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CHARACTERIZATION OF POLYACRYLONITRILE BASED CONDUCTING POLYMER ELECTROLYTE FILMS

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ABSTRACT

The conducting polymer electrolyte films composed of polyacrylonitrile (PAN) as the host polymer, $LiCF_3SO_3$ and $NaCF_3SO_3$ as inorganic salts were prepared by the solution cast technique. The pure PAN film was prepared as a reference. XRD studies show that the complexation has occurred in the PAN containing salt films and complexes formed are amorphous. These results correspond with surface morphology images obtained from SEM analysis. DSC analysis show that the glass transition temperature, T_g of PAN film has decreased on addition of salts. The ionic conductivity for the films is characterized using impedance spectroscopy. The room temperature conductivity for the PAN + 26wt.% $LiCF_3SO_3$ film and the PAN + 24wt.% $NaCF_3SO_3$ film is 3.04×10^{-4} Scm^{-1} and 7.13×10^{-4} Scm^{-1}, respectively. The PAN containing $NaCF_3SO_3$ film has a higher ionic conductivity compared to the PAN containing $LiCF_3SO_3$ film. These results can be explained based on the Lewis acidity of the alkali ions, i.e., the interaction between Li^+-ion and the nitrogen atom of PAN is stronger than that of Na^+-ion. The temperature dependence of the conductivity follows Arrhenius equation in the temperature range of 303 K to 353 K.

INTRODUCTION

The conducting polymer electrolyte film is one of the important components in electrochemical devices such as rechargeable batteries, fuel cells, electrochromic devices, etc [1-2]. Polymer electrolytes films have many advantages due to special properties like, good electrode-electrolyte contact, flexibility or processability, ease of preparation in thin film form, good mechanical and adhesive properties. In contrast to the liquid electrolytes, solid electrolytes have no, or very limited problems with leakage or pressure-related distortions [3].

The pioneering work of Armand et. al [4] and others [5-6] led to the development of polymer-based electrolyte for battery applications. Most of the early work carried out on conducting polymer electrolytes concentrate on polyethylene oxide (PEO) [7]. Generally, the cation-coordinating macromolecule is the majority component in the conducting polymer electrolytes and ionic transport occurs in amorphous regions of the materials, assisted by segmental motions of the host polymers [8]. Many lithium-ion-conducting polymer electrolytes have been reported using $LiBF_4$, $LiPF_6$, $LiCF_3SO_3$, and $LiClO_4$ [9-11]. Some studies in this field are devoted to PEO and poly(propylene carbonate) (PPO)-based electrolytes using sodium salts, e.g. NaI, $NaClO_4$, $NaCF_3SO_3$ and $NaYF_4$ [12-14].

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In the present work, the conducting polymer electrolyte films composed of polyacrylonitrile (PAN) as a host polymer, lithium trifluoromethanesulfonate ($LiCF_3SO_3$) and sodium trifluoromethanesulfonate ($NaCF_3SO_3$) as inorganics salts have been prepared. The films were characterized by impedance spectroscopic studies, where the influence of inorganic salts concentrations and temperature on the conductivity behavior will be investigated. The surface morphology, complexation and glass transition temperature, T_g were studied by Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and Differential Scanning Calorimetry (DSC) techniques.

EXPERIMENTAL METHODS

Sample Preparation

Polyacrylonitrile (PAN), with molecular weight of 150,000 g/mol, lithium trifluoromethanesulfonate ($LiCF_3SO_3$), sodium trifluoromethanesulfonate ($NaCF_3SO_3$) and dimethylformamide (DMF) were obtained from Aldrich. PAN was dissolved in DMF and the mixture was stirred at 60 °C until the solution turned into a clear and homogeneous. $LiCF_3SO_3$, and $NaCF_3SO_3$ salts were added accordingly. The mixtures continuously stirred with magnetic stirrer for several hours. After complete dissolution, the solutions were cast in petri dishes and left to dry under vacuum at 50 °C for 48 hours until the films were formed. The films were then kept in a desiccator for further drying until characterizations are to be carried out.

Characterization Techniques

To study the phase structure and complexation of the conducting polymer electrolyte films, XRD measurement was carried out using a PAN Analytical Expert Pro MPD in the range of 2θ from 10° to 80°.

