

## Comparative Studies on Plasticized and Unplasticized Polyacrylonitrile (PAN) Polymer Electrolytes Containing Lithium and Sodium Salts

(Kajian Perbandingan ke atas Elektrolit Polimer Berasaskan Poliakrilonitril (PAN) dengan Agen Pemplastik dan Tanpa Agen Pemplastik yang Mengandungi Garam Litium dan Garam Natrium)

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### ABSTRACT

*Polymer electrolytes based on polyacrylonitrile (PAN) containing inorganic salts; lithium triflate ( $\text{LiCF}_3\text{SO}_3$ ) and sodium triflate ( $\text{NaCF}_3\text{SO}_3$ ) and ethylene carbonate (EC) as plasticizer were prepared using solvent casting technique. In this study, five systems of plasticized and unplasticized polymer electrolyte films i.e. PAN-EC, PAN- $\text{LiCF}_3\text{SO}_3$ , PAN- $\text{NaCF}_3\text{SO}_3$ , PAN-EC- $\text{LiCF}_3\text{SO}_3$  and PAN-EC- $\text{NaCF}_3\text{SO}_3$  systems have been prepared. The structural and morphological properties of the films were studied using infrared spectroscopy and scanning electron microscopy (SEM) while the conductivity study was done by using impedance spectroscopy. The infrared results revealed that interaction had taken place between the nitrogen atoms of PAN and  $\text{Li}^+$  and  $\text{Na}^+$  ions from the salts. SEM micrographs showed that the plasticized film, PAN-EC- $\text{NaCF}_3\text{SO}_3$  has bigger pores than PAN-EC- $\text{LiCF}_3\text{SO}_3$  film resulting in the film containing  $\text{NaCF}_3\text{SO}_3$  salt being more conductive. On addition of salts and plasticizer, the conductivity of pure PAN increases to three orders of magnitude. The plasticized film containing  $\text{NaCF}_3\text{SO}_3$  salt has a higher conductivity compared to that containing  $\text{LiCF}_3\text{SO}_3$  salt. This result showed that the interaction between  $\text{Li}^+$ -ion and the nitrogen atom of PAN was stronger than that of  $\text{Na}^+$ -ion. The conductivity-temperature dependence of the highest conducting film from each system follows Arrhenius equation in the temperature range of 303 to 353 K. The conductivity-pressure study in the range of 0.01 - 0.09 MPa showed that the conductivity decreased when pressure was increased. This can be explained in term of free volume model.*

*Keywords: Conductivity; lithium triflate; plasticizer; polyacrylonitrile; sodium triflate*

### ABSTRAK

*Elektrolit polimer berasaskan poliakrilonitril (PAN) yang mengandungi garam tak organik; litium triflat ( $\text{LiCF}_3\text{SO}_3$ ) dan natrium triflat ( $\text{NaCF}_3\text{SO}_3$ ), etilena karbonat (EC) sebagai agen pemplastik telah disediakan dengan kaedah tuangan larutan. Dalam kajian ini, lima sistem elektrolit polimer filem yang mengandungi agen pemplastik dan tidak mengandungi agen pemplastik iaitu PAN-EC, PAN- $\text{LiCF}_3\text{SO}_3$ , PAN- $\text{NaCF}_3\text{SO}_3$ , PAN-EC- $\text{LiCF}_3\text{SO}_3$  dan PAN-EC- $\text{NaCF}_3\text{SO}_3$  telah disediakan. Sifat-sifat struktur dan morfologi filem telah dikaji dengan menggunakan spektroskopi inframerah dan mikroskop elektron imbasan (SEM) manakala kekonduksian dikaji dengan menggunakan spektroskopi impedans. Keputusan spektroskopi inframerah menunjukkan berlakunya interaksi di antara atom nitrogen daripada PAN dengan ion  $\text{Li}^+$  dan ion  $\text{Na}^+$  daripada garam. Mikrograf SEM menunjukkan bagi filem yang mengandungi agen pemplastik, filem PAN-EC- $\text{NaCF}_3\text{SO}_3$  mempunyai liang yang lebih besar daripada filem PAN-EC- $\text{LiCF}_3\text{SO}_3$  menyebabkan filem yang mengandungi  $\text{NaCF}_3\text{SO}_3$  lebih konduktif. Dengan penambahan garam dan agen pemplastik, kekonduksian bagi filem PAN tulen meningkat sebanyak tiga turutan magnitud. Filem yang mengandungi agen pemplastik dengan garam  $\text{NaCF}_3\text{SO}_3$  mempunyai nilai kekonduksian lebih tinggi daripada yang mengandungi garam  $\text{LiCF}_3\text{SO}_3$ . Ini menunjukkan interaksi di antara ion  $\text{Li}^+$  dengan atom nitrogen daripada PAN adalah lebih kuat daripada ion  $\text{Na}^+$ . Kajian kebergantungan kekonduksian terhadap suhu bagi filem yang mempunyai kekonduksian tertinggi daripada semua sistem menunjukkan ia mematuhi persamaan Arrhenius dalam julat suhu daripada 303 K hingga 353 K. Kajian kebergantungan kekonduksian terhadap tekanan dalam julat 0.01 - 0.09 MPa menunjukkan kekonduksian menurun dengan tekanan. Keputusan ini boleh diterangkan dengan model isipadu bebas.*

