

The interaction behavior of polymer electrolytes composed of poly(vinyl pyrrolidone) and lithium perchlorate (LiClO_4)

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Abstract

The interaction behavior of polymer electrolytes composed of poly(vinyl pyrrolidone) (PVP) and lithium perchlorate (LiClO_4) has been investigated in detail by solid-state NMR and FTIR spectroscopies. It is found that the N-atom of the PVP polymer is able to donate its lone pair electrons toward the C=O group, which results in a higher basicity of the C=O group. The complex bond of $\text{Li}^+ \cdots \text{C}=\text{O}$ is compartmented into two types: the tight primary complex bond of $\text{Li}^+ \cdots \text{C}=\text{O}$; and the secondary complex where Li^+ loosely complexed with several C=O groups simultaneously. The secondary complex is dominant when the [Li:O] ratio is greater than 0.281. The ClO_4^- anion is free in the diluted PVP/ LiClO_4 electrolyte. When the LiClO_4 concentration is increased, the ClO_4^- anion will interact with both N quasi-cation and/or Li^+ cation. Solvated Li^+ and “free” ClO_4^- ions are more favorable in diluted electrolyte; whereas neutral solvation-shared ion pair formation increases the incremental addition the LiClO_4 . © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer electrolytes; Interaction behavior; Poly(vinyl pyrrolidone)

1. Introduction

The interaction behavior of an alkaline ion within polymer electrolytes determines their applicability in high-energy density batteries and other solid-state electrochemical devices [1–4]. For most potential applications, it is desirable that the solid polymer electrolytes display a reasonable conductivity ($\sim 10^{-4} \text{ S cm}^{-1}$), dimensional stability, processability and flexibility in ambient conditions. Hence, the lithium salt-based electrolytes have been the focus of a wide variety of fundamental and application-oriented studies [5,6]. However, Li^+ -based polymer electrolytes exhibit several disadvantages that affect the commercialization of such cell. One major drawback is the low ionic conductivity of the electrolyte at ambient temperatures [7,8]. It is of vital importance to optimize the performance through understanding of the fundamentals of the ionic interaction behavior in full detail within polymeric electrolytes.

The poly(vinyl pyrrolidone) (PVP) is amorphous and possesses high T_g due to the presence of the rigid pyrrolidone group, which is known to form various complexes with many inorganic salts [9,10]. The pyrrolidone group is a

strong withdrawing group that makes the salt association with PVP different from other polymeric electrolytes, such as the PEO, PPO, PVDF, PAN, etc. Solid-state NMR and FTIR spectroscopies have been proven as powerful tools in characterizing the detailed structure of polymer solids [11–16]. A number of earlier works have demonstrated that the feature of IR spectroscopy in C=O absorbance range is very useful in determining the number of interactions [17–20]. In this article, we report the complex interaction behavior between PVP and LiClO_4 salt, which provides the direct evidence to support the proposed ionic interaction behavior in solid state. The ion interaction behavior of both Li^+ and ClO_4^- within PVP polymer electrolyte will be discussed in detail in this article.

2. Experimental section

2.1. Sample preparation

PVP with M_n of 90,000, was obtained from the Aldrich. The lithium perchlorate salt (LiClO_4), also from Aldrich, was dried in a vacuum oven at 140°C for 24 h, and then all stored in a desiccator before use. THF, also from the Aldrich, was refluxed at a suitable temperature under N_2 atmosphere before use.

