

Conductivity and FTIR Studies on PEO- NaCF₃SO₃ Solid Polymer Electrolyte Films

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Abstract— Solid polymer electrolytes electrolytes based Poly (ethylene oxide) (PEO) complexed with sodium trifluoromethanesulfonate (NaCF₃SO₃) salt were prepared by using solution cast technique. Ion-polymer ionic conductivity and interaction studies have been reported by Electrical Impedance spectroscopy (EIS) and Fourier transform infrared spectroscopy (FTIR). FTIR studies suggested that there are stronger interaction between Na⁺ ions and the polymer than interaction of anions cations of the salt. The temperature dependance electrical conductivity of polymer electrolyte films follow Arrhenius relation and the low activation energy 0.2993 eV was observed for PEO-18 wt. % NaCF₃SO₃ below 323 K.

Index Terms—Polymer Electrolytes, PEO, NaCF₃SO₃, EIS, FTIR

I. INTRODUCTION

Solid polymer electrolytes (SPEs) are promising materials electrolyte in solid state electrochemical devices such as lithium and sodium batteries. SPEs are used in solid state battery system because of easy to fabrication as thin films, their capability to form good contact with electrode material and better mechanical properties. Semi-crystalline phase of Polyethylene oxide (PEO) dissolves high concentrations of a wide variety of salts such as LiCF₃SO₃ and NaCF₃SO₃. However, conductivity of PEO at room temperature and mechanical strength is low because of its crystalline phase in nature limits the conductivity of PEO based electrolytes. The simplest method to overcome this problem is by modify solvating polymer in order to decrease the crystallinity of the polymer electrolyte. This can be done by introducing appropriate salt [1,2].

In this study, poly (ethylene oxide) (PEO) as polymer host and sodium trifluoromethanesulfonate (NaCF₃SO₃) as doping salt has been prepared by solution cast technique and the results obtained by FTIR and EIS are presented in this paper.

II. MATERIALS AND METHOD

A. Material and Sample Preparation.

The polymer electrolyte was prepared by solution cast technique. Poly(ethylene oxide) (PEO) with an average molecular weight of 600,000 and sodium

trifluoromethanesulfonate (NaCF₃SO₃) were obtained from Sigma Aldrich. One gram of PEO was dissolved in 40mL 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, 14 to 22 wt. % of NaCF₃SO₃ was added separately and the mixtures were stirred continuously until homogeneous solutions were obtained. The solutions were then poured into different glass petri dishes 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 further drying process.

III. RESULTS AND DISCUSSION

A.EIS

Figure 1 shows the temperature dependence of ionic conductivity of PEO-wt. % NaCF₃SO₃. The ionic conductivity is measured from 303 K to 373 K as shows in figure 1. The conductivity increase with increase temperature in all compositions of PEO-wt. % NaCF₃SO₃. There is a sudden increase in conductivity at 60 C - 70 C for Pure. However the ionic conductivity increase linearly beyond 70 C. Its due to the transition of the polymer from the crystalline to amorphous phase. These result was shown to exhibit an Arrhenius behavior with two different activation energies above and below melting temperature. As the temperature increase, the number of free ions also increases, thus increases the diffusion of ions through their free volumes. Thus the ionic conductivity increase when more the number of free ion can move into the free volume. The temperature conductivity relationship can be expressed by the equation:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)$$

where σ_0 is the pre-exponential factor, E_a is the activation energy and k is the Boltzmann constant. The low activation energy 0.2993 eV was observed for PEO-18 wt. % NaCF₃SO₃ below 323 K. [3–5]

