

Dielectric Studies of PEO-based Polymer Electrolytes Doped with LiTFSI Salt and EMIMTFSI Ionic Liquid

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Abstract

In this work, poly (ethylene oxide) (PEO) is doped with Lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) salt and 1-Ethyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide (EMIm-TFSI) ionic liquid, a plasticiser, for preparation of PEO-LiTFSI-EMImTFSI plasticised polymer electrolyte (PPE) system. Impedance spectroscopy is used to analyse the dependence of dielectric behaviour of the films on frequency and temperature. It is performed in the temperature range between 303K to 343K for frequencies between 50 Hz to 1 MHz. The cationic transport in the films may be explained from the dielectric constant, ϵ_r and dielectric loss, ϵ_i where they are found to increase with temperature at lower frequency and decrease at higher frequency, showing that the electrodes were being polarized. Both real parts, M_r and imaginary part, M_i of the modulus showed an increase at high frequency that indicates the spread of conductivity relaxation. The highest temperature (343K) achieved the lowest relaxation time, τ due to increase in number of ions and increase in mobility of ions in the polymer system indicating that conductivity in this system is thermally activated.

Keywords: Polymer electrolyte, Impedance spectroscopy, Dielectric properties, Electric modulus, Relaxation time.

1. Introduction

The demand for lithium ion batteries has been growing tandem globally. However, the conventional application for lithium ion batteries are limited due to the use of liquid organic electrolyte [1]. They suffer from safety problems because of their flammable nature. The conventional electrolyte can easily catch fire and even be explosive [1] if there are any short circuits, local overheating or misuse. Hence, polymer electrolyte, which is solid in nature, has been introduced as an alternative to replace the conventional liquid electrolyte. It has been widely studied and has been shown to be safe for use due to no leakage and overheating.

There are three different types of polymer electrolyte. Dry polymer electrolyte, plasticized/ gel polymer electrolyte (PPE) and composite polymer electrolyte [2]. PPE have received a lot of attention in recent years, as it possesses both cohesive property of solids and diffusive property of liquids. This hybrid system is formed by trapping a large amount of liquid electrolyte as lithium ion conducting organic solution in a polymer matrix [1]. This unique characteristic makes PPE garner various important applications [3] including as electrolyte in lithium batteries.

The main important component of a polymer electrolyte is the choice of polymer host. PEO has been studied widely as a polymer host due to its ability to coordinate ionic species and its local flexibility that allows for ionic mobility [4] and hence has been chosen in this work. Other important properties are its high melting point, good structure integrity and low toxicity [5].

Unfortunately, despite the advantages, some drawbacks are present which includes higher crystallinity at lower temperature resulting in lower room temperature ionic conductivity of the electrolytes (typically $\leq 10^{-5} \text{ cm}^{-1}$). Hence, in this work, LiTFSI salt is doped into PEO since it has a bulky anion, which suppresses crys-

tallization of the polymer [6] and it has low dissociation energy so that it can easily be dissociated into ions, which in turn contribute to ionic conductivity enhancement.

The polymer electrolyte PEO-LiTFSI is also incorporated with ionic liquid as plasticizer, which is thought to enhance both ionic conductivity and safety of the polymer electrolyte at the same time [7]. The ionic liquid helps to dissociate more salt leading to higher ionic conductivity since it increases the amorphous region, dissociate ion aggregates and lowers the glass transition temperature [8]. Also since the anion of the ionic liquid chosen is the same as the anion of the doping salt, cross contact ion pairs may be prevented.

The aim of this paper is to study the dependence of dielectric properties of PEO-LiTFSI-EMImTFSI polymer electrolyte system on frequency and temperature. This dependence is analysed using Impedance Spectroscopy for frequencies in the range of 50 Hz -1 MHz and for temperatures between 303K to 343K to understand the effects of temperature towards the conductivity of the PPE system studied in this work.

Impedance spectroscopy is a powerful tool usually employed to obtain the conductivity value of the polymer electrolyte. It is a useful technique for studying various aspects of solid ionics. Besides its versatility and simplicity, impedance spectroscopy also has its limitations. Relatively expensive equipment is required. Interpretation of data requires a good understanding of A.C. impedance theory. Care must also be taken in analyzing the impedance data to avoid the possibility of false interpretation of the data.

2. Experimental

2.1. Materials

PEO (Sigma-Aldrich, average molecular weight ca. 8 000 000 g mol⁻¹), EMIm-TFSI (C₈H₁₁F₆N₃O₄S₂) (Sigma-Aldrich and Methanol solution were purchased from Labchem Sdn. Bhd. Lithium salt, LiTFSI (LiCF₃SO₃) (Sigma-Aldrich) was received from ICC Lab, Faculty of Applied Sciences, Universiti Teknologi MARA.

