

CONDUCTIVITY AND DIELECTRIC STUDIES OF PURE AND DOPED POLY (ETHYLENE OXIDE) (PEO) SOLID POLYMER ELECTROLYTE FILMS

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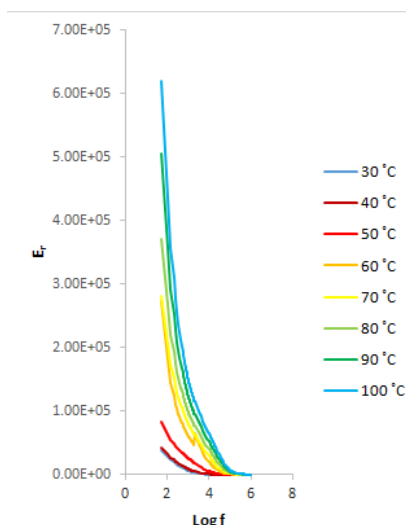
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Graphical abstract



Abstract

The solid polymer electrolytes (SPEs) composed of Poly (ethylene oxide) (PEO) with sodium trifluoromethanesulfonate (NaCF_3SO_3) salt has been prepared by solution casting technique. The conductivity and dielectric of the solid polymer electrolyte systems were studied within the broad frequency range of 50 Hz–1 MHz and within a temperature range of 30 °C to 100 °C. The samples were prepared by various salt concentrations ranging from 2 wt% to 22 wt%. The sample containing 18 wt% of NaCF_3SO_3 salt exhibit the highest ionic conductivity of $1.091 \times 10^{-5} \text{Scm}^{-1}$ at 30 °C. The conductivity of the SPEs has been found to depend on the salt concentration that was added to the sample. When higher salt concentration was added, ionic conductivity decreased due to the association of ions. The temperature of conductivity from 30 °C to 100 °C of SPEs was found to obey the Arrhenius rule. The dielectric permittivity decreased rapidly towards high frequencies due to the electrode polarization effects.

Keywords: SPEs, PEO, NaCF_3SO_3 , conductivity, dielectric

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1.0 INTRODUCTION

The Solid Polymer Electrolytes (SPEs) have received much interest because of their potential applications in solid state batteries. SPEs have many benefits such as ease of fabrication and handling batteries, excellent thermal stability and high ionic conductivity. However, the low ionic conductivity of SPE at room temperatures restrict practical applications of SPEs. Extensive effort has been focused on SPE to enhance the ionic conductivity [1].

Polyethylene oxide (PEO) dissolves high concentrations of a wide variety of salts and usually consists high crystalline phases at room temperature. PEO has a single a helical structure which helps fast ion

transport and good mechanical properties and electrochemical stability. However, conductivity of PEO-based electrolyte is limited because the amorphous phase of electrolytes made the most importance influence to ionic conductivity than crystalline phase. The simplest method to overcome this problem is to modify the solvating polymer in order to decrease the crystallinity of the polymer electrolyte is doped with salt. [2–5].

In this paper, Poly (ethylene oxide) (PEO) with sodium trifluoromethanesulfonate (NaCF_3SO_3) salt has been prepared by solution cast technique. . Electrical conductivity measurements and dielectric permittivity in the temperature ranging from 30 °C to 100 °C have been carried out to characterize solid polymer

electrolyte system and the results obtained are presented in this paper.

2.0 EXPERIMENTAL

2.1 Material and Sample Preparation

The polymer electrolyte was prepared by solution cast technique. Poly(ethylene oxide) (PEO) with an average molecular weight of 400,000 and sodium trifluoromethanesulfonate (NaCF_3SO_3) 98% with an average molecular weight of 172.06 was obtained from Sigma Aldrich. Acetonitrile is used as solvent. One gram of PEO was dissolved in 80mL of acetonitrile solution. The mixture was stirred continuously with a magnetic stirrer for few hours at room temperature until the PEO powder has completely dissolved. To these sets of solution, 2 to 22 wt. % of NaCF_3SO_3 was added separately and the mixtures were stirred continuously until homogeneous solutions were obtained. The solutions were then poured into different glass petri dish and left to dry at room temperature in order to allow complete evaporation of solvent. The thin films were kept in desiccators with silica gel desiccant for extra drying process.

