New Solid Polymer Electrolytes Based on PEO/PAN Hybrids

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ABSTRACT: Hybrid polymer dry electrolytes comprised of poly(ethylene oxide) (PEO), polyacrylonitrile (PAN), and $LiClO_4$ were investigated. The impedance spectroscopy showed that the effect of PAN on the ion conductivity of PEO-based electrolytes depends on the concentration of lithium salt. When the mole ratio of lithium to oxygen is 0.062 (15%$LiClO_4$-PEO), adding PAN will increase the ionic conductivity. Differential scanning calorimetry, NMR, and IR data suggested that the enhanced conductivity was due to both the decreasing of the PEO crystallinity and increasing of the degree of ionization of lithium salt. There was obviously no interaction between PAN and lithium ions, and PAN acts as a reinforcing filler, and hence contributes to the mechanical strength besides reducing the crystallinity of the polymer electrolytes. When the $LiClO_4$-PEO-PAN hybrid polymer electrolyte was heated at 200°C under N_2, PAN crosslinked partially, which further decreased the crystallinity of PEO and increased the ionic conductivity, and at the same time prevented the recrystallization of PEO upon sitting at ambient environment. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1530–1540, 2006

Key words: PEO; PAN; polymer electrolyte

INTRODUCTION

Solid polymer electrolytes (SPEs) have received considerable attention, because of their potential applications in solid-state batteries, electrochromic devices, and fundamental research of ion transport in disordered phases.[1–3] Classical solid electrolytes are formed by complexes between a lithium salt, LiX, and a high molecular weight polymer, containing Li^+ coordination sites, such as poly(ethylene oxide) (PEO). PEO-LiX polymeric electrolytes are among the most extensively studied polymer ionic conductors, because of the beneficial structure of PEO in supporting fast ion transport. The basic structure of LiX-PEO involves PEO chains coiled around the lithium cations, and this separates them from the X^- counterions.[4] Ionic conductivity is due to the motion of dissolved ionic species in a PEO matrix. The mechanism of ion transport in PEO is not totally understood, although it is recognized that cation–anion interaction, cation–polymer interaction, and polymer segmental motion play a critical role. It is also known that the ionic mobility is promoted by segmental motion of the polymer chains and that the conduction takes place in the amorphous phase of PEO matrix.[5] Therefore, suitable materials should be completely amorphous and should have a low glass transition temperature. Since PEO is a semicrystalline polymer, it must be stabilized against crystallization at ambient temperature, without giving up its conductivity and without degrading its mechanical properties. Nevertheless, the fast ion transport in PEO-LiX is a characteristic of the amorphous state, which is intrinsically reached above 70°C or artificially induced at low temperature by the addition of liquid plasticizers[6] or ceramic powders,[7–9] at the nanoscale particle size.[7]

Recognizing that the ionic conductivity of PEO-based electrolyte is facilitated in the amorphous phase, significant research efforts have been devoted in obtaining a polymer structure having a highly flexible backbone and a larger proportion of the amorphous phase. For instance, several comb-like polymers,[10] copolymers[11] and crosslinked polymers,[12] have been prepared, and their charge transport properties have been investigated. However, most of these polymers require a nontrivial synthetic process, and this is a serious drawback for practical applications. It is important to develop an easier method for preparing a SPE, with high ionic conductivity and dimensional stability. In this respect, the preparation of polymer electrolytes by blending other polymers is interest-

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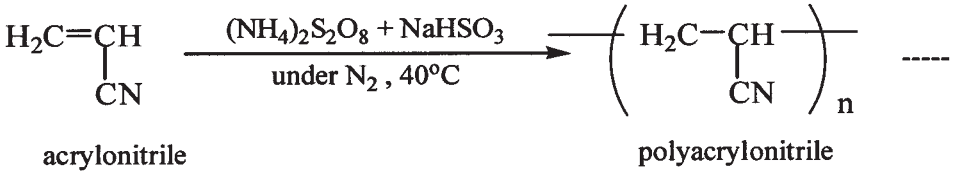
ing,[13,14] because it is a fast and an economic way to obtain materials with optimal thermal, mechanical, and adhesive properties. This is because for practical applications not only the high conductivity but also good physical properties, such as chemical stability and mechanical strength, have been considered.

In this article, a new solid electrolyte based on PEO/polyacrylonitrile (PAN) hybrid was reported. PAN, which consists of a saturated carbon backbone with a nitrile group on alternate carbon atoms, is a well-known precursor for conducting polymer[15] and carbon fiber.[16] Thermally treated PAN films show a rich evolution of structural as well as electronic properties. The polymer chains undergo cyclization at temperature above 200°C to form a conjugated-chain chemical structure,[17] which exhibits very good mechanical properties. The unique structure diversity and good mechanical properties of PAN after heat treatment made it very useful as matrix materials for polymer electrolytes. In $LiClO_4$-PEO-PAN, the higher segmental motion of PEO may lead to higher mobility of the dissolved ions, and the hard segment domains of partially crosslinked PAN can act as reinforcing fillers, and hence contribute to the mechanical strength of the polymer electrolytes. Furthermore, the poor-defined structure of low-temperature pyrolyzed PAN can avoid the crystallization of PEO, increasing the ionic conductivity of $LiClO_4$-PEO-PAN hybrid polymer electrolyte.

EXPERIMENTAL

Materials

$LiClO_4$ was dried under reduced pressure prior to use. PEO (MW = 100,000) was bought from Aldrich and used without further treatment. PAN was synthesized from acrylonitrile via radical initiation polymerization, as reported in literature.[18] The reaction scheme is listed in eq. (1) as follows:



(1)

Preparation of $LiClO_4$-PEO/PAN hybrid polymer electrolyte films

All the electrolyte films were prepared by solution-casting technique. The $LiClO_4$-PEO-PAN solutions were prepared by dissolving appropriate amounts of PAN (in DMF), PEO, and $LiClO_4$ (in acetonitrile) under vigorous stirring. The mixed solutions were poured into Teflon molders (1/3 full), kept in a vacuum oven, and heated at 60°C, 10^{-1} Torr, for 72 h. The solvent was evaporated, and the mechanically stable free standing films (190–350 μm thickness) can be peeled off from the Teflon molders. The electrolyte films were stored in a dry box, right after taking out of the vacuum oven, to avoid the absorption of moisture. In this article, the weight percentage of PAN is defined as the weight ratio of PAN to PEO, and the salt content is equal to the weight of the salt divided by the weight of PEO. For example, the weight ratio of $LiClO_4$ and PAN to PEO is 15 and 3%, respectively, in 15%$LiClO_4$-PEO-3%PAN hybrid polymer electrolyte.

