Studies of Ion Transport and Electrochemical Properties of Plasticized Composite Polymer Electrolytes
(Kajian Pengangkutan Ion dan Sifat Elektrokimia Komposit Pemplastik Polimer Elektrolit)

D. HAMBALI, Z. ZAINUDDIN, I. SUPA'AT & Z. OSMAN*

ABSTRACT

The composite polymer electrolytes (CPEs) composed of polyacrylonitrile (PAN) as host polymer, lithium tetraflouroborate (LiBF$_4$) as dopant salt, dissoÅlved in the mixture of ethylene carbonate (EC) and dimethyl phthalate (DMP) as plasticizing solvent, with the addition of silica (SiO$_2$) as inorganic filler were prepared by the solution casting technique. The CPE films were prepared by varying the concentrations of SiO$_2$ from 1 to 5 wt. %. The CPE film containing 3 wt. % of SiO$_2$ exhibits the highest ionic conductivity of 1.36×10^{-2} S cm^{-1} at room temperature while for temperature dependence studies, the plot obtained obeyed Arrhenius rule and the calculated activation energy was 0.11 eV. The ionic conductivity of the CPEs was found to depend on the concentration of ion pairs of dopant salt as showed by FTIR spectra. The calculated value of lithium ions transport number, t_{Li+} for the highest conducting CPE film was 0.15. This result indicates that anionic species are the main contributor to the total conductivity of the CPE. The CPE film has an electrochemical stability higher than the non-filler film.

Keywords: Composite polymer electrolytes; conductivity; FTIR; lithium tetraflouroborate; PAN

ABSTRAK

Komposit polimer elektrolit (CPEs) yang terdiri daripada poliakrilonitril (PAN) sebagai hos polimer, litium tetrafloroborat (LiBF$_4$) sebagai garam pendop telah larutkan di dalam campuran etilina karbonat (EC) dan dimetil ftalat (DMP) sebagai pelarut pemplastik, dengan silika (SiO$_2$) sebagai filer tak organik, telah disediakan melalui kaedah tuangan larutan. Filem CPE telah disediakan dengan pelbagai kandungan SiO$_2$ dari 1 hingga 5 % bt. Filem CPE yang mengandungi 3 % bt. SiO$_2$ memberikan nilai kekonduksian pada suhu yang bilik tertinggi iaitu 1.36×10^{-2} S cm^{-1}. Kekonduksian bagi CPEs didapati bergantung kepada kandungan pasangan ion daripada garam pendop seperti yang ditunjukkan oleh spektra FTIR. Nilai bagi nombor pengangkutan ion litium, t_{Li+} untuk CPE filem dengan kekonduksian tertinggi adalah 0.15. Keputusan ini menunjukkan spesies anion adalah penyumbang utama kepada kekonduksian CPE. Filem CPE mempunyai kestabilan elektrokimia lebih tinggi daripada filem tanpa filer.

Kata kunci: FTIR; kekonduksian; komposit polimer elektrolit; litium tetrafloroborat; PAN

INTRODUCTION

Safety issues concerning conventional liquid electrolytes such as leakage, volatility, spontaneous combustion of the electrolytes, limited temperature range of operation and lack of mechanical stability (Scrosati & Garche 2010) makes the solid polymer electrolytes (SPEs) as a potential substitution. Thus, there have been much interests on SPEs from the past few decades pioneered by Fenton et al. (1973) which prepared SPEs based on poly (ethylene oxide), (PEO) and produced an ionic conduction at room temperature. Meanwhile, suggestion made by Armand et al. (1979) which is the potential of such system for applied electrochemical on novels of materials, gives advantages on mechanical properties of SPE that include excellent stability and the elimination of electrolyte leakage problem. They also produced the first SPE based film battery. Since then, approaches on many types of polymers have been made such as poly(vinyl chloride) (PVC) (Ahmad et al. 2008) and polyacrylonitrile (PAN) (Yoon et al. 2004).

However, although SPEs can overcome the disadvantages of liquid electrolytes due to its non-volatility, low flammability and large electrochemical stability window (Manuel Stephan & Nahm 2006), the low value of ionic conductivity limits their performance especially in electrochemical devices. In addition, in order to be commercialised, SPEs should exhibit high ionic mobility that is closely coupled to the high local flexibility and high segmental motion of the polymer chain (Suthanthiraraj et al. 2009). These properties are important as the polar and flexibility of the main chain dissociate the salts to generate the carrier ions so that the ions can migrate through the amorphous region of the SPE systems via interchain/intrachain segmental motion (Agrawat & Mahipal 2011). The degree of amorphosity which predominantly controls the ion conduction in the polymer complex however can be greatly enhanced by the addition of plasticizers. As an examples, the incorporation of EC into the polymer electrolytes system have been worked effectively with

many types of polymers which are PAN (Isa et al. 2011) and poly glycidyl methacrylate (PGMA) (Imperiyka et al. 2014). Research done by Imperiyka et al. (2014) proved that the conductivity of system increased with EC concentration and reached a maximum value of 2.0×10^{-4} S cm^{-1} when 80 wt. % of EC concentration was added. This is due to the high value of dielectric constant of EC ($\epsilon_r = 85.1$) which reduce the inter-ion coulomb interactions and cohesive forces between the polymer chains and therefore increase the chain segmental mobility and consequently, the lithium ions contribution to the conductivity will be increased (Imperiyka et al. 2014).

Other plasticizer that works on polymer is dimethylphthalate (DMP). Research done by Rajendran et al. (2002a) showed that by adding DMP into the PMMA/PVDF-LiClO$_4$ system, the conductivity increases with the increase in the concentration of DMP. They claimed that, the purpose of adding plasticizers is to increase the free volume of the polymer electrolytes and hence increase the overall ionic mobility which enhances the ionic conductivity. The combination of both EC and DMP into the polymer system have been reported by our research group (Chong & Osman 2014) and obtained high values of conductivities up to 10^{-2} S cm^{-1}. Thus, this work is the continuity of our previous work by upgrading its properties with the dispersion of nano-sized ceramic filler into the optimum composition of solid polymer electrolytes films to produce composite polymer electrolytes (CPEs).

