

Preparation And Studies Of Polyacrylonitrile Ion Conducting Polymer Electrolytes

Z.Osman*, K.B.Md.Isa and A.Ahmad

Physics Department, University of Malaya, 50603 Kuala Lumpur

*Corresponding Author: zurinaosman@um.edu.my

Abstract

Polymer electrolyte systems composed of polyacrylonitrile (PAN) as the host polymer, ethylene carbonate (EC) and propylene carbonate (PC) as the plasticizers and LiCF_3SO_3 as the doping salt were prepared by the solution casting technique. In this work, five systems of polymer electrolyte films have been prepared. They are; the (PAN+EC) system, the (PAN+PC) system, the (PAN+ LiCF_3SO_3) system, the (PAN+EC+ LiCF_3SO_3) and the (PAN+PC+ LiCF_3SO_3) system. The pure PAN film was prepared as a reference. The ionic conductivity for each system was obtained by calculation using data from impedance spectroscopy. The room temperature conductivity of the pure PAN film is $1.51 \times 10^{-11} \text{ S cm}^{-1}$. The room temperature conductivity for the highest conducting film in the (PAN+ LiCF_3SO_3) system is $3.04 \times 10^{-4} \text{ S cm}^{-1}$. On addition of plasticizers, the room temperature conductivity of (PAN+ LiCF_3SO_3) film increases. The conductivity-temperature studies are then performed on the highest conducting film from the (PAN+ LiCF_3SO_3) system, the (PAN+EC+ LiCF_3SO_3) system and the (PAN+PC+ LiCF_3SO_3) system. The conductivity-temperature studies are conducted in the temperature range between 303 K and 373 K. XRD studies shown that the complexation has occurred in PAN films containing lithium salt and plasticizers and complexes formed are amorphous. The FTIR results confirmed the complexation has taken place between PAN and the lithium salt.

Keywords: polymer electrolytes, polyacrylonitrile, plasticizer, lithium triflate, conductivity

1. INTRODUCTION

The development of polymer electrolyte system with high ionic conductivity is one of the main objectives in polymer research. Various approaches have been made to modify the structure of polymer electrolytes in order to improve their electrical, electrochemical and mechanical properties. These approaches include: synthesizing new polymers, cross linking two polymers, blending of two polymers, adding plasticizers to polymer electrolytes and adding inorganic inert fillers to make composite polymer electrolytes [1]. Among these approaches, adding plasticizers to polymer electrolytes is a useful technique to enhance the conductivity of the polymer

system. The essence of plasticization is to enhance the conductivity of polymer electrolytes using low molecular weight and high dielectric constant additives such as propylene carbonate (PC) and ethylene carbonate (EC). These plasticizers increase the amorphous content of the polymer matrix and tend to dissociate ion-pairs into free cations and anions thereby leading to an overall enhancement in conductivity.

Among the host polymer used in plasticized polymer electrolytes are poly (vinylidene fluoride) (PVdF), poly (methylmethacrylate) (PMMA), poly (vinyl chloride) (PVC) and polyacrylonitrile (PAN). Reich and Michaeli [2] were the first to investigate PAN complexed with hydrated perchlorate salts

and reported ionic conductivities in the range 10^{-7} - 10^{-2} Scm^{-1} . Watanabe and his co-workers [3] prepared hybrid films by dissolving PAN and LiClO_4 in a plasticizer such as propylene carbonate (PC) or ethylene carbonate (EC).

In the present work, the plasticized polymer electrolyte systems composed of polyacrylonitrile (PAN) as a host polymer with plasticizers; ethylene carbonate (EC) and propylene carbonate (PC) containing lithium triflate (LiCF_3SO_3) have been prepared. The impedance of the samples was measured by ac impedance spectroscopy. Conductivity-temperature studies were carried out in the temperature range between 303 K and 373 K. The complexation of the PAN-based polymer electrolyte films will be investigated using the X-Ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) techniques.

2. EXPERIMENTAL METHODS

2.1. Sample Preparation

Polyacrylonitrile (PAN), with molecular weight of 150,000 g/mol, lithium triflate (LiCF_3SO_3), dimethylformamide (DMF) and ethylene carbonate (EC) were obtained from Aldrich. Propylene carbonate (PC) was obtained from Fluka. 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 , EC and PC were added accordingly. The mixtures were 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.