3.0 RESULTS AND DISCUSSION

3.1 Electrical Impedance Spectroscopy (EIS)

2.2 Electrical Impedance Spectroscopy (EIS)

The impedance of the samples was measured using HIOKI 3532-50 LCR Hi-Tester and the ESPEC SH-241 Bench-Top Type Temperature & Humidity Chamber which was interfaced to a computer. This instrument was set to measure the impedance in the frequency range from 50 Hz to 1M Hz and in a temperature range from 30 °C to 100 °C. The software controlling the measurements calculates the real and imaginary impedances. Complex impedance data, Z^* , can be represented by its real and imaginary parts, Z_r and Z_i . The conductivity (σ) was determined from the following equation:

$$\sigma = \frac{t}{R_b A} \quad (1)$$

Where t is the sample thickness, A is the area of contact between the electrode and sample, and R_b is the bulk resistance of the samples.

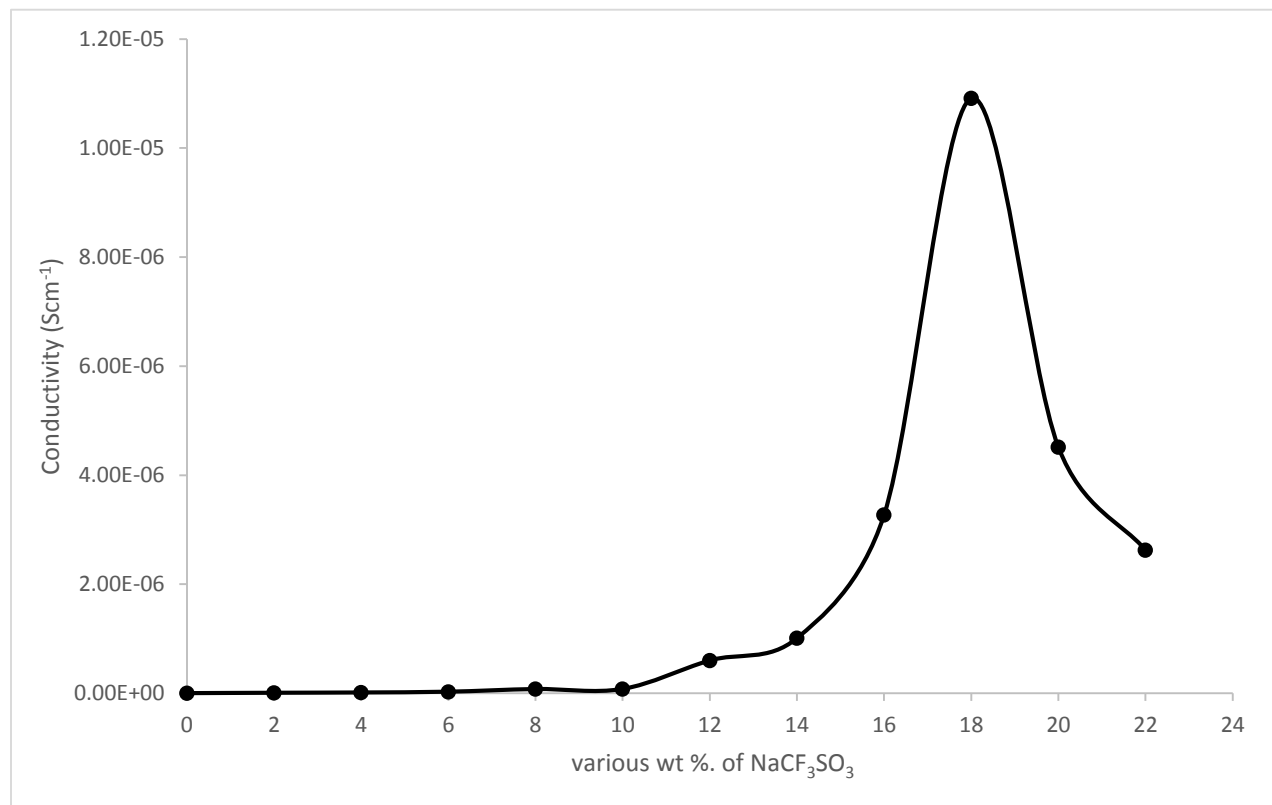


Figure 1 Ionic conductivity of PEO with various wt. % of NaCF_3SO_3 at 30 °

Figure 1 shows the 30 °C temperature complex impedance plots of PEO- NaCF_3SO_3 complex with different salt concentration. When NaCF_3SO_3 salt was dissolved in the pure PEO, the conductivity become increases compared to pure PEO due to of adding charge carriers. The reasons that, the availability of conducting ions provided by the salt and to the result of polymer-salt [1]. From the plot, conductivity of $1.091 \times 10^{-5} \text{Scm}^{-1}$ at 30 °C was obtained with additional of 18 wt. % NaCF_3SO_3 . It was found to be the most conductive electrolyte among the all salt

concentrations compare to pure PEO which have conductivity $3.57 \times 10^{-11} \text{Scm}^{-1}$. The conductivity values declined with further addition of NaCF_3SO_3 beyond 18 wt. % due to the mobility of ions decreased by the formation of ion pairs and higher aggregates. Beside, as the salt concentration increased, the number of charge carriers also increased, but the mobility of polymer chains would decrease [2]. This is because the higher rate of ion association than ion dissociation. Furthermore, ion aggregate at high salt concentration which do not support in the conduction process [6].

