Conductivity and Structural Studies of Plasticized Polyacrylonitrile (PAN) – Lithium Triflate Polymer Electrolyte Films

(Kekonduksian dan Struktur Filem Elektrolit Polimer Poliakrilonitril (PAN) – Litium Triflat yang Mengandungi Agen Pemplastik)

A. AHMAD, K.B. MD. ISA & Z. OSMAN*

ABSTRACT

The effect of different plasticizers on the properties of PAN– $LiCF_3SO_3$ polymer electrolytes has been studied. Propylene carbonate (PC) and ethylene carbonate (EC) having different values of donor numbers, dielectric constant and viscosity have been used as plasticizers. The highest room temperature conductivity for the film in the PAN– $LiCF_3SO_3$ system was 3.04×10^{-4} S cm^{-1}. The highest room temperature conductivity for the films in the PAN–EC– $LiCF_3SO_3$ system and the PAN–PC– $LiCF_3SO_3$ system was 1.32×10^{-3} and 8.64×10^{-4} S cm^{-1}. The addition of plasticizers has been found to enhance the conductivity of polymer electrolytes by increasing the amorphous content as well as by dissociating the ion aggregates present in polymer electrolyte. Conductivity temperature-dependence studies of these plasticized PAN-salt systems were carried out in the temperature range of 303 to 373 K. The conductivity versus temperature plots obeyed an Arrhenius type variation. The structural and complex formations were studied by X-ray diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy.

Keywords: Conductivity; lithium triflate; plasticizer; polyacrylonitrile; polymer electrolytes

ABSTRAK

Kesan penggunaan agen pemplastik yang berbeza terhadap sifat elektrolit polimer PAN– $LiCF_3SO_3$ telah dikaji. Propilina karbonat (PC) dan etilena karbonat (EC) mempunyai bilangan penderma, pemalar dielektrik dan kelikatan yang berbeza digunakan sebagai agen pemplastik. Nilai kekonduksian tertinggi pada suhu bilik bagi filem dalam sistem PAN– $LiCF_3SO_3$ adalah 3.04×10^{-4} S cm^{-1}. Nilai kekonduksian tertinggi pada suhu bilik bagi filem dalam sistem PAN–EC– $LiCF_3SO_3$ dan sistem PAN–PC– $LiCF_3SO_3$ adalah 1.32×10^{-3} dan 8.64×10^{-4} S cm^{-1}. Penambahan agen pemplastik didapati telah meningkatkan nilai kekoduksian elektrolit polimer melalui peningkatan kandungan amorfus dan penguraian kelompok ion yang wujud. Kajian kekonduksian terhadap suhu untuk sistem PAN-garam yang mengandungi agen pemplastik dilakukan pada julat suhu daripada 303 hingga 353 K. Plot bagi kekonduksian melawan suhu didapati mengikut Arrhenius. Struktur dan pembentukan kompleks dikaji dengan menggunakan pembelauan sinar-X (XRD) dan Spektroskopi Infra-merah (FTIR).

Kata kunci: Agen pemplastik; elektrolit polimer; kekonduksian; litium triflat; poliakrilonitril

INTRODUCTION

Polymer electrolytes have evolved extensively in the electrochemical field. Intensive research in this discipline is mainly driven by their significant application in power source like secondary lithium batteries. 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 (Baskaran et al. 2006). Among these approaches, adding plasticizers to polymer electrolytes is useful technique to enhance the conductivity of polymer system. The role of plasticization is to enhance the conductivity of polymer electrolytes using low molecular weight and high dielectric constant additives

such as propylene carbonate (PC)($\varepsilon = 64.4$) and ethylene carbonate (EC)($\varepsilon = 89.6$). These plasticizers impart salt-solvating power and high ion mobility to the polymer electrolytes and also 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 (vinylidine fluoride) (PVdF), poly (methylmethacrylate) (PMMA), poly (vinyl chloride) (PVC) and polyacrylonitrile (PAN). Reich and Michaeli (1975) were first to investigate polyacrylonitrile by examining the conductivity of PAN complexes with hydrated perchlorate salts with ionic conductivities in the range $10^{-7} – 10^{-2}$ S cm^{-1}. Hybrid polymer electrolyte films have also been prepared by dissolving PAN and LiClO$_4$ in a plasticizer such as propylene carbonate (PC) or ethylene carbonate (EC) (Cowie 1987).