The heat treatment of $LiClO_4$-PEO-PAN hybrid polymer electrolyte

The electrolyte film was cut into a disk, with a diameter of 10 mm. The disk was put in a glass tubing and heated in an oven under nitrogen flow for 1 h at 200°C. The heated $LiClO_4$-PEO-PAN film (with the glass tubing) was cooled in an ice bath immediately. When the film attains room temperature, the physicochemical studies was performed, and then, it was stored in a glove box.

Conductivity measurement

AC impedance and conductance measurements were performed over the frequency range of 1 MHz to 1Hz on an Autolab model Pgstat 30 potentiostae/Galvanostat. A refrigerated circulator temperature controller was used to control the temperature of the measurements. Samples (10 mm in diameter and 0.2–0.3 mm thick) for ionic conductivity measurements were prepared in a dry box filled with nitrogen, by sandwiching the polymer electrolyte films with two stainless steel disc electrodes of diameter 10 mm. Conductivity was calculated from bulk resistance, obtained from the impedance spectrum. Each sample was equilibrated at the experimental temperature for 30 min before measurement. The complex impedance spectra were measured from 25 to 80°C.

Physicochemical studies

Fourier transform infrared (FTIR) spectra were recorded as a free standing thin film or films on Si substrates, using a Bio-Rad 155 FTIR spectrometer, at the ambient temperature in the range of 400–4000 cm^{-1}, with a wavenumber resolution of 4 cm^{-1}. Band deconvolution of the infra red (IR) spectra was obtained by using a Gaussian–Lorentzian sum, and a constant baseline had been subtracted in the deconvolution figures to do the analysis. The maximum error associated with the fit was estimated to be less than 5%. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) studies were done with Hitachi S-800 at 15 kV. X-ray powder diffraction studies were carried out with a Shimadzu XRD-6000 X-ray diffractometer using Cu Kα radiation at 30 kV and 30 mA. High-resolution solid state ^{13}C NMR experiments were carried out on a Bruker MSL-300 spectrometer operating at resonance frequencies of 116.6 and 75.47 MHz for ^{7}Li and ^{13}C, respectively. The ^{13}C CP/magic angle spinning (MAS) spectra were measured at 4.1 μs, with 90° pulse angle, 500 μs contact time, 5 s acquisition time, and with 1000 scans. All NMR spectra were taken at 298 K with broad-band decoupling, normal crosspolarization pulse sequence, and an MAS of 3 kHz. Chemical shift was externally referenced to $LiClO_4$ solid at 0.0 ppm. Thermogravimetric analysis (TGA) was performed with a Perkin–Elmer TGA-7 thermal analysis system, using dry nitrogen (or oxygen) as a carrier gas, at a flow rate of 100 mL/s. The TGA experiments were conducted from 25 to 900°C, with a linear heating rate of 5°C/min. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Teledo DSC 822^{e} apparatus. Samples were heated from 25 to 80°C at a heating rate of 10°C/min, and then cooled to −60°C. Three heating–cooling cycles were recorded. Melting point (T_m) and melting enthalpy (ΔH_m) were determined from the DSC endothermic peaks on both the first and the second heating runs. Glass transition temperature (T_g) was estimated as the mean value between onset and endset temperature of the process. The crystallinity of PEO was calculated from the melting enthalpy (obtained from the DSC studies) of the PEO. To compare the crystallinity difference among electrolytes with different components, the degree of crystallinity of pure PEO with 10 wt % of $LiClO_4$ was defined as 100%. The crystallinity of the other polymer electrolytes was calculated from the following equation:

$$\chi_c(\%) = \frac{\Delta H_m(\mathrm{SPE})}{\Delta H_m(\mathrm{ST})} \times 100$$

χ_c (PSE) is the crystallinity of the polymer electrolyte,

ΔH_m (SPE) the melting enthalpy of the polymer electrolyte, and

ΔH_m (ST) is the melting enthalpy of the 10%$LiClO_4$-PEO film.

TABLE I
Room Temperature Conductivity of $LiClO_4$-PEO-PAN

Polymer electrolyte	Conductivity (S/cm)
10%$LiClO_4$-PEO	1.9×10^{-8}
10%$LiClO_4$-PEO-1%PAN	1.4×10^{-8}
10%$LiClO_4$-PEO-3%PAN	1.3×10^{-8}
10%$LiClO_4$-PEO-5%PAN	6.6×10^{-9}
10%$LiClO_4$-PEO-10%PAN	$<1.0 \times 10^{-10}$
15%$LiClO_4$-PEO	8.2×10^{-8}
15%$LiClO_4$-PEO-1%PAN	3.6×10^{-7}
15%$LiClO_4$-PEO-3%PAN	1.2×10^{-7}
15%$LiClO_4$-PEO-5%PAN	2.0×10^{-8}
20%$LiClO_4$-PEO	8.4×10^{-7}
20%$LiClO_4$-PEO-1%PAN	2.2×10^{-7}
20%$LiClO_4$-PEO-3%PAN	1.0×10^{-7}
20%$LiClO_4$-PEO-5%PAN	9.0×10^{-8}

RESULTS AND DISCUSSION

Ionic conductivity

Table I listed the room temperature conductivity for the hybrid polymer electrolytes, based on $LiClO_4$-PEO-PAN with various PAN and lithium salt concentration. The conductivity increased as the salt concentration increased. The conductivity maximum, 8.4 $\times 10^{-7}$ S/cm, at 25°C appeared at 20%$LiClO_4$-PEO for the all components explored in this work. Nevertheless, the mechanical property and dimensional stability of 20%$LiClO_4$-PEO are very poor. Addition of PAN can enhance the mechanical property and dimensional stability of the electrolyte films. However, the conductivity of $LiClO_4$-PEO-PAN polymer electrolyte decreased when the content of PAN increased. The optimal component of the hybrid polymer electrolyte is 15%$LiClO_4$-PEO-1%PAN. It could be also found that, when PAN content is less than 5 wt %, the conductivity of 15%$LiClO_4$-PEO-PAN is higher than that of the parent PEO polymer electrolyte. The difference in conductivity for the polymer electrolytes can be interpreted as due to the different salt solvating capability, polymer chain segmental motions, and lithium hopping motions in the electrolytes. The typical temperature-dependent conductivity of 15%$LiClO_4$-PEO with various amount of PAN is shown in Figure 1. The conductivity increased with increasing temperature, a typical behavior of lithium polymer electrolytes. Similar behavior was also observed in other hybrid electrolytes with different components. The temperature dependence of conductivity (σ) can be described by the Arrhenius equation eq. (3):

$$\sigma = \sigma_a \exp[-E_a/RT] \qquad (3)$$

where σ_o is the preexponential factor and E_a is the pseudoactivation energies. The parameter estimates from eq. (3) onto the data are given in Table II. The