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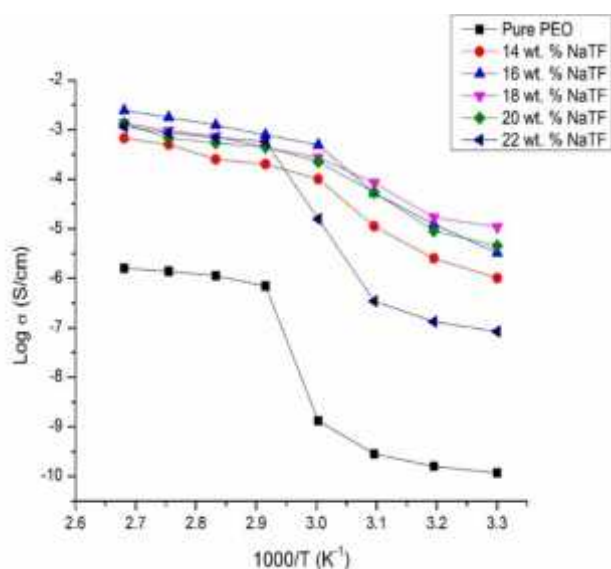


Fig.1. Temperature dependence of ionic conductivity of PEO- wt. % NaCF_3SO_3

B. FTIR

The band at 767 cm^{-1} and 630 cm^{-1} is assigned to $\nu_s(\text{CF}_3)$ and $\nu_s(\text{SO}_3)$ mode of triflate respectively. The addition of NaCF_3SO_3 to PEO results in new peak bands at 760 cm^{-1} , 756 cm^{-1} and 638 cm^{-1} . The band that appears at 630 cm^{-1} in pure NaCF_3SO_3 shifted to 638 cm^{-1} when addition of NaCF_3SO_3 to PEO. It shows, the complexation has occurred in the PEO- NaCF_3SO_3 films. To study the ion-ion interaction in these electrolytes the symmetric deformation mode of CF_3 [denoted as $\nu_s(\text{CF}_3)$] in the spectral region $1000\text{--}600\text{ cm}^{-1}$ has been investigated and is shown in Figure 2. This mode is very much sensitive to the ionic association present in the polymer-salt electrolytes. It is observed that no peak is present in pure PEO but with the addition of NaCF_3SO_3 salt to PEO, a peak appears at 766 cm^{-1} and 638 cm^{-1} [6].

In Figure 3, FTIR spectra of pure PEO, NaCF_3SO_3 and the films from the PEO- NaCF_3SO_3 system in the region between 1000 cm^{-1} and 1800 cm^{-1} are presented. The band that appears at 1036 cm^{-1} is due to the triflate symmetric (SO_3) stretching modes. According to many studies, it could be assigned that the component is describe to ion pairs, free ions, ion triple and ion cluster. This band decreases to 1030 cm^{-1} when increasing salt. It indicate that there is stronger interaction between Na^+ ions and the polymer than interaction of anions and cations salt. At higher salt concentrations most of of the band in this region slightly broadened. The change in shape, position and intensity of the peaks in this region confirms the complexation of PEO and NaCF_3SO_3 .

The width of C–O and C–H stretching band at 1093 cm^{-1} and 2877 cm^{-1} respectively decreases when salt are added compared to pure PEO. Therefore, the presence of new bands along with changes in existing bands in the FTIR spectra directly support complexation of PEO with NaCF_3SO_3 and is also responsible for distortion of crystalline PEO structure. [5].

The peak at 1258 cm^{-1} is shifted to 1278 cm^{-1} in the PEO- NaCF_3SO_3 complex. This prove that the interaction between PEO and NaCF_3SO_3 , which can be attributed to the change in environment for the CF_3SO_3^- ions in the complex. Since the cations of NaCF_3SO_3 are coordinated with the ether oxygen of PEO, the spectral changes are believed to be due to the influence of NaCF_3SO_3 or the C–O–C stretching mode and deformation. The presence of water can be identified by observing a broad peak at $3600\text{--}3200\text{ cm}^{-1}$ show in figure 3, which is characteristics for the –OH stretching vibrational mode. The spectrum is clearly observed at a frequency of 3501 cm^{-1} for NaCF_3SO_3 which is caused by the –OH stretching mode of hydrogen bonding. These observations imply the occurrence of interactions between the salt and polymer [3].