*Kata kunci: Agen pemplastik; kekonduksian; litium triflat; natrium triflat; poliakrilonitril*

### INTRODUCTION

Ionically conducting polymer electrolyte has in recent years been a candidate for a number of applications including high energy density rechargeable lithium batteries. Common features of the so-called traditional polymer electrolytes are that the cation of the inorganic salt coordinates with polymer and ionic transport occurs in amorphous region

of materials (Le Nest 1990). Most research activities on polymer electrolytes have focused on system related to poly (ethyleneoxide) (PEO). The first measurement of ionic conductivity in polymer electrolytes, PEO-salt complexes were carried out by Fenton (1973). However, Armand et al. (1979) was the first to realize the potential of polymer-salt complexes for use as electrolytes in lithium batteries.

Charge carrier concentration and ionic mobility are two important factors which influence the conductivity of the electrolyte. The conductivity of charge carriers present in an electrolyte generally depends upon the concentration of salt containing the mobile species as well as on the extent up to which the salt is dissociated. The mobility of smaller ions  $\text{Li}^+$  and/or  $\text{Mg}^{2+}$  is lower than that of cations with larger ions  $\text{Na}^+$  and/or  $\text{Zn}^{2+}$ . If the salt is completely dissociated, then almost all ions shall be available for conduction, but if the salt is not completely dissociated, then it will result in a decrease of numbers of charge carrier concentration which shall lower the conductivity. Adding plasticizers to polymer electrolytes is a useful technique to enhance the conductivity of 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. Lee et al. (2006) prepared SPEs based on polyethylene non-woven matrix and its conductivity could achieve  $3.1 \times 10^{-4} \text{ Scm}^{-1}$  at room temperature by adding PEG as a plasticizer. The addition of plasticizers in SPEs is considered one of the most effective approaches to obtain assist in improving the mobility of ionic or/and the interfacial interaction among ionic and polar groups in polymer chains (Bhide & Hariharan 2007; Egashira et al. 2008; Kuila et al. 2007; Pradhan et al. 2005).

Recently, attention has been drawn to the importance of measuring the electrical properties of electrolytes not only as function of temperature but as function of pressure. Pressure conductivity study is a very valuable tool to determine the nature of charge carriers and to investigate the ionic transport mechanism (Duclot et al. 2000). The present work was aimed to study the effect of plasticizer,  $\text{LiCF}_3\text{SO}_3$  and  $\text{NaCF}_3\text{SO}_3$  salts on the complexation, morphological and ionic conductivity of PAN-polymer electrolytes using Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM) and impedance spectroscopy. The effects of temperature and pressure on the electrical conductivity of the polymer electrolyte films were also investigated.

