Marwan Ali[b,d] and Muhd Zu Azhan Yahya[a,d,2]

[a]Faculty of Defence Science and Technology,
Universiti Pertahanan Nasional Malaysia, 57000 Kuala Lumpur, Malaysia
[b]Faculty of Applied Sciences, Universiti Teknologi MARA,
40450 Shah Alam, Selangor, Malaysia
[c]Centre of Foundation Studies, Universiti Teknologi MARA,
42300, Puncak Alam, Selangor, Malaysia
[d]Institute of Science, Universiti Teknologi MARA,
40450 Shah Alam, Selangor, Malaysia
E-mail: aomarupnm@gmail.com[1], mzay@upnm.edu.my[2]

ABSTRACT

Magnesium-based polymer gel electrolytes consist of magnesium triflate (MgTf) salt, a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) solvents as well as cellulose acetate as a polymeric agent were prepared via direct dissolution method. The highest ionic conductivity obtained for MgTf-EC:DEC(1:1) liquid electrolytes was 2.66 x 10^{-3} S cm^{-1} and enhanced to 2.73 x 10^{-3} S cm^{-1} with the addition of cellulose acetate. These results were in agreement with the activation energy obtained with the lowest value of 0.11. The best explanation on the enhancement in ionic conductivity of PGE is due to the "breathing polymeric chain model". The plots of conductivity–temperature were shown to obey an Arrhenius rule. The electrical properties of the sample with the highest conductivity were analyzed using electrical permittivity-based frequency and temperature dependence in the range of 100 Hz – 1 MHz and 303–373K, respectively. The variation in dielectric permittivity (e_r and e_i) as a function of frequency at different temperatures exhibited decays at higher frequencies and a dispersive behavior at low frequencies. Based on the observed electrical properties, it can be inferred that this polymer gel electrolyte could be a promising candidate as an electrolyte in electrochemical devices.

Keywords: *Magnesium triflate; cellulose acetate; ionic conductivity; polymer gel electrolyte; electrical properties component*

INTRODUCTION

The development of polymer electrolytes has drawn the attention of researchers from all over the globe. This is due to the many potential applications of polymer electrolytes in energy storage devices such as lithium batteries, magnesium batteries and supercapacitors. For applications in all and quasi solid-state electrochemical devices, polymer electrolytes should possess sufficient ionic conductivity, good mechanical properties and thermal stability [1,2] as well as should also be compatible with the electrodes used [3]. These polymer electrolytes can be classified into 3 types, *viz.* liquid electrolytes, gel electrolytes and solid electrolytes. In the case of polymer gel electrolytes (PGEs), they can be produced when the polymer swells up in an organic solvent and have many advantages compared to liquid electrolytes because of their physical properties enhancement and leak proof [4,5]. Moreover, PGEs can provide better interfacial contact between the electrode surface and electrolyte compared to the solid electrolytes [5,6].

Although many PGEs have been reported, however, few reports focused on Mg^{2+} ions compared to Li^+ ion-based conducting electrolytes [1,2,3]. The ionic radius of Li^+ and Mg^{2+} is about the same, i.e. 68 and 65 pm, respectively; hence, Mg^{2+} ions are possible to replace Li^+ ions as the charge carrier in polymer gel electrolytes. Besides, magnesium metal is more stable compared to lithium metal. Hence, it is easier to handle magnesium metal in oxygen or humid atmosphere compared to lithium metal. Moreover, magnesium metal is less expensive and more abundant in nature compared to lithium. Studies on polymer electrolytes using Mg^{2+} ions as the charge carriers were being intensively undertaken [7,8,9,10,11].

In this work, PGEs were prepared by adding cellulose acetate (CA) to liquid electrolytes comprising magnesium triflate (MgTf) or magnesium trifluoromethanesulfonate $Mg(CF_3SO_3)_2$ in binary solvent mixtures containing 1:1 ratio of ethylene carbonate (EC) and diethyl carbonate (DEC). Their ionic conductivity and dielectric properties based frequency and temperature dependence were thoroughly determined. This recognizes them as a promising candidate electrolyte for magnesium batteries.

EXPERIMENTAL METHOD

Sample Preparation

Cellulose acetate (CA) with an acetyl content of 39.8 wt.%, magnesium triflate (MgTf), ethylene carbonate (EC), diethyl carbonate (DEC) and acetone were purchased from Sigma–Aldrich and used as received without further purification. Prior to be dissolved in 0.4 M MgTf–EC-DEC (1:1) liquid electrolytes, CA with variation of weight ratios (1.0–6.0 wt.%) was dissolved in 10 mL acetone for several hours. All mixtures were stirred to obtain homogenous and transparent gels.