DSC measurement was carried out using a METTLER TORLEDO DSC882° at heating rate of 10 °C/min. The glass transition temperature, T_g was estimated from the DSC curves obtained from the second heating run after the first run of heating up to 120 °C and cooling to -50 °C at a cooling rate of 10 °C/min under nitrogen condition with a flow rate of 50 ml/min.

Impedance spectroscopy measurements were used to determine the conductivity of the films. The films were cut into a round shape that fit the size of the electrodes. The films were then sandwiched between the two stainless steel blocking electrodes with a diameter of 2 cm. A HIOKI 3532 LCR bridge that has been interfaced with a computer was used to perform the impedance measurement for each polymer electrolyte film in the frequency range of 50 Hz to 1 MHz. From the impedance plots obtained, the bulk resistance, R_b of each sample was determined and hence the conductivity (σ) of the samples were then calculated using $\sigma = t/R_bA$; where t is the sample thickness (cm), A the effective contact area of the electrode and the electrolyte (cm^2), and R_b is the bulk resistance (Ω). The temperature conductivity dependence studies were carried out in the range of temperature from 303 K to 353 K.

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The surface morphology of the films was observed by SEM (Stereoscan 420, Leica). The films were vacuumed after sputtering with gold at 25 mA for 40 s.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of pure PAN film, $LiCF_3SO_3$ salt, $NaCF_3SO_3$ salt, PAN + 24wt% $NaCF_3SO_3$ film and PAN + 26wt% $LiCF_3SO_3$ film. Figure (d) and 1(e) demonstrate that as the $LiCF_3SO_3$ and $NaCF_3SO_3$ salts are mixed with the PAN polymer, the individual diffraction patterns of the salts and PAN are not observed in the PAN containing salt films. These results reveal that the complexation has occurred and the complexes formed are amorphous. Berthier et al. [8] established that ionic conductivity in polymer electrolytes is associated with the amorphous phase of the studied samples.

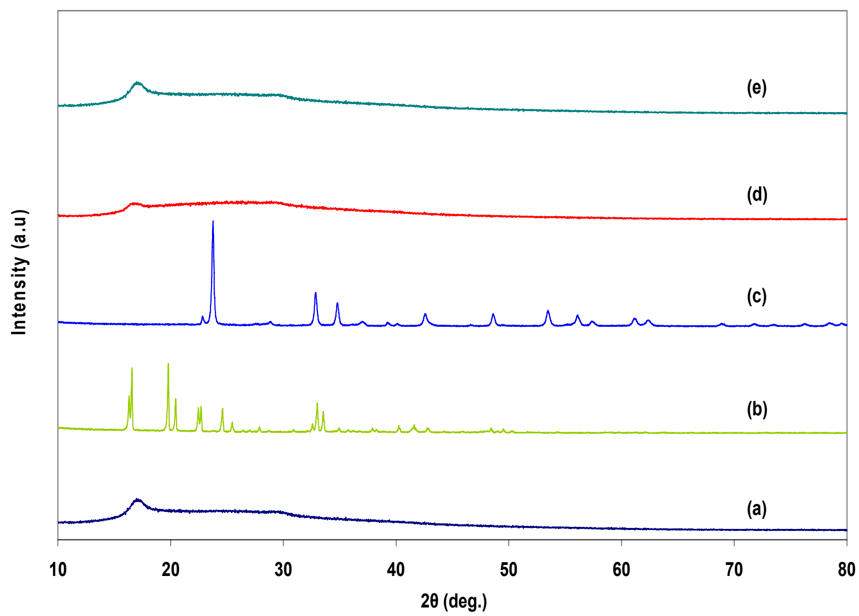

Figure 1: XRD patterns of (a) pure PAN film, (b) $LiCF_3SO_3$ salt, (c) $NaCF_3SO_3$ salt, (d) PAN + 26wt% $LiCF_3SO_3$ film and (e) PAN + 24wt% $NaCF_3SO_3$ film.

