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Enhanced Ionic Conductivity in PAN–PEGME-LiClO$_4$-PC Composite Polymer Electrolytes

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Poly(acrylonitrile) (PAN) and polyethyl glycol methyl ether (PEGME) blended with lithium perchlorate (LiClO$_4$) as dopant salt and propylene carbonate (PC) as plasticizer are prepared in the form of thin film. Fourier transform infrared studies show the evidence of the complexation between PAN, PEGME, and LiClO$_4$. The maximum conductivity of polymer electrolyte is up to 4.16 mS cm^{-1} at 90 ^{o}C by optimizing the composition of the polymers, salts, and plasticizer, and the temperature dependence of the conductivity of solid polymer electrolyte obeys the Vogel–Tamman–Fulcher (VTF) relationship. X-ray diffraction studies are carried out to reveal that the PAN phase changes from crystalline to amorphous when PEGME concentration increases.

Keywords: Conductivity, polymer electrolytes, Fourier transform infrared spectroscopy, polyethyl glycol methyl ether

1. INTRODUCTION

Research on polymer electrolytes has been growing since 1973 when Fenton et al. developed complexes of alkali metal ions with poly (ethylene oxide) (PEO) [1]. The interest in the study of polymer electrolyte system is due to the potential application of these materials in a great variety of electrochemical devices such as high energy density batteries, fuel cells, sensors, and electrochromic devices [2-12]. Generally, there are three types of polymer electrolytes: solid polymer electrolytes (SPEs), gel polymer electrolytes (GPEs), and composite polymer electrolytes (CPEs) [13-20].

In GPEs, polymer matrixes are required for the immobilization of electrolytes. Among the polymer matrixes that are promising for the application in GPE, polyacrylonitrile (PAN) [21,22], poly(vinylidene fluoride) (PVDF) [23,24], poly(methyl methacrylate) (PMMA) [25], and poly(ethylene oxide) (PEO) [26-29] based polymers have been most extensively studied. The use of poly (acrylonitrile) (PAN) as a host polymer was first reported by Reich and Michaeli [30] and then by many others [31]. Slane and Salomon [32] studied a composite polymer electrolyte that consisted of zeolite powders dispersed in PAN-based gels with $LiAsF_6$. PAN-based electrolytes showed interesting characteristics such as high ionic conductivity, high thermal stability, desirable morphology for electrolyte uptake and compatibility with the lithium electrodes [33]. Moreover, it has been revealed that –CN group in PAN could interact with Li^+ ions and PAN might provide rigidity to the polymer electrolytes with high lithium ion conduction [34].

The blending of polymers may lead to the increase in stability due to one polymer portraying itself as a mechanical stiffener and the other as a gelled matrix supported by the other. Monofunctional polyethylene glycols (methoxypolyethylene glycols, PEGME) can serve as lubricants, foam regulators, defoaming agents, emulsifiers, thickeners, superabsorbent polymers, stabilizers in emulsion and suspension polymerization, concrete superplasticizers, and textile auxiliaries [35]. Compared with poly(ethylene glycol) (PEG), PEGME only has a single free hydroxyl group, and some derivatives contain a polymerizable group that may allow incorporation of the MPEG group into PAN. Moreover, the lithium salts ($LiAsF_6$, $LiClO_4$, $LiCF_3SO_3$, $LiBF_4$, and $LiN(SO_2CF_3)_2$) are added so as to increase the amorphicity and the introduction of conducting moieties into the matrix. In the present work, hybrid solid polymer electrolyte films that consist of PAN, MPEG, $LiClO_4$, and propylene carbonate (PC) are examined to overcome the problem inherent to gel electrolytes. The choice of $LiClO_4$ salt is due to its smaller dissociation energy, and PAN–$LiClO_4$-based electrolytes have higher electrochemical stability than any of the other PAN Li^+ salt-based electrolytes [36]. The effect of PAN/ PEGME blend ratio on the ionic conductivity and mechanical stability has been investigated to optimize the appropriate concentration of plasticizer at which the electrolyte provides both maximum conductivity and good mechanical stability. The prepared polymer electrolyte films are characterized by XRD, FTIR, ac impedance, and Instron universal tester for the structural, complexation, conductivity, and mechanical properties, respectively.

2. EXPERIMENTAL

2.1. Materials

The starting materials polyethyl glycol methyl ether (PEGME) and poly(acrylonitrile) (PAN) with an average molecular weight of 2,000 and 150,000 obtained from Aldrich were dried at 373K under vacuum for 10 h. $LiClO_4$ (Aldrich) was dried at 343K under vacuum for 24 h. Plasticizer propylene carbonate (PC) (Alfa Aesar) was used without further purification.

2.2. Preparation of thin films

Appropriate weight percentage of PEGME, PAN, PC, and $LiClO_4$ were dissolved in DMF. The solution was stirred for 24 h at room temperature to obtain a homogenous mixture. The solution was then poured into a Petri dish and allowed to evaporate slowly inside a hood. This procedure yields mechanically stable and free standing thin films. The films were dried in a vacuum oven at 333K under a pressure of 10^{-3} Torr for 24 h. The resulting films were visually examined for their dryness and free-standing nature.

2.3. Measurements

FTIR studies were carried by using Perkin-Elmer FTIR Spectrophotometer Spectrum RX1. It was recorded in the range of 4,000 and 400 cm^{-1}, with resolution 4 cm^{-1}. X-ray diffractograms (XRD) were obtained at room temperature on a Rigaku RINT 2000 instrument, using Ni-filtered Cu Kα radiation (40 kV, 100 mA). An Instron universal tester model 3369 was used to study the mechanical properties. The load cell used was 5 kg and the crosshead rate was 5 mm/min. Measurements were performed with film specimens (1.35 cm wide, 6 cm long, and 50 ~ 60 mm thick). The ionic conductivity (Λ) of the gel polymer electrolytes was determined by AC impedance spectroscopy (CHI 627D). The membrane was sandwiched between two parallel stainless steel discs (d = 1 cm). The frequency ranged from 100 kHz to 10 Hz at a perturbation voltage of 10 mV. The ionic conductivity was calculated from the electrolyte resistance (R_b) (obtained from the intercept of the Nyquist plot with the real axis), the membrane thickness (l), and the electrode area (A) according to the equation:

$$\Lambda = \frac{l}{A} \cdot R_b \qquad (1)$$

3. RESULTS AND DISCUSSION

3.1. FTIR studies

Infrared spectral (IR) analysis is a powerful tool for identifying the nature of bonding and different functional groups present in a sample by monitoring the vibrational energy levels of the molecules, which are essentially the fingerprint of different molecules [37]. Fig. 1 shows the FTIR spectra of PAN/PEGME/PC (wt. %: 96/4/100) polymer matrix and Fig. 2 shows the FTIR spectra of polymer electrolytes prepared by blending various concentrations of $LiClO_4$ with PAN/PEGME/PC (wt. %: 96/4/100), among them, the most characteristic peaks of the interaction between polymer electrolytes and lithium salt are contributed to the –C=O group of PC, –C≡N group of PAN, and –CH_2–O–CH_2– group of PEGME. Fig. 3 shows the FT-IR spectra of –C=O group in polymer electrolytes prepared by blending 0, 150, 200, 250, 300, and 400 mg $LiClO_4$ with 1 g PAN/PEGME/PC (wt. %: 96/4/100), the characteristic frequency at 1790 cm^{-1} is assigned to the carbonyl stretching of PC in PAN/PEGME/PC electrolyte (wt. %: 96/4/100), the –C=O characteristic frequency of the propylene carbonate shifts to 1780 cm^{-1} gradually after the addition of $LiClO_4$, indicating the interaction of the plasticizer with $LiClO_4$ on complexation.