2.2. Characterization Techniques

2.2.1 Impedance Studies

Impedance spectroscopy measurements were used to determine the conductivity of the films. The films were cut into a circular

shape that fit the size of the electrodes. The films were then sandwiched between 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 from 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 was then calculated using equation:

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

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 conductivity-temperature studies were carried out in the temperature range from 303 K to 373 K.

2.2.2 XRD Studies

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°.

2.2.3 FTIR Studies

Fourier transform infrared (FTIR) spectra exhibited in this work were taken with a MAGNA-IR550 Spectrophotometer-Series II in the wavenumber region between 400 and 4000 cm^{-1} . The films used in this work were cut into suitable sizes and placed in the specimen holder of the spectrophotometer. In the present work, the FTIR spectrum of pure PAN film was also taken to serve as reference. The resolution of the spectrophotometer was 1 cm^{-1} .

3. RESULTS AND DISCUSSION

The room temperature conductivity of pure PAN film, (PAN+24 wt. % EC) film and (PAN+22 wt. % PC) film is 1.51×10^{-11} S cm^{-1} , 6.95×10^{-8} S cm^{-1} and 3.19×10^{-10}

S cm^{-1} , respectively. Fig. 1(a-c) depict the content for the (PAN+LiCF₃SO₃), (PAN+PC+LiCF₃SO₃), and the (PAN+EC+LiCF₃SO₃) systems, respectively. The conductivity of pure PAN film increases when more than 2 wt. % LiCF₃SO₃ was added and reached a maximum value at $3.04 \times 10^{-4} \text{ S cm}^{-1}$ when 26 wt. % LiCF₃SO₃ has been added to the film.

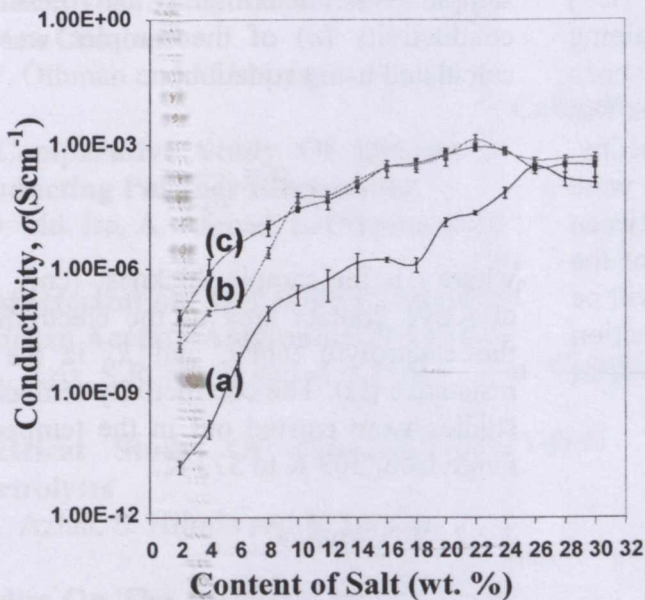


Fig. 1 The ionic conductivity versus salt content for the: (a) (PAN+LiCF₃SO₃), (b) (PAN+PC+LiCF₃SO₃) and (c) (PAN+EC+LiCF₃SO₃) systems at room temperature

The number of mobile ions increases with the increase of LiCF₃SO₃ concentration and since conductivity is proportional to the number of mobile ions the conductivity is therefore increased. The decrease in conductivity value at higher salt concentrations 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 [4].

On addition of 24 wt. % of EC and 22 wt. % of PC, the conductivity value of (PAN+LiCF₃SO₃) film increases to $1.32 \times 10^{-3} \text{ S cm}^{-1}$ and $8.62 \times 10^{-4} \text{ S cm}^{-1}$, respectively. It can be deduced that EC has dissociated more LiCF₃SO₃ salt compared to PC, thereby increasing the number of charge carriers in (PAN+EC+LiCF₃SO₃) film. The apparent roles of a plasticizer in a host

room temperature conductivity versus salt polymer are to decrease viscosity of the electrolyte and assist in the dissociation of the salt thereby increasing mobility and the number of charged carriers [5]. The effect of the plasticizer to dissociate the salt has also been observed by other workers [5-6].

