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Lithium complex in polyacrylonitrile/EC/PC gel-type electrolyte

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Abstract

Lithium complex with C≡N group of polyacrylonitrile (PAN) in the PAN-based electrolyte plasticized (7.5 wt% of the total weight) with binary mixture, ethylene carbonate (EC) and propylene carbonate (PC) are present. At low salt concentration, lithium is exchanged rapidly between the polymer substrate and the EC/PC mixture. But with increasing salt content the electrolyte viscosity increases, and the formation of a weak complex between lithium ion and the CN group in PAN is observed. Sudden increase in the ^{7}Li chemical shifts substantially broadened line-width in ^{7}Li NMR and the two-fold increase of the activation energy in variable temperature ^{7}LiT_1 relaxation measurements indicated clear presence of the complex. However, the conductivity is not substantially decreased with the appearance of the complex. The result suggested that the ion transport through the more direct lithium site-jump along the polymer chain is equally effective as the ion diffusion through the EC/PC solvent. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Gel-type electrolytes; Polyacrylonitrile; ^{7}Li NMR

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1. Introduction

Polymer electrolyte shows higher energy density and easier packaging properties when used in electronic devices such as secondary lithium battery [1,2], light emitting cell [3,4], glass tinting layer for smart window [5,6], chemical sensors [7,8], and capacitors [9]. Gel-type electrolytes (conductivity in the range of 10^{-3} S/cm at ambient temperature) are preferred as their conductive capacity is two to three orders higher than solvent free polymer electrolytes [10–12]. The most commonly electrolytes are produced by dissolving lithium salts, (such as $LiN(SO_2CF_3)_2$, $LiAsF_6$, $LiPF_6$, $LiSO_3CF_3$) in polyacrylonitrile (PAN) plasticized with ethylene carbonate (EC) and propylene carbonate (PC) where the conductivity is usually in the order of 10^{-3}–10^{-2} S/cm at room temperature. Ever since the early work of Watanabe et al. [13,14] to later improvements by Abraham et. al. [15] research has mostly focused on the temperature dependent conductivity, cycle efficiency and energy density. Factors governing these properties include relative concentrations of PAN, EC, PC, the type of lithium salt, and the passivation buildup between the electrode and the electrolyte. The ion conductivity in the binary mixture follows a weight averaged relationship and suggested that ion is rapidly exchanged between the two moieties [16]. Lithium self-diffusion employing pulse field gradient method clearly illustrated ion diffusion is closely related to conductivity [17].

Since lithium ion is capable of forming electric dipole interaction with both C=O of EC and PC, and C≡N of PAN, formation of a Li complex is possible. However, this issue has never been discussed or explored. Prior studies with polyethylene oxide (PEO) concluded that weak compelxation with ion through Columbic coordination with the electron-donating groups (oxygen) served to both dissociate the salt and to facilitate the ion transport [18,19]. Vibration Raman and FTIR spectra indicated attractive sites for both the solvent molecules and the cations in PAN-based system with preference given to the solvent [20]. In addition, static and dynamic light scattering measurements of salt interaction of high molecular weight PEO/$LiClO_4$/Methanol system indicated the (PEO/$LiClO_4$) adduct forms in the outer portion of the coil where charge–charge repulsion between the ionized chain expanded the interchain spacing [21]. In contrast, there were no detectable interactions found between the electrolyte and the polymer in PMMA-based gel electrolyte [22]. Though these studies provide vital information regarding the distribution of ions along the polymer chain, existence of a complex in the PAN-based gel-type electrolyte remains unclear. The presence of the complex structure would imply that PAN serve not only to improve the mechanical property, but also affect ion conduction.

Present studies illustrated the coordination characteristics using various ^{7}Li NMR methods to examine the gel-type

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Table 1
Variation of characteristic NMR parameters with $LiClO_4$ composition (^7Li chemical shift of $LiClO_4$ is −0.278 ppm in EC/PC solvent without PAN and ^7Li NMR chemical shift of $LiClO_4$ is −0.583 in EC/PC solution. The chemical shifts are measured with referenced to LiCl (0.3 N) methanol-d solvent)

$LiClO_4$ contents (wt%)	Li:N:O	T_1 relaxation time (s)	Chemical shift (ppm)	FWHM (ppm)
1	1:13.2:312.6	0.8297	−0.342	0.041
2	1:6.5:154.5	1.026	−0.351	0.037
5	1:2.5:60.0	1.545	−0.578	0.027
6.35	1:1.9:46.5	1.201	−0.573	0.02
10	1:1.2:28.5	0.776	−0.346	0.068
15	1:0.7:18.0	1.312	−0.72	0.02

PAN polymer electrolytes with low amount of PAN and demonstrated a complex formation between lithium and CN group in PAN. By correlating the conductivity with lithium ion mobility activation energy, the role that PAN played, and the manner by which the ion conducts (diffusion in solution mixture; along the polymer chain; or hopping cooperatively between polymer and solvents), can be clearly illustrated.

