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Magnesium Ion-Based Gel Polymer Electrolytes: Ionic Conduction and Infrared Spectroscopy Studies

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The gel polymer electrolyte (GPE) films based on polymethylmethacrylate (PMMA) containing the mixture of ethylene carbonate (EC) and propylene carbonate (PC) as a plasticizing solvent and various concentrations of magnesium triflate or $Mg(CF_3SO_3)_2$ salt have been prepared using the solution casting technique. The maximum room temperature ionic conductivity of 1.27 x 10^{-3} S cm^{-1} was obtained from the GPE film containing 20 wt.% of $Mg(CF_3SO_3)_2$ salt. The conductivity-temperature studies of the GPE films follow the Arrhenius behavior with activation energy for ionic conduction are determined to be 0.18 - 0.26 eV. The transport number of magnesium ions in the GPEs was evaluated using the combination of a.c. impedance spectroscopy and d.c. polarization techniques. Fourier Transform Infrared Spectroscopy (FTIR) studies confirmed the increased in conductivity is due to increase of free ions and decrease in ion aggregates.

Keywords: Gel polymer electrolytes; magnesium ion; ionic conductivity; transport number; FTIR spectroscopy

1. INTRODUCTION

Electrochemical energy storage systems have a tremendous role in technical applications such as supercapacitors, electrochemical devices, sensors, fuel cells, etc. [1-2]. In the midst of technologies emerging today, an even higher demand for rechargeable batteries with high specific energy, high power which provides good metal surface stability and high electrochemical stability are expected [2-4]. Although lithium batteries are widely been used in high power application due to its highest electrode potential with an average voltage of 3.8 V, the lithium itself has brought out serious environmental issues due to its reactive nature and safety concern to the device and even the users [5-6]. At the same time, the accessibility of the raw material for the conventional battery is a great challenge that is likely to impact its sustainability in the future. Therefore, an alternative energy sources which are less detrimental to the environment and cost effective has been discovered to replace lithium-based batteries.

Various studies have shown that magnesium, being the most abundance element on earth and its relative higher stability is more likely to be a good candidate for electrolyte materials [7-8]. In particular, magnesium-based systems have attracted interest in electrochemical research and development due to their electrochemical properties which are closed to lithium-based system as reported by Chusid et al. [9]. Yoshimoto et al. [10] have investigated the development of the electrochemistry of magnesium in a non aqueous media in connection with developing rechargeable magnesium batteries. In contrast to lithium batteries, rechargeable magnesium batteries are expected to have wide scope in the future since magnesium possesses a number of important characteristics as it is free from hazards, its stability is high with highly negative standard potential (-2.375 V), relatively low equivalent weight (12g per Faraday), high melting point ($649^{\circ}C$), low cost, high safety, ease of handling, and low toxicity which allows for urban waste disposal [11-13]. Girish Kumar and Munichandraiah [13-14] have successfully produced working magnesium cells by using poly(vinylidenefluoride) (PVDF) and poly(methylmethacrylate) (PMMA) as polymer hosts for the gel polymer electrolytes and manganese oxide (MnO_2) as cathode.

In batteries, electrolytes play the role as the medium for the transfer of charges between a pair of electrodes i.e. cathode and anode. At present, gel polymer electrolytes (GPEs) has gain much attention compared to both solid polymer electrolytes (SPEs) and liquid electrolytes. Feuillade and Perche [15] had demonstrated the idea of mixing solvent–salt–polymer hybrid system in which the salt solution is immobilized by the addition of a suitable polymer matrix. After the discovery, Sekhon et al. [16] affirm that the solvent provides the conducting medium whereas polymer provides mechanical stability to these electrolytes.

One of the host polymers that have been widely used as a promising matrix for an electrolyte material is PMMA. Appetecchi and co-workers [17] reported that PMMA-based gel electrolytes structure is the most beneficial to ionic conduction and has shown excellent interfacial stability towards electrodes. At the same time, chemical cross-linking of PMMA can remarkably increase the electrolyte solution retention ability as well as suppress salt dendrite formation in the GPE [18]. Asmara et. al [19] have investigated the variation of conductivity of GPE with various concentrations of PMMA in a binary solvent of EC:DEC and a fixed amount of magnesium triflate.

In the present work, gel polymer electrolyte films comprising PMMA, propylene carbonate (PC), ethylene carbonate (EC) and magnesium triflate ($Mg(CF_3SO_3)_2$) salt have been prepared. The effects of different concentrations of magnesium triflate on ionic conductivities have been measured by using impedance spectroscopy techniques. A combination of a.c. impedance and d.c. polarization methods were used to measure the transport number of magnesium ions in the GPE films. The transport number will reveal the contribution of magnesium ions in the ionic conductivity of the GPE films. FTIR spectroscopy was used to investigate the effect of free ions and ion aggregates from $Mg(CF_3SO_3)_2$) salt on the ionic conductivity of the GPE films.

2. MATERIAL AND METHODS

2.1. Materials

PMMA with molecular weight of 9.96 x 10^5 g/mol, propylene carbonate (PC), ethylene carbonate (EC), and magnesium triflate, $Mg(CF_3SO_3)_2$ salt were purchased from Sigma-Aldrich. These materials were used as received without further purification.