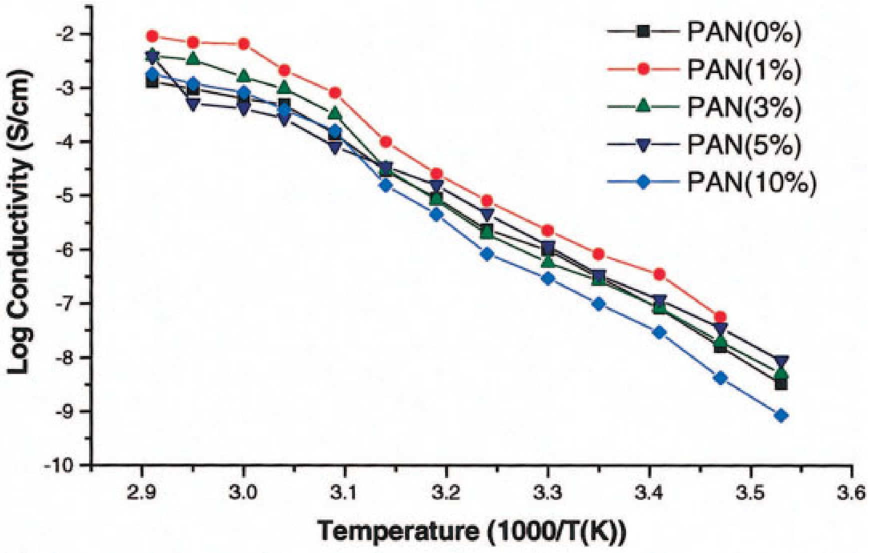


Figure 1 Variable temperature conductivity of 15%LiClO$_4$-PEO-PAN electrolytes with various PAN contents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

data showed that the activation energy of the polymer electrolytes decreased, as the content of lithium salt increased. The effect of adding PAN is rather complicated. The activation energy decreased when the PAN is less than 1 wt %. When the content of PAN is more than 1 wt %, the E_a increased compared to parent PEO electrolyte. This is because PAN is not a good promoter for lithium ion transport, and the presence of PAN will hamper the movement of lithium ions.

The thermal properties of LiClO$_4$-PEO-PAN hybrid polymer electrolytes

The thermal stability of the as-prepared polymer electrolytes was tested with TGA. It was shown that all polymer electrolytes were stable up to 300°C, and the thermal stability is independent of the PAN content.

TABLE II
The Conducting Activating Energy of LiClO$_4$-PEO-PAN

Polymer electrolyte	Activating energy (kJ/mol)
10%LiClO$_4$-PEO	86.5
10%LiClO$_4$-PEO-1%PAN	73.2
10%LiClO$_4$-PEO-3%PAN	89.0
10%LiClO$_4$-PEO-5%PAN	97.2
10%LiClO$_4$-PEO-10%PAN	–
15%LiClO$_4$-PEO	78
15%LiClO$_4$-PEO-1%PAN	72
15%LiClO$_4$-PEO-3%PAN	82
15%LiClO$_4$-PEO-5%PAN	82
20%LiClO$_4$-PEO	75
20%LiClO$_4$-PEO-1%PAN	71
20%LiClO$_4$-PEO-3%PAN	91
20%LiClO$_4$-PEO-5%PAN	89

Typical DSC curves of LiClO$_4$-PEO-PAN hybrid polymer electrolytes were displayed in Figure 2. The thermogram of the electrolyte exhibits an endothermal peak, an exothermal peak, and only one glass transition temperature, indicating that the electrolyte is semicrystalline and PAN is miscible in PEO. Apparently, the melting point and melting enthalpy of the first heating–cooling cycle is different from those of the second and third cycles (second and third cycles are identical). This implied that heat treatment will affect the structure of the electrolyte. The effect of heating on the properties of LiClO$_4$-PEO-PAN hybrid electrolytes will be discussed in detail later.

Since the conductivity of polymer electrolytes was measured without heat treatment, therefore, the DSC data shown in the first cycle represent the true thermal properties of the as-prepared polymer electrolytes. The thermal properties obtained from the first cycle of DSC curves of LiClO$_4$-PEO-PAN hybrid electrolytes were listed in Table III. It was found that for polymer electrolytes with low lithium salt concentration, the melting point and crystallinity (the definition of crystallinity was described in the experimental section) increased when PAN was added. On the other hand, both the melting point and crystallinity decreased when PAN was added for polymer electrolytes with high concentration of lithium salt. The DSC data suggested that the transient crosslinks between lithium salt and PEO decreased the crystallinity of PEO, promoting the mixing between PAN and PEO, and decreasing the crystallinity of PEO further. The room temperature conductivity–crystallinity relationship of LiClO$_4$-PEO-PAN hybrid polymer electrolytes was shown in Figure 3. In general, higher conductivity was observed in electrolytes with lower crystallinity (some