Complexes of PVP– LiClO_4 were prepared by dissolving

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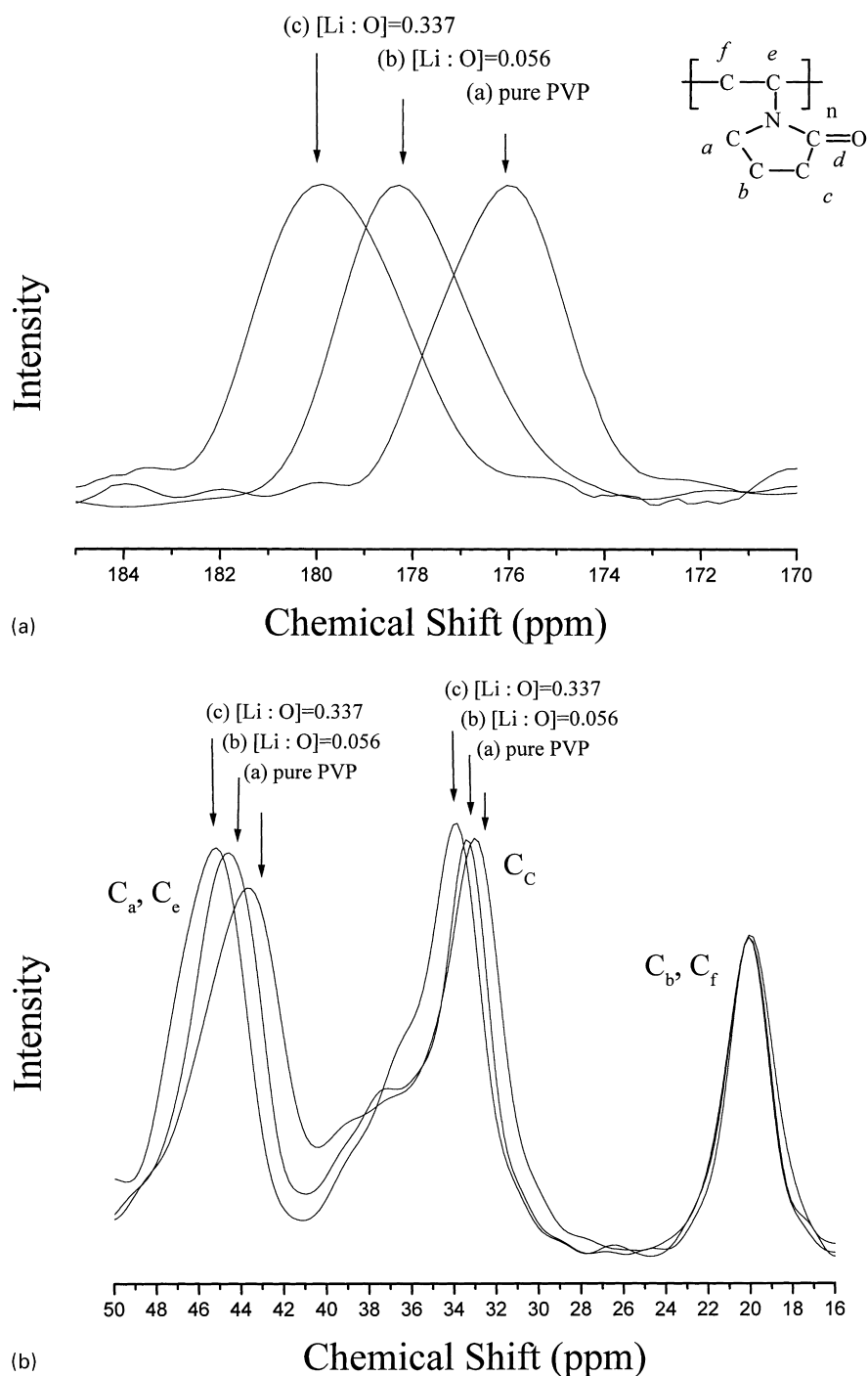


Fig. 1. (a) Scaled ^{13}C CP/MAS NMR spectra region of LiClO_4 -PVP complex ranging from 185 to 170 ppm, the $[\text{Li}:\text{O}]$ equivalent ratio of (a) 0, (b) 0.056, (c) 0.337. (b) Scaled ^{13}C CP/MAS NMR spectra region of LiClO_4 -PVP complex ranging from 50 to 16 ppm, the $[\text{Li}:\text{O}]$ equivalent ratio of (a) 0, (b) 0.056 (c) 0.337.

desired amount of the PVP and the vacuum-dried LiClO_4 salt in an anhydrous THF. After continuous stirring for 4 h at room temperature, the solutions were allowed to stand at 40 – 50°C for 24 h to facilitate the evaporation of the solvent, and then further dried under vacuum at room temperature for additional 12 h. All these complexes were stored at N_2 atmosphere to avoid contact with moisture from air.