2.2. Preparation of the gel polymer electrolytes

The solution casting method was used to prepare gel polymer electrolyte (GPE) films. In this method, magnesium triflate, $Mg(CF_3SO_3)_2$ salt was first dissolved in the mixture of EC and PC with continuous stirring at 60°C for several hours. The polymer, PMMA, was then added to this solution and the mixture was further stirred until complete homogenization of the mixture was achieved. The viscous solution thus obtained was cast on a petri-dish and allowed to dry at room temperature to form the free standing GPE films. In this work, the GPE films were prepared by varying the amounts of $Mg(CF_3SO_3)_2$ salt from 5wt% to 30wt% in a fixed amount (by weight) of PMMA and the plasticizing solvent, (EC and PC). The mass ratio of (EC+PC) to PMMA was 3:2.

2.3. Characterizations

The ionic conductivity of the GPE films was evaluated using an electrochemical cell by sandwiching the GPE films between two stainless steel electrodes. a.c. impedance measurements were carried out using HIOKI 3532 LCR impedance analyzer over the frequency range from 1 Hz to 1 MHz at room temperature. The ionic conductivity was also measured as a function of temperature in the temperature range of 303 K to 373 K for the GPE films containing 5wt.%, 20wt.% and 30wt.% of $Mg(CF_3SO_3)_2$ salt. The conductivity, σ of the GPE was calculated using the following equation;

$$\sigma = \frac{t}{R_b A} \tag{1}$$

where t is the thickness of the GPE films, R_b is the bulk resistance obtained from the Cole-Cole plot of a.c. impedance measurement and A is the contact area between the electrodes and electrolyte.

The total ionic transport number, t_{ion} was measured using the d.c. polarization method [20]. In this method, the d.c. current is monitored as a function of time on the application of fixed d.c. voltage (0.5 V) across the SS|GPE|SS (SS: stainless steel). The stainless steel acted as blocking electrodes. The value of t_{ion} was determined by using the following equation;

$$t_{ion} = \frac{i_T - i_e}{i_T} \tag{2}$$

where i_T and i_e are the total current and residual current, respectively. The transport number, t_+ of Mg^{2+} ions in the GPE was evaluated by the method that proposed by Evans et al. [21] using the combination of a.c. impedance spectroscopy and d.c. polarization of Mg|GPE|Mg cell. According to this method, the cells were polarized by applying a constant voltage, $\Delta V = 0.3$ V for 20 hours and subsequently initial and final currents were recorded. The cells were subjected to a.c. impedance measurements prior to and after the polarization. The values of electrode-electrolyte contact resistances were obtained from the impedance plots. The transport number, t_+ values were determined using the equation;

$$t_i = \frac{I_s(\Delta V - R_o I_o)}{I_o(\Delta V - R_s I_s)} \quad (3)$$

where I_o and I_s are initial current and final current, respectively. R_o and R_s are cell resistances before and after the polarization, respectively. FTIR spectra of GPE films were taken using Thermo Scientific Nicolet iS10 Smart ITR spectrometer [19] in the wavenumber range from 650 to 4000 cm^{-1} and resolution of 1 cm^{-1}.

3. RESULTS AND DISCUSSION

3.1. Ionic conductivity measurements

In the present work, the binary solvent of EC and PC are used as a plasticizing solvent. EC and PC are chosen because of their high dielectric constant, ε (ε for EC = 89 and ε for PC = 64) which is beneficial for the dissolution of $Mg(CF_3SO_3)_2$ salt. At room temperature, EC is present in powder form and hence a co-solvent is required to dissolve it. Therefore in this work, PC is used as co-solvent for EC which at room temperature PC is in liquid form and its viscosity, η = 2.53 cP. Thus, a binary mixture of EC and PC is a good solvent combination for polymer electrolyte with characteristics of high dielectric constant and low viscosity.

In order to get the appropriate EC:PC ratio that would give the highest conductivity on incorporation of $Mg(CF_3SO_3)_2$ salt in GPE films, prior to this work, we have prepared the GPE films containing mass ratio of EC:PC = 1:1 in a fixed amount of PMMA (2 g) with various concentrations of $Mg(CF_3SO_3)_2$ salt, from 0.2 g to 1.0 g. The conductivity values of these GPE films are given in Table 1. It can be observed that the conductivity values are in the order of 10^{-4} S cm^{-1} with the highest conductivity is obtained from the sample containing 0.6 g $Mg(CF_3SO_3)_2$ salt. It is noticed that the GPE films in this system were inhomogeneous and not flexible; this might be due to lower proportions of (EC+PC). We have also prepared the GPE films with higher proportion of PC (EC:PC = 1:2) and the obtained films exhibited poor mechanical and electrical properties which is not favorable for battery applications. Since the formation of GPE requires optimum quantity of the liquid components, i.e. binary solvent mixtures (EC+PC), therefore the mass ratio of EC:PC used in the present study was fixed at 2:1. Kumar and Munichandraiah [14] obtained the highest conductivity of 3.75 x 10^{-4} S cm^{-1}

from the GPE sample containing 1 g PMMA, 2 g (PC + EC) and 0.5 $Mg(CF_3SO_3)_2$ salt. In their work, the mass ratio of PC:EC was 1:1. This conductivity value is about the same order of magnitude with our previous GPE system as listed in Table 1.