2. Experimental

2.1. Material

PAN (Polysciences, Warrington, PA, $M_n = 100{,}000$) is dried in vacuum at 40°C for 24 h. EC (Baxter, USA) and PC (Scientific Products, USA) are distilled under nitrogen atmosphere. Water and contaminant of $LiClO_4$ (Aldrich Chemical Co.) is removed by drying in vacuum ($<10^{-4}$ Torr) at 120°C for 24 h.

2.2. Electrolyte preparation

In order to assure complete dissociation of the lithium salt, 1–15 wt% of extensively dried $LiClO_4$ salt is dissolved first in the plasticizer composed of EC and PC (1:1 mole ratio) before mixing with the PAN solution. Dry PAN (with PAN: EC + PC weight ratio 1:14) is than well-mixed and dried under vacuum at 135°C until light yellow to deep yellow gel-type electrolyte is formed. The Li:N:O mole ratio in these electrolytes is summarized in Table 1.

2.3. Instruments

Solution ^{13}C and ^7Li NMR are performed using a Bruker DRX 200 spectrometer. For ^7Li NMR, chemical shifts are measured with shift referenced to $LiClO_4$ (0.3 N) methanol-d solvent. $^7LiT_1$ relaxation time is obtained through inversion recovery techniques with temperatures ranging from 270 to 330 K. The temperature is calibrated to within ±1 K for all samples following standard procedure.

3. Results and discussion

Lithium chemical shift range is relatively smaller compared with other metal nuclei in the range of 10 ppm. This is attributed to the smaller paramagnetic contribution to the shielding of lithium nuclei, which leads to a near-cancellation of the diamagnetic term [23]. ^7Li ($I = 3/2$) is chosen over ^6Li ($I = 1$) due to the larger gyromagnetic ratio, higher natural abundance (92.58%), greater chemical shift dispersion and sensitivity. Fig. 1 shows the ^7Li NMR spectra for PAN/EC/PC samples containing 1.0, 2.0, 5.0, 10.0, and 15.0 wt% $LiClO_4$ salt. The ^7Li resonance shows a general upfield shifting with increasing salt content, however, the 10 wt% salt sample exhibits much smaller δ values and broader line-width. Since the chemical shift is the average from the exchange of lithium in sites with different chemical shifts, the gradual upfield shift implied that less shielding due to rapid exchange between sites occurs. The chemical

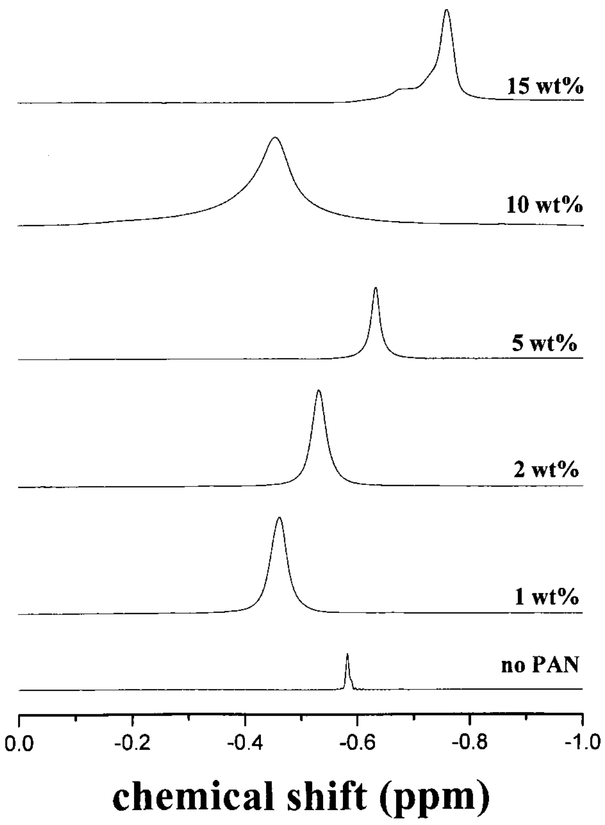

Fig. 1. Li NMR spectra of the five electrolytes. Li: (a) 1%; (b)2%; (c) 5%; (d) 10%; and (e) 15%.