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$_3$SO$_3$) have been prepared. The conductivity of the samples was measured by ac impedance spectroscopy. The 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 was investigated using the X-Ray diffraction (XRD) and Fourier Transform Infrared (FTIR) technique.

EXPERIMENTAL DETAILS

SAMPLE PREPARATION

Polyacrylonitrile (PAN), with molecular weight of 150,000 g/mol, lithium triflate (LiCF$_3$SO$_3$), 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$_3$SO$_3$, 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 52°C for 48 h until the films were formed. The films were then kept in a desiccator for further drying.

CHARACTERIZATION TECHNIQUES

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 measure the impedance 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 was then calculated using equation;

$$\sigma = t/R_b A \qquad (1)$$

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 dependence study was conducted in the temperature range of 303 K to 373 K. 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°. Fourier Transform Infrared (FTIR) spectra were obtained 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}.

RESULTS AND DISCUSSION

The room temperature conductivity of the pure PAN film, the (PAN+24 wt%EC) film and (PAN+22 wt%PC) film was $1.51 \times 10^{-11}, 6.95 \times 10^{-8}$ and 3.19×10^{-10} S cm^{-1}, respectively. The room temperature conductivity versus salt content for the (PAN+LiCF$_3$SO$_3$) system, the (PAN+PC+LiCF$_3$SO$_3$) system and the (PAN+EC+LiCF$_3$SO$_3$) system is presented in Figures 1(a), 1(b) and 1(c), respectively. It can be observed that the conductivity of pure PAN film increases when more than 2 wt% of LiCF$_3$SO$_3$ was added and reached maximum value when 26 wt% LiCF$_3$SO$_3$ has been added to the film. The highest room temperature conductivity film in the (PAN+LiCF$_3$SO$_3$) system is 3.04×10^{-4} S cm^{-1}.
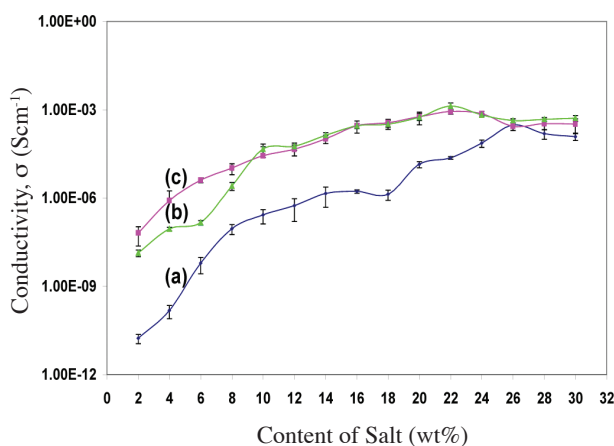

FIGURE 1. The ionic conductivity versus salt content for the: (a) (PAN+LiCF$_3$SO$_3$) system, (b) (PAN+PC+LiCF$_3$SO$_3$) system and (c) (PAN+EC+LiCF$_3$SO$_3$) system at room temperature

The number of mobile ions increased with the increase of LiCF$_3$SO$_3$ concentration and because conductivity was proportional to the number of mobile ions the conductivity was therefore increased. The decrease in the 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 (Ramya et al. 2007).