Impedance Measurement

Electrical impedance spectroscopy (EIS) technique was performed on the electrolytes using HIOKI 3532-50 LCR Hi Tester interfaced to a computer with a frequency range from 100 Hz to 1 MHz. The measurement was conducted in the temperature range between 303 K and 373 K. The conductivity (σ) was determined using the following equation:

$$\sigma = t/RA \tag{1}$$

where t is the distance between the electrodes (cm), A is the contact area between the electrolyte and the electrodes (cm^2), and R is the bulk resistance of the sample.

Dielectric constant (ε_r) and dielectric loss (ε_i) by Eqs. (2) to (3):

$$e_r\,(w) = Z_i / [w\, C_o\, (Z_r^{\,2} + Z_i^{\,2})] \tag{2}$$

$$e_i\,(w) = Z_r / [w\, C_o\, (Z_r^{\,2} + Z_i^{\,2})] \tag{3}$$

where C_0 is equal to $\varepsilon_0 A/t$ and ε_0 is the permittivity of the free space.

RESULTS AND DISCUSSION

The effect of CA concentration on ionic conductivity at room temperature (303 K) is depicted in Figure 1. The conductivity pattern of PGE slightly increases at low CA concentration and starts declining with increasing CA content. The highest ionic conductivity obtained for MgTf-EC:DEC(1:1) liquid electrolytes was 2.66 x 10^{-3} S cm^{-1} and enhanced to 2.73 x 10^{-3} S cm^{-1} with the addition of cellulose acetate (Figure 1). The conductivity reaches a maximum value with the lowest bulk resistance (Figure 2) at 4.0 wt.% CA. These results were in agreement with the activation energy obtained with the lowest value of 0.11. The best explanation on the enhancement in ionic conductivity of PGE is due to the "breathing polymeric chain model" [5,12], in which PGE presumably contains dissociated ions (Mg^{2+} cation and triflate anion), ion pairs, solvent, and polymer chains. By adding a small amount of CA, an increase in the pressure in the system occurs because the polymer chains "breathe" (open or fold) and occupy different volumes. This pressure wave assists in the dissociation of salts, which increases the number of Mg^{2+} ions functioning as charge carriers and enhances the mobility. Thus, conductivity increases. However, increasing the CA concentration beyond 4.0 wt.% results in an increase in bulk resistance and, thus, a decrease in conductivity.

The temperature dependence conductivity plots for the MgTf-EC-DEC–CA system (Figure 3) shows the regression values are in the range 0.97 to 0.99. The plot proves that the conductivity of PGE is proportional to the temperature. Thus, the conductivity–temperature relationship of PGE characteristically obeys the Arrhenius rule in behavior, implying that the conductivity is thermally activated. As temperature increases, the polymer chain acquires faster internal modes, in which bond rotations produce segmental motion that favors hopping interchain and intrachain ion movements and, consequently, increasing PGE conductivity [11]. This behavior is also in agreement with reports by Abidin *et al.* [5] who had investigated on electrical properties of polymer electrolyte-based cellulose acetate.

The activation energy of the electrolyte is obtained using the equation:

$$s = s_0 \exp\left(-E_A/kT\right) \qquad (4)$$

where σ_0 is the pre-exponential factor, E_A is the activation energy, k is the Boltzmann constant, and T is the absolute temperature. The highest-conducting sample provides the lowest activation energy [4,5,11]. Activation energy is the free energy barrier that is associated with the ions hopping between two sites. Consequently, the lowest activation energy also implies that the distance between transit sites is short because CA at low concentration has contributed more sites for transit, which is in between the sites provided by EC:DEC (1:1).