The conductivity-temperature dependence studies for the (PAN + 24 wt. % EC + 22 wt. % LiCF₃SO₃), (PAN + 22 wt. % PC + 22 wt. % LiCF₃SO₃) and (PAN + 26 wt. % LiCF₃SO₃) films are represented in Figure 2(a), (b) and (c), respectively. The plot shows that as the temperature increases, the conductivity also increases. The calculated regression values for the films are close to unity signifying that all points lie on a straight line. This indicates that the plots obey Arrhenius rule,

$$\sigma(T) = \sigma_o \exp\left(\frac{-E_A}{kT}\right) \quad (2)$$

where σ_o is the conductivity pre-exponential factor and E_A is the activation energy for conduction. As the conductivity temperature relationship 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 [7]. It is also understood that the increase in conductivity with temperature can be linked to the decrease in viscosity and hence increased chain flexibility [8].

The activation energy, E_A can be evaluated from the slope of the plots [9]. The E_A for the (PAN+26 wt. % LiCF₃SO₃), (PAN+24 wt. % EC+22 wt. % LiCF₃SO₃) and (PAN+22 wt. % PC + 22 wt. % LiCF₃SO₃) films have been calculated to be 0.30 eV, 0.26 eV and 0.27 eV, respectively. It can be observed that (PAN+24 wt. % EC+22 wt. % LiCF₃SO₃) film has the highest ionic conductivity and lowest activation energy.

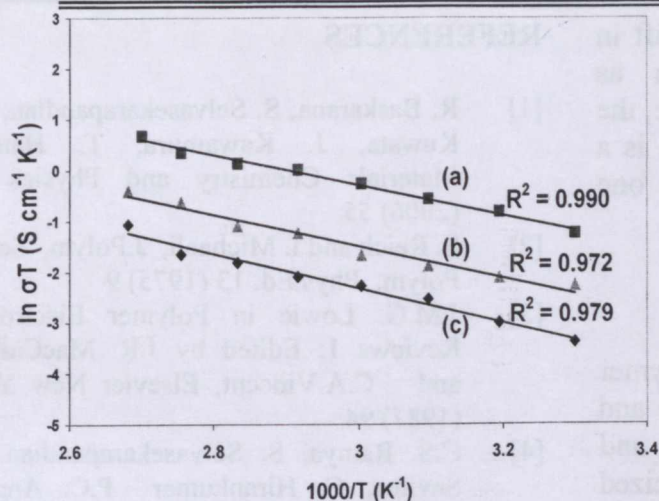


Fig. 2 Arrhenius plot for the (a) PAN+24 wt. % EC+22 wt. % LiCF_3SO_3 , (b) PAN+22 wt. % PC+22 wt. % LiCF_3SO_3 and (c) PAN+26 wt. % LiCF_3SO_3 films

Fig. 3 represents the XRD patterns for the films of pure PAN and of the highest conducting films from (PAN + EC), (PAN + PC), (PAN + LiCF_3SO_3), (PAN + EC + LiCF_3SO_3) and (PAN + PC + LiCF_3SO_3) systems.