The dispersion of ceramic fillers is an attractive approaches due to the improvement of ionic conductivity and mechanical stability (Rajendran et al. 2002a). According to Yang et al. (2006), on addition of Al$_2$O$_3$, TiO$_2$ and BaTiO$_3$ filler into the PVdF-PEGDA-PMMA system, the ionic conductivities were higher than that of electrolyte without fillers. They claimed that this effect may be due to the fact that ceramic fillers retain the electrolytes and provide a route for ion transfer. On the other hand, the nano-sized of the ceramic filler itself is very significant as it will provide maximum possible surface area. As the conductivity enhancement is believed to be associated with the nature of the number of Lewis acid-base groups in the surface of the fillers, therefore in this case, the conductivity value is likely to be increased (Jayathilaka et al. 2002). The dispersion of ceramic fillers plays an important role in the ionic transport of polymer electrolytes and also helps to improve the thermal stability and ability to retain conductivity over time (Ramesh & Lu 2008). It was also proven that the ceramic filler can help in electrochemical stability of the CPE system due to its strong influence on the nature of the passivation layer formed (Shin & Passerini 2004).

In the present work, we have studied the effects of SiO$_2$ filler on the prepared PAN based CPEs containing plasticizers DMP and EC as well as LiBF$_4$ salt. The work was focused on the electrical, structural and electrochemical properties of the CPE films upon the addition of SiO$_2$ filler. These properties of the CPE films are expected to show improvements compared to the film without the

SiO$_2$ filler as reported before (Chong & Osman 2014). Although several works have been reported on the addition of SiO$_2$ in the polymer matrix, however to the best of our knowledge, no literature has been reported for PAN-based polymer electrolytes containing SiO$_2$ filler.

MATERIALS AND METHODS

PAN with an average molecular weight of 1.5×10^5 g/mol and SiO$_2$ with particle size of (5-15) nm were obtained from Sigma-Aldrich while DMP was purchased from Merck Schrucharat OHG. Meanwhile, EC was obtained from Fluka, LiBF$_4$ was obtained from Acros Organics and dimethylformamide (DMF) was obtained from R & MII Chemicals.

SAMPLE PREPARATION

The solution casting technique was used in preparing CPEs. In this technique, PAN was first dissolved in DMF and EC and DMP were then added as plasticizers. LiBF$_4$ and SiO$_2$ powder were dissolved in DMF separately. All the solutions were mixed and stirred until they turned clear and homogeneous. The mixtures of LiBF$_4$ and SiO$_2$ solutions were then poured into the solution of PAN-plasticizers and continuously stirred for several hours. After complete dissolution, the solution was then poured onto the petri dishes and dried thoroughly under vacuum at 50°C for 24 h until films were formed. The optimised composition of PAN, EC, DMP and LiBF$_4$ was determined by preparing the solid polymer electrolyte films with different weight ratio as reported in our previous work (Chong & Osman 2014). The highest conducting film from this system i.e. the film with weight ratio composition for PAN: EC: DMP: LiBF$_4$ of 24:18:18:40 was chosen as CPE without filler as a reference. The contents of SiO$_2$ in the prepared CPE system were varied from 1 to 5 wt. % and the compositions of each film are shown in Table 1.

CHARACTERIZATION METHODS

Ionic conductivity studies of the CPE films were carried out by using A.C. impedance technique. The CPE films were cut into circular shape to fit the stainless steel electrode and sandwiched between them. Impedance measurements were then performed for each CPE film by using a computer-interfaced HIOKI 3532 LCR bridge over the frequency range of 50 Hz to 1 M Hz. Then, by using (1);

$$\sigma = \frac{t}{R_b A},\tag{1}$$

where t is the thickness of the CPE film (cm); A is the effective contact area between the electrode and the film; and R_b is the bulk resistance (Ω) determined from the Cole-Cole plot, the value of conductivity (σ) was then calculated.

The conductivity temperature dependence studies were also carried out for the selected CPE films by varying the temperature from 303 K to temperature below the glass transition temperature, T$_g$ of pure PAN film i.e 353 K. From

thermal analysis, pure PAN film exhibited a distinct, T_g at 85°C (308 K) (Osman et al. 2010).

In order to determine the molecular structure of the CPE films, Fourier Transform Infrared (FTIR) spectroscopy was carried out. It is a useful technique that provides information on the molecular structure and chemical bonding of materials. In this work, Nicolet is 10 (Thermo Scientific) spectrophotometer in the wavenumber region between 650 and 4000 cm^{-1} with a resolution of 1 cm^{-1} was used.

Ionic transport number was then determined by direct current (D.C.) polarization method proposed by Watanabe et al. (1983). In this method, a constant voltage was applied across the highest conducting film that is sandwiched between the two stainless steel (SS) electrodes SS/CPE/SS which act as blocking electrodes and the resulting current is measured as a function of time. The value of ionic transport number, t_i was calculated using (2);

$$t_i = i_T - \frac{i_e}{i_T},$$ (2)

where i_e is the electronic current; and i_T is the total current. Cationic transport number, t_{Li+}, was evaluated using the combined A.C. impedance and D.C. polarization measurement techniques as proposed by Evans et al. (1987). Lithium foil was used and the highest conducting CPE film with cell configuration of Li/CPE/Li. The cell was prepared inside the vacuum glove box to prevent oxidation of the lithium foils. The cell has been polarized by applying a constant voltage for 5 h and the value of initial and final currents, I_0 and I_s were recorded. A.C. impedance was measured before and after polarization to obtain the values of electrode-electrolyte resistances. Thus, the cationic transport number, t_{Li+} can be determined using (3);

$$t_{Li+} = \frac{I_s R_f}{I_0 R_i} \left[\frac{\Delta V - I_0 R_0}{\Delta V - I_s R_s} \right],$$ (3)

where I_0 is the initial current; and I_s is the final current. R_i and R_f represent initial and steady-state resistances of the electrolytes while R_0 and R_s are the initial and steady-state resistances of the passivation layers on the lithium electrodes (Abraham et al. 1997).