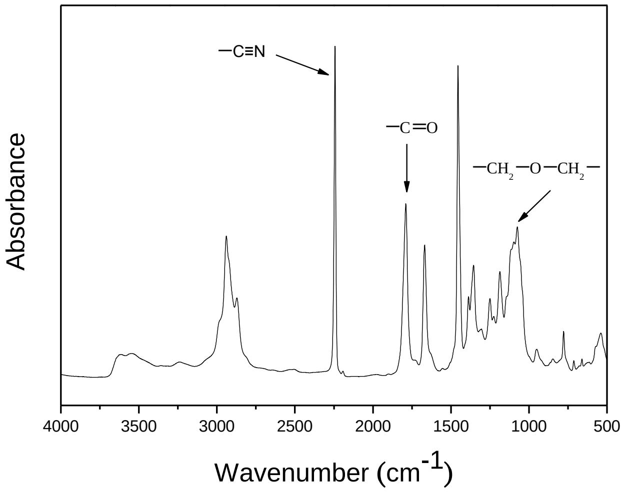

Figure 1. The FT-IR spectrum of PAN/PEGME/PC (wt. %: 96/4/100).

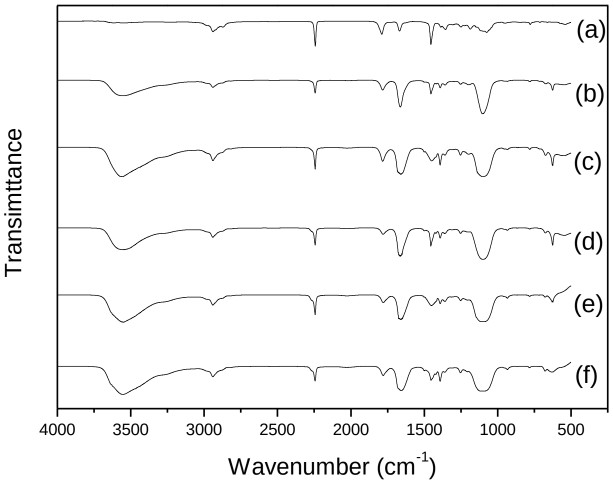

Figure 2. The FT-IR spectra of polymer electrolytes prepared by blending (a) 0, (b) 150, (c) 200, (d) 250, (e) 300, and (f) 400 mg $LiClO_4$ with 1 g PAN/PEGME/PC (wt. %: 96/4/100).

The C≡N group stretching spectra of SPEs based on PAN is presented in Fig. 4, the group frequency at 2242 cm^{-1} is assigned to C≡N stretching frequency of neat PAN. After the addition of $LiClO_4$ gradually, a new component (at 2270 cm^{-1} in Li-based PAN) split from the C≡N stretching band of free C≡N at 2242 cm^{-1} was observed, demonstrating the Li^+ ion coordination with the C≡N group of PAN [38]. The relative peak intensity at 2270 cm^{-1} increases with salt concentration due to an increase in the number of carrier ion. The characteristic frequency at 2270 cm^{-1} is not clear in low

$LiClO_4$ concentration, but it’s obvious in high $LiClO_4$ concentration, this can be attributed to the following two factors: (1) the bonding energy of –C≡N group is stronger than –C=O group, accordingly, the –C≡N characteristic peak is not clear, (2) as shown in Fig. 5, several factors influence the interaction between polymer matrix and lithium salt, such as the interaction between lithium ion and plasticizer may decrease the bonding opportunity between lithium ion and the –C≡N group of PAN.

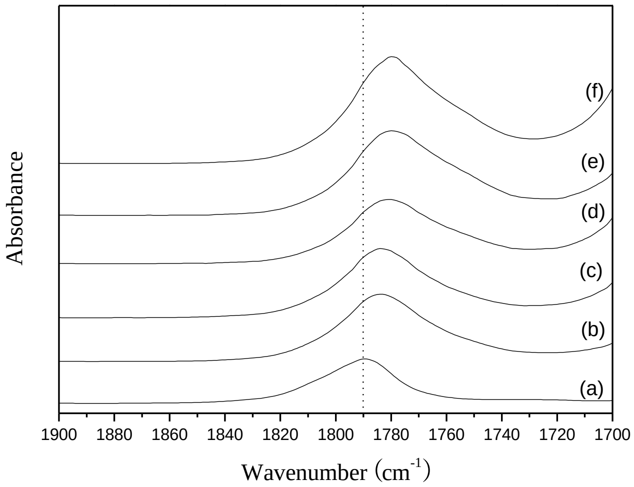

Figure 3. The FT-IR spectra of –C=O group in polymer electrolytes prepared by blending (a) 0, (b) 150, (c) 200, (d) 250, (e) 300, and (f) 400 mg $LiClO_4$ with 1 g PAN/PEGME/PC (wt. %: 96/4/100).

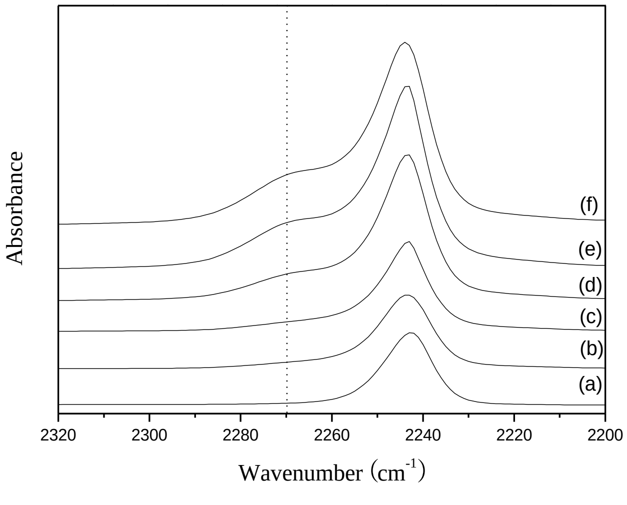

Figure 4. The FT-IR spectra of –C≡N group in polymer electrolytes prepared by blending (a) 0, (b) 150, (c) 200, (d) 250, (e) 300, and (f) 400 mg $LiClO_4$ with 1 g PAN/PEGME/PC (wt. %: 96/4/100).