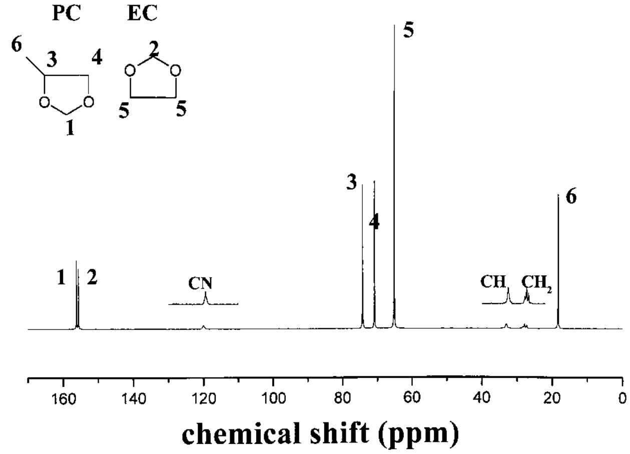

Fig. 2. Representative ^{13}C NMR spectra of the five electrolytes. The insert shows the blow up portion corresponding to PAN.

shift of lithium ions has been investigated in connection with ion pairing, salvation, and complexation. A range of nearly 6 ppm was found for $\delta(^7\text{Li})$ due to the weak interactions in various solvents and sudden shifts are also frequently observed on the formation of complexes with defined stoichiometry [24]. The jump discontinuity in the shift of the 10 wt% sample thus suggested unusual changes in both the chemical environment and lithium mobility. At 15 wt% $LiClO_4$, there appeared two peaks located at −0.72 and −0.63 ppm. In this case, the two types of lithium correspond to two unique structures, modulated by an exchange with a time scale slower than their shift difference.

Representative ^{13}CNMR spectra are summarized in Fig. 2, the peak assignments are also indicated. In spite of the visible ^{7}Li shift, there are no detectable differences in the EC/PC carbons even for the 15 wt% salt. As lithium coordinates only through electron dipole interaction with O and N, it appears that the interaction with the ion is too weak to induce sufficient electron charge to affect the adjacent carbon shift. However, carbon resonance of CN group shows a typical unequal doublet feature originated from