On addition of 24 wt% of EC and 22 wt% of PC, the conductivity value of (PAN+LiCF$_3$SO$_3$) film increased to 1.32×10^{-3} and 8.62×10^{-4} S cm^{-1}, respectively. It can be deduced that EC with higher dielectric constant allowed greater dissolution of the electrolyte salt resulting in increased number of charge carriers hence conductivity. The apparent roles of a plasticizer in a host polymer are to decrease viscosity of the electrolyte and assist in the dissociation of the salts thereby increasing the number

of charged carriers (MacFarlane et al. 1995). The effect of the plasticizer to dissociate the salt has also been observed by other workers (Forsyth et al. 1995; Souquet et al. 1994).

The conductivity-temperature dependence studies for the (PAN+24 wt%EC+22 wt%LiCF$_3$SO$_3$) film, the (PAN+22 wt%PC+22 wt%LiCF$_3$SO$_3$) film and (PAN+26 wt%LiCF$_3$SO$_3$) film is represented in Figures 2(a), 2(b) and 2(c), respectively. The plots show that as the temperature increases, the conductivity also increases. The calculated regression values for all the films are close to unity signifying that all points lie on a straight line. This indicates that the plots obey Arrhenius rule,

$$\sigma(T) = \sigma_o \, exp \, (-E_a/RT) \qquad (2)$$

where σ_o is the conductivity pre-exponential factor and E_a is the activation energy for conduction. As the conductivity temperature-dependence studies 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 (Souquet et al. 1994). It is also understood that the increase in conductivity with temperature can be linked to the decrease in viscosity and hence increased chain flexibility (Rajendran et al. 2004)

The activation energy, E_a, can be evaluated from the slope of the plots (Ramesh & Arof 2001) The E_a for the (PAN+26 wt%LiCF$_3$SO$_3$) film, the (PAN+24 wt%EC+22 wt%LiCF$_3$SO$_3$) film and (PAN+22 wt%PC+22 wt%LiCF$_3$SO$_3$) film have been calculated to be 0.28, 0.22 and 0.27 eV, respectively. The low activation energy for the lithium ion transport was due to the completely amorphous nature of the polymer electrolytes that facilitate the fast Li$^+$ ion motion in the polymer network. The completely amorphous nature also provided a bigger free volume in the polymer electrolyte system upon increasing the temperature (Michael et al. 1997).
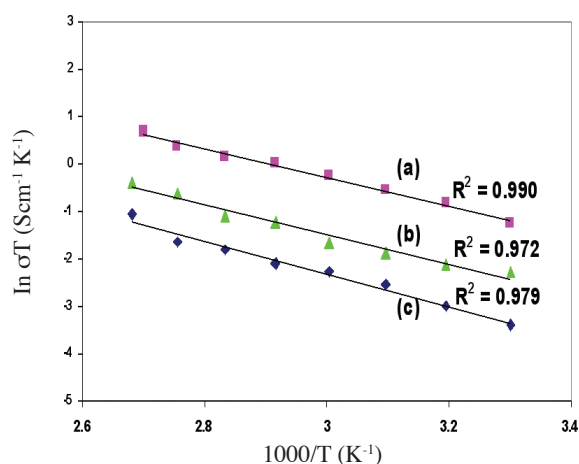

FIGURE 2. Arrhenius plot for the (a) PAN+24 wt% EC+22 wt%LiCF$_3$SO$_3$ film, (b) PAN+22 wt%PC+22 wt% LiCF$_3$SO$_3$ film and (c) PAN+26 wt% LiCF$_3$SO$_3$ film