Fig. 6 shows the FTIR spectra of PEGME $–CH_2–O–CH_2–$ group in solid polymer electrolytes prepared by blending 0, 150, 200, 250, 300, and 400 mg $LiClO_4$ with 1 g PAN/PEGME/PC (wt. %: 96/4/100). The characteristic frequency of $–CH_2–O–CH_2–$ group at 1035~1185 cm^{-1} increases with the increasing $LiClO_4$ concentration, this change is expected because of the well known coordination of lithium ions to the un-bonded electrons of the ether oxygen [39].

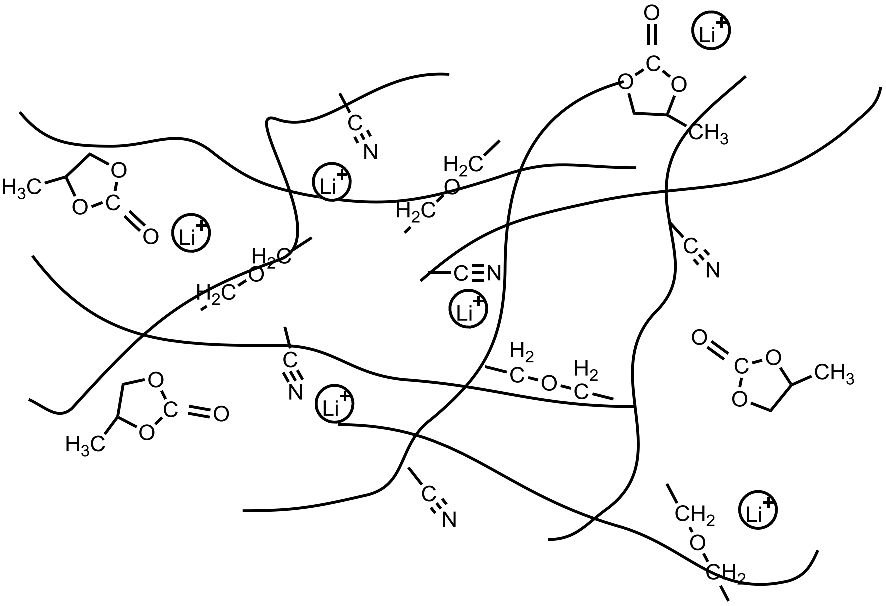

Figure 5. The interaction mechanism of lithium ion, plasticizer, and polymer matrix.

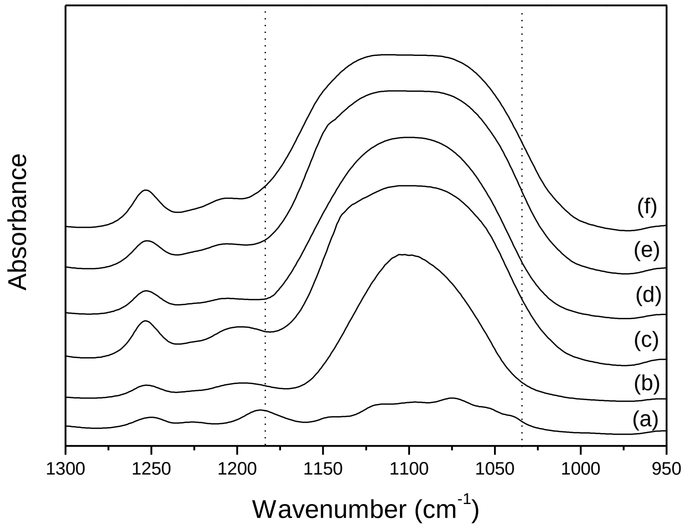

Figure 6. The FT-IR spectra of $–CH_2–O–CH_2–$ group in polymer electrolytes prepared by blending (a) 0, (b) 150, (c) 200, (d) 250, (e) 300, and (f) 400 mg $LiClO_4$ with 1 g PAN/PEGME/PC (wt. %: 96/4/100).

The dissociation of lithium salt is an important parameter that determines the ionic conductivity of the electrolyte, the absorption peak of $LiClO_4$ can be de-convoluted into two components centered at 624 and 640 cm^{-1}, respectively. Among them, the 624 cm^{-1} band can be attributed to the free ClO_4^- and the 640 cm^{-1} mode is assigned to the ion-pair formation or the contact of ClO_4^- with lithium ion [40]. Fig. 7 shows the FT-IR spectra of ClO_4^- in polymer electrolytes prepared by blending 400 mg $LiClO_4$ with 1 g PAN/PEGME/PC. Weight percentage of PAN/PEGME/PC is 96/4/100, 90/10/100, and 80/20/100. The ratio of peak areas (624 cm^{-1}/640 cm^{-1}) can be used as an index of the degree of ionization of the lithium salt in the polymer electrolytes. The dissociation of $LiClO_4$ increased with the PEGME content in Fig. 7, indicating that the PEGME segment promoted the dissociation of lithium salt in electrolytes.

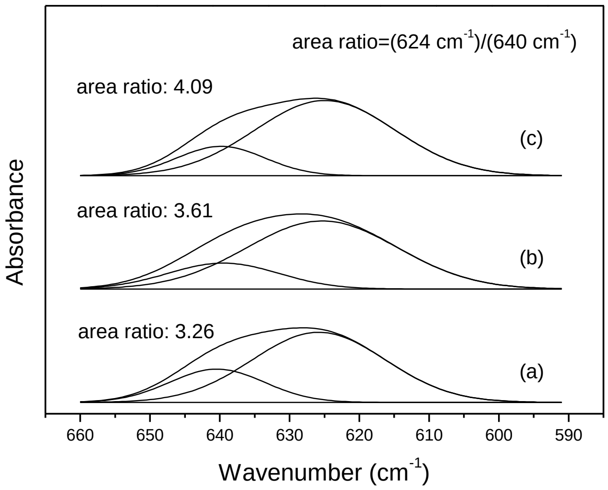

Figure 7. The FT-IR spectra of the ClO_4^- in polymer electrolytes prepared by blending 400 mg $LiClO_4$ with 1 g PAN/PEGME/PC. (a) wt. % of PAN/PEGME/PC is 96/4/100, (b) wt. % of PAN/PEGME/PC is 90/10/100, and (c) wt. % of PAN/PEGME/PC is 80/20/100.

3.2. Conductivity studies

The ionic conductivity of a polymer electrolyte depends on the concentration of carriers and on their mobility. Generally, the ionic conductivity of polymer solid electrolytes increase with temperature due to the higher segmental motion of polymer chain in the amorphous phase. The investigation of conductivity contain two topics in this study, one studies the conductivity of SPEs by blending various $LiClO_4$ concentrations with PAN/PEGME/PC (wt %: 96/4/100), the other one studies the conductivity of SPEs by blending various polymer concentrations (PAN/PEGME/PC wt %: 96/4/100, 90/10/100, and 80/20/100) with the same $LiClO_4$ concentration.