## MATERIALS AND METHODS

### SAMPLE PREPARATION

Polyacrylonitrile (PAN), with molecular weight of 150,000 g/mol, lithium triflate ( $\text{LiCF}_3\text{SO}_3$ ), dimethylformamide (DMF) and ethylene carbonate (EC) were obtained from Aldrich. Sodium triflate was obtained from Fluka. PAN was dissolved in DMF and the mixture was stir at  $60^\circ\text{C}$  until the solution turned into a clear and homogeneous.  $\text{LiCF}_3\text{SO}_3$ ,  $\text{NaCF}_3\text{SO}_3$  and EC were added accordingly. The mixtures were continuously stirred for several hours. After complete dissolution, the solutions were cast in petri dishes and left to dry under vacuum at  $50^\circ\text{C}$  for 48 h until the films were

formed. The films were then kept in a desiccator for further drying until the characterizations are to be carried out.

### CHARACTERIZATION TECHNIQUES

To study the complexation of the conducting polymer electrolyte films, infrared measurements were recorded using a MAGNA-IR550 Spectrophotometer-Series II in the wavenumber region between 400 and  $4000 \text{ cm}^{-1}$ . In the present work, the infrared spectrum of pure PAN film was also taken to serve as a reference. The resolution of the spectrophotometer was  $1 \text{ cm}^{-1}$ . The surface morphology of the films was observed by SEM using SEC Mini-SEM-Bruker Eds System.

Impedance spectroscopy measurements were used to determine the conductivity of the films. A HIOKI 3532 LCR bridge that was 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. The conductivity-temperature and conductivity-pressure studies were carried out in the range between 303 and 353 K, and 0.01 and 0.09 MPa, respectively.

### RESULTS AND DISCUSSION

The infrared spectra of pure PAN, PAN-EC, PAN- $\text{LiCF}_3\text{SO}_3$ , PAN- $\text{NaCF}_3\text{SO}_3$ , PAN-EC- $\text{LiCF}_3\text{SO}_3$  and PAN-EC- $\text{NaCF}_3\text{SO}_3$  are shown in Figure 1. The nitrile band,  $\text{C}\equiv\text{N}$  assigned to stretching band in the IR spectrum is appears at  $2247 \text{ cm}^{-1}$  for pure PAN film. The nitrile band was displaced toward the lower wavenumber around  $2244 \text{ cm}^{-1}$  due to

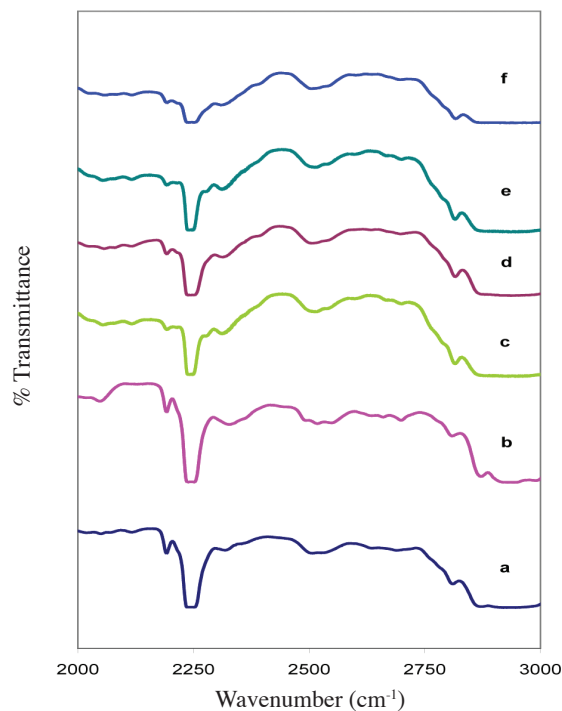


FIGURE 1. FTIR spectrum of (a) pure PAN (b) PAN-EC (c) PAN- $\text{LiCF}_3\text{SO}_3$  (d) PAN- $\text{NaCF}_3\text{SO}_3$  (e) PAN-EC- $\text{LiCF}_3\text{SO}_3$  and (f) PAN-EC- $\text{NaCF}_3\text{SO}_3$  films

inductive effect created by the interaction N atom in  $C\equiv N$  with  $Li^+$  and  $Na^+$ . It also can be observed that the intensity of absorption band at  $2247\text{ cm}^{-1}$  was reduced when the plasticizer and the salts were added, as shown in Figures 1 (c) to 1 (f). This shows that the complexation had occurred between PAN and the salts.