2.2. NMR experiments

High-resolution solid-state ^{13}C NMR experiments were carried out on a Bruker DSX-400 spectrometer operating at resonance frequencies of 400.23 and 100.61 MHz for ^1H and ^{13}C , respectively. The ^{13}C CP/MAS spectra were measured with $3.9 \mu\text{s}$, 90° pulse angle, 3 s pulse delay

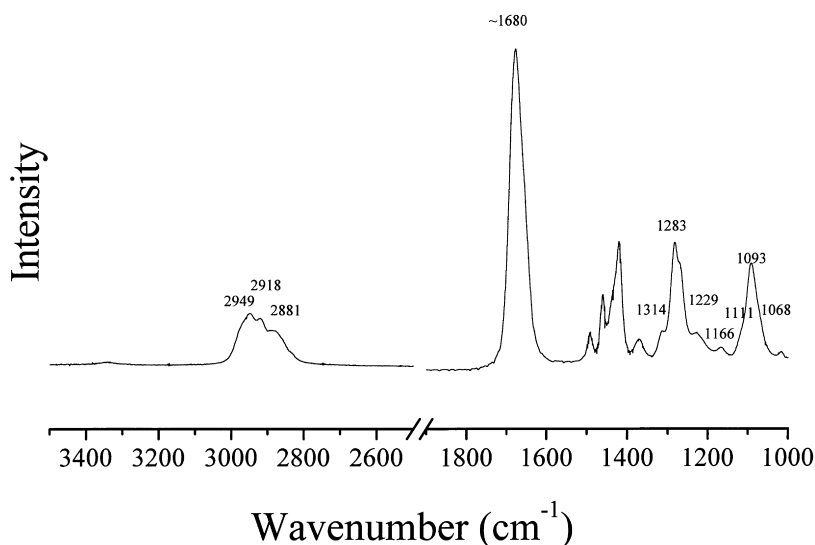


Fig. 2. Infrared spectrum of PVP/LiClO₄ ([Li:O] equivalent ratio 0.056) complex in the spectral region between 3500 and 1000 cm⁻¹ at 140°C.

time, 30 ms acquisition time, 1 ms contact time and with 2048 scans. All NMR spectra were taken at 300 K with broad band decoupling, normal cross-polarization pulse sequence, and a magic angle spinning (MAS) of 10 kHz.

2.3. Infrared spectra

Infrared spectra of polymer complex films were determined by using the conventional NaCl disk method. The THF solution containing the complex was cast onto NaCl disk and dried under conditions similar to those used in the bulk preparation. Infrared spectra recorded on elevated temperature were obtained by using a heating cell mounted inside the sample compartment of the spectrometer. Temperature was controlled within $\pm 0.1^\circ$. All infrared spectra were obtained at a resolution of 2 cm⁻¹ on a Nicolet AVATR 320 FTIR spectrometer at 140°C.

3. Results and discussions

3.1. The interaction behavior of PVP observed from solid-state NMR

The solid-state NMR spectrum is used to characterize the interaction behavior between PVP and LiClO₄ complex. The electron-donated carbon produces small perturbation to the magnetic shield on the nucleus and results in downfield chemical shift as compared to the ones without the complex interaction [21,22]. On the contrary, the electron-accepted carbon tends to shift upfield. The extent of such field shift reflects the strength of the complex interaction [21]. Fig. 1(a) and (b) shows the scale expanded ¹³C CP/MAS NMR spectra and the corresponding peak assignments of various PVP–LiClO₄ complex compositions at room temperature. The C=O resonance of the pure PVP (C_d) is

assigned at 176.1 ppm. It shifts downfield, when LiClO₄ is added, to 179.9 ppm (shift downfield ~ 3.8 ppm) at the [Li:O] equivalent ratio of 0.337. This observed chemical shift of the complexed C=O is greater than that of an ordinary H-bonding (~ 2 ppm), an indication of the strong complex interaction. It is obvious that the basicity of PVP C=O group is increased with the increasing [Li:O] equivalent ratio, implying that the C=O group is able to act as a strong electron donor to interact with Li⁺ ion.