The temperature dependence of the ionic conductivity of the polymer electrolytes is generally following by either an Arrhenius Eq. (2) [41,42] or a Vogel–Tamman–Fulcher (VTF) Eq. (3) equation [43-52],

$$\sigma = A[\frac{-E_a}{k_B T}] \quad (2)$$

$$\sigma = \frac{A}{\sqrt{T}} \exp[\frac{-B'}{k_B(T\text{-}T_0)}] \quad (3)$$

where A is a constant that is proportional to the number of carrier ions, B' is the pseudo-activation energy for the redistribution of the free volume, k_B is the Boltzmann constant (1.38 × 10^{-23} J K^{-1}), E_a is the activation energy, and T_o is a reference temperature, normally associated with the ideal T_g at which the free volume is zero or with the temperature at which the configuration entropy becomes zero [53].

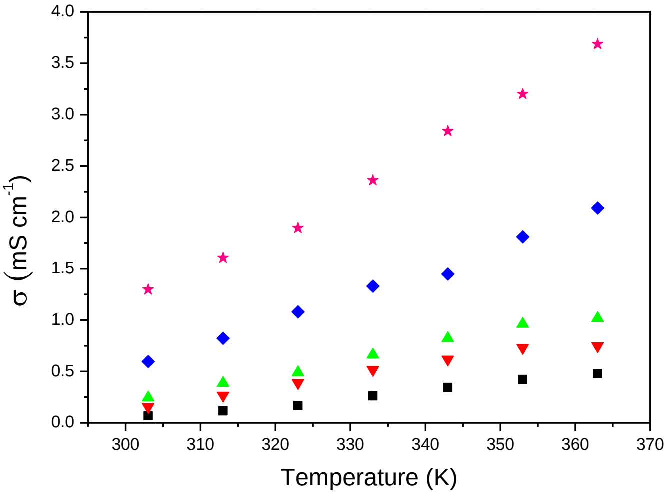

Figure 8. σ vs. T plot of polymer electrolytes prepared by blending 150 (■), 200 (▼), 250 (▲), 300 (◆), and 400 mg (★) $LiClO_4$ with 1 g PAN/PEGME/PC (wt. %: 96/4/100).

Eq. 4 is Eyring equation, a linear relationship is obtained from the plot of $\ln(\frac{\sigma h}{k_B T})$ vs. $1/T$, the slope is $-\Delta H$, and the intercept is ΔS. Accordingly, the Arrhenius active energy (E_a), entropy (ΔS), and enthalpy (ΔH) can be estimated from Arrhenius equation and Eyring equation [54-58]:

$$R\ln(\frac{\sigma h}{k_B T}) = \frac{-\Delta H}{T} + \Delta S \quad (4)$$

where h is Planck's constant (6.63 x 10^{-34} J s), ΔH is the enthalpy of electrolyte, ΔS is the entropy of electrolyte.

3.2.1 Conductivity of SPEs prepared by blending various $LiClO_4$ concentrations with PAN/PEGME/PC (wt %: 96/4/100)

Fig. 8 shows the conductivity vs. temperature plot of polymer electrolytes prepared by blending 150, 200, 250, 300, and 400 mg $LiClO_4$ with 1 g PAN/PEGME/PC, weight ratio of PAN/PEGME/PC is 96/4/100, and the conductivity of SPEs is summarized in Table 1. When 1 g PAN/PEGME/PC blends with 400 mg $LiClO_4$, the conductivity of SPEs is up to 3.69×10^{-3} S cm^{-1} at 90 ^{o}C. Fig. 9 shows the VTF plot of SPEs ionic conductivity at various temperatures, the observed temperature dependences of conductivity are well fitted by Vogel–Tammann–Fulcher (VTF) equation, the VTF fitting parameters of the ionic conductivity for these SPEs are summarized in Table 2.

Table 1. Conductivity of polymer electrolytes prepared by blending various $LiClO_4$ concentrations with 1 g PAN/PEGME/PC.

	Concentration of $LiClO_4$ (mg $LiClO_4$ / g PAN/PEGME/PC)				
T / K	150 [a]	200	250	300	400
303	6.92×10^{-2} [b]	1.55×10^{-1}	2.45×10^{-1}	5.96×10^{-1}	1.31
313	1.15×10^{-1}	2.67×10^{-1}	3.86×10^{-1}	8.23×10^{-1}	1.62
323	1.68×10^{-1}	3.90×10^{-1}	4.92×10^{-1}	1.08	1.89
333	2.63×10^{-1}	5.18×10^{-1}	6.64×10^{-1}	1.33	2.36
343	3.44×10^{-1}	6.19×10^{-1}	8.23×10^{-1}	1.45	2.84
353	4.22×10^{-1}	7.31×10^{-1}	9.64×10^{-1}	1.81	3.20
363	4.78×10^{-1}	7.47×10^{-1}	1.02	2.09	3.69

[a] The polymer electrolytes is prepared by blending 150 mg $LiClO_4$ with 1 g PAN/PEGME/PC, the weight ratio of PAN:PEGME:PC is 96:4:100.

[b] The unit of conductivity is mS cm^{-1}.

Table 2. VTF parameters of polymer electrolytes prepared by blending various $LiClO_4$ concentrations with 1 g PAN/PEGME/PC.

	Concentration of $LiClO_4$ (mg $LiClO_4$ / g polymer)				
	150 [a]	200	250	300	400
σ_o / mS cm^{-1}	11.21	2.32	4.13	9.06	28.15
T_o / K	212.82	264.5	247.23	229.16	181.95
B' / KJ $mole^{-1}$	458.95	103.83	157.35	200.87	374.21
R^2 [b]	0.998	0.999	0.998	0.998	0.998

[a] The polymer electrolytes is prepared by blending 150 mg $LiClO_4$ with 1 g PAN/PEGME/PC, the weight ratio of PAN:PEGME:PC is 96:4:100.

[b] Correlation coefficient.

Fig. 10 shows the Arrhenius plot of polymer electrolytes prepared by blending 150, 200, 250, 300, and 400 mg $LiClO_4$ with 1 g PAN/PEGME/PC (wt%: 96/4/100), the Arrhenius active energy (E_a), entropy (ΔS), and enthalpy (ΔH) can be estimated from Arrhenius equation and Eyring equation, and are summarized in Table 3. E_a, Δ*S*, and Δ*H* decreases with increasing concentration of $LiClO_4$, depicting lower E_a facilitates the lithium ion hopping in polymer backbone.

Table 3. The E_a, Δ*S*, and Δ*H* of polymer electrolytes prepared by blending various $LiClO_4$ concentrations with 1 g PAN/PEGME/PC.