Figure 2 shows the SEM micrographs of (a) pure PAN (b) PAN- $LiCF_3SO_3$  (c) PAN- $NaCF_3SO_3$  (d) PAN-EC- $LiCF_3SO_3$  and (e) PAN-EC- $NaCF_3SO_3$ . The surface morphology of the pure PAN film appears smooth and homogenous. However, when  $LiCF_3SO_3$  and  $NaCF_3SO_3$  salts were added the surface becomes rough and uneven.

It also can be observed the pores are appears in the salted films as shown in Figures 2 (b) and (c). In Figures 2 (d) and (e), on addition of EC in the salted-PAN film the pores size have been increased. The pores size in PAN-EC- $NaCF_3SO_3$  film is bigger than PAN-EC- $LiCF_3SO_3$  film resulting in the  $NaCF_3SO_3$  salt being more conductive which corresponds with the conductivity results. This implies that the presence of the plasticizer will lead to ion mobility, hence higher conductivity.

The conductivity of pure PAN film and the PAN- 22 wt.% EC at room temperature is  $1.51 \times 10^{-11}$  and  $3.43 \times 10^{-11}\text{ S cm}^{-1}$ , respectively. The highest room temperature

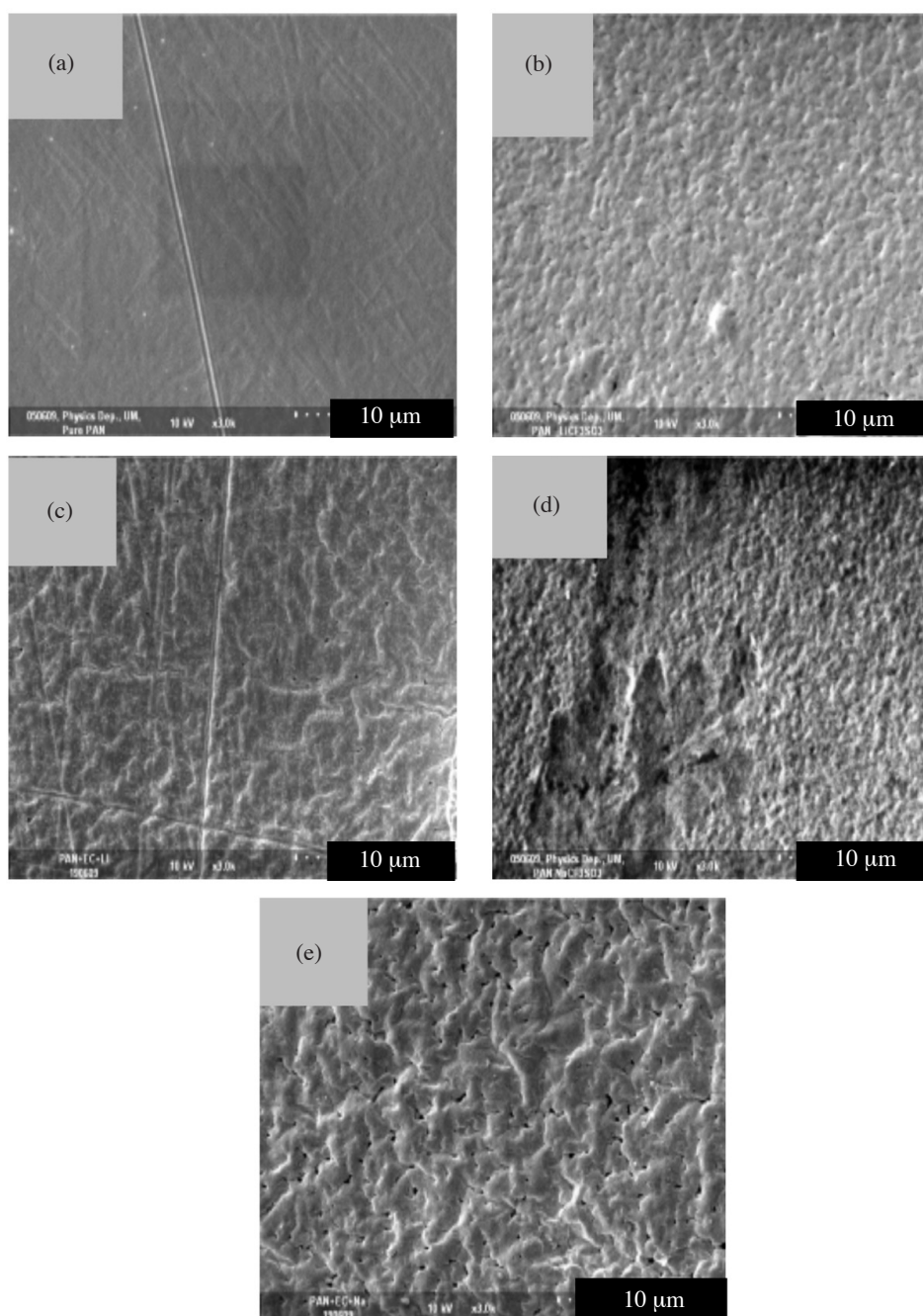


FIGURE 2. SEM micrographs of (a) pure PAN (b) PAN- $LiCF_3SO_3$  (c) PAN- $NaCF_3SO_3$  (d) PAN-EC- $LiCF_3SO_3$  and (e) PAN-EC- $NaCF_3SO_3$  films