The glass transition temperatures of the PAN-based conducting polymer electrolyte films have been estimated from DSC curves. DSC curve of pure PAN film revealed a distinct T_g at 88.3 ^oC. The T_g for PAN + 24wt% $NaCF_3SO_3$ film and PAN + 26wt% $LiCF_3SO_3$ film is 84.7 ^oC and 85.3 ^oC, respectively. It can be seen that T_g of the PAN containing salt films has decreased compared to that of pure PAN film. This is in agreement with observation of Chen-Yang et al. [15]. These results indicate that there is some interaction between the salts and PAN as inferred from XRD studies.

Figure 2 shows the impedance plots for the PAN + 24wt% $NaCF_3SO_3$ film and the PAN + 26wt% $LiCF_3SO_3$ film. The disappearance of a depressed semicircle at high

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frequency for the films reveals the absence of capacitive nature of the samples. The inset figure shows the impedance plot for the pure PAN film. The intercept of the depressed semicircle with the real axis gives the electrolyte bulk resistance, R_b from which the conductivity can be determined.

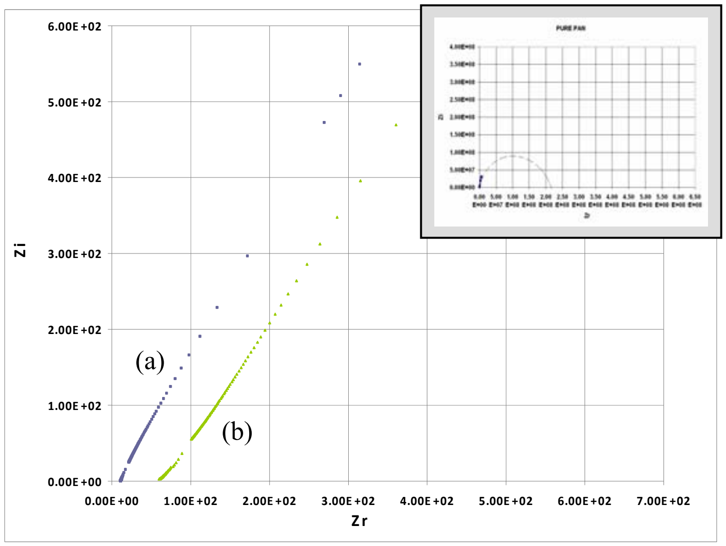

Figure 2: Impedance plots for the PAN containing salt films and the pure PAN film (inset).

The ionic conductivity versus salt content for the PAN + $NaCF_3SO_3$ system and the PAN + $LiCF_3SO_3$ system at room temperature is presented in Figure 3(a) and 3(b), respectively. It can be observed that the conductivity of pure PAN film increases an order of magnitude when 6 wt.% of $NaCF_3SO_3$ salt was added and continues to do so until 24 wt.% $NaCF_3SO_3$ has been added to the film. Hence 24 wt.% $NaCF_3SO_3$ is the conductivity optimizing concentration. The conductivity for PAN+$LiCF_3SO_3$ system is gradually increases when more than 2 wt.% of $LiCF_3SO_3$ was added and reached maximum value when 26 wt.% $LiCF_3SO_3$ has been added to the film. On addition of more than 10wt% of salts, the value of conductivity for the $NaCF_3SO_3$ salt containing films is higher than that of the $LiCF_3SO_3$ salt containing films. The highest room temperature conductivity film in the PAN + $NaCF_3SO_3$ system and the PAN + $LiCF_3SO_3$ system is 7.13 x 10^{-4} and 3.04 x 10^{-4} S cm^{-1}, respectively. Ionic conductivity of electrolytes depends on the charge carrier concentration, n and carrier mobility, μ as described by relation $\sigma = nq\mu$, where q representing the charge of mobile carrier. The increase in the ionic conductivity with increasing salt concentrations can be related to the increase in the number of mobile charge in the conducting polymer electrolyte films. The decrease in conductivity value at higher salt concentration is observed and can be explained by aggregation of the ions, leading to the formation of ion cluster, thus decreasing the number of mobile charge carriers and hence the mobility [16].