	Concentration of $LiClO_4$ (mg $LiClO_4$ / g polymer)				
	150 [a]	200	250	300	400
ΔH / kJ mole^{-1}	27.33	21.11	19.11	15.77	13.36
ΔS / J mole^{-1}K^{-1}	-176.05	-189.17	-192.58	-196.67	-198.71
E_a / kJ mole^{-1}	30.09	23.86	21.87	18.53	16.12

[a] The polymer electrolytes is prepared by blending 150 mg $LiClO_4$ with 1 g PAN/PEGME/PC, the weight ratio of PAN:PEGME:PC is 96:4:100.

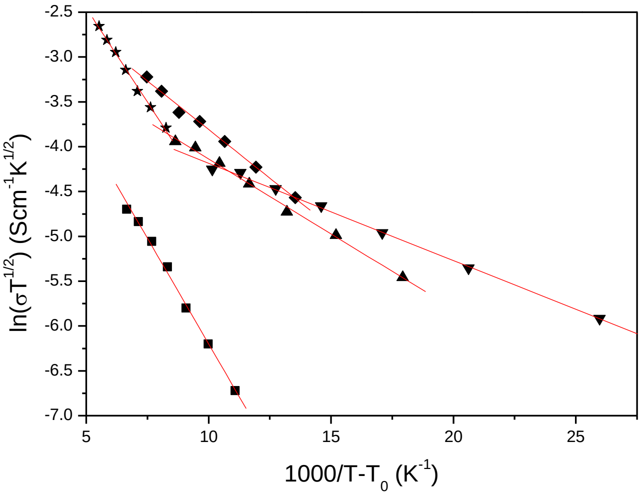

Figure 9. VTF plot of ionic conductivity for 1 g PAN/PEGME/PC (wt %: 96/4/100) doped with (■) 150, (▼) 200, (▲) 250, (◆) 300, and (★) 400 mg $LiClO_4$.

3.2.2 The conductivity of SPEs prepared by blending various polymer concentrations (PAN/PEGME/PC wt %: 96/4/100, 90/10/100, and 80/20/100) with the same $LiClO_4$ concentration

Fig. 11 shows the σ vs. *T* plot of polymer electrolytes prepared by blending 400 mg $LiClO_4$ with 1 g PAN/PEGME/PC, weight ratio of PAN/PEGME/PC is 96/4/100, 90/10/100, and 80/20/100, and the conductivity of SPEs is summarized in Table 4. SPEs prepared by PAN/PEGME/PC (wt %: 80/20/100) show conductivity of 1.5×10^{-3} S cm^{-1} at 30 °C, and 4.16×10^{-3} S cm^{-1} at 90 °C, the conductivity increases with the increasing weight ratio of PEGME, implying the incorporation of –CH_2–O–CH_2– group in PEGME facilitates ionic transport of electrolyte. The observed temperature dependences of conductivity are well fitted by Vogel–Tammann–Fulcher (VTF) equation, and the VTF fitting parameters of the ionic conductivity for these SPEs are summarized in Table 5. Fig. 12 shows the Arrhenius plot of polymer electrolytes prepared by blending 400 mg $LiClO_4$ with 1 g PAN/PEGME/PC, weight ratio of PAN/PEGME/PC is 96/4/100, 90/10/100, and 80/20/100, the Arrhenius active energy (E_a), entropy (ΔS), and enthalpy (ΔH) can be estimated from Arrhenius equation and Eyring equation, and are summarized in Table 6. E_a decreases with increasing weight ratio of PEGME, demonstrating the $–CH_2–O–CH_2–$ group in PEGME facilitates the lithium ion hopping in polymer electrolytes.

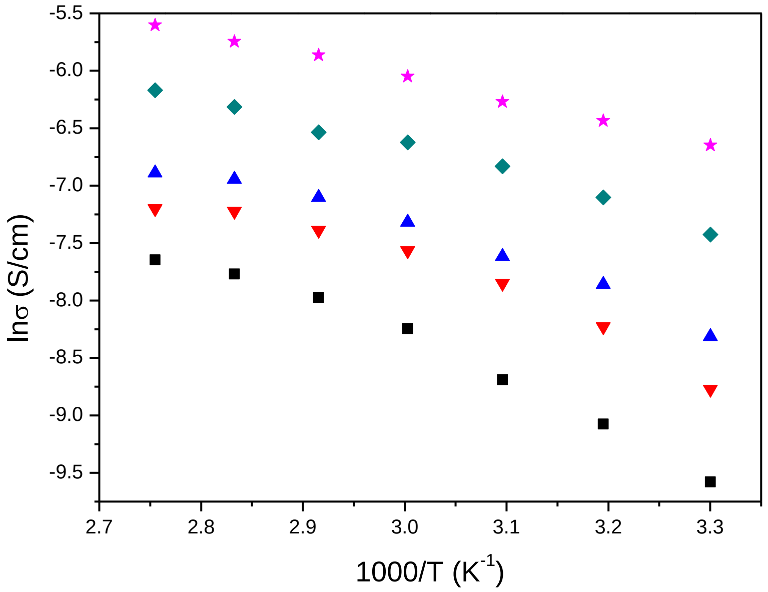

Figure 10. Arrhenius plot of ionic conductivity vs. *T* for polymer electrolytes prepared by blending (■) 150, (▼) 200, (▲) 250, (◆) 300, and (★) 400 mg $LiClO_4$ with 1 g PAN/PEGME/PC (wt. %: 96/4/100).

Table 4. Conductivity of polymer electrolytes prepared by blending 400 mg $LiClO_4$ with 1 g PAN/PEGME/PC.

	PAN/PEGME (wt. %)		
T / *K*	96/4 [a]	90/10	80/20
303	1.30 [b]	1.41	1.50
313	1.60	1.74	1.85
323	1.89	2.10	2.20
333	2.36	2.54	2.73
343	2.84	2.91	3.19
353	3.20	3.37	3.75
363	3.69	3.72	4.16

[a] The polymer electrolytes is prepared by blending 400 mg $LiClO_4$ with 1 g PAN/PEGME/PC, the weight ratio of PAN:PEGME:PC is 96:4:100.

[b] The unit of conductivity is mS cm^{-1}.

Table 5. VTF parameters of polymer electrolytes prepared by blending 400 mg $LiClO_4$ with 1 g PAN/PEGME/PC.

	PAN/PEGME (wt. %)		
T / K	96/4 [a]	90/10	80/20
σ_o / mS cm^{-1}	28.15	43.14	39.14
T_o / K	181.95	154.43	170.11
B' / kJ mol^{-1}	374.21	508.05	434.81
R^2 [b]	0.998	0.999	0.998

[a] The polymer electrolytes is prepared by blending 400 mg $LiClO_4$ with 1 g PAN/PEGME/PC, the weight ratio of PAN:PEGME:PC is 96:4:100.

[b] Correlation coefficient.

Table 6. The E_a, ΔS, and ΔH of polymer electrolytes prepared by blending 400 mg $LiClO_4$ with 1 g PAN/PEGME/PC.