conductivity in the PAN-LiCF<sub>3</sub>SO<sub>3</sub>, PAN-NaCF<sub>3</sub>SO<sub>3</sub>, PAN-EC-LiCF<sub>3</sub>SO<sub>3</sub> and PAN-EC-NaCF<sub>3</sub>SO<sub>3</sub> systems is  $3.04 \times 10^{-4}$ ,  $7.13 \times 10^{-4}$ ,  $1.32 \times 10^{-3}$  and  $5.49 \times 10^{-3}$  S cm<sup>-1</sup>, respectively. Figure 3 shows the plots of conductivity versus salt content for the unplasticized-salted and plasticized-salted systems. It can be seen that at room temperature the conductivity increased with salt concentrations, with maximum value at 26, 24, 22 and 34 wt% of LiCF<sub>3</sub>SO<sub>3</sub> and NaCF<sub>3</sub>SO<sub>3</sub> for PAN-LiCF<sub>3</sub>SO<sub>3</sub>, PAN-NaCF<sub>3</sub>SO<sub>3</sub>, PAN-EC-LiCF<sub>3</sub>SO<sub>3</sub> and PAN-EC-NaCF<sub>3</sub>SO<sub>3</sub>, respectively, and then decreased with the salt concentrations. It can be observed that the films containing NaCF<sub>3</sub>SO<sub>3</sub> salt had a higher ionic conductivity than the films containing LiCF<sub>3</sub>SO<sub>3</sub> salt. 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 (Sagane et al. 2005). 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 (Ramya et al. 2007). On addition of plasticizer to the salted-PAN films, the conductivity is further increased. This indicates that the plasticizer has helped to dissociate the salt into mobile ions so that the conductivity of films can be enhanced.