The difference in molecular segmental mobility between the “free” and the “complexed” C=O group is rather significant. Consequently, the difference in resonance intensity between the “free” and “complexed” C=O groups can be resolved in the different efficiency of the cross-polarization (CP) in ¹³C NMR spectra [23]. Based on the normalized solid-state NMR spectra with 1 ms contact time, the intensity of the “free” C=O component is relatively weaker than the complexed C=O component. Only insignificant fraction of the “free” C=O group can be detected in NMR spectra for the composition having higher LiClO₄ salt concentration. Therefore, it is difficult to quantify the extent of the complexed C=O species accurately from the solid-state NMR spectra.

The resonances C_a and C_e are assigned at 43.6 ppm; C_c is at 33.1 ppm; and, C_b and C_f are at 20.1 ppm, respectively [24]. The resonances of C_a, C_e and C_c as well as the C=O resonance (C_d) shift downfield with the increase of [Li:O] equivalent ratio, as shown in Fig. 1(b). The C_a, C_e and C_c show the character of electron-donors. The resonances of C_a and C_e, adjacent to the N atom, downshift more severely than that of C_c. It is inferred that the N atom pushes more severely on the electron of C_a and C_e than the C=O group pushing on C_c. The strong electron withdrawing character of the N atom is able to function as a quasi-cation within the PVP chain to attract the anion. In addition, the resonances of

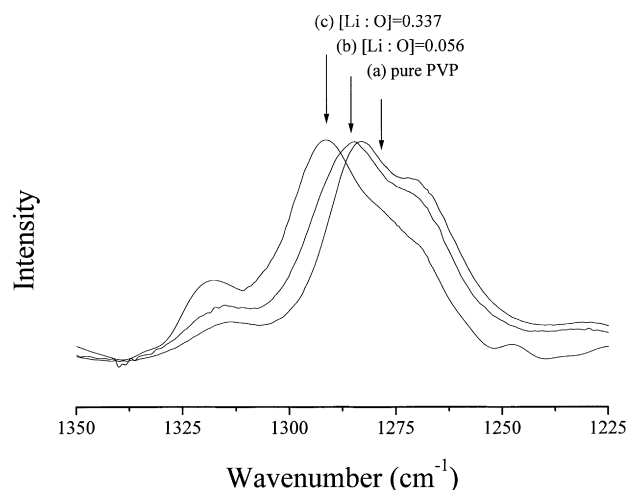
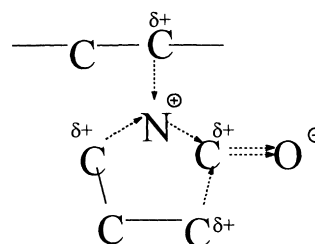


Fig. 3. Mid-infrared spectra region from 1350 to 1225 cm^{-1} with various LiClO_4 salt concentrations at 140°C , the $[\text{Li}:\text{O}]$ equivalent ratio of (a) 0, (b) 0.056, (c) 0.337.

C_b and C_f are nearly independent of the $[\text{Li}:\text{O}]$ equivalent ratio because both carbons are far away from the active group.

Fig. 2 shows the IR spectrum of the PVP– LiClO_4 ($[\text{Li}:\text{O}]$ equivalent ratio = 0.056) complex measured at 140°C . The assignments for major bands are listed in Table 1. Fig. 3 shows the FTIR spectra in the mid-IR region from 1350 to 1225 cm^{-1} of various PVP– LiClO_4 complex compositions at 140°C . It is possible to assign different IR bands in a polymer–salt complex to various vibrational modes of different interaction strengths. Fig. 3(a) shows the IR spectrum of the pure PVP that has a major peak at 1283 cm^{-1} and a minor peak at 1314 cm^{-1} corresponding to the CH_2 wagging motion. These CH_2 peaks shift to higher frequencies gradually with the increase of the $[\text{Li}:\text{O}]$ equivalent ratio, its electron surroundings have been deprived by the higher electronegativity of N or/and $\text{C}=\text{O}$. It is reasonable to assume that the withdrawing group (N or/and $\text{C}=\text{O}$) is partially compensated by drawing electrons from the neighboring C atoms, and results in a slight positive charge on these neighboring C atoms [26,27].

The dipole moment within the PVP chain induced by the



Scheme 1.

LiClO_4 salt based on results from solid-state NMR and FTIR spectra is depicted in Scheme 1.