Figure 3 represents the XRD patterns for the pure PAN film and for the the highest conducting films from (PAN+EC), (PAN+PC), (PAN+LiCF$_3$SO$_3$), (PAN+EC+LiCF$_3$SO$_3$) and (PAN+PC+LiCF$_3$SO$_3$) systems. The XRD pattern in the Figure 3(a) for pure PAN film shows that the film is semicrystalline and a crystalline peak at 2θ=17° and it corresponds to orthorhombic PAN (110) reflection (Rajendran et al. 2001; Sawai et al. 2000; Zhang et al. 2001). These diffraction peak intensity is markedly reduced in the complexes. The diffraction patterns in Figures 3(d), 3(e) and 3(f) also show that most of the peaks pertaining to plasticizers and pure LiCF$_3$SO$_3$ 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 complex formed are amorphous. Berthier et al. (1983) reported that ionic conductivity in polymer electrolytes is associated with the amorphous phase of the samples.
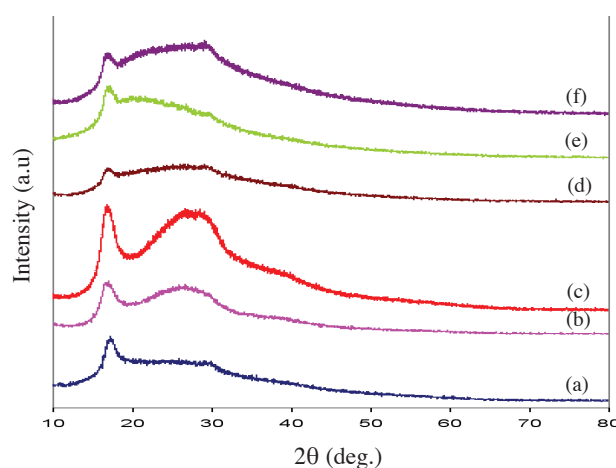

FIGURE 3. XRD patterns of the (a) pure PAN (b) PAN+24 wt%EC (c) PAN+22 wt%PC (d) PAN+26 wt%LiCF$_3$SO$_3$ (e) PAN+24 wt%EC+22 wt% LiCF$_3$SO$_3$ and (f) PAN+22wt%PC+22 wt% LiCF$_3$SO$_3$

In order to investigate the complex formation in the polymer matrices, FTIR studies have been carried out. The FTIR spectrum in the wavenumber range between 2000 and 3000 cm^{-1} of pure PAN and the highest conducting films from (PAN+EC), (PAN+PC),(PAN+LiCF$_3$SO$_3$), (PAN+EC+LiCF$_3$SO$_3$) and (PAN+ PC+LiCF$_3$SO$_3$) systems are shown in Figure 4. The nitrile band, C≡N assigned to stretching band in the infrared spectrum is appears at 2247 cm^{-1} for the pure PAN film. The nitrile band was displaced toward the lower wavenumber around 2244 cm^{-1} due to inductive effect created by the interaction N atom in C≡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 Figures 4(b) and 4(c). Hence, the PAN+EC system and PAN+PC system is a mixed phase with no interaction with one another.
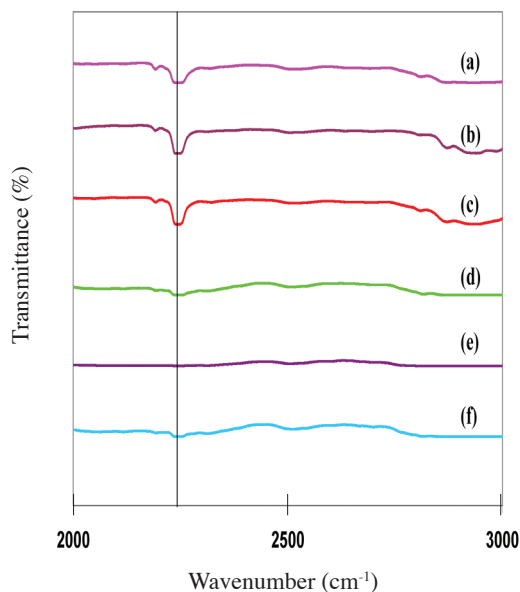
694

FIGURE 4. FTIR spectra of the (a) pure PAN (b) PAN+22 wt% PC
(c) PAN+24 wt% EC (d) PAN+26 wt% LiCF$_3$SO$_3$
(e) PAN+22 wt%PC+22 wt% LiCF$_3$SO$_3$
(f) PAN+24 wt%EC+22 wt% LiCF$_3$SO$_3$ films