Figure 4 represents the Arrhenius plot for the highest conducting films from the PAN-LiCF<sub>3</sub>SO<sub>3</sub> and PAN-NaCF<sub>3</sub>SO<sub>3</sub>, PAN-EC-LiCF<sub>3</sub>SO<sub>3</sub> and PAN-EC-NaCF<sub>3</sub>SO<sub>3</sub> systems. The linear plots show that, in the temperature range, the ionic conductivity data of these systems follow Arrhenius equation,

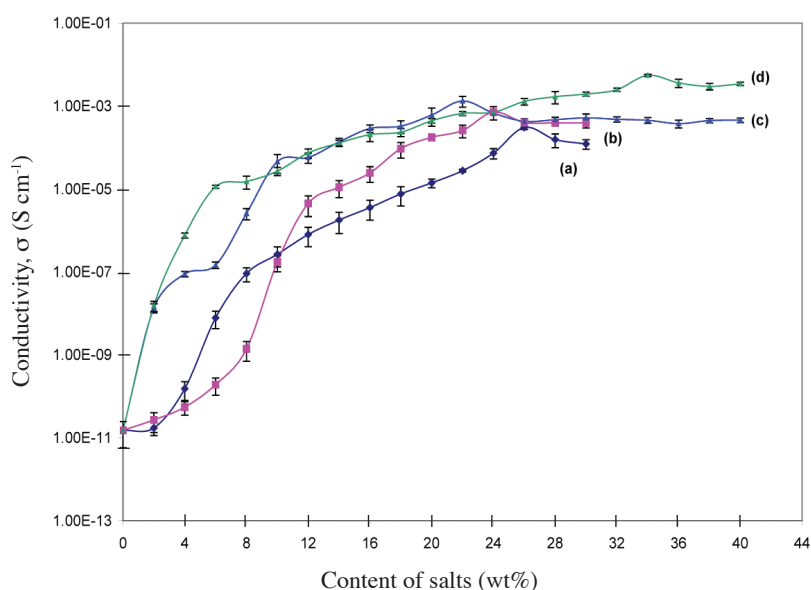


FIGURE 3. Variation of electrical conductivity with salt content in (a) PAN-LiCF<sub>3</sub>SO<sub>3</sub>, (b) PAN-NaCF<sub>3</sub>SO<sub>3</sub>, (c) PAN-EC-LiCF<sub>3</sub>SO<sub>3</sub> and (d) PAN-EC-NaCF<sub>3</sub>SO<sub>3</sub> systems

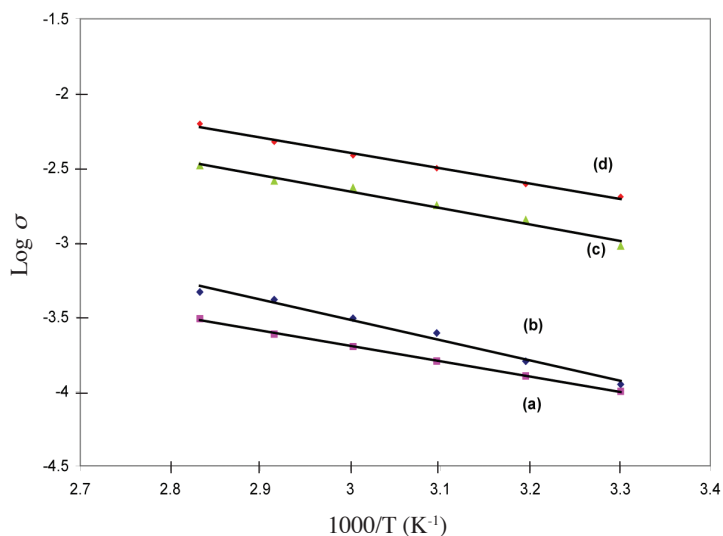


FIGURE 4. Conductivity-temperature dependence for the highest conducting film of the (a) PAN-LiCF<sub>3</sub>SO<sub>3</sub>, (b) PAN-NaCF<sub>3</sub>SO<sub>3</sub>, (c) PAN-EC-LiCF<sub>3</sub>SO<sub>3</sub> and (d) PAN-EC-NaCF<sub>3</sub>SO<sub>3</sub> systems

$$\sigma(T) = \sigma_0 \exp\{-E_a/RT\} \quad (1)$$

where  $\sigma_0$  is the conductivity pre-exponential factor and  $E_a$  is the activation energy for conduction. The activation energy,  $E_a$ , can be evaluated from the slope of the plots. The  $E_a$  for the PAN-LiCF<sub>3</sub>SO<sub>3</sub>, PAN-NaCF<sub>3</sub>SO<sub>3</sub>, PAN-EC-LiCF<sub>3</sub>SO<sub>3</sub> and PAN-EC-NaCF<sub>3</sub>SO<sub>3</sub> films have been calculated to be 0.28, 0.23, 0.22 and 0.19 eV, respectively.