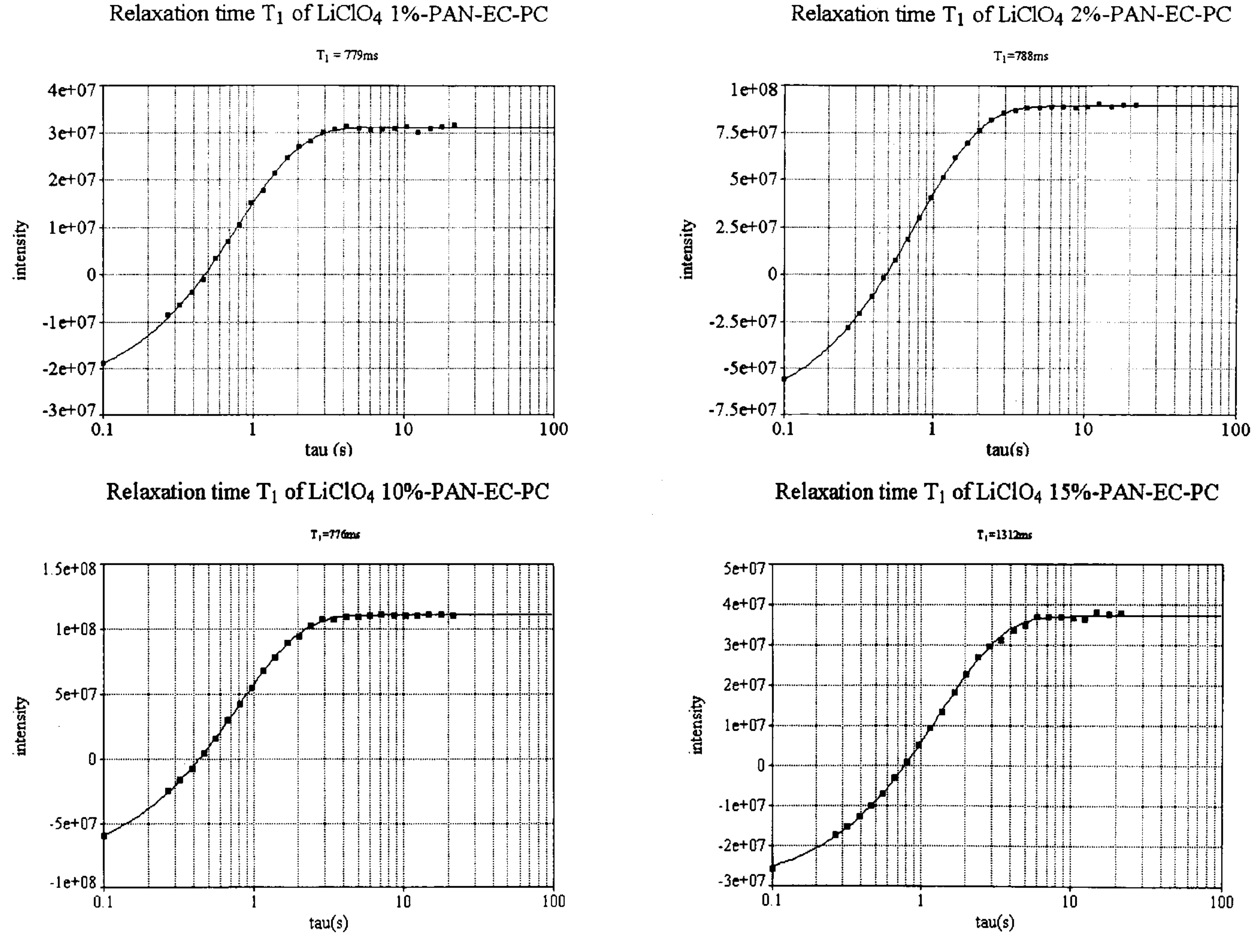

Fig. 3. ^{7}Li relaxation time inversion recovery curves for: (a) 1%; (b) 2%; (c) 10%; and (d) 15% $LiClO_4$ salt.

unaveraged dipolar coupling with the quadrupolar nuclei, $^{14}N(I = 1)$ [25]. This is not observed in a small molecule but is typical for a viscous solvent.

^{7}Li Longitudinal (spin-lattice) relaxation time T_1 is shown to be dominated by fluctuations of the $Li(I = 3/2)$ nucleus electric field gradient modulated by the molecular reorientation, while the Li–H dipolar interaction contribution is less [26]. This measurement provides a most convenient means to gauge the change of quadrupolar interaction, which revealed the lithium mobility and diffusion behavior. Fig. 3 shows the change of lithium magnetization in the inversion recovery process of 0, 2.0, 5.0, 10.0, and 15.0 wt% samples. For gel-type electrolytes, the ion diffusion constant appears in the order of 10^{-7}–10^{-8} cm^2/s. Therefore simple exponential recovery is a good approximation of the recovery process when the diffusion is weak [27]. The T_1 results are summarized in Table 1 where an increasing trend with salt content except for the dramatic jump for the 10 wt% sample is found. Knowledge of spin-lattice relaxation time suggests that the increase revealed slower Li fluctuation, which corroborated with the fact that viscosity of the electrolyte is increased with increasing salt content. Thus, the much larger T_1 of the 10 wt% sample, indicated the possibility that an exotic structure or dynamics may have appeared. These results are reproduced with repeated sample preparations and measurements.

Fig. 4 corroborates both T_1 and ^{7}Li peak half-height with $LiClO_4$content. With increasing salt content, the ^{7}Li linewidth (full width of a half-maximum, FWHM) narrows, which reaches a minimum at 6.36 wt%, indicating that signaled lithium mobility is highest at this composition. However, FWHM increases rapidly with 10 wt% salt which decreases again at 15 wt%. Additional broad down field peak is also observed for the 15 wt% sample. The linewidths, T_1 relaxation and the chemical shift variations unanimously suggested that the anomalous lithium structure and dynamics occurred near the 10 wt% composition.