The electrochemical stability of the selected CPE films was determined by using linear sweep voltammetry (LSV). In this method, stainless steel was used as working electrode while lithium foil act as reference electrode with cell configuration of SS/CPE/Li at a scan rate of 1 mVs^{-1}. The current response was plotted as a function of voltage.

RESULTS AND DISCUSSION

IONIC CONDUCTIVITY STUDIES

The value of R_b was determined from the intercept of the Z_r-axis of the Cole-Cole plot of each film and hence, the value of conductivity, σ was calculated using (1).

The variation of conductivity with SiO$_2$ filler for the CPE film was then plotted as shown in Figure 1. It can be observed the two maximum after the addition of SiO$_2$ filler. The first maximum conductivity is obtained when 1 wt. % of SiO$_2$ was added. This maximum observed at a lower content of SiO$_2$ is related with the generation of free ions followed by their re-association. The second maximum is obtained when 3 wt. % of SiO$_2$ filler was added and this behaviour is related to the formation of a surface-charge layer at the polymer-filler interface as the weight percentage of SiO$_2$ increases (Kumar 2004). This effect can be explained mainly due to the instantaneous presence of SiO$_2$ and BF$_4^-$ species and such charged layer are responsible for the generation of free ions and mobility, thus enhance the conductivity. The decrease in conductivity after the achievement of the second maximum is because of the two possible reasons: The space charge layer may cause a blocking effect at high
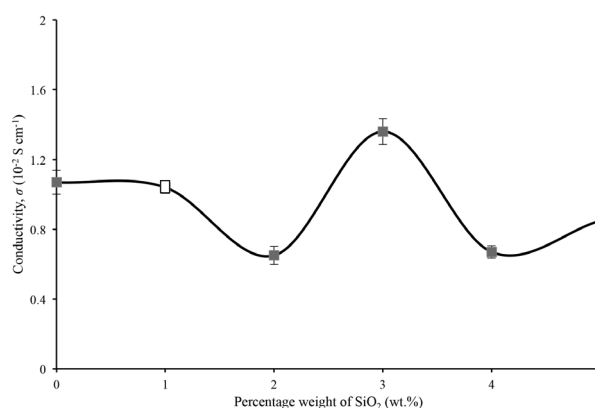

FIGURE 1. The variation of conductivity with SiO$_2$ filler for the CPE films

TABLE 1. The compositions of the prepared CPE films

Samples	Composition in gram				SiO$_2$ content in wt. %	Conductivity values (S cm^{-1})
	PAN	EC	DMP	LiBF$_4$		
CPE0	2	1.5	1.5	3.3	0	1.07×10^{-2}
CPE1	2	1.5	1.5	3.3	1	1.04×10^{-2}
CPE2	2	1.5	1.5	3.3	2	0.65×10^{-2}
CPE3	2	1.5	1.5	3.3	3	1.36×10^{-2}
CPE4	2	1.5	1.5	3.3	4	0.67×10^{-2}
CPE5	2	1.5	1.5	3.3	5	0.85×10^{-2}

concentration of SiO_2 particles which limits the ions mobility; the generated free ions under the influence of a local electric field may be re-associated to form ion pairs and thus decrease the conductivity (Kumar & Hashmi 2010). As conclusion, the addition of SiO_2 gives improvement in conductivity that is when 3 wt. % of SiO_2 was added and obtained a maximum value of 1.36×10^{-2} S cm^{-1}.

TEMPERATURE-DEPENDENCE IONIC CONDUCTIVITY STUDIES

The ionic conductivities was also measured for CPE films containing 2, 3 and 5 wt. % of SiO_2, in a temperature range of 303 K to 353 K. Figure 2 shows the linear plots of log σ against 1000/T for CPE films containing 2, 3 and 5 wt. % of SiO_2. The regression values, R^2 were calculated and were found to be closed to unity and this indicates that the plots obey Arrhenius rule as specified by (4);

$$\sigma(T) = \sigma_o \exp - (E_a/kT), \qquad (4)$$

where σ_o is the conductivity pre-exponential factor; and E_a is the activation energy for conduction, the value of E_a hence was calculated. The values of σ_o, E_a and R^2 were tabulated in Table 2. It is understood that in Arrhenius behaviour, the nature of cation transport of polymer electrolytes can be deduced to be similar to that in ionic crystals, where ions jump into neighbouring vacant sites (Gadjourova et al. 2001; Louis 1994; Md Isa et al. 2011; Osman et al. 2010; Othman et al. 2013, 2007; Zainol et al. 2013). As expected, the value of activation energy is

the lowest for the CPE film containing 3 wt. % SiO_2 of 0.11 eV, which has the highest conductivity value. A low value of activation energy can be related to the decrease in viscosity and hence increased the polymer chain flexibility (Rajendran et al. 2008, 2004, 2002b) thus facilitate the fast lithium ions motion in the polymer network (Hema et al. 2008).

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

FTIR was carried out to study the interaction between PAN, EC, DMP, LiBF$_4$ salt and SiO_2 filler in CPE films. The vibrational modes of each material used are tabulated in Table 3.