Table 1. The conductivity values of GPEs containing PMMA (2g), (EC:PC) (1:1) (2g) and various amounts of $Mg(CF_3SO_3)_2$ salt

Amount of $Mg(CF_3SO_3)_2$ salt (g)	Conductivity (S cm^{-1})
0.2	2.43×10^{-4}
0.4	3.75×10^{-4}
0.6	6.08×10^{-4}
0.8	2.80×10^{-4}
1.0	2.59×10^{-4}

Fig. 1 shows the variation of conductivity with the concentration of $Mg(CF_3SO_3)_2$ salt. It can be observed that at low salt concentrations (5 wt.% and 10 wt.%), the conductivity values are in order of 10^{-5} S cm^{-1}. On addition of 15 wt.% of $Mg(CF_3SO_3)_2$ salt, the value of conductivity is found to be (5.58 ± 0.5 x 10^{-4}) S cm^{-1}. This value is about the same with that reported by Kumar and Munichandraiah [14], they obtained a conductivity of 2.1 x 10^{-4} S cm^{-1} for the GPE film containing 1 g PMMA, 2 g (PC + EC) and ~ 12 wt.% of $Mg(CF_3SO_3)_2$ salt .

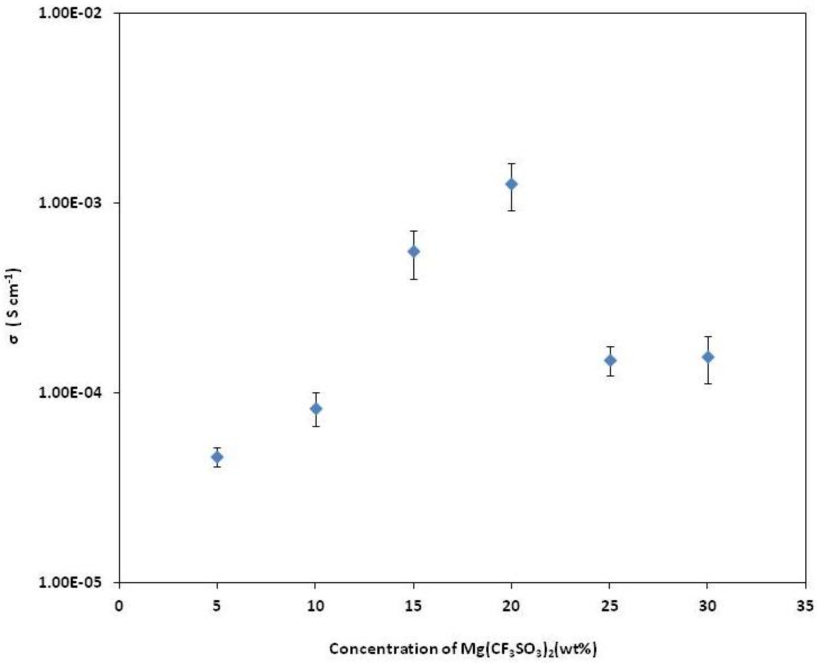


Figure 1. Ionic conductivity (σ) of GPE films as a function of $Mg(CF_3SO_3)_2$ salt concentration

In the present work, the value of conductivity increases until it reaches a maximum value of (1.27 ± 0.3 x 10^{-3}) S cm^{-1} when 20 wt.% of $Mg(CF_3SO_3)_2$ salt has been added. The GPEs exhibits high ionic conductivity due to the presence of $Mg(CF_3SO_3)_2$ salt dissolved in EC and PC, which is encapsulated in the matrix of PMMA [22]. The increase in the ionic conductivity with the increase of salt concentration can be related to the increase in the number of mobile charge carriers in the polymer electrolytes [23]. Further increase in concentration of $Mg(CF_3SO_3)_2$ salt (25 wt.% and 30 wt.%), the conductivity decreased to order of 10^{-4} S cm^{-1}. This result may be attributed to the ions aggregation, leading to the formation of ion pairs and ion aggregates, thus reduces the number of mobile charge carriers [24].

The conductivity-temperature dependence studies have been done on the GPEs containing 5 wt.%, 20 wt.% and 30 wt.% of $Mg(CF_3SO_3)_2$ salt. The films were sandwiched between two blocking electrodes and were subjected to a.c. impedance measurements in the temperature range from 303 K to 373 K. Fig. 2 shows the plots are fairly linear with activation energy, E_a obtained from the films containing 5wt.%, 20wt.%, and 30wt.% of $Mg(CF_3SO_3)_2$ are in the range between 0.18 and 0.26 eV. The regression value, R^2 for the plot of log σ versus 1000/T is almost unity suggesting that the plot can be considered linear thus obeying the Arrhenius behavior. The low value of E_a suggests that ionic conduction is facile in GPE films due to the completely amorphous nature that facilitates the fast Mg^{2+} ion motion in the polymer network. In this study, the value of E_a is a minimum of 0.18 eV for the highest conducting GPE film. The values of conductivity, σ and activation energy, E_a obtained in this present work are within the range that reported by other researchers as presented in Table 2.