Variable temperature T_1 relaxation time measurements are performed to analyze the ion transport behavior. As the dynamics are incoherent in the polymer gel, the generic Blombergen–Purcell–Pound relation [28] can be used to derive the averaged lithium ion correlation activation energy:

$$\frac{1}{T_1} = \frac{C_1}{r^6}\left(\frac{\tau_c}{1 + \omega_L^2\tau_c^2} + \frac{4\tau_c}{1 + 4\omega_L^2\tau_c^2}\right), \tag{1}$$

where

$$\tau_c = \tau_0 \exp\left(\frac{-E_a}{RT}\right). \tag{2}$$

E_a corresponds to the activation energy of lithium ion dynamics. The Arrhneius relationship ($\ln(T_1)$ versus inverse temperature) for all samples are shown in Fig. 5. Gorecki et. al [29] reported the temperature dependent T_1 results for ^{7}Li in PEO, which shows well behaved V-shape relation as predicted by the single activation process by Blombergen's relationship [29]. For the gel-type electrolyte, however, the result displayed inverse N-shape relationship where a weak recovery of relaxation time is found in between the high temperature and the low temperature regime. Careful examination shows that the transition occurs when the electrolyte turns from a clear solution (high T) into a cloudy suspension (low T). Physically, the cloudy behavior corresponds to PAN being separated from the EC/PC solution. In the current system, the cloud temperature is found to decrease with increasing salt content, consistent with the study of PEO in methanol solution [21]. The fact that the lithium salt depressed the cloud temperature is shown to be due to an enhanced miscibility of the PAN and the solvent [30]. Within the temperature region examined, lithium ion experiences two types of mobility which relaxes via different $E_a(T_1)$. The transition is not related to EC crystallization around 30–40°C, since there is no sign of such crystallization from DSC.

As evident from Fig. 5, the slopes on the low temperature side (cloudy sample) are roughly equal regardless of salt content, but on the high temperature side (clear solution), they become steeper for the 6.35 and 10 wt% samples. Simulations by Eqs. (1) and (2) with the experimental values give E_a and τ. The results for both the high and the low

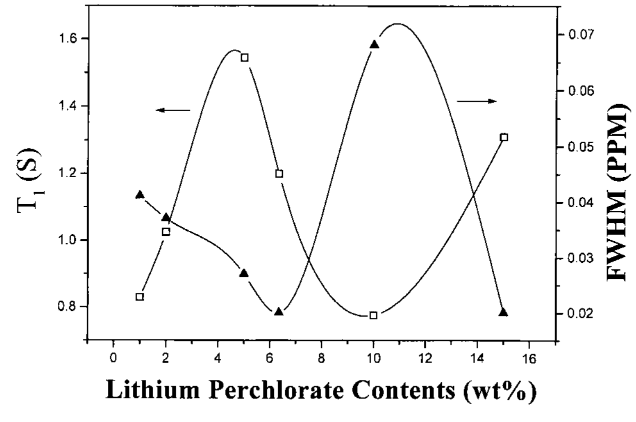

Fig. 4. Variation of room temperature T_1 relaxation time and the peak width with salt composition.

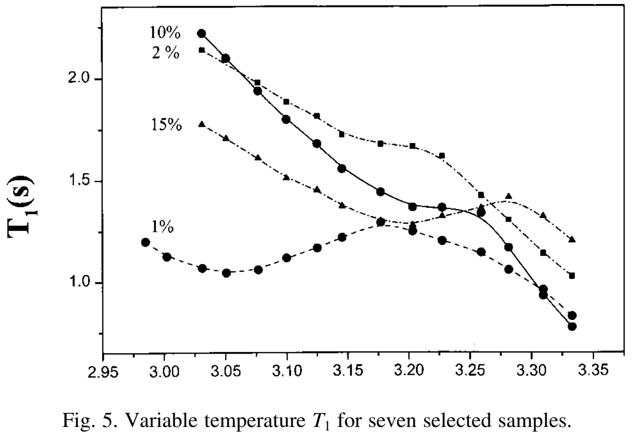

Fig. 5. Variable temperature T_1 for seven selected samples.

temperature regimes are summarized in Table 2. In the clear solution temperature regime, the activation energy is about twice higher for 10 wt% salt sample compared with the other electrolytes. But below the cloud temperature, E_a for all samples are higher and reach the 30–60 kJ/mol ranges. The higher activation energy near 10 wt% salt concentration implied that the lithium ion is experiencing stronger restriction and exhibits slower mobility compared with other samples. The most plausible cause for the unusual increase of $E_a(T_1)$ would be the formation of a weak complex with PAN, where lithium nucleus fluctuation is greatly reduced.