The conductivity-pressure dependence studies are carried out in the range of pressure between 0.01 and 0.09 MPa for the highest conducting films from the PAN-LiCF<sub>3</sub>SO<sub>3</sub> and PAN-NaCF<sub>3</sub>SO<sub>3</sub>, PAN-EC-LiCF<sub>3</sub>SO<sub>3</sub> and PAN-EC-NaCF<sub>3</sub>SO<sub>3</sub> systems. Conductivity was observed to decrease with increasing pressure for all systems. The linear dependence of logarithmic variation of electrical conductivity versus pressure allows a volume  $\Delta V^*$  can be calculated by using (1) (Bendler et al. 2003):

$$\left( \frac{\partial \ln \sigma}{\partial P} \right)_T = - \left( \frac{\Delta V^*}{RT} \right) \quad (2)$$

Because the conductivity of all systems follows an Arrhenius type law at constant pressure, this volume is called an "activation volume". The activation volume is the difference in volume between a mole of moving species in its activated transition state and its volume at normal equilibrium. The decrease of conductivity values with increasing pressure are related to the basis of the free volume model. Because free volume is the volume available for motion and the activation volume is the volume change required for motion, large activation volumes are associated with small free volume and vice versa (Fontanella et al. 1986; Stallworth et al. 1999). The  $V^*$  values and the conductivity values for each system are summarized in Table 1.

## CONCLUSIONS

Plasticized and unplasticized PAN polymer electrolyte films containing LiCF<sub>3</sub>SO<sub>3</sub> and NaCF<sub>3</sub>SO<sub>3</sub> salts have been prepared and studied. The infrared spectra exhibited the nitrile C≡N band that was shifted towards the lower frequency. This result showed that the interaction occurred between the nitrogen atoms of PAN with Li<sup>+</sup> and Na<sup>+</sup> ions from the salts. The plasticized film containing NaCF<sub>3</sub>SO<sub>3</sub> salt had higher conductivity and lower activation energy than that containing LiCF<sub>3</sub>SO<sub>3</sub> salt. This result was consistent with the SEM studies. The plasticizer, EC helps to dissociate the salt thereby increasing the number of mobile ions and lead to conductivity enhancement. The temperature dependence of the conductivity follows Arrhenius equation in the temperature range of 303 K – 353 K. The decrease of conductivity with increasing pressure was discussed in term of free volume model.

TABLE 1. The room temperature conductivity,  $\sigma$  and activation volume,  $\Delta V^*$  for PAN-LiCF<sub>3</sub>SO<sub>3</sub>, PAN-NaCF<sub>3</sub>SO<sub>3</sub>, PAN-EC-LiCF<sub>3</sub>SO<sub>3</sub> and PAN-EC-NaCF<sub>3</sub>SO<sub>3</sub> films

System	Conductivity, $\sigma$ (S cm <sup>-1</sup> )	Activation Volume, $\Delta V^*$ (cm <sup>3</sup> /mol)
PAN-LiCF <sub>3</sub> SO <sub>3</sub>	$3.04 \times 10^{-4}$	$30.4 \times 10^{-3}$
PAN-NaCF <sub>3</sub> SO <sub>3</sub>	$7.13 \times 10^{-4}$	$28.6 \times 10^{-3}$
PAN-EC-LiCF <sub>3</sub> SO <sub>3</sub>	$1.32 \times 10^{-3}$	$13.7 \times 10^{-3}$
PAN-EC-NaCF <sub>3</sub> SO <sub>3</sub>	$5.49 \times 10^{-3}$	$11.1 \times 10^{-3}$