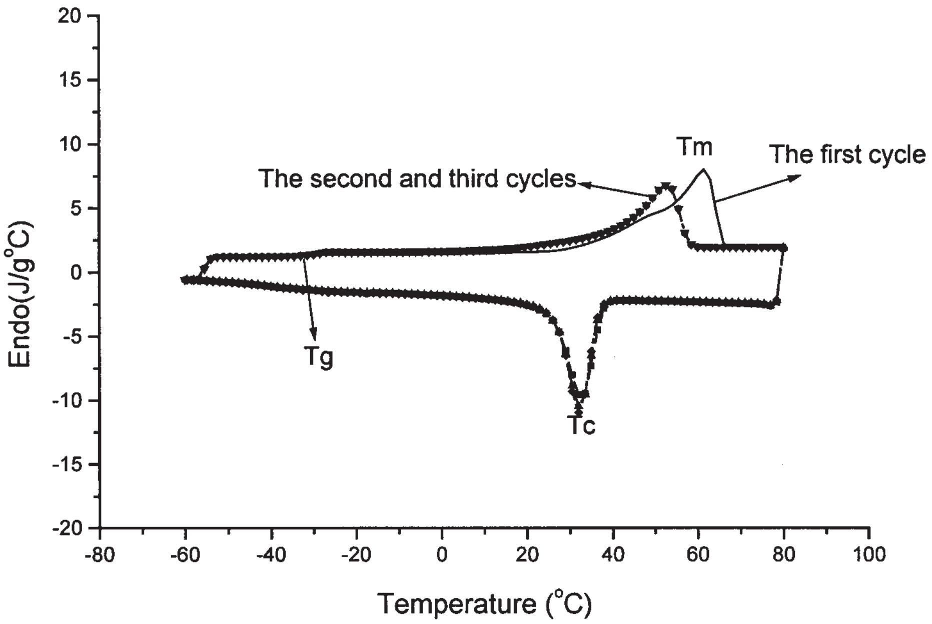


Figure 2 DSC thermograms of 10%$LiClO_4$-PEO-3%PAN film.

swings in the data were observed, because other parameters may also affect the conductivity). Nevertheless, in parent PEO-based electrolyte, when the crystallinity of PEO is low, the electrolyte film becomes very soft and loses its mechanical strength. The mechanical strength enhanced significantly when small amount of PAN was added. PAN in $LiClO_4$-PEO-PAN hybrid polymer electrolytes acts as a reinforcing filler, and hence contributes to the mechanical strength of the polymer electrolytes.

TABLE III
The Thermal Data of $LiClO_4$-PEO-PAN

Polymer electrolyte	Cycle number	Melting point (°C)	T_g (°C)	Crystallinity ≪?1≫^{a}(%)
10%$LiClO_4$-PEO	1	56	-	100
	2 and 3	52	-	105
10%$LiClO_4$-PEO-1%PAN	1	59	−32	171
	2 and 3	59	-	142
10%$LiClO_4$-PEO-3%PAN	1	66	−28	189
	2 and 3	59	-	161
10%$LiClO_4$-PEO-5%PAN	1	62	−39	151
	2 and 3	57	-	135
15%$LiClO_4$-PEO	1	62	−30	77
	2 and 3	52	−26	56
15%$LiClO_4$-PEO-1%PAN	1	60	−33	59
	2 and 3	52	−30	44
15%$LiClO_4$-PEO-3%PAN	1	61	−32	77
	2 and 3	52	−28	57
15%$LiClO_4$-PEO-5%PAN	1	59	−30	63
	2 and 3	52	−26	41
20%$LiClO_4$-PEO	1	57	−25	44
	2 and 3	44	−37	24
20%$LiClO_4$-PEO-1%PAN	1	52	−35	44
	2 and 3	42	−38	11
20%$LiClO_4$-PEO-3%PAN	1	50	−32	34
	2 and 3	42	−32	–
20%$LiClO_4$-PEO-5%PAN	1	43	-	36
	2 and 3	36	−46	16

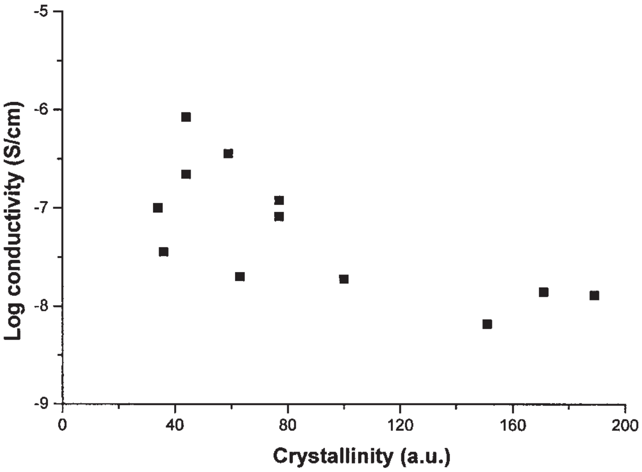
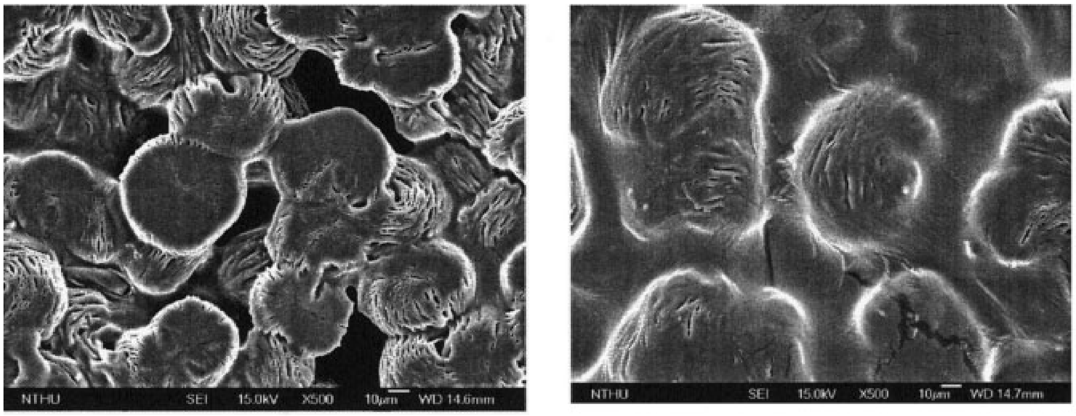


Figure 3 Conductivity versus crystallinity of $LiClO_4$-PEO-PAN polymer electrolytes.