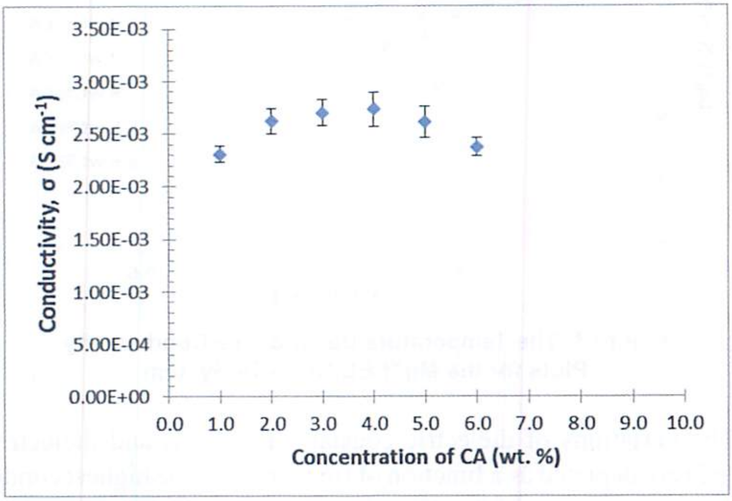

Figure 1: Variation of Conductivity with CA Concentration for PGE

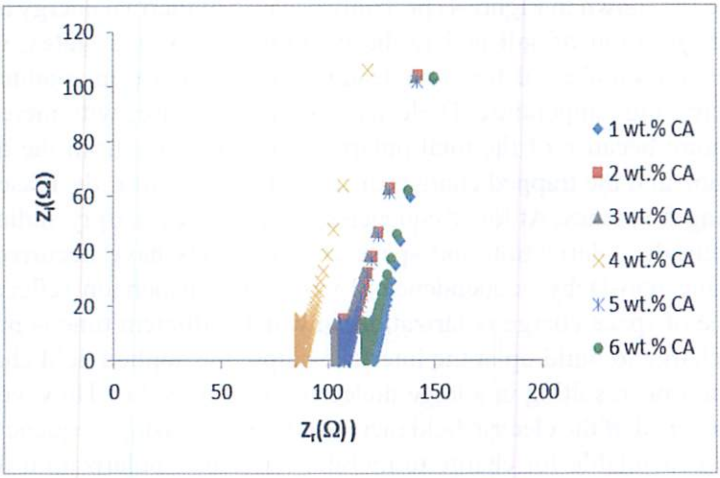

Figure 2: Cole-cole Plot of Various CA Concentrations of PGE

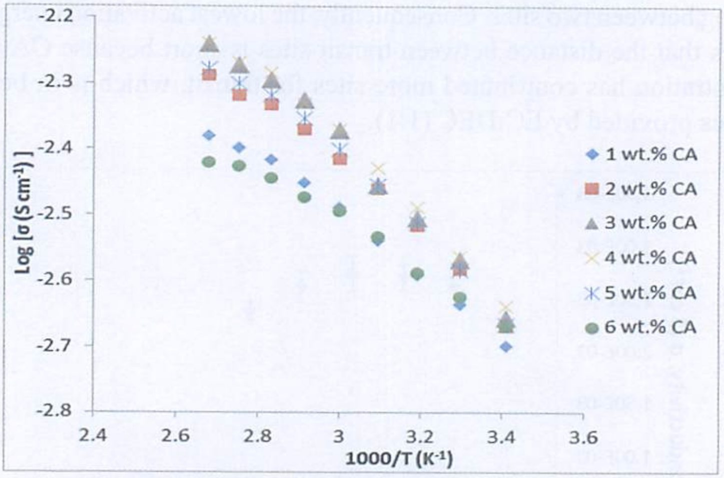

Figure 3: The Temperature Dependence Conductivity Plots for the MgTf-EC:DEC–CA System

The variations of dielectric constant (Figure 4) and dielectric loss (Figure 5) are depicted as a function of frequency for the highest conducting PGE sample containing 4.0 wt.% CA at different selected temperatures in the range 303 to 373 K. The increase in dielectric constant with temperature occurred (as shown in Figure 4) probably because of thermal energy assists in the dissolution of salt and re-dissociation of ion aggregates, which increases the number of free ions leading to an increase in conductivity with increasing temperature. Dielectric constant increases with increasing temperature because of the total polarization that comes from the dipole orientation and the trapped charge carriers. The values of ε_r decrease with increasing frequency. At low frequencies, the plot rises sharply, indicating that electrode polarization and space charge effects have occurred and confirming non-Debye dependence [13,14]. This dispersion reflects the existence of space charge polarization, in which sufficient time is present for the charge to build up at the interface before the applied field changes direction, thus resulting in a large dielectric constant value. However, the rate of reversal of the electric field increases with increasing frequency, and no time is available for charge to mobile. Therefore, polarization due to charge accumulation decreases, which results in a decrease in the dielectric constant value.