Figure 3 shows the FTIR spectra of pure PAN, PAN + (EC+DMP), PAN + (EC+DMP) + LiBF$_4$ and PAN + (EC+DMP) + LiBF$_4$ + SiO_2 (1-5 wt. %) films in wavenumber range between 1000 and 3200 cm^{-1}. After the addition of SiO_2 into the PAN+(EC+DMP) film, it is observed that the vibrational band of 1658 cm^{-1} which indicates the CH asymmetrical stretching of pure PAN is shifted to 1654-1660 cm^{-1} for PAN films containing SiO_2 and the intensity of this band has decreased. The intensity of C≡N stretching of pure PAN films at 2242 cm^{-1} decreases for samples containing 1, 3 and 5 wt. % SiO_2 and increases for samples containing 2 and 4 wt. % SiO_2. On the other hand, the vibrational band of 2935 cm^{-1} in pure PAN film corresponds to CH$_2$ symmetrical is shifted to 2934-2936 cm^{-1} in all samples containing SiO_2. The intensity of this band is also decreases. The characteristic peak of SiO_2 at 1078 cm^{-1} which indicates the Si-O-Si functional group disappears in all PAN-composite polymer electrolyte film. The disappearance and shifting of
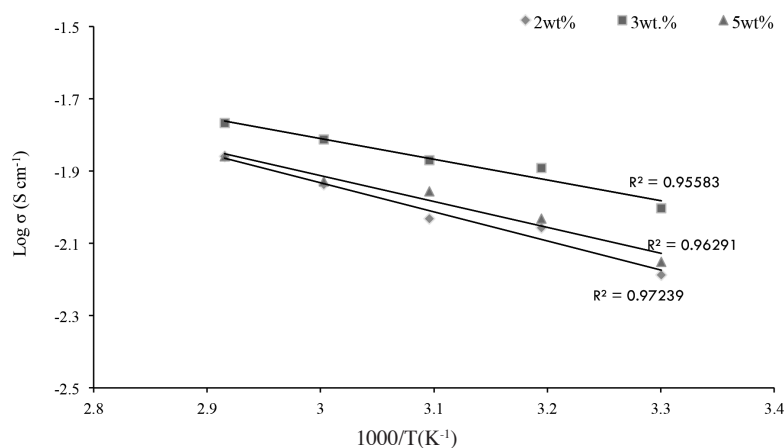

FIGURE 2. Plot of log σ against 1000/T for CPE films containing 2, 3 and 5 wt. % of SiO_2

TABLE 2. The values of conductivity pre exponential factor (σ_o), activation energy (E_a) and regression (R^2) of CPE films

Samples	σ_0(S cm^{-1})	E_a(eV)	R^2
CPE2	3.04	0.16	0.97
CPE3	0.81	0.11	0.96
CPE5	1.72	0.14	0.96

TABLE 3. The vibrational bands of PAN, EC, DMP, LiBF$_4$ and SiO$_2$

| Material	Wavenumber (cm^{-1})	Assignments of bands	References
PAN	1664	CH asymmetrical stretching	(Rajendran et al. 2008)
	2242	C≡N stretching	(Rajendran et al. 2008)
	2940	CH$_2$ symmetrical stretching	(Rajendran et al. 2008)
EC	1053	Ring breathing	(Huang 1996)
	1396	CH$_2$ (wagging)	(Huang 1996)
	1471	CH$_2$ (bending)	(Frech 1996)
	1768	C=O (stretching)	(Huang 1996)
DMP	1432	C-C (stretching)	(Kumar 2004)
	2953	CH (stretching)	(Kumar 2004)
LiBF$_4$	766	υ_1 (BF$_4$) free ions	(Qiao et al. 2008)
	770	υ_1 (BF$_4$) ion pairs	(Qiao et al. 2008)
	782	dimers	(Qiao et al. 2008)
SiO$_2$	1078	Si-O-Si	(Qiao et al. 2008)
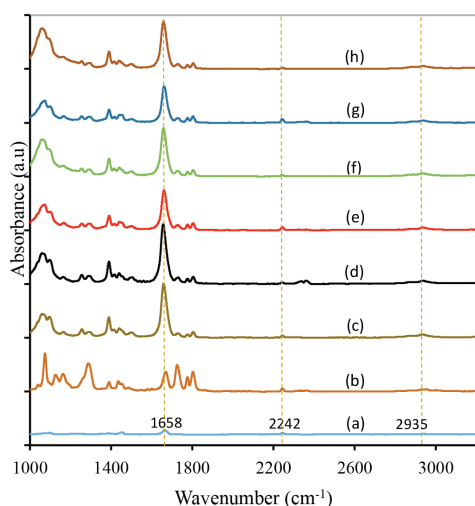
FIGURE 3. FTIR spectra of (a) pure PAN film, (b) PAN + EC + DMP, (c) PAN + EC + DMP + LiBF$_4$, PAN + EC + DMP + LiBF$_4$ with (d) 1 wt. % SiO, (e) 2 wt. % SiO$_2$, (f) 3 wt. % SiO$_2$, (g) 4 wt. % SiO$_2$ and (h) 5 wt. % SiO$_2$

the bands as well as decreasing in the band intensity have proved that there are interactions between PAN, EC, DMP, LiBF$_4$ and SiO$_2$ and complexation has occurred between them.

The FTIR deconvolution was then carried out to study the ion association involving BF$_4^-$. The band at 766 cm^{-1}

of LiBF$_4$ corresponds to free ions while the band at 770 cm^{-1} is the contact ion pairs. The FTIR spectra of CPE films containing 1 to 5 wt. % of SiO$_2$ is then deconvoluted at the region between 730 to 800 cm^{-1} to obtain the integrated area of free ions and ion pairs as shown in Figure 4. However, the free ions band was found to be overlapped at 766 cm^{-1} with the aromatic C-H band of DMP and a single band was formed at 752 cm^{-1} as reported before (Chong & Osman 2014). Therefore, only the ion pairs band will be studied as the free ions band is less reliable to be referred. The integrated area of the ion pairs band for each CPE films and film without SiO$_2$ is calculated and the values are tabulated as shown in Table 4. From the table, it can be observed that the area of the bands follow the trend of ionic conductivity that is high value of conductivity depicts low value of integrated area of ion pairs and vice versa. This shows that less ion pairs exists in the CPE film with highest conductivity value.