3.2. The interaction behavior of Li^+ cation within PVP– LiClO_4 complex

Measuring the degree of the complexed IR $\text{C}=\text{O}$ stretching as function of blend composition is the most frequently employed method to quantify the relative fraction of “free”¹ and “complexed” $\text{C}=\text{O}$ sites within the PVP chain [9,28,29]. As shown in Fig. 4, the band of $\text{C}=\text{O}$ stretching is broadened gradually with the increase of the $[\text{Li}:\text{O}]$ equivalent ratio. The fraction of the “free” and the complexed $\text{C}=\text{O}$ group of compositions with different $[\text{Li}:\text{O}]$ equivalent ratios can be measured by decomposing its $\text{C}=\text{O}$ stretching band into three Gaussian peaks. Those peaks are composed of one “free” $\text{C}=\text{O}$ absorptions (centered at $\sim 1683\text{ cm}^{-1}$ with the half width ($w_{1/2}$) of $\sim 25\text{ cm}^{-1}$ and two “complexed” $\text{C}=\text{O}$ absorptions (centered at $\sim 1657\text{ cm}^{-1}$), respectively. The band of the “complexed” $\text{C}=\text{O}$ group is actually composed of two Gaussian peaks; a narrower peak ($w_{1/2} \cong 25\text{ cm}^{-1}$) is assigned as primary complex; and the wider peak ($w_{1/2} \cong 65\text{ cm}^{-1}$) is assigned as the secondary complex with wider bond distance distribution within complex [1,30,31], as shown in Fig. 4(g). Table 2 and Fig. 5 summarize the fractional area, width and location of the “free” and two the “complexed” $\text{C}=\text{O}$ bands for comparison. The relative fraction of the “free” $\text{C}=\text{O}$ group decreases exponentially with the increase of $[\text{Li}:\text{O}]$ equivalent ratio. The fractions of the primary and secondary complexes of the Li^+ ion increase with the increase of the $[\text{Li}:\text{O}]$ equivalent ratio up to 0.225. After that, the fraction of the primary complex begins to decrease while the secondary complex fraction continuously increases. Apparently, the formation of the primary complex shifts gradually into the secondary complex when the concentration of LiClO_4 salt increases. It evidences that the secondary complex is favorable in higher concentration of ClO_4^- anion. That will be shown in following IR spectrum. On the other hand, it is understandable that not all the added Li^+ ions are able to associate with the $\text{C}=\text{O}$ by forming the polymer–salt complex; some “free” $\text{C}=\text{O}$ groups are still present in the composition, even with high LiClO_4 salt concentration. In other words, the Li^+

Table 1

Observed frequencies and assignments of infrared bands of PVP– LiClO_4 complex, the $[\text{Li}:\text{O}] = 0.056$, in a cast film at 140°C [25]

PVP– LiClO_4 complex (cm^{-1})	Assignments
2949, 2918, 2881	CH_2 or CH stretching
~ 1680 (strong and broad)	$\text{C}=\text{O}$ stretching
1314, 1283, 1229	CH_2 deformation
1166	$\text{C}-\text{CH}_2$ stretching
1093	$\text{Cl}-\text{O}$ stretching (free ClO_4^-)
1111, 1068 (shoulder at 1093)	$\text{Cl}-\text{O}$ (ion pair)

¹ Here “free” identified as no coordination with lithium ion.