2.2 Preparation of Plasticised Polymer Electrolyte Film

1g of PEO was dissolved in 50 ml methanol solution at 50°C. Once it is fully dissolved, 30 wt. % of LiTFSI (following the equation xPEO – [1-x] LiTFSI, where x is wt. % of PEO) is added into the PEO solution and stirred for 24 hours at 50°C until a homogenous solution is obtained. Then, 8 wt. % of EMImTFSI (following the equation 1) is added into the PEO-LiTFSI system and stirred for further 24 hours at room temperature [9]. The solution is casted into Teflon petri dishes and allowed to evaporate slowly at room temperature [5]. Flexible and free standing films of thickness between 145 - 150 µm is obtained and is stored in a desiccator for continuous drying.

$$\text{wt. \% of IL} = \frac{\text{wt. of ionic liquid}}{\text{wt. of PEO} + \text{wt. of lithium salt} + \text{wt. of ionic liquid}} \times 100\% \quad (1)$$

2.4 Characterisation of Polymer Electrolyte Film

The study on dielectric properties is carried out for the PPE with 8 wt. % of EMImTFSI (PEIL08) using Impedance Spectroscopy in the frequency range of 50 Hz to 1 MHz for temperatures between 303K to 343K. The analysis is carried out by sandwiching the PPE between two stainless steel (SS) blocking electrodes with diameter of 1 cm with configuration SS/PPE/SS. Impedances of the films were measured using the HIOKI 3531 Z LCR Hi-tester impedance meter interfaced to a computer. The impedance data obtained is converted into both dielectric (ϵ) and electric modulus (M) formalisms using the following equations:

$$\epsilon_r(\omega) = Z_i / \omega C_o (Z_r^2 + Z_i^2) \quad (2)$$

$$\epsilon_i(\omega) = Z_r / \omega C_o (Z_r^2 + Z_i^2) \quad (3)$$

$$M_r(\omega) = \epsilon_r / (\epsilon_r^2 + \epsilon_i^2) \quad (4)$$

$$M_i(\omega) = \epsilon_i / (\epsilon_r^2 + \epsilon_i^2) \quad (5)$$

where Z_i and Z_r are imaginary and real impedance respectively, C_o is vacuum capacitance ($C_o = \epsilon_o A / t$, t is thickness of the electrolyte, A is the surface area of contact, ϵ_o is the permittivity of free space) and ω is the angular frequency, being $2\pi f$. These formalisms are chosen since they display different aspects of the dielectric behavior; for example, the dielectric formalism (ϵ) highlights the effects of polarization whereas the electric moduli formalism (M) suppresses the effects of polarization but instead highlights the bulk dielectric behavior.

3. Results and Discussion

Dielectric constant, ϵ_r also known as the real part of dielectric constant is associated with a material's capacity to store charge, represents the amount of dipole alignment in a given volume and hence is a measure of the material's polarization. Since the number of ions present affects the amount of charge stored, then, if the number of ions increase, the number of charge stored increases. While for imaginary dielectric constant, also known as dielectric loss, ϵ_i , it is used to measure the dissipation of energy generated

from transportation of charge carriers and alignment of dipoles when the polarity of electric field reverses and hence is a measure of polarization effects of charge carriers [10] where it is related to the electrical conductivity of the material.

Fig. 1(a) and (b) shows the dependence of dielectric constant and dielectric loss as a function of frequency at various temperatures for PEIL08. The nature of dielectric permittivity for free dipoles oscillating in an alternating field may be described in the following manner. At very low frequencies ($\omega \ll 1/\tau$, τ is the relaxation time), dipoles follow the field and the value of dielectric constant $\epsilon_r = \epsilon_s$ (value of dielectric constant at quasistatic fields) [4, 11]. As the frequency increases (with $\omega < 1/\tau$), the dielectric constant drops (relaxation process). At very high frequencies ($\omega \gg 1/\tau$), dipoles can no longer follow the field and $\epsilon_r = \epsilon_\infty$ (high frequency value of ϵ_r).