TRANSPORT NUMBER STUDIES

Ionic transport number is a dimensionless parameter which symbolizes the contribution of a particular charged species present in the electrolyte to the overall charge transport across the cell. The normalized current versus time plot for the highest conducting CPE film was plotted as shown in Figure 5. The value of ionic transport number calculated using (2) (Pandey & Hashmi 2009) was 0.98. This shows

TABLE 4. The position and integrated area of ion pairs band corresponds to BF$_4^-$ ions in CPE films with different concentrations of SiO$_2$

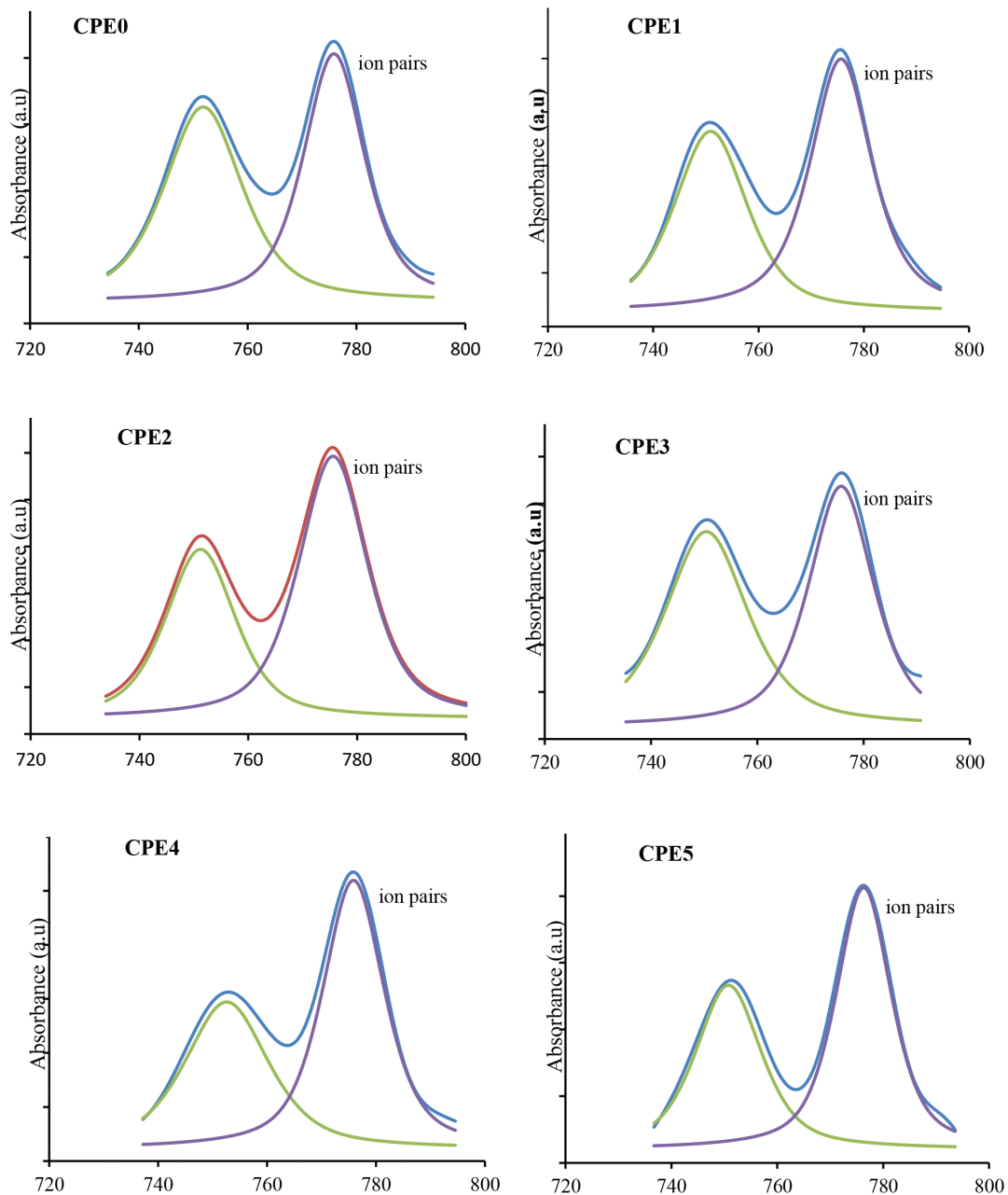| CPE films	Position (cm^{-1})	Integrated area (%)
CPE0	776	50.4
CPE1	775	55.9
CPE2	775	60.5
CPE3	776	49.3
CPE4	775	57.5
CPE5	776	57.3

FIGURE 4. FTIR spectra of the υ_1 mode of BF_4^- from 730-800 cm^{-1} for CPE films with different concentrations of SiO_2 in PAN-EC-DMP-LiBF$_4$ system

that the charge carriers in the CPE film were predominantly ions (Chen-Yang et al. 2009).