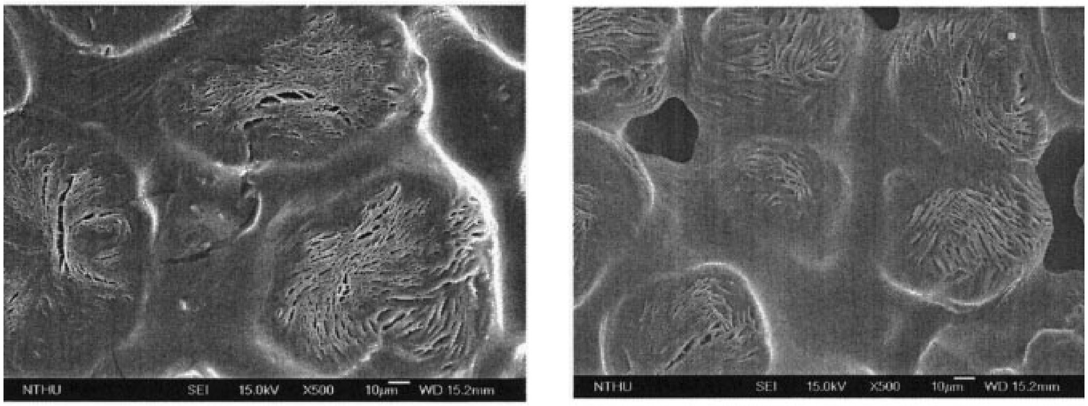
Morphology characterization

Figure 4 shows the SEM micrographs for $LiClO_4$-PEO-PAN hybrid electrolytes, containing various amount of PAN. It is clear that there is no phase separation in the hybrid polymer film and both crystalline (spherical morphology) and amorphous (fiber texture) were observed in parent $LiClO_4$-PEO and $LiClO_4$-PEO-PAN hybrid polymer films. However, as the percentage of PAN increased, the electrolyte film becomes smoother, and the size of spheroids also increased, and the boundaries of individual spheroids become indistinct. According to MacCallum and Vincent[19] report, spheroids occur *via* sporadical nucleation, and grow radially until they impinge upon each other at boundaries. This is a typical morphological behavior of crystalline polymers with flexible chains. Although the bigger spheroids in 15%$LiClO_4$-PEO-5%PAN and 15%$LiClO_4$-PEO-3%PAN hybrid electrolytes may suggest higher crystallinity, if we look into one of the spheroid carefully, we can find that more fiber texture (amorphous phase) was formed within the spheroid com-



15% $LiClO_4$-PEO

15% $LiClO_4$-PEO-PAN(1%)



15% $LiClO_4$-PEO-PAN(3%)

15% $LiClO_4$-PEO-PAN(5%)

Figure 4 SEM micrographs of 15%$LiClO_4$-PEO-PAN polymer electrolytes.

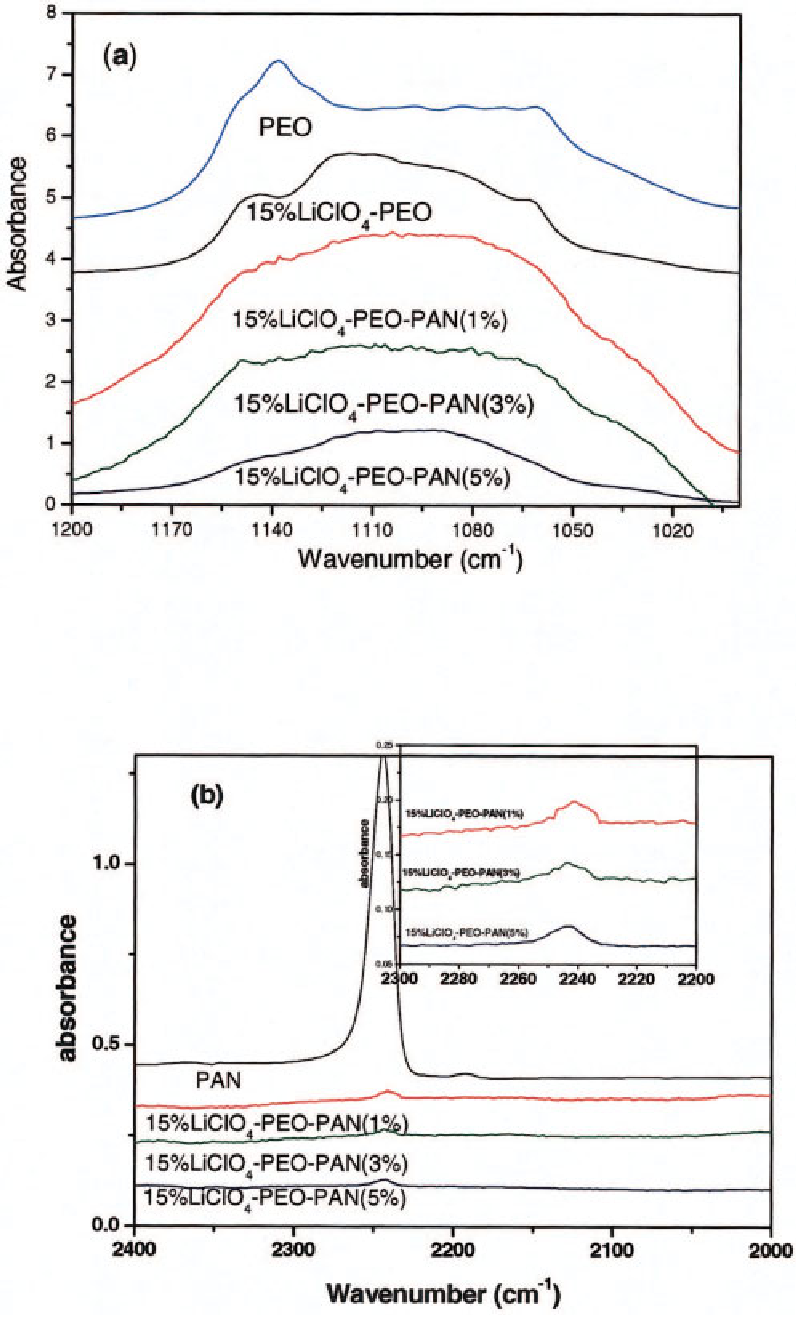


Figure 5 IR spectra of LiClO$_4$-PEO-PAN films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

pared to that of 15%LiClO$_4$-PEO. Therefore, the crystallinity of the PEO-based polymer electrolyte slightly decreased after blending with PAN. Furthermore, the rim (formed by mixing of PEO and PAN) of the spheroid acts as a framework for the polymer electrolyte, providing dimensional stability of the free-standing polymer electrolyte films.