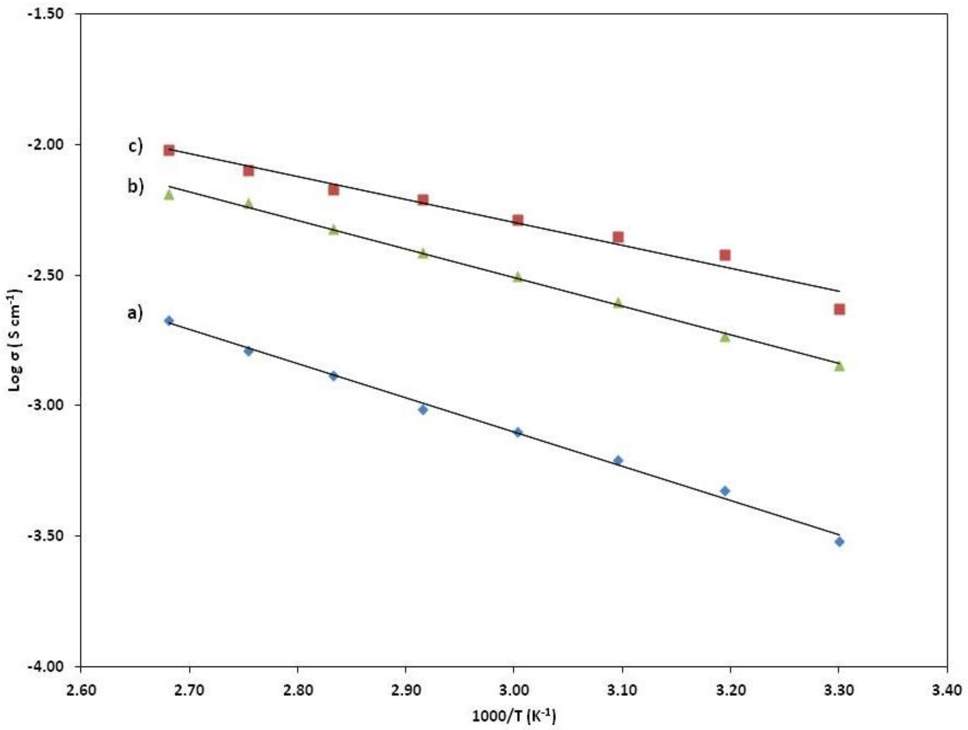


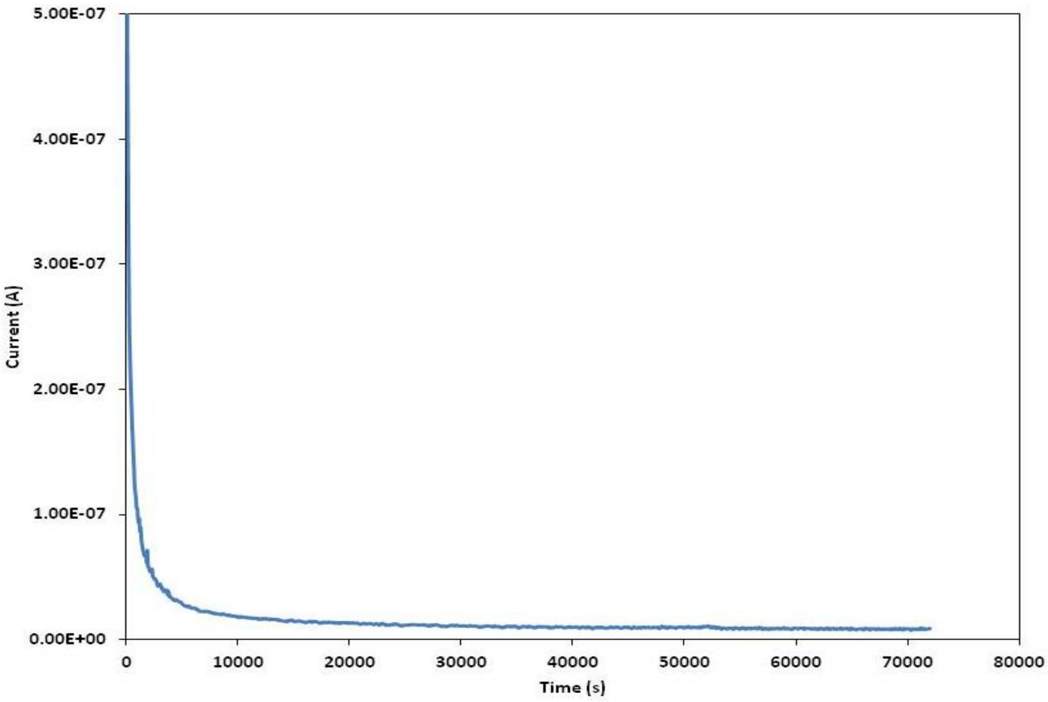
Figure 2. Temperature dependence of ionic conductivity of PMMA-EC-PC-$Mg(CF_3SO_3)_2$ gel polymer electrolyte films for the film containing (a) 5wt.%, (b) 30wt.% and (c) 20wt.% of $Mg(CF_3SO_3)_2$ salt

Table 2. The conductivity and activation energy values of GPE films using various types of magnesium salt