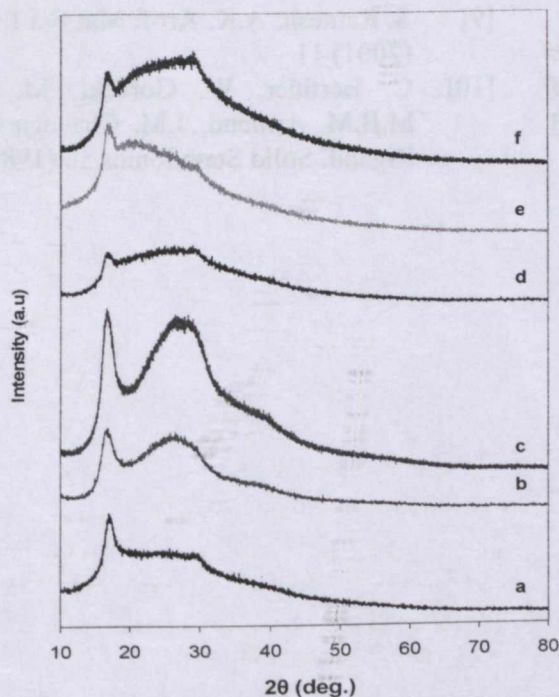


Fig. 3 XRD patterns of the (a) pure PAN (b) PAN + 24 wt. % EC (c) PAN + 22 wt. % PC (d) PAN + 26 wt. % LiCF_3SO_3 (e) PAN + 24 wt. % EC + 22 wt. % LiCF_3SO_3 and (f) PAN + 22 wt. % PC + 22 wt. % LiCF_3SO_3 films.

The diffraction patterns in Fig. 3(d), (e) and (f) show that most of the peaks pertaining to plasticizers and pure LiCF_3SO_3 salt are absent in the complexes that indicate the complete dissolution of the plasticizers and

salt in the polymer matrix. Thus, the XRD studies confirm that complexation has occurred in the polymer matrices and the complexes formed are amorphous. Berthier et al. [10] reported that ionic conductivity in polymer electrolytes is associated with the amorphous phase of the samples.

In order to investigate the complex formation in the polymer matrices, FTIR studies have been carried out. The FTIR spectra in the wavenumber range between 2000 cm^{-1} to 3000 cm^{-1} of pure PAN and that of the highest conducting films from (PAN + EC), (PAN + PC), (PAN + LiCF_3SO_3), (PAN + EC + LiCF_3SO_3) and (PAN + PC + LiCF_3SO_3) systems are shown in Fig. 4.

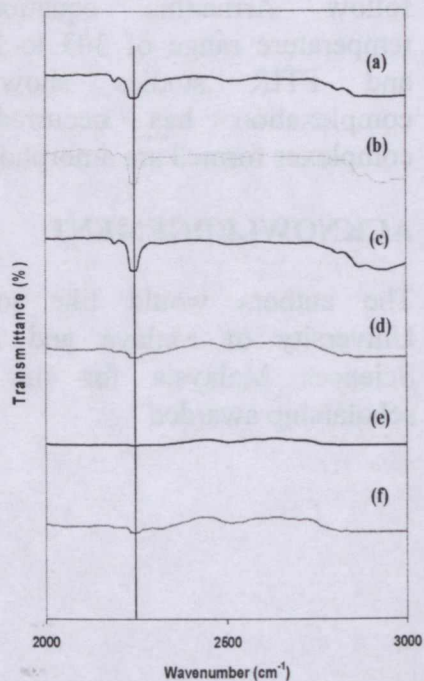


Fig. 4 FTIR spectra of the (a) pure PAN (b) PAN + 22 wt. % PC (c) PAN + 24 wt. % EC (d) PAN + 26 wt. % LiCF_3SO_3 (e) PAN + 22 wt. % PC + 22 wt. % LiCF_3SO_3 and (f) PAN + 24 wt. % EC + 22 wt. % LiCF_3SO_3 films

The nitrile band, $\text{C}\equiv\text{N}$ assigned to stretching band in the infrared spectrum is observed at 2247 cm^{-1} for the pure PAN film. The nitrile band is displaced towards lower frequency around 2244 cm^{-1} due to inductive effect created by the interaction between the N atom in $\text{C}\equiv\text{N}$ with Li^+ . It can also be observed that the intensity of absorption band at 2247 cm^{-1} is reduced when salt is added. This shows that the complexation has occurred between PAN and lithium triflate

salt. There is hardly any noticeable shift in peaks of the plasticized-PAN film as presented in Figure 4(b) and 4(c). Hence, the PAN+EC system and PAN+PC system is a mixed phase with no interaction with one another.

4. CONCLUSIONS

The PAN based ion conducting polymer electrolyte films containing EC, PC and LiCF_3SO_3 films have been prepared and studied. The conductivity of the plasticized PAN-salt complexes is due to the salt and can be enhanced by plasticization. EC has dissociated more LiCF_3SO_3 salt compared to PC. The conductivity-temperature studies follow Arrhenius equation in the temperature range of 303 to 373 K. XRD and FTIR studies show that the complexation has occurred and the complexes formed are amorphous.

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