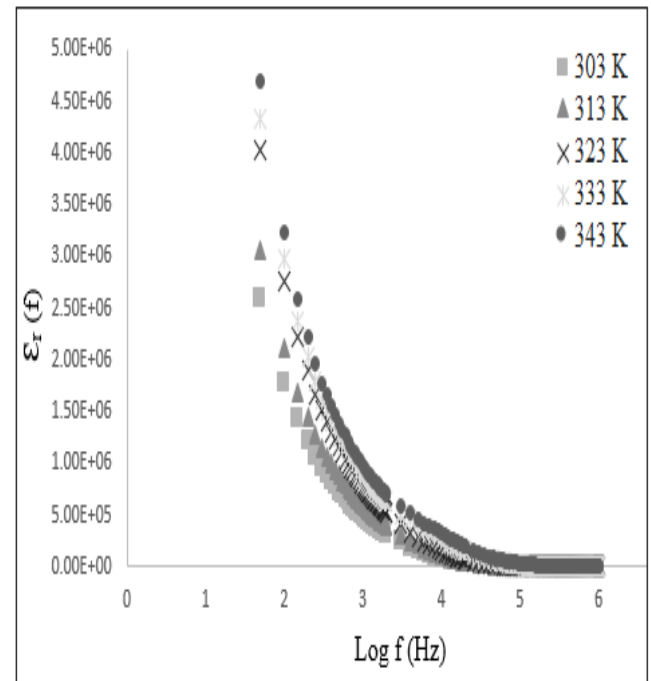


Fig. 1(a): Variation of dielectric constant with log frequency at various temperatures.

Qualitatively the above described behavior is observed in Fig. 1 (a) and (b). The dielectric constant at low frequency is observed to be rather high, is found to decrease with frequency at first, and then becomes more or less stabilized. The high value of ϵ_r at frequencies lower than 100 Hz, which increases with decreasing frequency and increasing temperature, corresponds to bulk effect of the system. Higher value of dielectric constant observed at high temperature and very low frequencies may be attributed to free charge buildup at the interfaces within the bulk of the sample (interfacial polarization) and at the interface between the sample and the electrodes (space-charge polarization) indicating that the sample at 343K has the highest amount of charge stored and hence the highest conductivity.

The dielectric loss is also rather high at low frequency but falls quickly with rising frequency. Similar to the dependence of dielectric constant on temperature, the dielectric loss increases with increasing temperature. This indicates the thermally activated nature of dielectric relaxation of the polymer electrolyte system and that heat or temperature increases the degree of salt dissociation and redissociation of ion aggregates and hence increases conductivity due to higher ion content. The thermally activated behaviour is also apparent from the displacement of the rise in both dielectric constant and dielectric loss to higher frequencies at higher temperatures indicating that the number of charges and hence ion present increases with temperature.

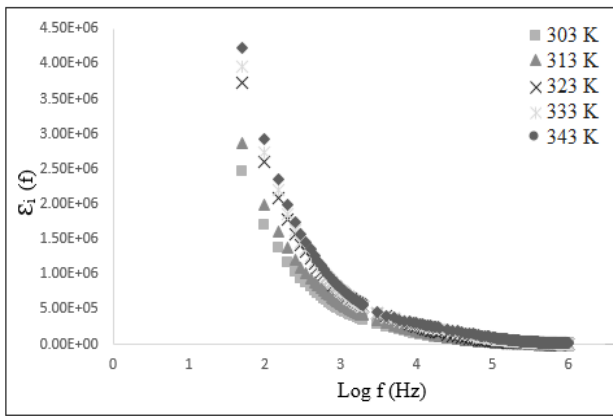


Fig. 1(b): Variation of dielectric loss with log frequency at various temperatures.

In order to analyse the relaxation processes, dielectric moduli analysis is presented to highlight the bulk dielectric behavior and suppress the effects of electrode polarization [12]. Fig. 2 (a) and (b) depicts both real and imaginary part of the electric moduli at temperatures between 303K to 343K for PEIL08.

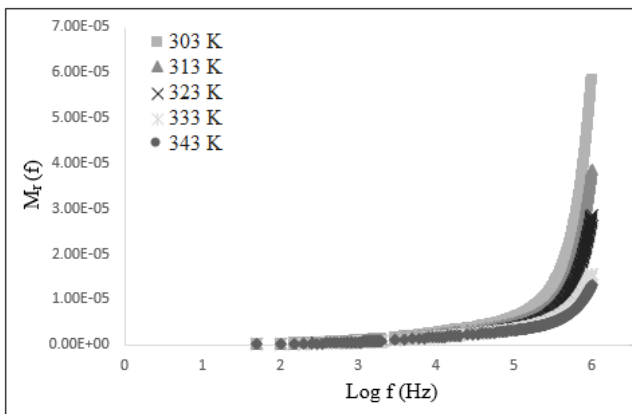


Fig. 2(a): Variation of real part of electric modulus with log frequency at various temperatures.