The structure of LiClO$_4$-PEO-PAN hybrid polymer electrolytes

IR and NMR spectroscopy have proved to be powerful tools to probe salt–polymer interactions and the type of lithium ions responsible for the conduction. This is important for determining the species of the microstructures in the electrolyte, by exploring the spectral changes of the interesting functional groups in the polymer electrolyte. FTIR spectroscopy was employed to study the interaction behavior between the ion and the polymer host. Introduction of a salt in a polymer blend can change the intermolecular interactions. Among the possible interactions for the LiClO$_4$-PEO-PAN system, three types of possible complexes are proposed. Type 1 complex is PEO-Li-PEO, formed by the interaction of lithium ion with the oxygen atom on

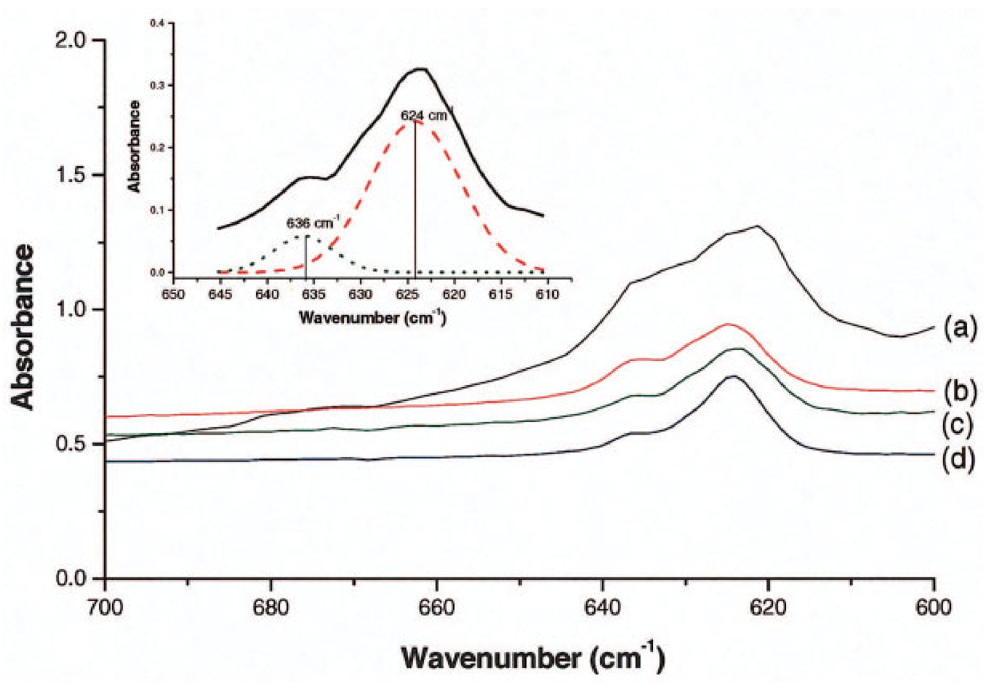


Figure 6 IR spectra (in the range of 600–700 cm^{-1}) of (a) 15%$LiClO_4$-PEO, (b) 15%$LiClO_4$-PEO-1%PAN, (c) 15%$LiClO_4$-PEO-3%PAN and (d) 15%$LiClO_4$-PEO-5%PAN.[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

PEO, as generally observed in PEO-based electrolyte.[20] Type 2 complex could be PAN-Li-PEO, in which an interaction between lithium ions with a PEO segment and a PAN segment takes place. Type 3 complex may be described as PAN-Li-PAN, in which the lithium ion was surrounded by PAN chains. Figure 5(a) showed the IR spectra of electrolyte films within the region 1200–1000 cm^{-1}. The three absorption peaks between 1050 and 1150 cm^{-1}, which represent the C—O—C stretchings of PEO segment interacts with lithium ion,[21] and becomes indistinct when small amount of PAN was added, indicating that PAN has altered the conformation of PEO, and in turn, changed the interaction between PEO and lithium ions. The interaction between PAN and lithium ion can be brought out by IR absorption associated with CN group at 2244 cm^{-1}, as showed in Figure 5(b). It was found that the CN vibration peaks in $LiClO_4$-PEO-PAN are similar to that in PAN. This result indicated that there is no interaction between PAN and lithium ion, in contrast to what was reported by previous workers.[22] They observed a weak shoulder at around 2270 cm^{-1} as a result of the interaction between the CN and lithium ions. The very weak interaction between PAN and lithium ion in our system is because of the interaction being very strong between PEO and Li^+, and this restricts the Li^+ interaction with CN or the CN peak is too weak to see a shoulder.

The dissociation of lithium salt, i.e., the concentration of lithium ions, is one of the parameters that determines the ionic conductivity of the electrolyte. IR is also a good tool to probe the degree of the dissociation of lithium salt in different polymer matrices. In Figure 6, the exemplary spectrum obtained for the electrolytes in the 600–650 cm^{-1} range is shown. The absorption peak can be separated by two components centered at 624 and 636 cm^{-1} (The deconvolution of the region was done by the Gaussian function and analyzed for the changes in peak frequencies and band area). Salmon[23] *et al.* and Wieczorek[24] attributed the 624 cm^{-1} band to the free ClO_4^- anion and the 636

TABLE IV
The Degree of Ionization of Lithium Salt in $LiClO_4$-PEO-PAN Polymer Electrolytes

Polymer electrolyte	Ratio of 623 cm^{-1}/635 cm^{-1} peak area
10%$LiClO_4$-PEO	3.6
10%$LiClO_4$-PEO-1%PAN	3.0
10%$LiClO_4$-PEO-3%PAN	4.1
10%$LiClO_4$-PEO-5%PAN	3.2
15%$LiClO_4$-PEO	1.9
15%$LiClO_4$-PEO-1%PAN	3.1
15%$LiClO_4$-PEO-3%PAN	3.7
15%$LiClO_4$-PEO-5%PAN	3.4
20%$LiClO_4$-PEO	2.2
20%$LiClO_4$-PEO-1%PAN	2.4
20%$LiClO_4$-PEO-3%PAN	2.8
20%$LiClO_4$-PEO-5%PAN	3.1