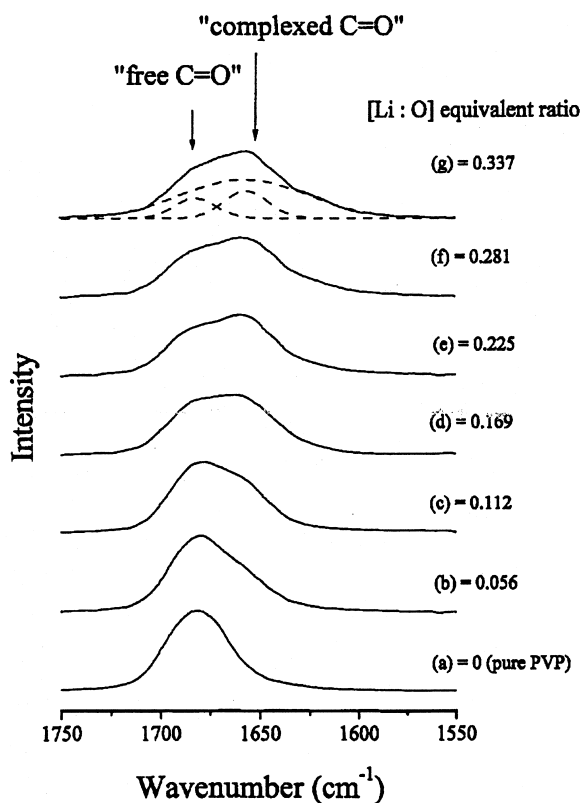


Fig. 4. Infrared spectra of C=O stretching region of PVP–LiClO₄ complex at 140°C, the [Li:O] equivalent ratio of (a) 0, (b) 0.056, (c) 0.112, (d) 0.169, (e) 0.225, (f) 0.281, (g) 0.337.

ion is involved in equilibrium with both ClO₄[−] and C=O simultaneously in the complex.

3.3. The dissolved behavior of the ClO₄[−] anion

The change of relative intensity and/or location of a particular band (ClO₄[−] stretching) within the complex depends on the concentration of the LiClO₄ salt. Therefore, the interaction involving the ClO₄[−] anion can be assigned to such change. Fig. 6 gives the IR spectra of the neat PVP and various PVP–LiClO₄ complexes showing the ClO₄[−] stretching band ranging from 1150 to 1025 cm^{−1} at 140°C. There are a number of bands originating from the intermolecular

interaction of the ClO₄[−] anion; each component representing a different environment for the ClO₄[−] anion (i.e. “free” anion and ion pair). The major band appears at 1092 cm^{−1} when small amount of the LiClO₄ salt is added into the PVP resin (Fig. 6(b)). It is reasonable to assign this 1092 cm^{−1} band as the “free” ClO₄[−] anti-symmetric stretching mode $\nu_{as}(\text{Cl-O})$. When the LiClO₄ salt is added incrementally, two new bands appear centered at 1112 and 1065 cm^{−1} and their intensities increase gradually. These two newly formed bands can be attributed to the cation–anion interaction (i.e. including both solvation–shared ion pair Li⁺⋯ClO₄[−] and the complexation with the N quasi-cation of PVP). The relative intensities of these two newly formed bands increase more rapidly than that of the 1092 cm^{−1} peak with increasing salt concentration, and eventually become dominant when the [Li:O] equivalent ratio is greater than 0.281. This can be interpreted as the ClO₄[−] anion interacting gradually with the Li⁺ and the N quasi-cation of PVP to facilitating the cation–anion interaction with increasing LiClO₄ salt concentration.

On the other hand, the increasing Li⁺ ion concentration also induces the N atom to become quasi-cation more severely, which prompts the electrostatic N atom to pull the anion allowing cation–anion interaction. The interaction of Li⁺ ion is more complicated in concentrated ClO₄[−] anion, when the primary complex converts into the secondary complex gradually, similar to Fig. 5.

3.4. The formation of PVP–LiClO₄ salt complex

Summarizing results from the above solid-state NMR and FTIR spectra of the PVP–LiClO₄ complex, it is reasonable to assume that the Li⁺ cation is able to have different interactions with C=O groups simultaneously (primary and secondary complexes) and with the ClO₄[−] anion. Similarly, the ClO₄[−] anion is able to interact not only with the Li⁺ cation but also with N atom of the PVP in a concentrated LiClO₄ salt electrolyte. We can depict such multiple interactions and the related ionic interaction behavior of the PVP–LiClO₄ complex in Fig. 7. Complex type I describes the solvated Li⁺ cation complexed with C=O. The complex type II describes the “free” ClO₄[−] anion within PVP electrolyte. It is inferred that the Li⁺ cation can migrate through the

Table 2

Curve-fitting data of infrared spectra of C=O stretching region of PVP/LiClO₄ complexes with various compositions at 140°C