The possibility also explains the anomalous line-width and shift results. In the complex, lithium becomes severely shielded by the CN group and the partial negative charge in CN is dispersed to the coordinated lithium. As a result, ^{7}Li resonance is most down field in the 10 wt% sample. The complex which localized lithium broadens the ^{7}Li line-width and yields higher activation energy at variable temperature T_1. Since viscosity is proportional to the coil hydrodynamic volume, viscosity in the gel increases with increasing salt content, as observed by Yelhiraj [30]. For samples with lower salt concentrations, the rapid exchange with the solvent in the less viscous medium gives rise to a sharper peak. Previous Raman and laser light scattering experiments, show that the majority of lithium is solvated through electric dipole linkage with EC/PC [31]. However, the measurement is carried out in the low salt concentration range (<5 wt%). This does not exclude the complex formation at higher salt content. From this result, one can also concluded that the extra shoulder for 15 wt% composition has originated from the complex, but the exchange with EC/PC solvent has shifted the peak upfield. The exchange between the two lithium configurations is slower due to the increased viscosity at high salt content leading to resolved resonances. It can be estimated from the spectra that the majority of lithium (~60 mol%) is solvated by EC and PC and an additional component weakly coordinated with CN(~40 mol%). The ^{7}Li spectra width (10 wt%) is reduced from 6 to 2.5 Hz as temperature increased from 300 to 380 K which suggested that exchange also occurred between the complex and the solvent. However, the 2.5 Hz width at high temperature is still broader than other samples at room temperature, and reflected the influence of the complex. The Li:N ratio for the 10 wt% is close to unity at 1:1.25, but this can hardly justify that the complex is in 1:1 (Li:N) ratio, since the amount of exchanging lithium with EC/PC is not determined.

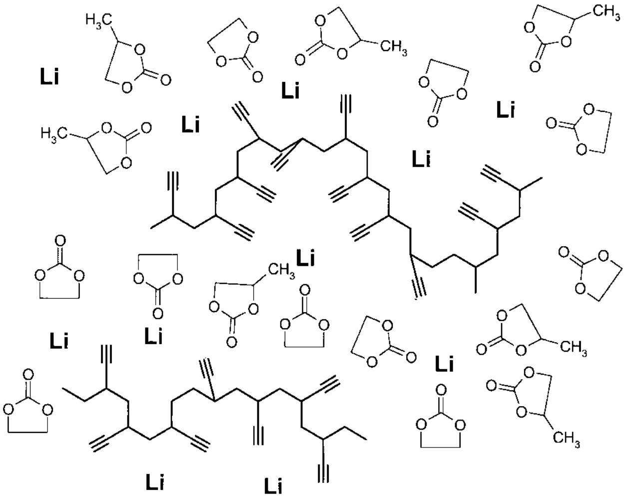

Fig. 6. Possible lithium structures in the EC/PC/PAN electrolyte.

Fig. 6 shows all possible lithium configurations within the gel-type electrolytes. The coordination complex between lithium and PAN is apparent near 10 wt% salt concentration, but for all other samples, (including the 15 wt% sample) lithium ions are heavily solvated by EC/PC. For the 15 wt% sample, both complex and solvating forms existed with slower exchange. Ion pairing of Li$^+$ and ClO$_4^-$ is negligible in the gel electrolyte, as judged from the almost identical activation energy from the T_1 measurements. Few factors maybe responsible for the formation of the complex. With increasing salt content, charge repulsion between polymer chain increases [32]. When charge accumulation reaches a certain threshold value, lithium ion begins to complex with the CN group in PAN. Further increase in the salt content, enhances the miscibility of EC/PC with the complex. Beyond the threshold concentration, no more complex is formed and the salt is again solvated with the solvent. One may argue, based on electron negativity that lithium should experience stronger affinity with oxygen from EC and PC than with C≡N in PAN. However, the association with the small molecule is short-lived compared with PAN. Recent neutron scattering studies show that the residence time in Li:O is shorter than a microsecond [33]. This weak complexation with PAN thus restrict lithium motion and limit its exchange with the EC/PC solvent. The current results are obtained with 7.5 wt% of PAN in the electrolyte. For samples with 14 wt% of PAN as used by Abraham et. al. [15,27] the threshold value where a complex can form should be close to 20 wt% LiClO$_4$. This