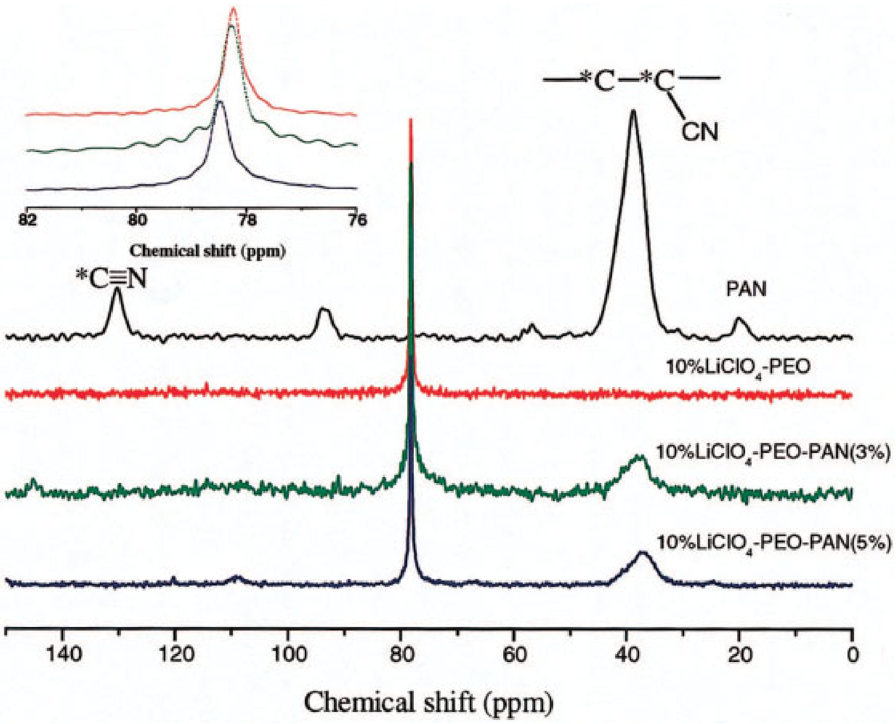


Figure 7 ^{13}C MAS NMR spectra of PAN and 10%LiClO$_4$-PEO-PAN with various PAN contents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

cm^{-1} mode to ion-pair formation or contact of ClO$_4^-$ anion with lithium. The ratio of 624 cm^{-1}/636 cm^{-1} peak area can be used as an indication for the degree of ionization of lithium salt in polymer matrices. Table IV summarized the IR data obtained from the electrolytes, with various amount of lithium salt and PAN. It was found that the dissociation of LiClO$_4$ increased when PAN was added. The ratio (peak area) of 624 cm^{-1}/636 cm^{-1} is 1.9 for parent PEO electrolyte, with 15 wt % of lithium salt, and it increased to 3.7 when 3 wt % of PAN was added. Furthermore, both PEO and LiClO$_4$ are very hydrophilic, the LiClO$_4$-PEO film exhibits strong absorption at about 3500 cm^{-1} after standing in air for a few seconds. Nevertheless, the IR spectra of LiClO$_4$-PEO-PAN electrolyte films, standing at the similar condition, showed weaker absorption at 3500 cm^{-1}. This result indicated that LiClO$_4$-PEO-PAN is more hydrophobic material, in which the absorbed water can be removed easily by heating. This point is very important, because water will react with lithium electrode, and hence it must be avoided concerning the application in lithium batteries.

Solid-state NMR analysis

Most methods used to characterize the polymer electrolytes, such as ionic conductivity, thermal properties, and others, do not separate the roles of the anions and cations. Solid-state NMR has the advantage of being able to selectively measure the dynamics of the different species in the polymer electrolytes.[25–30] For example, measurements of spin–lattice relaxation rates, as a function of temperature, have been used to study the correlation between the cationic and the polymer chain segmental motions in SPEs. We used ^{13}C CP/MAS NMR spectrum to characterize the interactions between PEO (or PAN) and LiClO$_4$ in LiClO$_4$-PEO-PAN hybrid polymer electrolyte. Figure 7 showed the ^{13}C CP/MAS NMR spectra of LiClO$_4$-PEO-PAN at room temperature. The C resonance of the PEO was assigned at 75–85 ppm, and the peaks centered at 30–50 and 120–140 ppm were assigned to the resonance of CC and CN group in PAN respectively. Upon adding PAN, the peak at 78.5 ppm broadened slightly. This broadening indicated that the presented PAN causes a little bit more complicated distribution of the PEO segment environments and reduces the segment motion of the PEO chains or both. The former is due to the mixing of PEO and PAN, and the latter results from the hindering of the PAN chains, which is not a good promoter for lithium ion conduction. Interestingly, the peak centered at 30–50 ppm in LiClO$_4$-PEO-PAN has an upfield shift compared to that of pure PAN. The upfield ^{13}C chemical shifts have been correlated to oxygen–cation interaction of PEO.[31] Did the ^{13}C NMR data suggest that

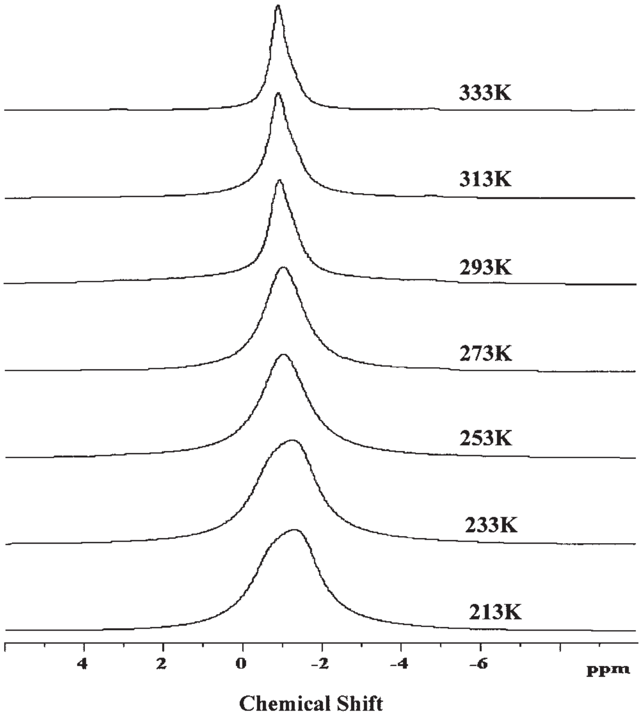


Figure 8 Variable temperature ^{7}Li NMR spectra of 10%$LiClO_4$-PEO-3%PAN.

there is a weak interaction between CN and lithium ions, which cannot be detected with IR spectroscope? More studies on this issue are underway.