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## REFERENCES

- Armand M.B., Chabango, J.M. & Duclot, M.J. 1979. In. Vashishta P., Mundy J.N. & Shenoy G.K. (ed.) *Fast Ion Transport in Solids*, 131-136. North-Holland, Amsterdam.
- Bendler, J.T., Fontanella, J.J., Shlesinger, M.F. & Wintersgill, M.C. 2003. The need to reconsider Traditional Free Volume Theory for Polymer Electrolytes. *Electrochimica Acta* 48: 2267-2272.
- Bhide, A. & Hariharan, K. 2007. Ionic Transport Studies on (PEO)<sub>6</sub>: NaPO<sub>3</sub> Polymer Electrolyte Plasticized with PEG<sub>400</sub>. *European Polymer Journal* 43: 4253-4270.
- Duclot, M., Alloin, F., Brylev, O., Sanchez, J.Y. & Souquet, J.L. 2000. New Alkali Ionomers: Transport Mechanism from Temperature and Pressure Conductivity Measurements. *Solid State Ionics* 136-137: 1153-1160.
- Egashira, M., Todo, H., Yoshimoto, N. & Morita, M. 2008. Lithium Ion Conduction in Ionic Liquid-Based Gel Polymer Electrolyte. *Journal of Power Sources* 178: 729-735.
- Fenton, B.E., Parker, J.M. & Wright, P.W. 1973. Complexes of Alkali Metal Ions with Poly (ethylene oxide). *Polymer* 14: 589
- Fontanella, J.J., Wintersgill, M.C., Smith, M.K., Semancik, J. & Andeen, C.G. 1986. Effect of High Pressure on Electrical Relaxation in Poly (Propylene Oxide) and Electrical Conductivity in Poly (Propylene Oxide) Complexed with Lithium Salts. *Journal of Applied Physics*. 60: 2665-2671.
- Kuila, T., Acharya, H., Srivastava, S.K., Samantaray B.K. & Kureti, S. 2007. Enhancing the Ionic Conductivity of PEO Based Plasticized Composite Polymer Electrolyte by LaMnO<sub>3</sub> nanofiller. *Material Science Engineering B* 131: 217-224.
- Lee, Y.M., Ko, D.H., Lee, J.Y. & Park, J.K. 2006. Highly Ion-Conductive Solid Polymer Electrolytes Based on Polyethylene Non-Woven Matrix. *Electrochimica Acta* 52: 1582-1587.
- Le Nest, J.F. & Gandini, A. 1990. In. Scrosati, B (ed.). *Second International Symposium on Polymer Electrolytes*. pp. 129. London, New York: Elsevier Appl. Sci.
- Pradhan, D.K., Samantaray, K., Choudhary, N.P. & Thakur, A.K. 2005. Effect of Plasticizer on Structure-Property Relationship in Composite Polymer Electrolytes. *Journal of Power Sources* 13: 384-393.
- Ramya, C.S., Selvasekarapandian, S., Savitha, T., Hirankumar, G. & Angelo, P.C. 2007. Vibrational and Impedance Study on PVP-NH<sub>4</sub>SCN Based Polymer Electrolytes. *Physica B* 393: 11-17.

Sagane, F., Iriyama, Y., Abe, T. & Ogumi, Z. 2005. Li<sup>+</sup> and Na<sup>+</sup> Transfer Through Interfaces between Inorganic Solid Electrolytes and Polymer or liquid Electrolytes. *Journal of Power Sources* 146(1-2): 749-752.

Stallworth, P.E., Fontanella, J.J., Wintersgill, M.C., Scheidler, C.D., Immel, J., Greenbaum, S.G. & Gozdz, A.S. 1999. NMR, DSC and High Pressure Electrical Conductivity Studies of Liquid and Hybrid Electrolytes. *Journal of Power Sources* 81-82: 739-747.

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