For cationic transport number, it was defined as the net number of faradays of charge carriers across the reference plane by the cationic species in the direction of the cathode, during the passage of one faraday of charge across the plane (Chen-Yang et al. 2009). Thus, it was used to determine the contribution of the cationic species in the CPE film to the overall conductivity. Figure 6 shows the D.C. polarization plot for the highest conducting film from which the values of initial and final currents were obtained. As shown in the figure, there is an initial current, I_o at the very beginning of the polarization and after a duration of

polarization time about 4 h, a steady-state current, I_s is established. When an electric field is applied to the CPE film, the cationic species, Li$^+$, Li$_2$BF$_4$, is carried toward the cathode while anionic species, BF$_4^-$, Li(BF$_4$)$_2^-$, migrates toward the anode. Hence, the movement of both cationic and anionic species contribute to the total conductivity (Choe et al. 1997). The difference between the fluxes of Li-containing species directed toward the cathode and anode was measured as the cationic transport number. When a steady-state is developed, the current drop due to the growth of passivation layers on the Li electrodes and this establishes the concentration gradient. The cationic transport number, t_{Li+} was calculated using (3). The values
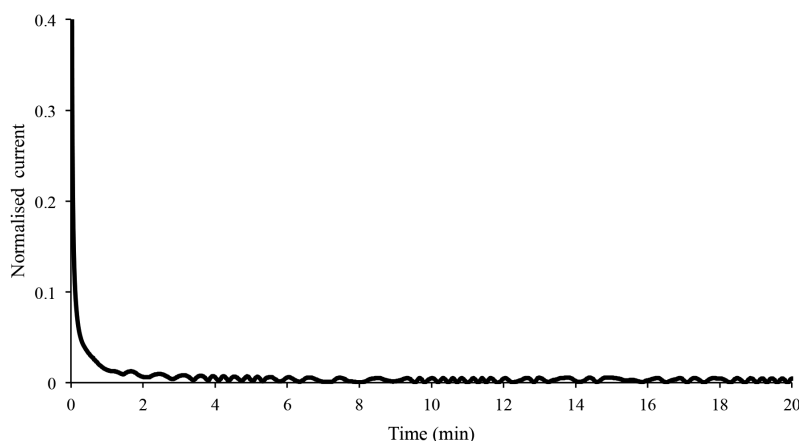
FIGURE 5. Normalized current versus time plot for CPE film containing 3 wt. % SiO$_2$

of R_i, R_f, R_o and R_s were obtained from the impedance plots as shown in the inset of Figure 6. The t_{Li+} for the highest conducting film was calculated as 0.15 and this result indicates that anionic species are the main contributor to the total conductivity of the CPE film. The t_{Li+} value obtained in this present work is within the range of 0.1 to 0.3 for PAN-based polymer electrolytes as reported by Chen-Yang et al. (2009) and Choe et al. (1997). This behaviour illustrates the similarity in the conductivity mechanisms of plasticized polymer electrolytes and conventional liquid electrolytes (Jayathilaka et al. 2002).

LINEAR SWEEP VOLTAMMETRY (LSV)

LSV was used to evaluate the electrochemical window stability which is another important parameter of the polymer electrolytes system that must be considered for application in a lithium polymer battery (Adnan & Mohamed 2014; Lee et al. 2000). The technique was performed by applying a voltage sweep from -5 up to 5 V for the highest conducting CPE film and the non-filler film. Figure 7 shows the plot of current as a function of voltage for the highest conducting CPE film while the inset graph shows the plot for non-filler film. It can be observed that the current is very stable up to 3.6 V for the non-filler film and increased rapidly above 3.6 V at which the decomposition of the electrolyte takes place (Yang et al. 2006). For the highest conducting film, the current is stable up to 4.0 V. As lithium rechargeable batteries generally operate between 3.0 and 4.5 V, therefore both films are suitable to be used as an electrolyte in lithium polymer battery. These results showed that the anodic stability which is the capability of the polymer electrolyte to withstand high voltages at the cathode interface (Lee et al. 2000) is higher for CPE film containing SiO$_2$ filler compared to the non-filler film. Thus, it shows that the addition of SiO$_2$ filler can increase the anodic stability of the film.
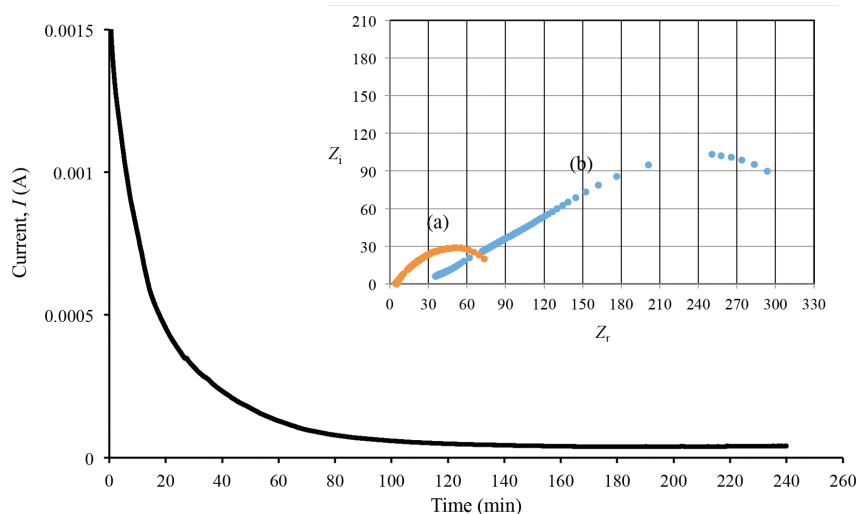