To gather the information regarding the lithium ion environment, high resolution ^{7}Li MAS NMR were employed. The proton-decoupled ^{7}Li MAS NMR spectra of 10%$LiClO_4$-PEO-5%PAN hybrid polymer electrolyte recorded from 213 to 333 K were displayed in Figure 8. The peak width increased as the temperature decreased. Although they are only partially resolved, when the temperature is lower than 233 K (below the glass transition temperature of the polymer electrolyte), the peak shape becomes asymmetric and two components are visible. NMR data suggested that there are two distinct lithium species with different local environments. The microphase-separated structure of the polymer backbone can result in heterogeneous lithium environment at low temperature. Li^+ mobility in polymer electrolytes has been explored by measuring the line width of solid state ^{7}Li MNMR spectra.[32] The broader the ^{7}Li- NMR line width the slower the Li mobility, because of this the peak width observed is the result of increased quadrupolar or internuclear dipole–dipole interactions. As the temperature increases, the peak width decreases as a result of increased lithium mobility and hence averaging of these interactions. The ^{7}Li line width at different temperature for $LiClO_4$-PEO and $LiClO_4$-PEO-PAN electrolytes was shown in Figure 9. It was found that the line width evolution with temperature can be described by a curve composed of two plateaus separated by a temperature range, in which rapid change of line width occurs. At the temperature below T_g (233 K), the line is broad, suggesting that the lithium ion is not mobile and thus not conductive. When the temperature increased, the line widths are motionally narrowed, with the onset of narrowing correlating to the T_g of the electrolyte. Interestingly, the line widths of $LiClO_4$-PEO-PAN are similar to those of $LiClO_4$-PEO at high temperature. Nevertheless, at temperature below T_g, the line width of $LiClO_4$-PEO-PAN is smaller than that of parent $LiClO_4$-PEO, implying that the presence of PAN can avoid the recrystallization of PEO at low temperature, consistent with the conductivity and DSC data.

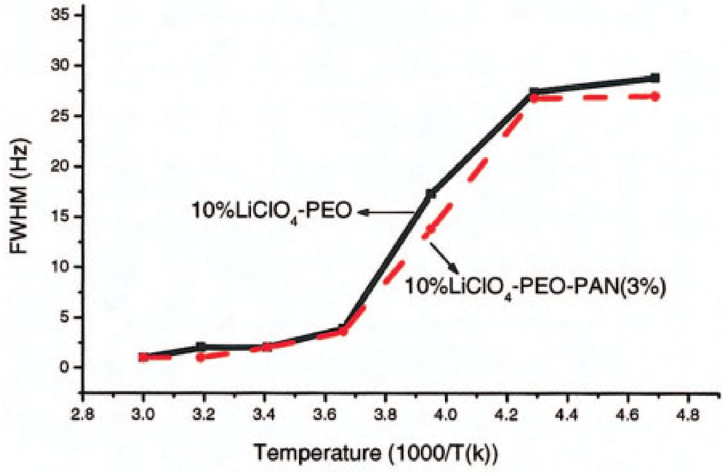


Figure 9 ^{7}Li NMR line width versus temperature of 10%$LiClO_4$-PEO-3%PAN.[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE V
Changing of Room Temperature Conductivity Upon Heating of $LiClO_4$-PEO-PAN Polymer Electrolytes

	Conductivity (S/cm)	
Polymer electrolyte	As-prepared sample	Heated sample at 200°C
10%$LiClO_4$-PEO	1.9×10^{-8}	3.1×10^{-7}
10%$LiClO_4$-PEO-1%PAN	1.4×10^{-8}	1.5×10^{-7}
10%$LiClO_4$-PEO-3%PAN	1.3×10^{-8}	5.5×10^{-8}
10%$LiClO_4$-PEO-5%PAN	6.6×10^{-9}	3.8×10^{-8}
10%$LiClO_4$-PEO-10%PAN	$<1.0 \times 10^{-10}$	–
15%$LiClO_4$-PEO	8.2×10^{-8}	1.9×10^{-7}
15%$LiClO_4$-PEO-1%PAN	3.6×10^{-7}	4.0×10^{-7}
15%$LiClO_4$-PEO-3%PAN	1.2×10^{-7}	1.2×10^{-8}
15%$LiClO_4$-PEO-5%PAN	2.0×10^{-8}	3.4×10^{-8}
20%$LiClO_4$-PEO	8.4×10^{-7}	2.5×10^{-7}
20%$LiClO_4$-PEO-1%PAN	2.2×10^{-7}	2.2×10^{-7}
20%$LiClO_4$-PEO-3%PAN	1.0×10^{-7}	1.2×10^{-7}
20%$LiClO_4$-PEO-5%PAN	9.0×10^{-8}	7.9×10^{-8}

The effect of heat treatment on the properties of $LiClO_4$-PEO/PAN hybrid polymer electrolyte

The room temperature conductivity of $LiClO_4$-PEO and $LiClO_4$-PEO-PAN after heat treatment was displayed in Table V. It was shown that heating increased the ionic conductivity slightly. The enhanced conductivity was due to the decreasing crystallinity (as revealed with DSC data), and therefore, leads to a greater degree of dissociation of the salt. The detailed studies focus on the effects of heating on the properties of $LiClO_4$-PEO-PAN hybrid polymer electrolytes which will be reported elsewhere.

CONCLUSIONS

Solid electrolytes based on PEO/PAN hybrid polymer doping with $LiClO_4$ were investigated. Spectroscopic and conductivity data showed that, blending small amount of PAN in 15%$LiClO_4$-PEO can increase its ionic conductivity, due to both the decreasing of crystallinity and increasing of ionization of lithium salt. The decreasing of crystallinity was caused by the mixing of PEO with PAN. The increasing of the degree of ionization of lithium salt is probably because of the low crystallinity of PEO as well as the weak interaction between PAN and Li^+, as revealed by NMR data. Upon heating, partially crosslinked reaction of PAN occurs, the crystallinity of the hybrid polymer electrolyte decreased further, although the ionic conductivity did not obviously change, and the mechanical property and dimensional stability enhanced. The function of PAN in $LiClO_4$-PEO-PAN hybrid polymer electrolytes can be regarded as a reinforcing filler. It can support the electrolyte film effectively, because of its solid-like medium, while the PEO functions as a tunnel for ion transport to provide high ionic conductivity comparable with that containing no PAN. Nevertheless, PAN is not a good promoter for ion transport in solid state, and small amounts of PAN can raise the mechanical properties and high PAN content will reduce the conductivity of the hybrid polymer electrolyte.

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