CONCLUSIONS

The PAN based ion conducting polymer electrolyte films containing EC, PC and LiCF$_3$SO$_3$ films have been prepared and studied. The conductivity of the plasticized PAN–salt complexes was due to the salt and can be enhanced by plasticization. EC has dissociated more LiCF$_3$SO$_3$ salt compared to PC. The conductivity-temperature studies follow Arrhenius equation in the temperature range of 303 to 373 K. FTIR studies show that the complexation has taken place and the complexes formed are amorphous and these results correspond with XRD analysis.

ACKNOWLEDGEMENTS

REFERENCES

Baskaran, R., Selvasekarapandian, S., Kuwata, N., Kawamura, J. & Hattori, T. 2006. AC impedance, DSC and FT-IR investigations on (*x*) PVAc–(1 – *x*) PVdF blends with LiClO$_4$. *Materials Chemistry and Physics* 98: 55-61.
Berthier, C., Gorecki, W., Minier, M., Armand, M.B., Chabagno, J.M. & Rigaud, P. 1983. Microscopic investigation of ionic conductivity in alkali metal salts-poly(ethylene oxide) adducts. *Solid State Ionics* 11: 91-95.

Cowie, J.M.G. 1987. In MacCallum, J.R. & Vincent, C.A. (ed.) *Polymer Electrolyte Reviews 1*, 69-102. New York: Elsevier.
Forsyth, M., Meakin, P. & MacFarlane, D.R. 1995. A ^{13}C NMR study of the role of plasticizers in the conduction mechanism of solid polymer electrolytes. *Electrochimica Acta* 40: 2339-2342.
MacFarlane, D.R., Sun, J., Meakin, P., Fasoulopoulos, P., Hey, J. & Forsyth, M. 1995. Structure-property relationships in plasticized solid polymer electrolytes. *Electrochimica Acta* 40: 2131-2136.
Michael, M.S., Jacob, M.M.E., Prabaharan, S.R.S. & Radhakrishna. S. 1997. Enhanced lithium ion transport in PEO-based solid polymer electrolytes employing a novel class of plasticizers. *Solid State Ionics* 98: 167-174.
Rajendran, S., Sivakumar, M. & Subadevi, R. 2004. Investigations on the effect of various plasticizers in PVA–PMMA solid polymer blend electrolytes. *Materials Letters* 58: 641-649.
Ramesh, S. & Arof, A.K. 2001. Ionic conductivity studies of plasticized poly (vinyl chloride) polymer electrolytes. *Mat Sci Eng B* 85: 11-15.
Ramya, C.S., Selvasekarapandian, S., Savitha, T., Hirankumar, G. & Angelo, P.C. 2007. Vibrational and impedance spectroscopic study on PVP–NH$_4$SCN based polymer electrolytes. *Physica B* 393: 11-17.
Reich, S. & Michaeli, I. 1975. Electrical conductivity of small ions in polyacrylonitrile in the glass–transition region. *J. Polym. Sci. B-Polym. Phys.* 13: 9-18.
Sawai, D., Miyamoto, M., Kanamoto, T. & Ito, M. 2000. Lamellar thickening in nascent poly(acrylonitrile) upon annealing. *J. Polym. Sci. Part B-Polym. Phys.* 38: 2571-2579.
Souquet, J.L., Levy, M. & Duclot, M. 1994. A single microscopic approach for ionic transport in glassy and polymer electrolytes. *Solid State Ionics* 70-71: 337-345.
Zhang, Z., Zhang, L., Wang, S., Chen, W. & Lei, Y. 2000. A convenient route to polyacrylonitrile/silver nanoparticle composite by simultaneous polymerization–reduction approach. *Polymer* 42: 8315-8318.

Physics Department
University of Malaya
50603 Kuala Lumpur
Malaysia

*Corresponding author; email: zurinaosman@um.edu.my