Figure 4(a) and 4(b) represent the variation of ionic conductivity with the reciprocal temperature for the PAN + 24wt% $NaCF_3SO_3$ film and the PAN + 26wt% $LiCF_3SO_3$

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film, respectively. The linear variation of log σ versus 1000/T plots revealed that in the temperature range between 303 K and 353 K, the ionic conductivity data follow Arrhenius equation, $\sigma(T) = \sigma_o \exp(-E_a/RT)$, where σ_o is the conductivity pre-exponential factor and E_a is the activation energy for conduction. As the conductivity temperature-dependence data obeys Arrhenius relationship, the nature of cation transport is quite similar to that occurring in ionic crystal, where ions jump into neighboring vacant sites and, hence, increase conductivity to higher value [17].

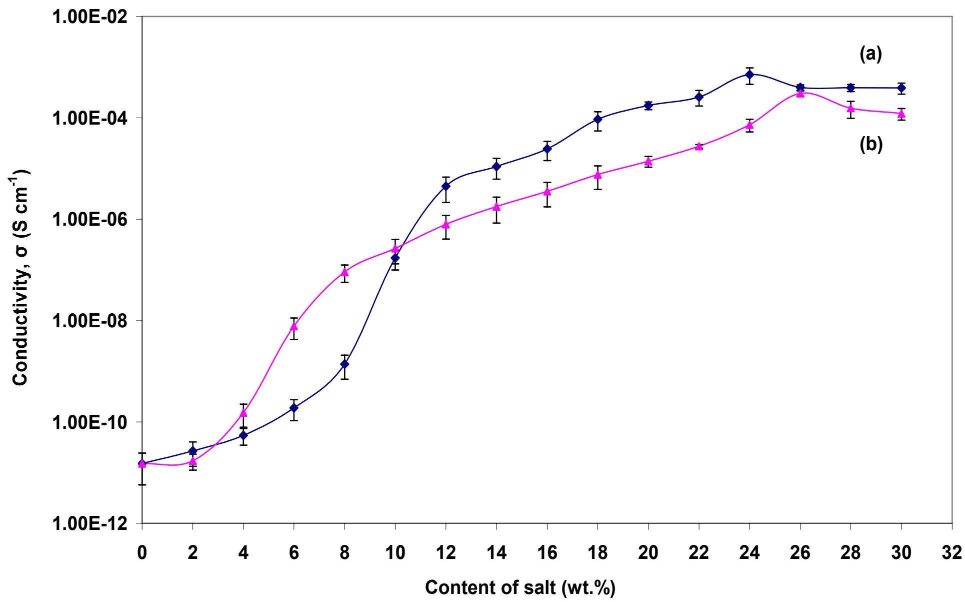

Figure 3: The ionic conductivity versus salt content for the (a) PAN + $NaCF_3SO_3$ system and (b) PAN + $LiCF_3SO_3$ system at room temperature.

The activation energy, E_a, which is a combination of the energy of defect formation and the energy of defect migration, can be evaluated from the slope of the plots [18]. The E_a for the PAN + 24wt% $NaCF_3SO_3$ film and PAN + 26wt% $LiCF_3SO_3$ film have been calculated to be 0.23 eV and 0.30 eV, respectively. It can be observed that PAN + 24wt.% $NaCF_3SO_3$ film has a higher ionic conductivity and lower activation energy compared to PAN + 26wt.% $LiCF_3SO_3$ film. This result can be explained based on the Lewis acidity of the alkali ions, i.e., the strength of the interaction of cations with the Lewis base of the polymer electrolyte [19]. The interaction between Li^+-ion and the nitrogen atom of PAN is stronger than that of Na^+-ion. Thus, Li^+-ion transfer requires higher activation energy than Na^+-ion in polymer electrolytes. These results agree well with the works reported by Sagane et al. and Abe et al. [19-21].