	PAN/PEGME (wt. %)		
T / K	96/4 [a]	90/10	80/20
ΔH / kJ $mole^{-1}$	13.36	13.11	12.17
ΔS / J $mole^{-1}K^{-1}$	-198.71	-198.35	-201.81
E_a / kJ $mole^{-1}$	16.62	15.85	14.92

[a] The polymer electrolytes is prepared by blending 400 mg $LiClO_4$ with 1 g PAN/PEGME/PC, the weight ratio of PAN:PEGME:PC is 96:4:100.

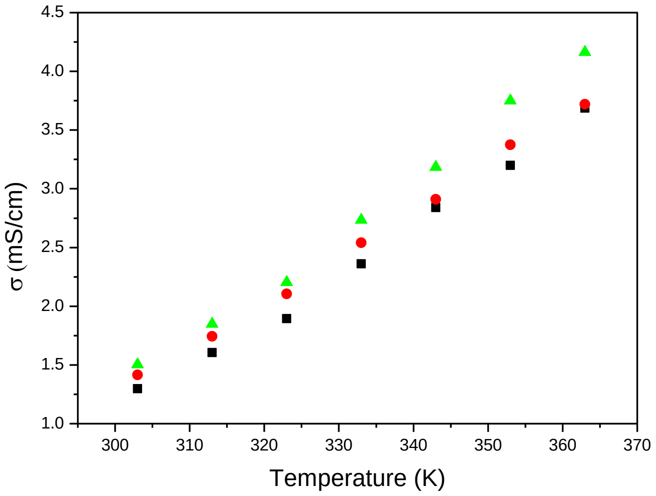

Figure 11. σ vs. T plot of polymer electrolytes prepared by blending 400 mg $LiClO_4$ with 1 g PAN/PEGME/PC. (a) wt. % of PAN/PEGME/PC is 96/4/100 (■), (b) wt. % of PAN/PEGME/PC is 90/10/100 (●), (c) wt. % of PAN/PEGME/PC is 80/20/100 (▲).

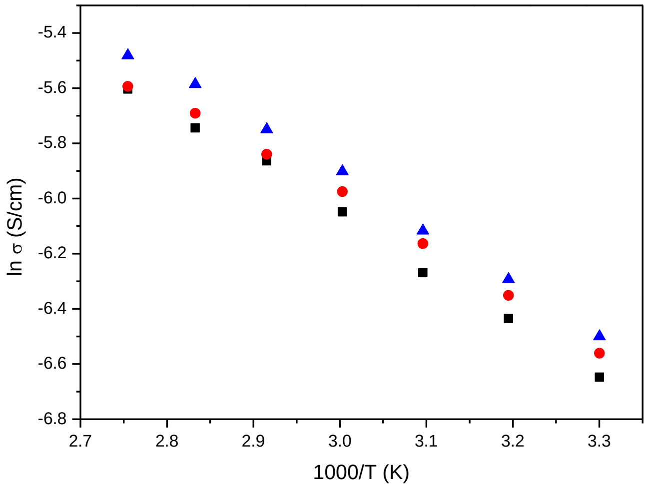

Figure 12. Arrhenius plot of ln σ vs. T for polymer electrolytes prepared by blending 400 mg $LiClO_4$ with 1 g PAN/PEGME/PC. (a) wt. % of PAN/PEGME/PC is 96/4/100 (■), (b) wt. % of PAN/PEGME/PC is 90/10/100 (●), (c) wt. % of PAN/PEGME/PC is 80/20/100 (▲).

3.3. Mechanical properties of PAN/PEGME/PC electrolytes

It is known that the mechanical properties of the SPEs are as important as the ionic conductivity at room temperature for their practical applications. The stress–strain properties of three PAN/PEGME/PC electrolytes are summarized in Table 7, which may be used to evaluate the mechanical properties of corresponding SPEs. The Young's Modulus of the SPEs follow the order: (wt % of PAN/PEGME/PC is 96/4/100) > (wt % of PAN/PEGME/PC is 90/10/100) > (wt % of PAN/PEGME/PC is 80/20/100), SPEs possess higher PAN weight ratio shows higher Young's Modulus, whereas SPEs possess higher PEGME weight ratio shows lower Young's Modulus, this can be attributed to PEGME is soft matter, incorporate PEGME into PAN decreases the mechanical properties of SPEs.

Table 7. The mechanical properties of PAN/PEGME/PC electrolytes.

PAN/PEGME/PC	Max of tensile stress / MPa	Tensile strain / %	Young's modulus / GPa
96/4/100 [a]	67.15	3.04	3.11
90/10/100	46.82	3.42	2.82
80/20/100	23.19	4.96	1.98

[a] The weight ratio of PAN:PEGME:PC is 96:4:100.

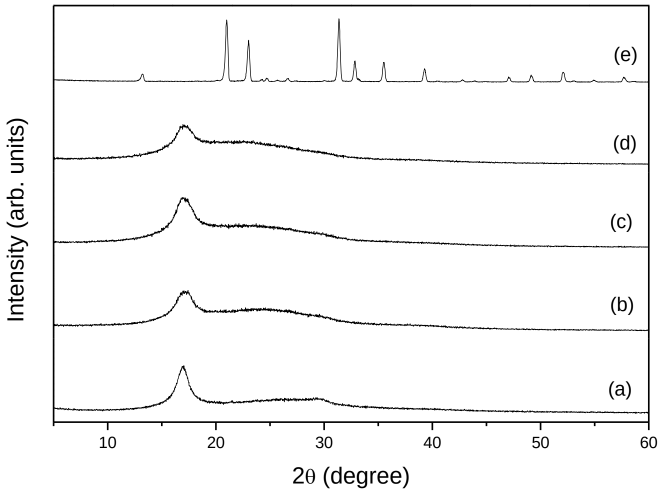

Figure 13. XRD pattern of (a) neat PAN, (b) PAN/PEGME (wt %: 96/4), (c) PAN/PEGME (wt %: 90/10), (d) PAN/PEGME (wt %: 80/20), and (e) neat $LiClO_4$.

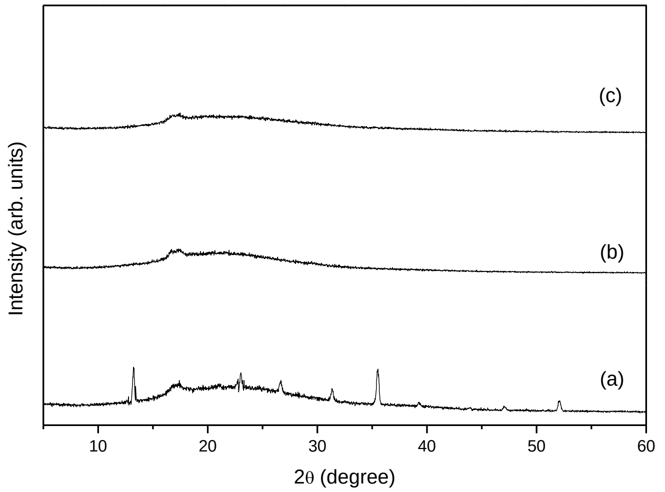

Figure 14. XRD pattern of polymer electrolytes prepared by blending 400 mg $LiClO_4$ with 1 g PAN/PEGME/PC. (a) wt. % of PAN/PEGME/PC is 96/4/100, (b) wt. % of PAN/PEGME/PC is 90/10/100, (c) wt. % of PAN/PEGME/PC is 80/20/100.