Dielectric loss is the direct measure of dissipated energy and generally contributes to ionic transport and polarization of the charge. As shown in the plot in Figure 5, dielectric loss follows the same pattern as the dielectric constant. The high value of dielectric loss at lower frequencies is due to the build-up of free Mg^{2+} ions at the electrode–electrolyte interface, but the opposite is observed at higher frequencies. The variations of imaginary electric modulus for PGE with 4.0 wt.% CA, defeat the effects of the mobile ion polarization. The plot exhibits a long tail at lower frequencies. This tail is associated with long-range ionic motion, in which ions can successfully hop from one site to a neighboring site. The small value of imaginary electric modulus corresponding to the large capacitance makes a negligible contribution to electric modulus [15]. This finding further confirms the non-Debye behaviour in the sample [5]. However, no definitive peak can be observed in this plot because the frequency range on the lower side of the peak frequency determines the range in which charge carriers are mobile over long distances.

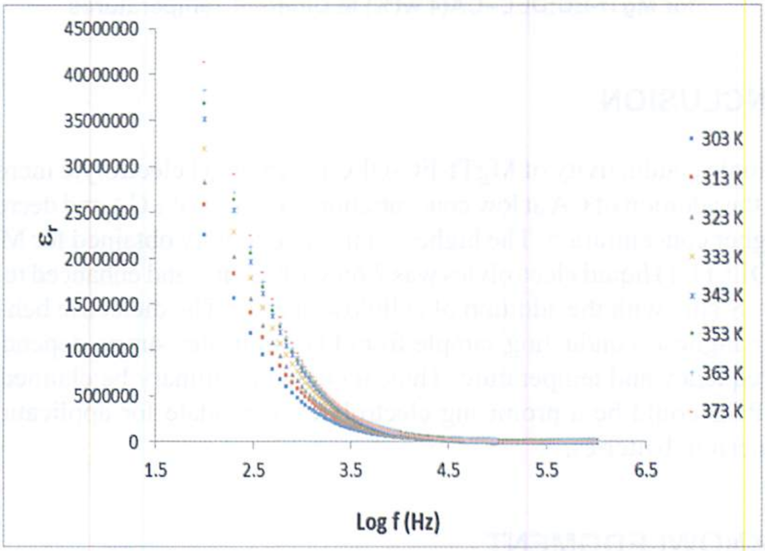

Figure 4: Dielectric Constant vs Frequency for MgTf-EC:DEC–CA(4 wt%) at Different Temperatures

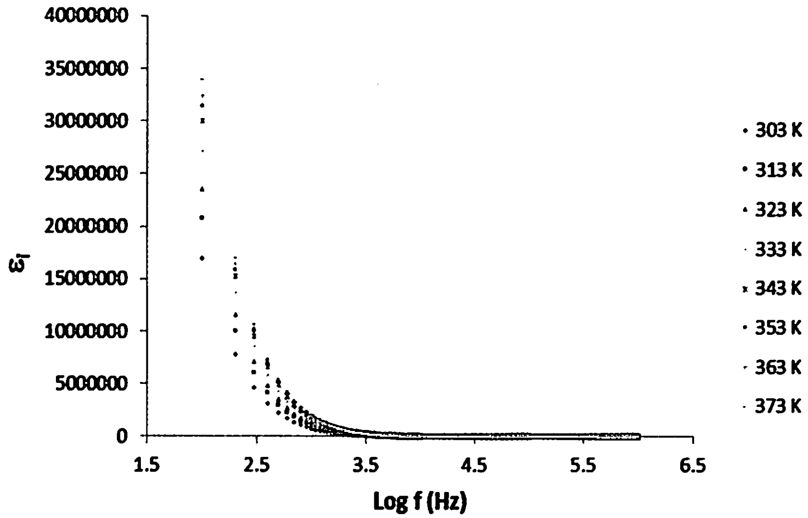

Figure 5: Dielectric Loss vs Frequency for MgTf-EC:DEC–CA(4 wt%) at Different Temperatures

CONCLUSION

The ionic conductivity of MgTf-EC-DEC polymer gel electrolyte increases with the addition of CA at low concentration up to 4.0 wt% CA and decreases at higher concentration. The highest ionic conductivity obtained for MgTf-EC:DEC(1:1) liquid electrolytes was 2.66 x 10^{-3} S cm^{-1} and enhanced to 2.73 x 10^{-3} S cm^{-1} with the addition of cellulose acetate. The dielectric behavior of the highest- conducting sample from PGE indicates strong dependence on frequency and temperature. Thus, it could preliminary be claimed that this PGE could be a promising electrolyte's candidate for application in magnesium batteries.