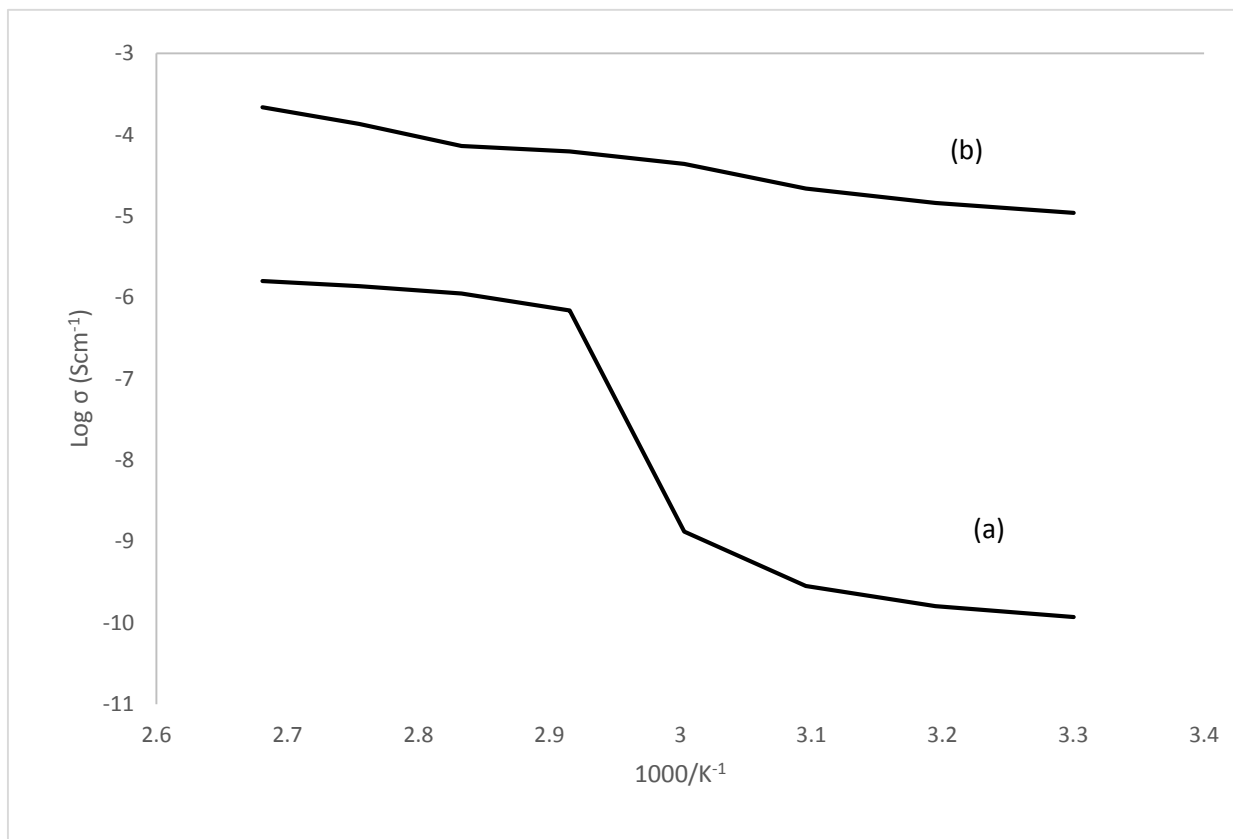


Figure 2 Conductivity dependence temperature of solid polymer electrolytes (a) Pure PEO (b) PEO-18 wt. % NaCF_3SO_3

Figure 2 shows the Arrhenius plot of the conductivity dependence temperature for the SPE. The ionic conductivity increases with increasing temperature from 30 °C to 100 °C. This can be explained from the free volume model of the system. When temperature increases, the free volume of the system can enlarge easily and facilitate the motion of ionic charge. So more ions, solvated molecules, or the polymer segments can travel into the free volume. This improves the ion and polymer segmental mobility

which make enhances the ionic conductivity [3]. Pure PEO electrolyte at 60 °C to 70 °C as shows there is sudden increase in conductivity. Still, the ionic conductivity increase linearly beyond 70 °C [7]. It is because may due to the transition of the polymer from the crystalline to amorphous phase [4]. But for PEO- NaCF_3SO_3 electrolyte with higher salt concentration, figure 2 (b) show did not exhibit such obvious transition.