3.4. X-ray diffraction studies

Fig. 13 shows the XRD patterns of SPEs (PAN/PEGME/PC) with various PAN/PEGME weight ratio compared with neat PAN and $LiClO_4$. The XRD pattern of neat PAN (Fig. 13a) shows a crystalline peak at $2\theta = 17^{o}$ and it corresponds to orthorhombic PAN (1 1 0) reflection [59-61]. The XRD pattern of $LiClO_4$ (Fig. 13e) shows intense peaks at angles $2\theta = 23.2$, 32.99, and 36.58^{o}, which represent the crystalline nature of the salt. As shown in Fig. 13b, 13c, and 13d, the XRD pattern of SPEs (PAN/PEGME/PC) with various PAN/PEGME weight ratio show the incorporation of PEGME into PAN decrease the crystallinity of PAN electrolyte. Fig. 14 shows the XRD patterns of Li-based PAN/PEGME/PC, most of the peaks pertaining to $LiClO_4$ disappeared in the Li-based SPEs complexes, this indicates the complete dissolution of the $LiClO_4$ in the polymeric matrix. It is evident from Fig. 14b and 14c that the amorphous nature is predominant in the Li-based SPEs complexed system.

4. CONCLUSIONS

PAN–PEGME–$LiClO_4$–PC blended polymer electrolytes have been prepared by a solvent casting technique. FTIR and XRD studies revealed the occurrence of complexation between PAN, PEGME, and $LiClO_4$ in the composite matrix polymer. Ionic conductivity studies reveal that polymer electrolyte prepared using 1 g PAN/PEGME/PC (wt. % of PAN/PEGME is 96/4) blends with 400 mg $LiClO_4$ has the highest ionic conductivity of 3.69 mS cm^{-1} at 90 ^oC, whereas polymer electrolyte prepared using 1 g PAN/PEGME/PC (wt. % of PAN/PEGME is 80/20) blends with 400 mg $LiClO_4$ has the highest ionic conductivity of 4.16 mS cm^{-1} at 90 ^oC. The temperature dependence conductivity of the PAN–PEGME–$LiClO_4$–PC blended polymer electrolytes obeys the VTF relationship, and the active energy (E_a), entropy (ΔS), and enthalpy (ΔH) of polymer electrolytes are estimated. SPEs possess higher PAN weight ratio shows higher Young’s Modulus, indicating PEGME is soft matter.

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References

1. D.E. Fenton, J.M. Parker, P.V. Wright, *Polymer,* 14 (1973) 589.
2. J. Gao, J. Liu, W. Liu, B. Li, Y. Xin, Y. Yin, Z. Zou, *Int. J. Electrochem. Sci.,* 6 (2011) 6115.
3. L.C. Xuan, Y.X. An, W. Fang, L.X. Liao, Y.L. Ma, Z.Y. Ren, G.P. Yin, *Int. J. Electrochem. Sci.,* 6 (2011) 6590.
4. M.S.M. Eldin, M.A. Abu-Saied, A.A. Elzatahry, K.M. El-Khatib, E.A. Hassan, K.M. El-Sabbah, *Int. J. Electrochem. Sci.,* 6 (2011) 5417.
5. J.H. Kim, S.K. Kim, Y.Z. You, D.I. Kim, S.T. Hong, H.C. Suh, K.S. Weil, *Int. J. Electrochem. Sci.,* 6 (2011) 4365.
6. A. Anis, S.M. Al-Zahrani, A.K. Banthia, S. Bandyopadhyay, *Int. J. Electrochem. Sci.,* 6 (2011) 2461.
7. A. Anis, S.M. Al-Zahrani, A.K. Banthia, S. Bandyopadhyay, *Int. J. Electrochem. Sci.,* 6 (2011) 2652.
8. W.H. Chen, T.H. Ko, J.H. Lin, C.H. Liu, C.W. Shen, C.H. Wang, *Int. J. Electrochem. Sci.,* 6 (2011) 2192.
9. C.H. Wan, J.M. Wei, M.T. Lin, C.H. Lin, *Int. J. Electrochem. Sci.,* 6 (2011) 889.
10. B.C. Ng, H.Y. Wong, K.W. Chew, Z. Osman, *Int. J. Electrochem. Sci.,* 6 (2011) 4355.