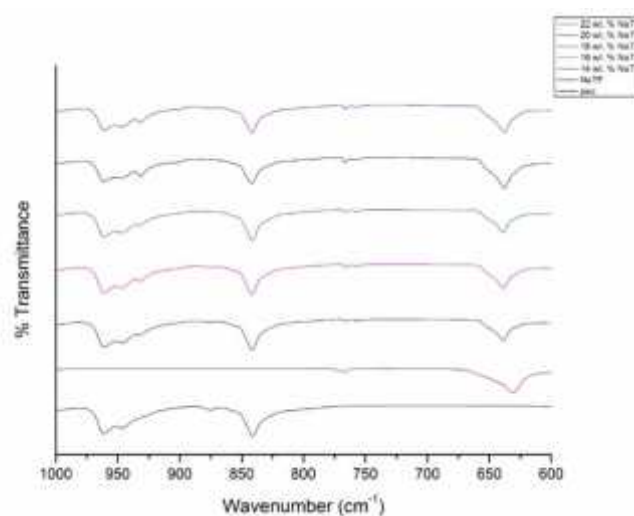


Fig. 2. FTIR spectra of pure PEO, pure NaCF_3SO_3 and various composition of PEO-wt.% NaCF_3SO_3 film band between 100 cm^{-1} and 600 cm^{-1}

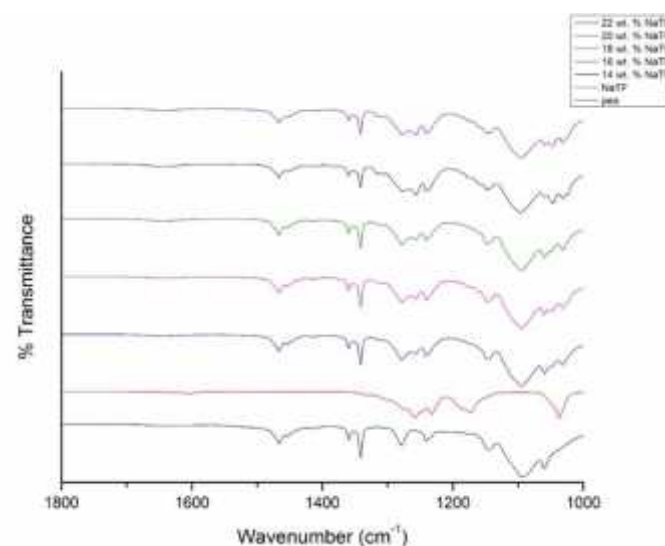


Fig. 3. FTIR spectra of pure PEO, pure NaCF_3SO_3 and various composition of PEO-wt.% NaCF_3SO_3 film band between 1800 cm^{-1} and 1000 cm^{-1}

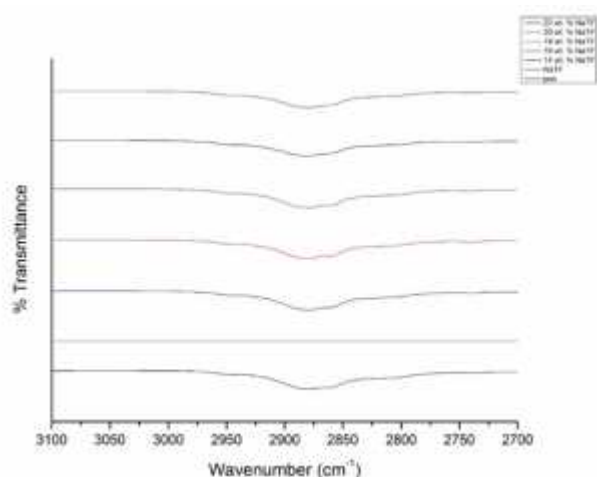


Fig. 4. FTIR spectra of pure PEO, pure NaCF_3SO_3 and various composition of PEO-wt.% NaCF_3SO_3 film band between 3100 cm^{-1} and 2700 cm^{-1}

IV. CONCLUSIONS

Solid polymer electrolytes consisting of Poly (ethylene oxide) (PEO) and sodium trifluoromethanesulfonate (NaCF_3SO_3) were prepared by solution cast technique. From EIS, the temperature dependence of ionic conductivity of PEO- NaCF_3SO_3 obeyed the Arrhenius relationship and low activation energy obtained for optimum composition PEO- NaCF_3SO_3 . Analysis of the thin films by FTIR indicates that interaction in PEO- NaCF_3SO_3 has occurred.

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