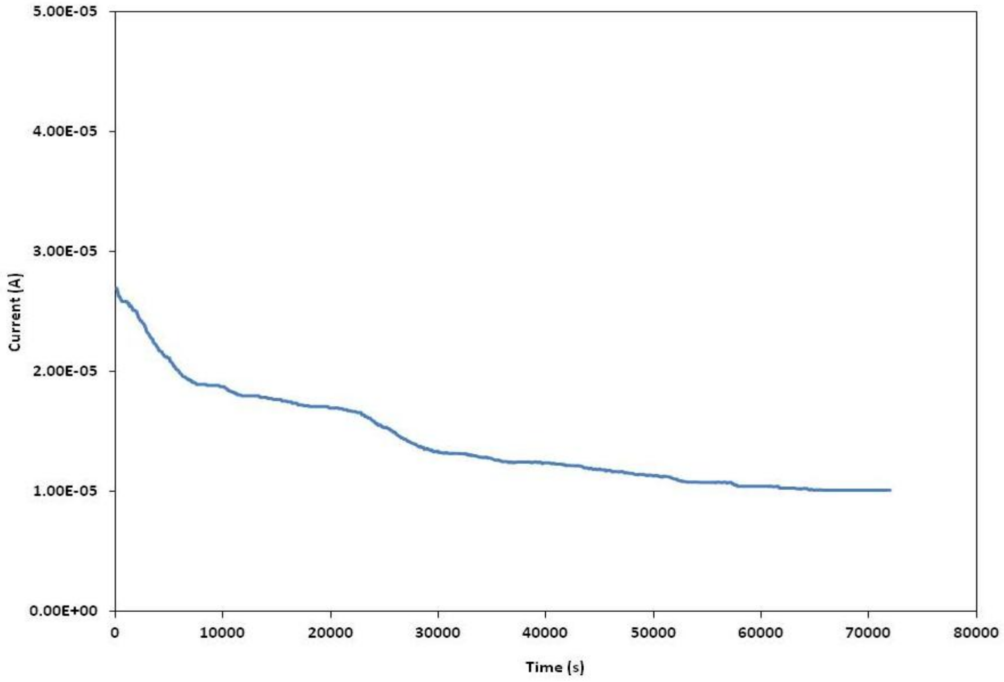
GPE composition	Conductivity (Scm^{-1})	E_a (eV)	Reference
PMMA+PC+$Mg(ClO_4)_2$	1.59×10^{-2} (Resistivity, $\rho = 62.8\ \Omega$ cm)	0.21 (19.8 kJ/mol)	[25], [26]
PMMA+PC+$Mg(ClO_4)_2$	2.38×10^{-4} (Resistivity, $\rho = 4200\ \Omega$ cm)	0.21 (19.8 kJ/mol)	[27]
PMMA+PC+EC+ $Mg(CF_3SO_3)_2$	4.20×10^{-4}	0.038	[14]
PAN+PC+EC+ $Mg(CF_3SO_3)_2$	1.80×10^{-3}	0.13 – 0.16	[22]
PVdF-HFP+EC+PC+$Mg(ClO_4)_2$+MgO	8.0×10^{-3}	0.235	[28]

3.2. Transport Number

The value of t_{ion} has been evaluated using Eq. (2) and found to be > 0.99 for each GPE film. This result indicates that the overall conductivity of the GPE film is predominantly ionic as shown in Fig. 3(a). The cationic transport number measurement is an important study to determine the performance of the GPE film from its application point of view, i.e. magnesium rechargeable batteries.



(a)



(b)

Figure 3. (a) The variation of current with respect to time across the cell SS|GPE|SS (b) d.c. polarization curve of the cell Mg|GPE|Mg for the highest conducting GPE film.

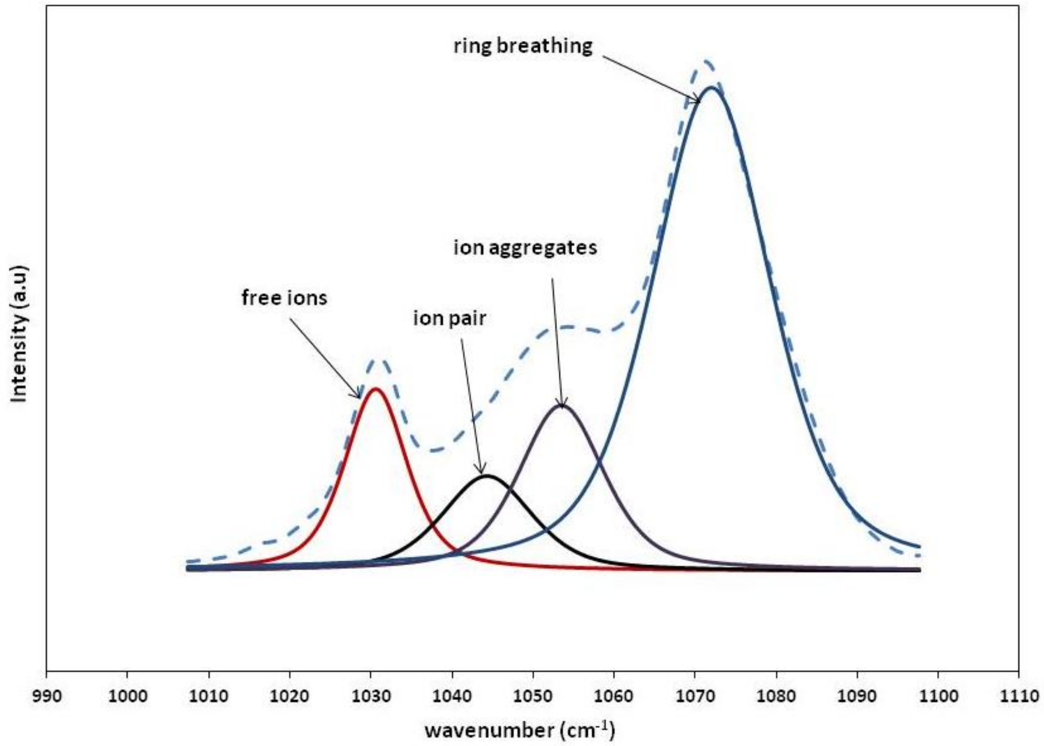
In this present work, the transport number of Mg^{2+} ions in the GPE films was measured using the combination of a.c. and d.c techniques, as described above. The d.c. polarization curve of the GPE film containing 20 wt.% of $Mg(CF_3SO_3)_2$ salt is shown in Fig. 3(b). The value of Mg^{2+} ions transport number has been calculated using Eq. (3) and the value has found to 0.38 for the highest conducting GPE film. This value is about the same that reported by Asmara et al. [19]. In their work, they obtained the value of Mg^{2+} ions transport number of 0.37 for 0.4 M $Mg(CF_3SO_3)_2$ dissolved in a binary solvent of EC:DEC containing 40wt.% PMMA. Kumar et al. [14] obtained the value of Mg^{2+} ions transport number of 0.33 at room temperature for PMMA-based GPE using 0.5 g of $Mg(CF_3SO_3)_2$ salt.