FIGURE 6. D.C. polarization plot for CPE film containing 3 wt. % SiO$_2$. Inset graph shows impedance plots; (a) before and (b) after D.C. polarization
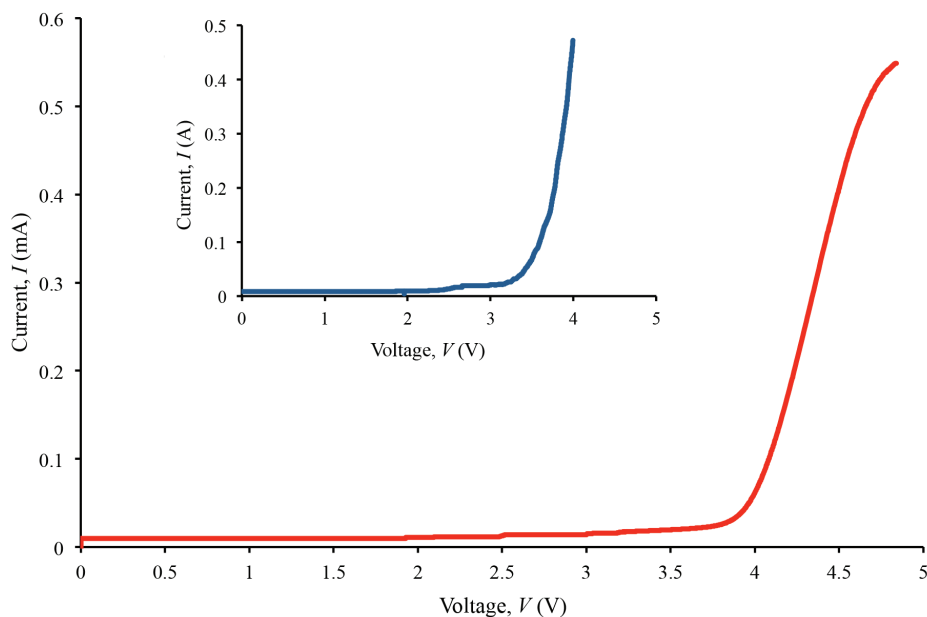
FIGURE 7. Plot of current as a function of voltage for CPE film containing 3 wt. % SiO$_2$. Inset graph shows plot of current as a function of voltage for non-filler film

CONCLUSION

Polyacrylonitrile (PAN) based composite polymer electrolytes (CPEs) have been prepared with variation of SiO$_2$ filler from 1 to 5 wt. % and were characterized. The highest room temperature ionic conductivity of 1.36×10^{-2} S cm^{-1} was obtained from the CPE film containing 3 wt. % of SiO$_2$. The conductivity-temperature dependence studies for the highest conducting film obeyed Arrhenius rule with activation energy, E$_a$ of 0.11 eV. The relationship between ionic conductivity and ion pairs of the dopant salt have been proved by FTIR spectroscopy analysis. The calculated value of ionic transport number for the highest conducting film was 0.98 and therefore the charge carriers that exist in the CPE film were predominantly ions. In addition, the lithium ions transport number of 0.15 was obtained from the highest conducting CPE film and showed that anions gave significant contribution to the overall conductivity. A higher value of anodic stability was observed when 3 wt. % of SiO$_2$ filler was added compared to the non-filler film. As a whole, there are some improvements obtained through characterizations upon the addition of SiO$_2$ filler with the nature of a stable, free standing film itself. The films also have the potential to maintain the ionic conductivity after some times which shows they are less sensitive to the surrounding and will be an important factor to achieve good quality of results.

REFERENCES

Abraham, K.M., Jiang, Z. & Carroll, B. 1997. Highly conductive PEO-like polymer electrolytes. *Chemistry of Materials* 9(9): 1978-1988.

Adnan, S.B.R.S. & Mohamed, N.S. 2014. Properties of novel Li4-3xCrxSiO4 ceramic electrolyte. *Ceramics International* 40(3): 5033-5038.

Agrawat, R.C. & Mahipal, T.K. 2011. Study of electrical and electrochemical behaviour on hot-press synthesized nano-composite polymer electrolyte (NCPE) membranes: [(70PEO: 30 KNO3) + X SiO2. *International Journal of Electrochemical Science* 6: 867-881.

Ahmad, A., Rahman, M.Y.A. & Su'ait, M.S. 2008. Preparation and characterization of PVC-LiClO4 based composite polymer electrolyte. *Physica B: Condensed Matter* 403(21-22): 4128-4131.

Armand, M.B., Chabagno, J.M. & Duclot, M. 1979. *Fast Ion Transport in Solids*, edited by Vahisha, P., Mundy, J.N. & Shenoy, G.K. North Holland, New York: Elsevier.

Chen-Yang, Y.W., Chen, Y.T., Chen, H.C., Lin, W.T. & Tsai, C.H. 2009. Effect of the addition of hydrophobic clay on the electrochemical property of polyacrylonitrile/LiClO4 polymer electrolytes for lithium battery. *Polymer* 50(13): 2856-2862.

Choe, H.S., Carroll, B.G., Pasquariello, D.M. & Abraham, K.M. 1997. Characterization of some polyacrylonitrile-based electrolytes 9(1): 367-379.

Chong, W.G. & Osman, Z. 2014. The effect of carbonate-phthalate plasticizers on structural, morphological and electrical properties of polyacrylonitrile-based solid polymer electrolytes. *Journal of Polymer Research* 21(3): 381.

Evans, J., Vincent, C.A. & Bruce, P.G. 1987. Electrochemical measurement of transference numbers in polymer electrolytes. *Polymer* 28(13): 2324-2328.

Fenton, D.E., Parker, J.M. & Wright, P.V. 1973. Complexes of alkali metal ions with poly(ethylene oxide). *Polymer* 14(11): 589.

Gadjourova, Z., Andreev, Y.G., Tunstall, D.P. & Bruce, P.G. 2001. Ionic conductivity in crystalline polymer electrolytes. *Letters to Nature* 412: 520-523.

Hema, M., Selvasekerapandian, S., Sakunthala, A., Arunkumar, D. & Nithya, H. 2008. Structural, vibrational and electrical characterization of PVA - NH 4 Br polymer electrolyte system. *Physica B: Condensed Matter* 403(17): 2740-2747.