3.2 Dielectric Permittivity Studies

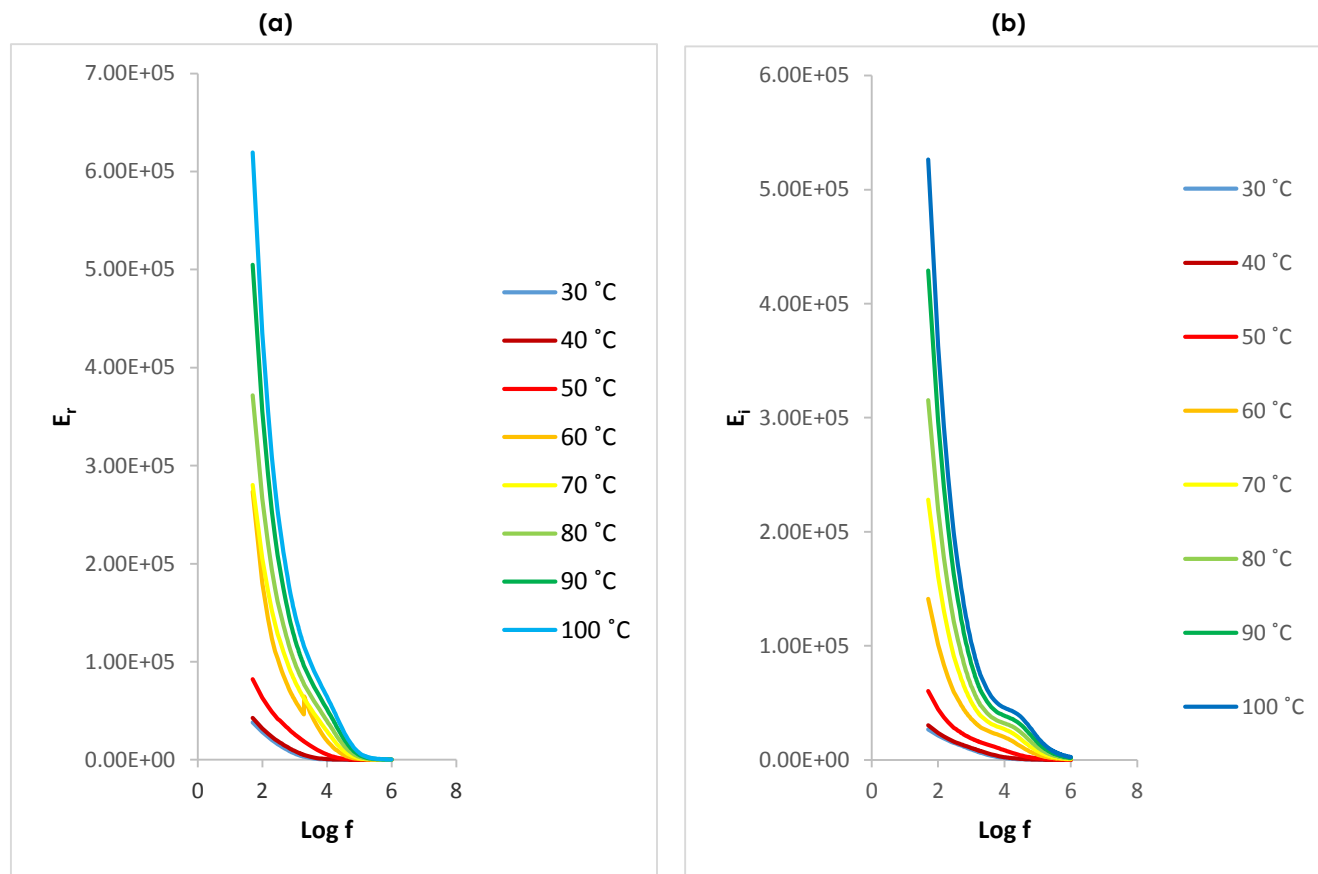


Figure 3 (a) Dielectric constant (ϵ_r) and (b) Dielectric loss (ϵ_i) of PEO-18 wt. % NaCF_3SO_3 at different temperature

Fig. 3 shows the relationship between dielectric constant (ϵ_r) and (b) dielectric loss (ϵ_i) of PEO-18 wt. % NaCF_3SO_3 at different temperature. The values of ϵ_r and ϵ_i increase with the addition of salt. At high frequency, the dielectric constants decrease nonstop until reaches a constant value at about 10 kHz. It is observed from figure 3 that at low frequency, dielectric permittivity increases rapidly due to the mobile ions accumulate at the electrode/electrolyte interface and electrode polarization effect. On the other hand, at high frequencies, the dielectric permittivity decrease due to periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction field and polarization due to charge accumulation decrease. [6, 8, 9]

4.0 CONCLUSION

In this work, by using PEO as the polymer host and NaCF_3SO_3 as doped salt, the solid polymer electrolyte could be prepared by using the solution cast technique. The highest conductivity of the polymer electrolyte PEO-18 wt% NaCF_3SO_3 was $1.091 \times 10^{-5} \text{ Scm}^{-1}$ at 30 °C. Arrhenius plot also showed that the ionic

conductivity increased with an increase in temperature from 30 °C to 100 °C. The dielectric behavior of PEO and its complexes had also been studied. The dielectric constant and dielectric loss of PEO were found to increase upon the addition of NaCF_3SO_3 salt. The dielectric permittivity increased rapidly towards low frequencies.

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