At low frequencies, M_r and M_i approaches zero for all temperatures indicating that electrode polarization phenomenon makes negligible contribution [13]. The presence of the long tail at the low frequency end is attributed to the large capacitance associated with the electrodes [14], which gives added evidence of the suppression of electrode polarization. It can be observed that both M_r and M_i have low values at lower frequencies and slowly increase as the frequencies increased. The rise in both M_r and M_i is displaced towards higher frequencies at higher temperatures giving indication of a thermally activated behavior implying higher conductivity at higher temperatures. The high value at higher frequencies is due to conductivity relaxation spreading over the range of frequencies studied [15], i.e. the existence of a temperature-dependent electrical relaxation phenomenon in the system. It also indicates that ionic conduction motion and polymer segmental motion are strongly coupled in the system. This implies that as temperature increased, the polymer segmental motion increases giving it more flexibility which in turn aids in the transport of ions. In other words, as the polymer segments become more flexible with temperature the mobility of ion increases and so does the conductivity. This is in line with the very fundamental concept of conductivity described by the equation:

$$\sigma = nq\mu \tag{6}$$

Where σ is conductivity, n is number of charge carriers/ions and μ is the mobility. Also it is to be noted that at higher temperatures

n , the number of ions increases as evidenced by the graph in Fig. 1 (a), where the value of ϵ_r is the highest at the highest temperature.

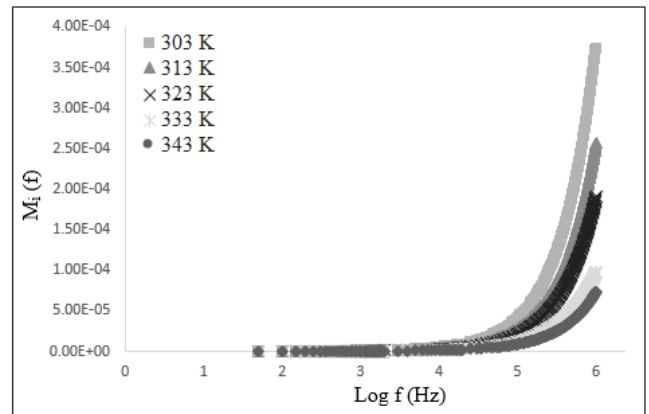


Fig. 2(b): Variation of imaginary part of electric modulus with log frequency at various temperatures.

The relaxation phenomenon may be interpreted from a graph of loss tangent ($\tan \delta$) versus frequency at various temperatures as shown in Fig. 3 for PEIL08. The rising trend of $\tan \delta$ at low frequencies is representative of the presence of DC conductivity in the polymer electrolyte system. At low frequencies, $\tan \delta$ increased due to the active compound (ohmic) being more dominant than the reactive component (capacitive). At higher frequencies, $\tan \delta$ decreased with frequency since the ohmic portion is independent of frequency and the reactive compound increased in proportion to the frequency [16].

The shift of $\tan \delta$ peaks to higher frequencies for samples at higher temperatures indicate that the charge carriers/ions are thermally activated and the highest conducting sample (343K) has the lowest peak intensity. The occurrence of relaxation time, τ can be obtained from the peak of $\tan \delta$ using the relation [17]:

$$\tau = 1/\omega_{\text{peak}} \tag{7}$$

where, $\omega = 2\pi f$ and f is the frequency of the relaxation peak.

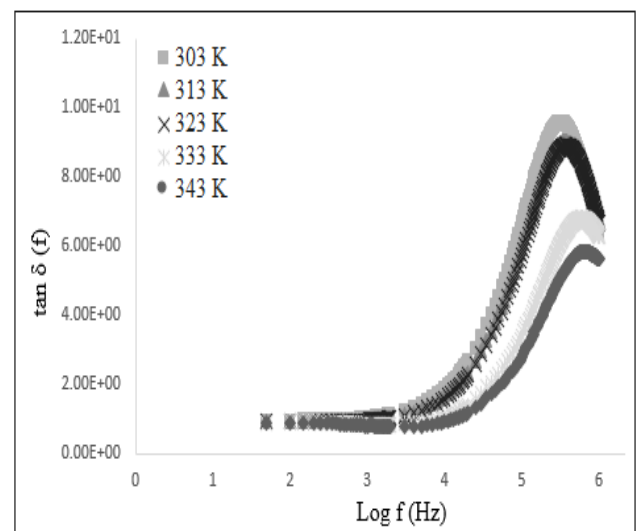


Fig. 3: Variation of loss tangent with frequency at various temperatures.