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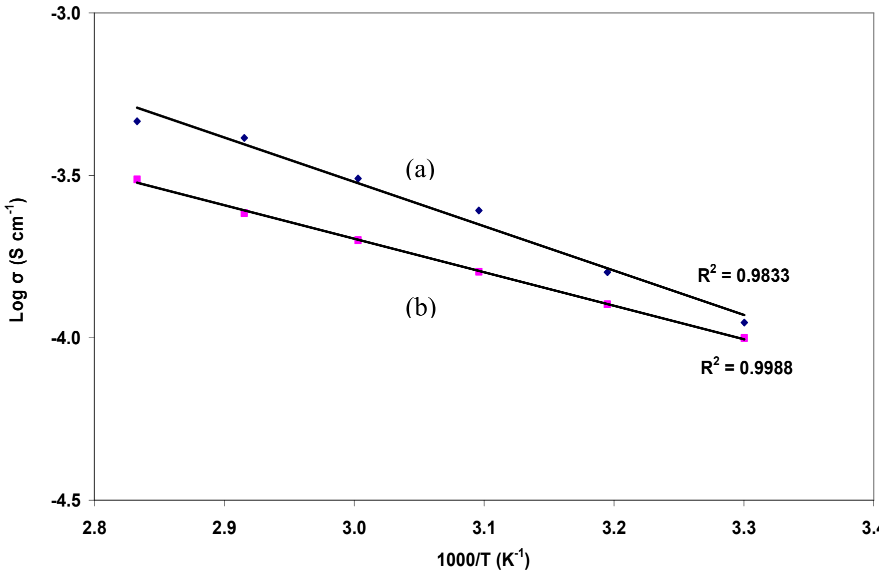
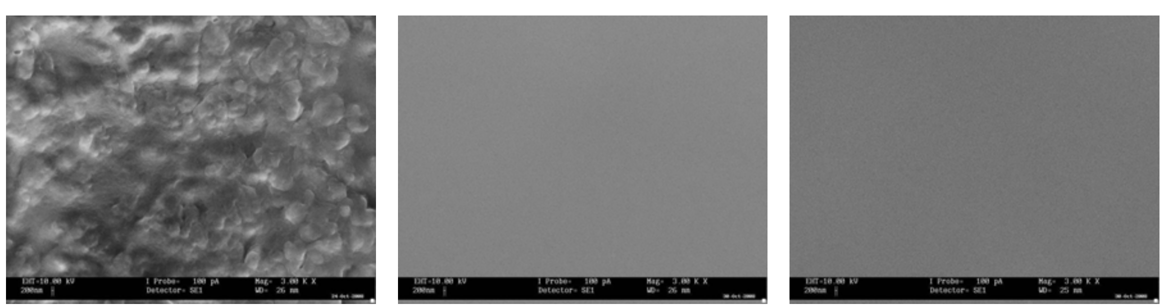


Figure 4: Log σ versus 1000/T plot for the (a) PAN + 26wt.% $LiCF_3SO_3$ film and (b)PAN + 24wt.% $NaCF_3SO_3$ film.

Figure 5 depicts the SEM micrographs of pure PAN film, PAN + 24wt% $NaCF_3SO_3$ film and PAN + 26wt% $LiCF_3SO_3$ film. A flaky surface with unevenly sized pores was discovered in the SEM micrograph of pure PAN film as shown in Figure 5(a). This result shows that the pure PAN is semicrystalline polymer as confirmed by XRD pattern, Figure 1(a). The surface morphology of the PAN containing salt films is smooth and homogeneous and is expected to continue in the bulk as depicted in Figure5(b) and 5(c). These results correspond with the amorphous phase in XRD patterns of the PAN containing salt films and higher conductivity of the PAN containing salt films than the pure PAN film.



(a) (b) (c)

Figure 5: SEM images of (a) pure PAN film, (b) PAN + 26wt.% $LiCF_3SO_3$ film and (c)PAN + 24wt.% $NaCF_3SO_3$ film.

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CONCLUSIONS

The conducting PAN polymer electrolytes containing $LiCF_3SO_3$ and $NaCF_3SO_3$ salts films have been prepared and studied. XRD studies show that the complexation has occurred and complexes formed are amorphous. These results correspond with SEM analysis. The T_g of the PAN film has decreased on addition of salts. The temperature dependence of the conductivity follows Arrhenius equation in the temperature range of 303 – 353 K. The PAN containing $NaCF_3SO_3$ film has a higher ionic conductivity and lower activation energy compared to the PAN containing $LiCF_3SO_3$ film. The results indicate that the interaction between Li^+-ion and the nitrogen atom of PAN is stronger than that of Na^+-ion.

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