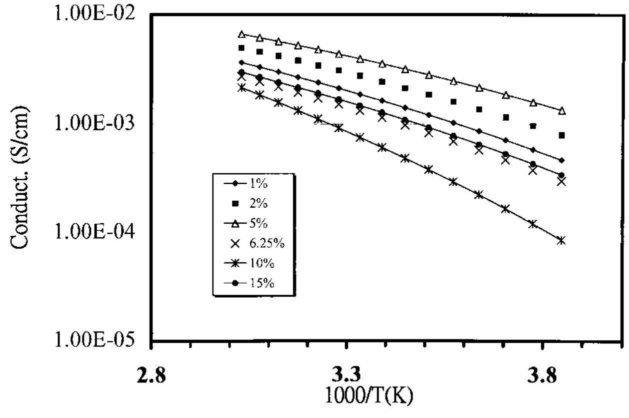

Fig. 7. Variable temperature conductivity and the VTF fit for samples of different LiClO$_4$ salt content.

Table 2
Li correlation time activation energy measured from variable temperature T_1 (E_a from conductivity measurements is about 25 kJ/mol)

$LiClO_4$ contents (wt%)	E_a(kJ/mol) low temperature	E_a(kJ/mol) high temperature	Conductivity E_a (kJ/mol)
1	32.00	16.08	18.25
2	30.34	15.29	16.37
5	–	12.3	14.22
6.35	–	18.14	19.68
10	67.34	26.85	28.73
15	13.05	16.62	19.24

explains why such complex has never been reported when the salt content is lower than 15 wt% in these electrolytes.

As ion diffusion contributes to ion conduction, it is pertinent to compare the activation energy derived from T_1 relaxation time with that deduced from the conductivity measurements. Fig. 7 shows the variable temperature conductivity for the six samples taken within the same temperature range of the T_1 measurements. The conductivity gradually rose with increasing salt content, but showed a drop for the 10 wt% sample with greater temperature dependence. The conductivity modeled by Vogel–Tamman–Fulcher (VTF) relationships are shown in the solid line. The glass temperature (~ -89°C) is used in the VTF for deducing the activation energy. Except for the case of 10 wt% $LiClO_4$ salt sample, the activation energy $E_a(\sigma)$ are within the bulk-part of that reported by Abraham et. al. [27] which are summarized in the last column in Table 2. It is interesting to note that the lowest $E_a(\sigma)$ is found for the sample where the $E_a(T_1)$ is lowest, and highest at 10 wt% sample where the $E_a(T_1)$ is also highest. Though the two values are not directly proportional, since other factor also influences ion conduction, the similarity in both measurements suggest that transport through cooperative PAN chain is also an efficient path as the random ion diffusion via the EC/PC solution.

Although presence of complexes does not substantially hinder the ion conductivity, such complexation may play a critical role in terms of the resistance to redox cycle, physical stability and mechanical properties of the electrolytes. This feature would influence both physical properties and charge–discharge recycle efficiency and should be acknowledged. Neutron scattering to derive the residence time of lithium ion in the complex and other moieties is currently in progress.

4. Conclusions

^{7}Li NMR shows anomalous ^{7}Li chemical shift and variable temperature spin-lattice relation time and reveal slower lithium motion (higher activation energy) in the 10 wt% of $LiClO_4$ salt. All spectroscopic results point toward the possible formation of a weak complex between lithium ion and cyanide group of PAN above this composition. At low salt content (<10 wt%) the two lithium species exhibit rapid exchange with preference given to the EC/PC solvent, as evident from the gradual upfield change of the lithium shift. In these cases, conduction is established mainly through the EC/PC binary solution. Near the 10 wt% threshold concentration, additional conduction channel is established via the formation of Li–CN complex. In this case, Li exchange with the solvent is much suppressed, resulting in a broader linewidth with higher activation energy in lithium mobility. Above this threshold concentration, the ion mobility is reduced due to the increased viscosity in the presence of the complex, conductivity is not decreased substantially since both solvated ions, and the complex contribute comparably to ion conductivity. The more direct lithium conduction (compared with the random diffusion motion in EC/PC) by hopping alone the PAN polymer chain may compensate its restricted mobility and give rise to comparable conductivity as the diffusion within the EC/PC solvent. This result raised the issue that diffusion in EC/PC medium is not the sole conducting mechanism, but the weak complex with PAN is also beneficial to ion transport. However, even higher salt content does not necessarily improve the conductivity, as the increased viscosity begins to deteriorate the ion mobility.

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