Imperiyka, M., Ahmad, A., Hanifah, S.A., Mohamed, N.S. & Rahman, M.Y.A. 2014. Investigation of plasticized UV-curable glycidyl methacrylate based solid polymer electrolyte for photoelectrochemical cell (PEC) application. *International Journal of Hydrogen Energy* 39(6): 3018-3024.

Md Isa, K.B., Othman, L. & Osman, Z. 2011. Comparative studies on plasticized and unplasticized polyacrylonitrile (PAN) polymer electrolytes containing lithium and sodium salts. *Sains Malaysiana* 40(7): 695-700.

Jayathilaka, P.A.R.D., Dissanayake, M.A.K.L., Albinssom, I. & Mellandar, B.E. 2002. Effect of nano-porous Al2O3 on thermal, dielectric and transport properties of the (PEO)9LiTFSI polymer electrolyte system. *Electrochimica Acta* 47: 3257-3628.

Kumar, B. 2004. From colloidal to composite electrolytes: Properties, peculiarities, and possibilities. *Journal of Power Sources* 135(1-2): 215-231.

Kumar, D. & Hashmi, S.A. 2010. Ion transport and ion-filler-polymer interaction in poly(methyl Methacrylate)-based, sodium ion conducting, gel polymer electrolytes dispersed with silica nanoparticles. *Journal of Power Sources* 195(15): 5101-5108.

Lee, K.H., Lee, Y.G., Park, J.K. & Seung, D.Y. 2000. Effect of silica on the electrochemical characteristics of the plasticized polymer electrolytes based on the P(AN-Co-MMA) copolymer. *Solid State Ionics* 133(3-4): 257-263.

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(1): 337-345.

Manuel Stephan, A. & Nahm, K.S. 2006. Review on composite polymer electrolytes for lithium batteries. *Polymer* 47(16): 5952-5964.

Osman, Z., Md Isa, K.B., Ahmad, A. & Othman, L. 2010. A comparative study of lithium and sodium salts in PAN-based ion conducting polymer electrolytes. *Ionics* 16(5): 431-435.

Othman, L., Md Isa, K.B., Osman, Z. & Yahya, R. 2013. Ionic conductivity, morphology and transport number of lithium ions in PMMA based gel polymer electrolytes. *Defect and Diffusion Forum* 334-335: 137-142.

Othman, L., Chew, K.W. & Osman, Z. 2007. Impedance spectroscopy studies of poly(methyl methacrylate)-lithium salts polymer electrolyte systems. *Ionics* 13: 337-342.

Pandey, G.P. & Hashmi, S.A. 2009. Experimental investigations of an ionic-liquid-based, magnesium ion conducting, polymer gel electrolyte. *Journal of Power Sources* 187(2): 627-634.

Rajendran, S., Babu, R.S. & Sivakumar, P. 2008. Investigations on PVC/PAN composite polymer electrolytes. *Journal of Membrane Science* 315(1-2): 67-73.

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.

Rajendran, S., Mahendran, O. & Kannan. R. 2002a. Ionic conductivity studies in composite solid polymer electrolytes based on methylmethacrylate. *Journal of Physics and Chemistry of Solids* 63(2): 303-307.

Rajendran, S., Mahendran, O. & Mahalingam, T. 2002b. Thermal and ionic conductivity studies of plasticized PMMA/PVdF blend polymer electrolytes. *European Polymer Journal* 38(1): 49-55.

Ramesh, S. & Lu, S.C. 2008. Effect of nanosized silica in poly(methyl methacrylate)-lithium bis(trifluoromethanesulfonyl)imide based polymer electrolytes. *Journal of Power Sources* 185(2): 1439-1443.

Scrosati, B. & Garche, J. 2010. Lithium batteries: Status, prospects and future. *Journal of Power Sources* 195(9): 2419-2430.

Shin, J.H. & Passerini, S. 2004. Effect of fillers on the electrochemical and interfacial properties of PEO-LiN(SO2CF2CF3)2 polymer electrolytes. *Electrochimica Acta* 49(9-10): 1605-1612.

Suthanthiraraj, S.A., Kumar, R. & Paul, B.J. 2009. FT-IR spectroscopic investigation of ionic interactions in PPG 4000: AgCF3SO3 polymer electrolyte. *Spectrochimica Acta. Part A, Molecular and Biomolecular Spectroscopy* 71(5): 2012-2015.

Watanabe, M., Kanba, M., Nagaoka, K. & Shinohara, I. 1983. Ionic conductivity of hybrid films composed of polyacrylonitrile, ethylene carbonate, and LiClO4. *Journal of Polymer Science Part B: Polymer Physics Edition* 21: 939-948.

Yang, C.M., Kim, H.S., Na, B.K., Kum, K.S. & Cho, B.W. 2006. Gel-type polymer electrolytes with different types of ceramic fillers and lithium salts for lithium-ion polymer batteries. *Journal of Power Sources* 156(2): 574-580.

Yoon, H.K., Chung, W.S. & Jo, N.J. 2004. Study on ionic transport mechanism and interactions between salt and polymer chain in PAN based solid polymer electrolytes containing LiCF3SO3. *Electrochimica Acta* 50: 289-293.

Zainol, N.H., Samin, S.M., Othman, L., Md Isa, K.B., Chong, W.G. & Osman, Z. 2013. Magnesium ion-based gel polymer electrolytes: Ionic conduction and infrared spectroscopy studies. *International Journal of Electrochemical Science* 8: 3602-3614.

D. Hambali, Z. Zainuddin & Z. Osman*
Centre for Ionics, University of Malaya
50603 Kuala Lumpur, Federal Territory
Malaysia

D. Hambali, Z. Zainuddin & Z. Osman*
Department of Physics, University of Malaya
50603 Kuala Lumpur, Federal Territory
Malaysia

I. Supa'at
Centre for Foundation Studies in Sciences
University of Malaya
50603 Kuala Lumpur, Federal Territory
Malaysia

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