11. P.C. Barbosa, M. Fernandes, S.M.F. Vilela, A. Goncalves, M.C. Oliveira, E. Fortunato, M.M. Silva, M.J. Smith, R. Rego, V.D. Bermudez, *Int. J. Electrochem. Sci.*, 6 (2011) 3355.
12. T.Y. Wu, H.C. Wang, S.G. Su, S.T. Gung, M.W. Lin, C.B. Lin, *J. Chin. Chem. Soc.*, 57 (2010) 44.
13. A.M. Stephan, K.S. Nahm, *Polymer*, 47 (2006) 5952.
14. J.C. Cruz, V. Baglio, S. Siracusano, V. Antonucci, A.S. Arico, R. Ornelas, L. Ortiz-Frade, G. Osorio-Monreal, S.M. Duron-Torres, L.G. Arriaga, *Int. J. Electrochem. Sci.*, 6 (2011) 6607.
15. T.Y. Wu, B.K. Chen, L. Hao, Y.C. Lin, H.P. Wang, C.W. Kuo, I.W. Sun, *Int. J. Mol. Sci.*, 12 (2011) 8750.
16. M.R. Johan, L.M. Ting, *Int. J. Electrochem. Sci.,* 6 (2011) 4737.
17. R.C. Agrawal, Y.K. Mahipal, *Int. J. Electrochem. Sci.*, 6 (2011) 867.
18. N.A. Aini, M.Z.A. Yahya, A. Lepit, N.K. Jaafar, M.K. Harun, A.M.M. Ali, *Int. J. Electrochem. Sci.*, 7 (2012) 8226.
19. H.N. Su, B.J. Bladergroen, S. Pasupathi, V. Linkov, S. Ji, *Int. J. Electrochem. Sci.*, 7 (2012) 4223.
20. S. Siracusano, V. Baglio, M.A. Navarra, S. Panero, V. Antonucci, A.S. Arico, *Int. J. Electrochem. Sci.*, 7 (2012) 1532.
21. S. Rajendran, R.S. Babu, P. Sivakumar, *Ionics*, 14 (2008) 149.
22. X.H. Flora, M. Ulaganathan, S. Rajendran, *Int. J. Electrochem. Sci.*, 7 (2012) 7451.
23. M.S. Mohy Eldin, M.A. Abu-Saied, A.A. Elzatahry, K.M. El-Khatib, E.A. Hassan, M.M. El-Sabbah, *Int. J. Electrochem. Sci.*, 6 (2011) 5417.
24. N. Ataollahi, A. Ahmad, H. Hamzah, M.Y.A. Rahman, N.S. Mohamed, *Int. J. Electrochem. Sci.,* 7 (2012) 6693.
25. K.W. Chew, K.W. Tan, *Int. J. Electrochem. Sci.,* 6 (2011) 5792.
26. S. Ibrahim, M.R. Johan, *Int. J. Electrochem. Sci.,* 6 (2011) 5565.
27. E.M. Fahmi, A. Ahmad, N.N.M. Nazeri, H. Hamzah, H. Razali, M.Y.A. Rahman, *Int. J. Electrochem. Sci.,* 7 (2012) 5798.
28. S. Ibrahim, M.R. Johan, *Int. J. Electrochem. Sci.,* 7 (2012) 2596.
29. M.R. Johan, S.M.M. Yasin, S. Ibrahim, *Int. J. Electrochem. Sci*., 7 (2012) 222.
30. S. Reich, I. Michaeli, *J. Polym. Sci. Phys. Ed.*, 13 (1975) 9.
31. C.R. Yang, J.T. Perng, Y.Y. Wang, C.C. Wan, *J. Power Sources*, 62 (1996) 89.
32. S. Slane, M. Salomon, *J. Power Sources*, 55 (1975) 7.
33. M.M. Rao, J.S. Liu, W.S. Li, Y. Liang, Y.H. Liao, L.Z. Zhao, *J. Power Sources*, 189 (2009) 711.
34. A.I. Gopalan, P. Santhosh, K.M. Manesh, J.H. Nho, S.H. Kim, C.G. Hwang, K.P. Lee, *J. Memb. Sci.*, 325 (2008) 683.
35. K.S. Kazanskii, G. Lapienis, V.I. Kuznetsova, L.K. Pakhomova, V.V. Evreinov, S. Penczek, *Polym. Sci. Ser. A*, 42 (2000) 585.
36. H.S. Kim, B.W. Cho, K.S. Yun, H.S. Chun, *KIChE*, 1 (1995) 49.
37. T. Nagamoto, C. Ichikawa, O. Omoto, *J. Electrochem. Soc.*, 134 (1987) 305.
38. U.-S. Park, Y.-J. Hong, S.M. Oh, *Electrochem. Acta*, 41 (1996) 849.
39. W.H. Hou, C.Y. Chen, C.C. Wang, Y.H. Huang, *Electrochim. Acta*, 48 (2003) 679.
40. H.L. Wang, H.M. Kao, M. Digar, T.C. Wen, *Macromolecules*, 34 (2001) 529.
41. T.Y. Wu, H.C. Wang, S.G. Su, S.T. Gung, M.W. Lin, C.B. Lin, *J. Taiwan Inst. Chem. Eng.,* 41 (2010) 315.
42. T.Y. Wu, S.G. Su, S.T. Gung, M.W. Lin, Y.C. Lin, C.A. Lai, I.W. Sun, *Electrochim. Acta*, 55 (2010) 4475.
43. T.Y. Wu, B.K. Chen, L. Hao, K.F. Lin, I.W. Sun, *J. Taiwan Inst. Chem. Eng.*, 42 (2011) 914.
44. T.Y. Wu, B.K. Chen, L. Hao, C.W. Kuo, I.W. Sun, *J. Taiwan Inst. Chem. Eng.*, 43 (2012) 313.
45. T.Y. Wu, S.G. Su, S.T. Gung, M.W. Lin, Y.C. Lin, W.C. Ou-Yang, I.W. Sun, C.A. Lai, *J. Iran. Chem. Soc.,* 8 (2011) 149.
46. T.Y. Wu, I.W. Sun, S.T. Gung, B.K. Chen, H.P. Wang, S.G. Su, *J. Taiwan Inst. Chem. Eng.*, 42 (2011) 874.

47. T.Y. Wu, S.G. Su, H.P. Wang, I.W. Sun, *Electrochem. Commun.*, 13 (2011) 237.
48. T.Y. Wu, L. Hao, C.W. Kuo, Y.C. Lin, S.G. Su, P.L. Kuo, I.W. Sun, *Int. J. Electrochem. Sci.*, 7 (2012) 2047.
49. T.Y. Wu, S.G. Su, Y.C. Lin, H.P. Wang, M.W. Lin, S.T. Gung, I.W. Sun, *Electrochim. Acta*, 56 (2010) 853.
50. T.Y. Wu, B.K. Chen, L. Hao, Y.C. Peng, I.W. Sun, *Int. J. Mol. Sci.*, 12 (2011) 2598.
51. T.Y. Wu, I.W. Sun, S.T. Gung, M.W. Lin, B.K. Chen, H.P. Wang, S.G. Su, *J. Taiwan Inst. Chem. Eng.*, 42 (2011) 513.
52. T.Y. Wu, I.W. Sun, M.W. Lin, B.K. Chen, C.W. Kuo, H.P. Wang, Y.Y. Chen, S.G. Su, *J. Taiwan Inst. Chem. Eng.*, 43 (2012) 58.
53. M. Salomon, M. Xu, E.M. Eyring, S. Petrucci, *J. Phys. Chem.*, 98 (1994) 8234.
54. I.W. Sun, Y.C. Lin, B.K. Chen, C.W. Kuo, C.C. Chen, S.G. Su, P.R. Chen, T.Y. Wu, *Int. J. Electrochem. Sci.*, 7 (2012) 7206.
55. T.Y. Wu, S.G. Su, H.P. Wang, Y.C. Lin, S.T. Gung, M.W. Lin, I.W. Sun, *Electrochim. Acta*, 56 (2011) 3209.
56. I.W. Sun, H.P. Wang, H. Teng, S.G. Su, Y.C. Lin, C.W. Kuo, P.R. Chen, T.Y. Wu, *Int. J. Electrochem. Sci.*, 7 (2012) 9748.
57. T.Y. Wu, S.G. Su, K.F. Lin, Y.C. Lin, H.P. Wang, M.W. Lin, S.T. Gung, I.W. Sun, *Electrochim. Acta*, 56 (2011) 7278.
58. T.Y. Wu, L. Hao, P.R. Chen, J.W. Liao, *Int. J. Electrochem. Sci.*, 8 (2013) 2606.
59. D. Sawai, M. Miyamoto, T. Kanamoto, M. Ito, *J. Polym. Sci. B Polym. Phys.*, 38 (2000) 2571.
60. Z. Zhang, L. Zhang, S. Wang, W. Chen, Y. Lei, *Polymer*, 42 (2001) 8315.
61. S. Rajendran, R. Kannan, O. Mahendran, *Mater. Lett.*, 48 (2001) 331.