Table 1 shows the relaxation time at each temperature and from this table, it is observed that the highest temperature (343 K) achieved the lowest relaxation time due to increase in number of ions and increase in mobility of ions in the polymer system, which in turn decreased the relaxation time. The results show that relaxation is a thermally activated process where the relaxation time decreased when temperature increased.

Table 1: Conductivity, σ and Relaxation Time, τ for PEO-LiTFSI-EMIm-TFSI at 8 wt. % of EMIm-TFSI as a Function of Temperature.

| Temperature (K) | Relaxation Time, τ (s) | Conductivity, σ (S/cm ¹) |
|-----------------|-----------------------------|---|
| 303 | 3.84×10^{-7} | 1.44×10^{-3} |
| 313 | 3.66×10^{-7} | 2.05×10^{-3} |
| 323 | 3.50×10^{-7} | 2.80×10^{-3} |
| 333 | 2.67×10^{-7} | 5.13×10^{-3} |
| 343 | 1.99×10^{-7} | 7.10×10^{-3} |

These results may be corroborated by the graph of ϵ_r and ϵ_i versus temperature and M_r and M_i versus temperature as shown in Fig. 4 and Fig. 5.

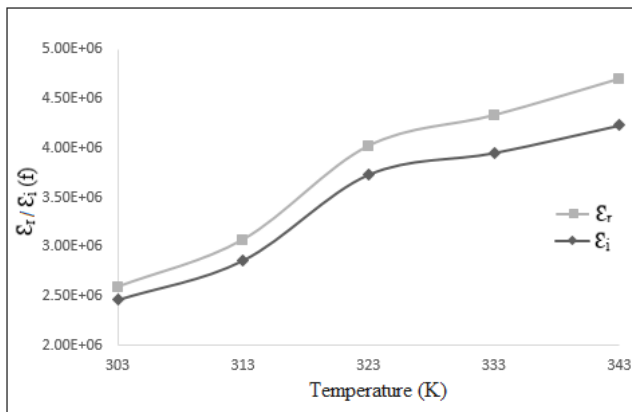


Fig. 4: ϵ_r and ϵ_i versus temperature

From the graph of temperature dependence, at low temperature, the charge carriers cannot orient themselves with respect to the direction of applied field [18], as they did not get enough thermal energy. When the temperature increased, it led to dissociation of more ions that caused increase in the number of free ions [19]. The charge carriers also get enough thermal energy to be excited and hence, they were able to obey the change in the external field and contributed to polarization, which in turn led to an increase of dielectric constant and dielectric loss value in the samples [20]. This is due to more energy being dissipated. The highest ionic conductivity value at 343K, thus has the highest ϵ_r and ϵ_i proving that ϵ_r and ϵ_i are thermally activated [21] and the lowest M_r and M_i showing the spread of conductivity relaxation, an indication of temperature-dependence relaxation phenomenon [15]. The shift of M_r and M_i towards the higher frequency side also implies that the thermally activated ionic conduction relaxation is due to hopping of charge carriers [15].

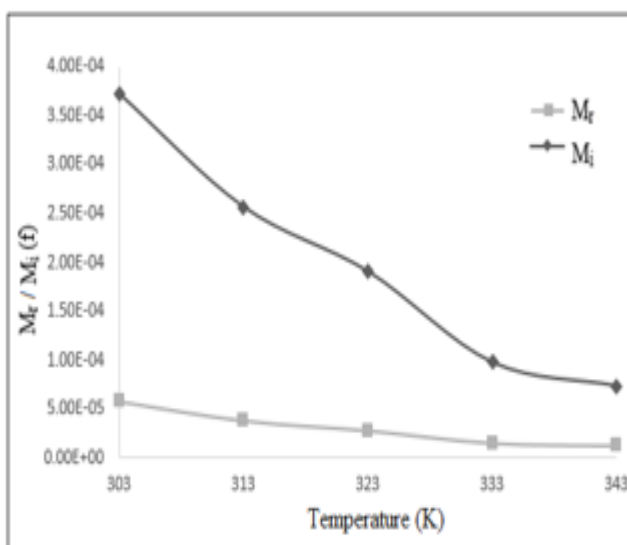


Fig. 5: M_r and M_i versus temperature

4. Conclusion

The electrical relaxation process occurring in PEO-LiTFSI-EMIMTFSI system has been found to be temperature and frequency dependent. The lowest relaxation time is achieved at the highest temperature, which is 343K.

Acknowledgement

The authors would like to thank the Ministry of Higher Education for the Sports Scholarship awarded and Faculty of Applied Sciences, Universiti Teknologi MARA for the opportunity given.

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