ACKNOWLEDGMENT

The authors express their gratitude to the Ministry of Education (MOE) for the research funding under the RAGS grant (600-RMI/RAGS 5/3 (26/2012)), and Universiti Teknologi MARA (UiTM) for the facilities. In addition, A. Omar thanks UPNM for the scholarship and postgraduate funding.

REFERENCES

[1] A. Manuel Stephan, 2006. Review on gel polymer electrolytes for lithium batteries, *Eur. Polym. J.*, *Vol. 42*, no. 1, pp. 21–42.

[2] G. B. Appetecchi, F. Croce, and B. Scrosati, 1995. Kinetics and stability of the lithium electrode in poly(methylmethacrylate)-based gel electrolytes, *Electrochim. Acta*, *Vol. 40*, no. 8, pp. 991–997.

[3] B. Scrosati, F. Croce, and S. Panero, 2001. Progress in lithium polymer battery R&D, *J. Power Sources*, *Vol. 100*, no. 1–2, pp. 93–100.

[4] A. S. Kamisan, T. I. T. Kudin, A. M. M. Ali, and M. Z. A. Yahya, 2011. Electrical and physical studies on 49% methyl-grafted natural rubber-based composite polymer gel electrolytes, *Electrochim. Acta*, *Vol. 57*, pp. 207–211.

[5] S. Z. Z. Abidin, M. Z. A. Yahya, O. H. Hassan, and A. M. M. Ali, 2014. Conduction mechanism of lithium bis(oxalato)borate-cellulose acetate polymer gel electrolytes, *Ionics*, 10.1007/s11581-014-1127-y, ISSN: 09477047.

[6] S. Z. Z. Abidin, M. F. M. Taib, T. I. T. Kudin, A. M. M. Ali, O. H. Hassan, and M. Z. A. Yahya, 2013. *International Journal of Electroactive Materials, Vol. 1*, pp. 36–42.

[7] G. Girish and N. Munichandraiah, 1999. Reversibility of Mg/Mg^{2+} in a gel polymer electrolyte, *Electrochimica Acta*, *Vol. 44*, pp. 2663–2666.

[8] G. P. Pandey and S. A. Hashmi, 2009. Experimental investigations of an ionic-liquid-based, magnesium ion conducting, polymer gel electrolyte. *Journal of Power Sources*, *Vol. 187*. pp. 627–634.

[9] J. Sharma and S. A. Hashmi, 2013. Magnesium ion transport in poly (ethylene oxide)-based polymer electrolyte containing plastic-crystalline succinonitrile. *J. Solid State Electrochem.*, *Vol. 17*, no. 8, pp. 2283–2291.

[10] P. Bian, Y. Nu Li, Z. Abudoureyimu, J. Yang, and J. Wang, 2014. A novel thiolate-based electrolyte system for rechargeable magnesium batteries. *Electrochim. Acta, Vol. 121*, pp. 258–263.

[11] S. N. Asmara, M. Z. Kufian, S. R. Majid, and A. K. Arof, 2011. Preparation and characterization of magnesium ion gel polymer electrolytes for application in electrical double layer capacitors. *Electrochim. Acta, Vol. 57*, pp. 91–97.

[12] G. Eason, B. Noble, and I. N. Sneddon, 1955. On Certain Integrals of Lipschitz-Hankel Type Involving Products of Bessel Functions, vol. A247, pp. 529–551

[13] M. Z. A. Yahya and A. K. Arof, 2003. Effect of oleic acid plasticizer on chitosan–lithium acetate solid polymer electrolytes. *Eur. Polym. J., Vol. 39*, no. 5, pp. 897–902.

[14] N. H. Zainol, S. M. Samin, L. Othman, K. B. Isa, W. G. Chong, and Z. Osman, 2013. Magnesium Ion-Based Gel Polymer Electrolytes : Ionic Conduction and Infrared Spectroscopy Studies. *International Journal of Electrochemical Science, Vol. 8*, pp. 3602–3614, 2013.

[15] N. I. Harun, R. M. Ali, A. M. M. Ali, and M. Z. A. Yahya, 2011. Dielectric behaviour of cellulose acetate-based polymer electrolytes. *Ionics (Kiel)., Vol. 18*, no. 6, pp. 599–606.