[Li:O] equivalent ratio	“Free” C=O			The primary complexed C=O			The secondary complexed C=O		
	ν (cm ^{−1})	$w_{1/2}$ (cm ^{−1})	A_f (%)	ν (cm ^{−1})	$w_{1/2}$ (cm ^{−1})	A_c (%)	ν (cm ^{−1})	$w_{1/2}$ (cm ^{−1})	A_c (%)
0	1682	29.15	100.00						
0.056	1682	25.76	67.73	1658	23.97	14.14	1666	69.64	18.14
0.112	1682	25.41	45.25	1657	21.76	25.3	1664	55.58	29.45
0.169	1681	30.28	33.95	1656	22.94	32.1	1647	39.29	33.95
0.225	1686	23.30	22.36	1658	27.26	37.29	1655	69.67	35.44
0.281	1686	22.24	17.01	1658	28.89	33.85	1658	68.71	49.16
0.337	1682	21.05	12.26	1656	22.65	17.62	1657	63.40	70.11

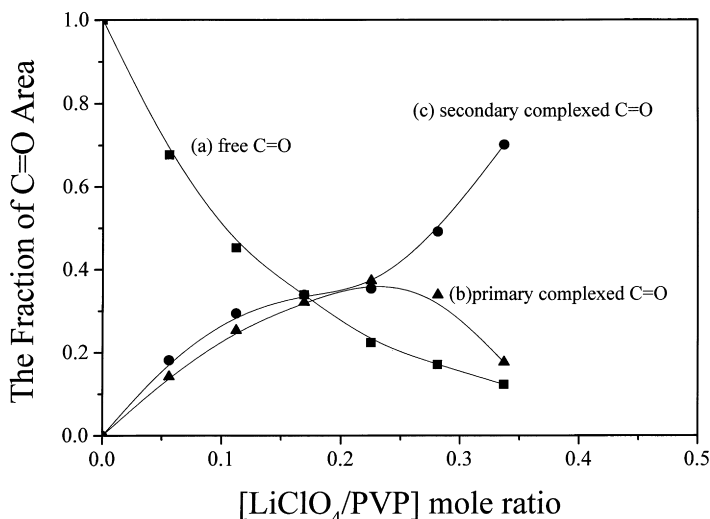


Fig. 5. The dependence of “free” and “complexed” C=O band on LiClO₄ salt concentration: (a) “free”; (b) the “primary complexed”; and (c) the “secondary complexed” C=O band.

alternations among the primary, secondary bonded complexes and the “free” C=O sites along the electric field within the matrix. The mechanism of the Li⁺ cation alternations provide an environment for ionic conduction. By increasing the [Li:O] equivalent ratio, the Li⁺ cation interacts simultaneously with C=O group and ClO₄⁻ anion and becomes a neutral solvation-shared ion pair as shown as type III in Fig. 7. In fact, migration of these neutral species neither makes any contribution to the ionic conductivity, nor influences the transference number [1].

The N atom of the PVP indeed prompts the intermolecular attraction of the “free” anion when the Li⁺ anion concentration is high enough to induce the N atom to be quasi-cation. It is reasonable to assume that the migration of the “free” ClO₄⁻ anion in this system is not as easy as that in other electrolyte systems (such as PEO,

PVDF, PAN etc.) [1] because the strong interaction between the ClO₄⁻ and the N quasi-cation limits the mobility of the ClO₄⁻ anion in the electrolyte. Further work is in progress in order to obtain more relationships between conductivity and ionic interaction within PVP–LiClO₄ electrolyte.

4. Conclusions

The present study describes in detail the ionic interaction behavior within the PVP–LiClO₄ polymer electrolyte throughout solid-state NMR and FTIR techniques. The N atom, a quasi-cation within PVP, is able to donate its electron to increase the basicity of the C=O. The solvated Li⁺ cation within the PVP electrolyte is comparted into two types of interactions. The primary and tight complex of Li⁺...C=O