3.3. FTIR Analysis

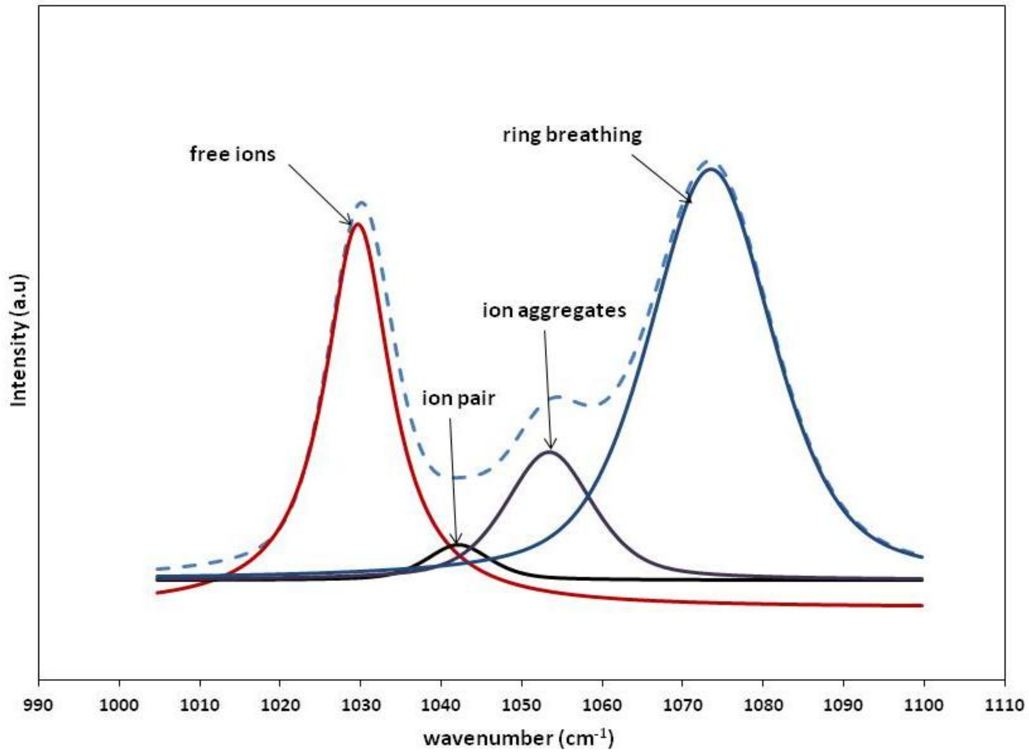
Table 3. Assignment of triflate anion $(CF_3SO_3)^-$ [19, 29-32]

FTIR bands	Wavenumber(cm^{-1})	Assignment
SO_3 symmetric	1032	free triflate ions
stretching SO_3	1040	Ion pairs; $[Mg(CF_3SO_3)_2]$,
symmetric stretching		$[Mg(CF_3SO_3)_2]_2^-$, $[Mg(CF_3SO_3)_2]_3^{2-}$
	1051	$[Mg_2(CF_3SO_3)_2]^+$ aggregate
SO_3 symmetric	1062	$[Mg_3(CF_3SO_3)_2]^{2+}$ aggregates
stretching		
SO_3 symmetric		
stretching		