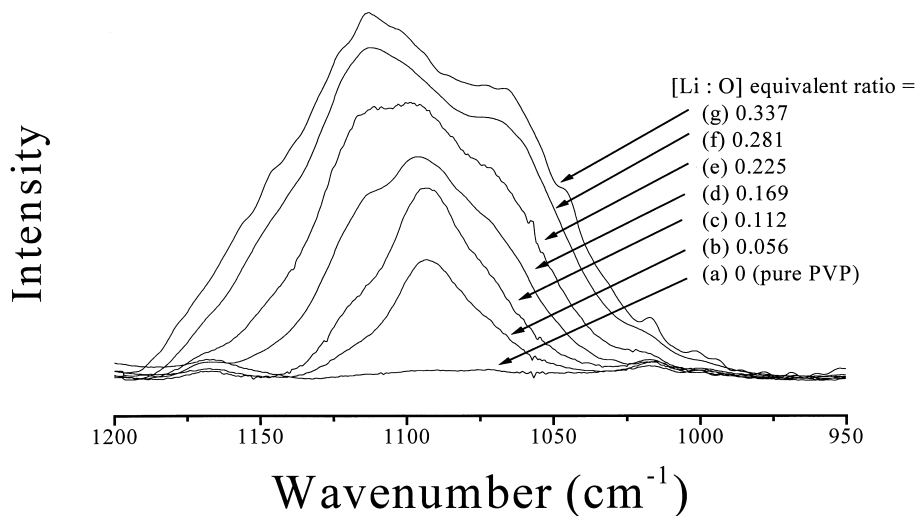


Fig. 6. Mid-infrared spectra region from 1200 to 950 cm⁻¹ PVP–LiClO₄ complex with various LiClO₄ salt concentrations at 140°C, the [Li:O] equivalent ratio of (a) 0, (b) 0.056, (c) 0.112, (d) 0.169, (e) 0.225, (f) 0.281, (g) 0.337.

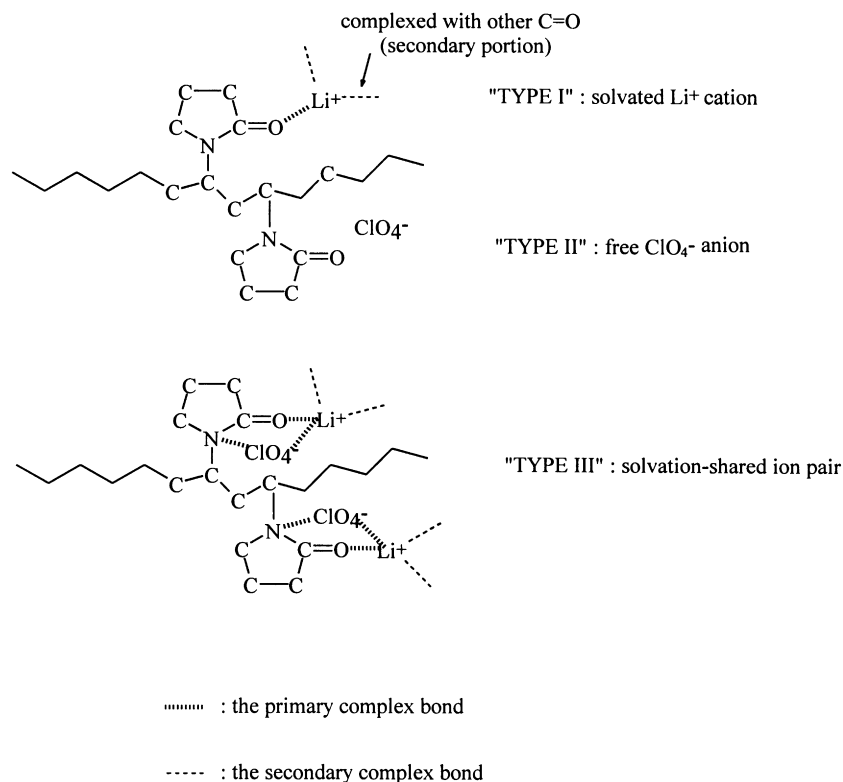


Fig. 7. Schematic drawing of three types of the ionic association of polymer electrolytes—PVP— LiClO_4 complex.

has shorter bond distance. The secondary complex interaction involves the Li^+ cation interacting with several C=O groups simultaneously with wider bond distance distribution. The secondary complex interaction is dominant when the [Li:O] ratio is greater than 0.281, and further increase in [Li:O] ratio results in more interaction with ClO_4^- anion. On the other hand, the ClO_4^- anion is essentially “free” in very dilute salt concentration. When the salt concentration is increased, the ClO_4^- anion begins to interact with Li^+ cation and N quasi-ation. It implies that the solvated Li^+ cation ion and the “free” ClO_4^- anion are favored in the diluted LiClO_4 salt electrolyte; whereas the solvation-shared ion pair is formed in the concentrated LiClO_4 salt electrolyte.

Acknowledgements

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