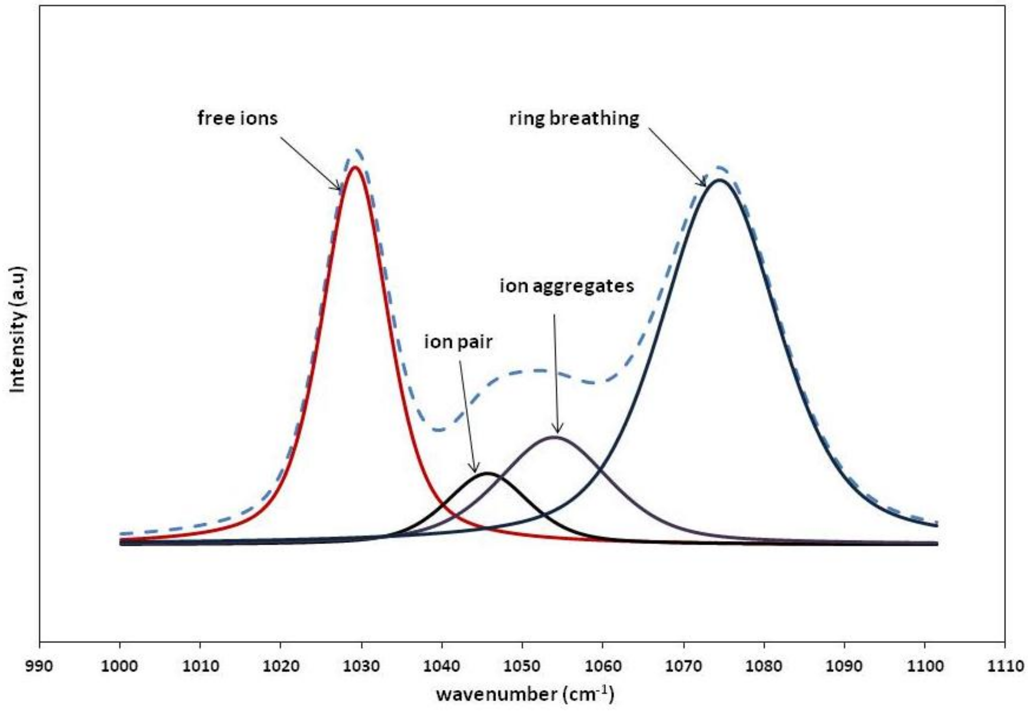
As discussed in the results of ionic conductivity, the increases in room temperature ionic conductivity of GPE films is dependent on the number of charge carriers while the decreases in conductivity are probably due to the formation of ion pairs and ion aggregates.



(a)



(b)



(c)

Figure 4. Symmetric SO_3 mode for GPE films containing (a) 5wt.% (b) 20wt.% and (c) 30wt.% of $Mg(CF_3SO_3)_2$ salt

FTIR spectroscopic measurements were carried out to investigate the presence of free ions, ion pairs and ion aggregates in the GPE films with various concentrations of magnesium triflate salt.

Table 3 summarizes the assignments for FTIR bands of triflate anion $(CF_3SO_3)^-$. Jeong et at. [30] reported that the distinctions between free ions, ion pairs, ion aggregates and large ion aggregates can be observed from the FTIR spectra of triflate anion. According to them, ion association occurs at the SO_3 end of the anion and the symmetric SO_3 mode is highly sensitive to change in the coordination state of the anion. Fig. 4 (a)-(c) display the FTIR spectra of GPE films containing 5 wt.%, 20 wt.% and 30 wt.% $Mg(CF_3SO_3)_2$ salt in the wavenumber region from 1000 to 1100 cm^{-1}. In all spectra, it can be observed four decomposed bands that peak at approximately 1030, 1041, 1051 and 1071 cm^{-1} which assigned to free ions, ion pairs, ion aggregates of triflate anion and ring breathing of a binary solvent (EC:PC), respectively. The amount of the entities i.e free ions, ion pairs and ion aggregates were represented by the area of each band.

Fig. 5 and 6 show the relationship between the conductivity and area of free ions band and ion aggregates band as a function of $Mg(CF_3SO_3)_2$ salt concentration, respectively. It is to be noted that in this work, the amount of PMMA and the plasticizing solvent, (EC+PC) are fixed. In Fig. 5, it can be observed that at salt concentrations above 20 wt.% the area of free ions band decreased with increasing salt concentration, while in Fig. 6, the area of ion aggregates increased. The curves of ion pairs and ion aggregates are similar with that reported by Asmara et al. [19] for PMMA-(EC+DEC)-$Mg(CF_3SO_3)_2$ gel polymer electrolytes. The free ions curve exhibits a maxima and the ion aggregates curve exhibits a minimum at 20 wt.% salt concentration, i.e. the highest conducting GPE film. As salt concentration increases from 5 wt.% to 20 wt.%, the plasticizing solvent, EC and PC play a vital role in dissociating ion aggregates into mobile ions.

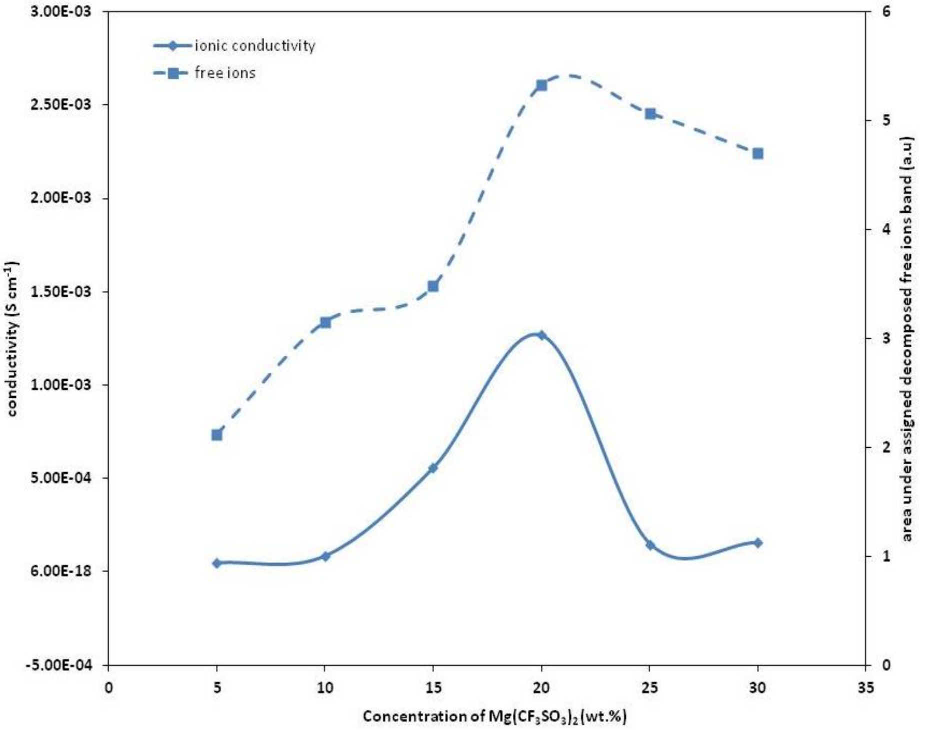


Figure 5. The relationship between area under assigned decomposed free ions band with conductivity as a function of $Mg(CF_3SO_3)_2$ salt concentration

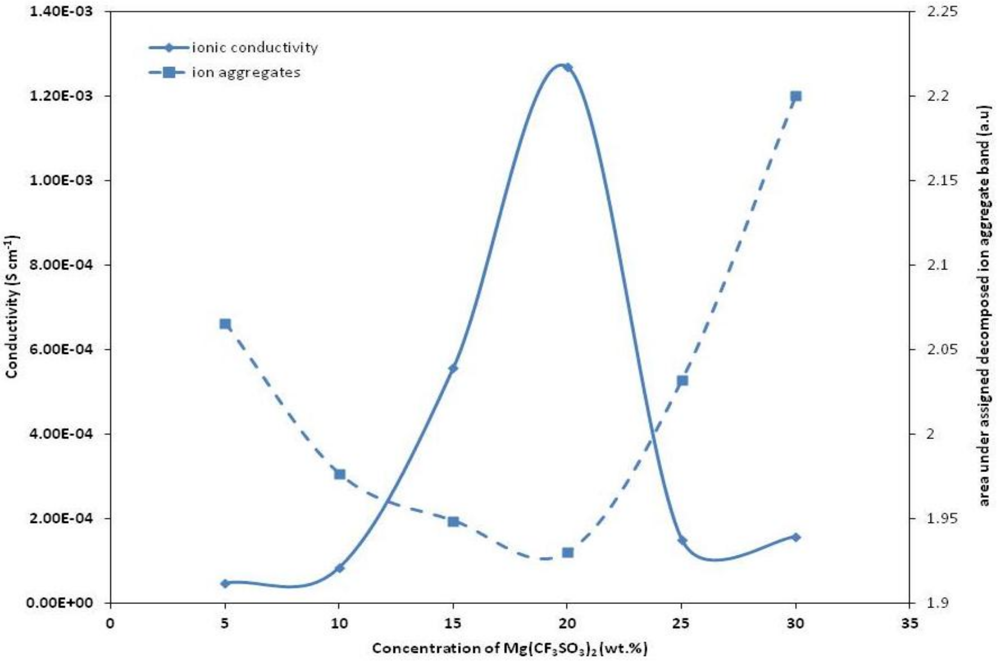


Figure 6. The relationship between area under assigned decomposed ion aggregates band with conductivity as a function of $Mg(CF_3SO_3)_2$ salt concentration

In these GPE films, the amount of free ions is much higher (up to 3 times) than ion aggregates as can be seen in Figure 5 and 6. However, above 20 wt.% salt concentration ion association becomes significant compared to dissociation. Therefore, on addition of 25 wt.% and 30 wt.% $Mg(CF_3SO_3)_2$ salt, the decrease in conductivity can be explained by the decrease in free ions and the increase in ion aggregates. The results presented in Fig. 5 and 6 can be correlated with the curve of conductivity-$Mg(CF_3SO_3)_2$ salt concentration (Fig. 1). Thus, FTIR studies have shed some light on the variation of conductivity with the $Mg(CF_3SO_3)_2$ salt concentration.

4. CONCLUSIONS

The magnesium ion conducting gel polymer electrolytes consisting of magnesium triflate salt dissolved in a plasticizing solvent, EC and PC, immobilized in a host polymer PMMA have been synthesized and characterized. The highest room temperature ionic conductivity of 1.27 x 10^{-3} S cm^{-1} is obtained from the GPE film containing 20 wt.% of $Mg(CF_3SO_3)_2$ salt. The temperature-dependence study shows that it follows the Arrhenius relationship with activation energy of 0.18 eV. The Mg^{2+} ions transport number has been evaluated using a combination of a.c. impedance and d.c. polarization techniques and the value is found to be 0.38 for the highest conducting GPE film. FTIR studies proved the increased in conductivity is due to the increase of free ions and decrease in ion aggregates.

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