

Chapter IV The Interaction Behavior of Polymer Electrolytes Composed of Poly(vinyl pyrrolidone) and Lithium Perchlorate (LiClO₄)

4-1 Introduction

The interaction behavior of 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 ($\sim 10^{-4}$ S cm⁻¹), dimensional stability, processability and flexibility in ambient condition. 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 temperature.^(7,8) It is vital important to optimize the performance through understanding the fundamental of the ionic interaction behavior in full details 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 withdraw group that makes the salt associations with PVP different from other polymeric electrolytes, such as the PEO, PPO, PVDF, PAN...etc. Solid-state NMR and FT-IR spectroscopy have been proven as powerful tools in characterizing

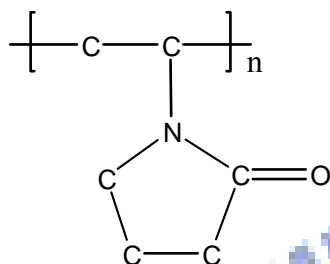
detailed structure of polymer solids.^(11~16) A number of earlier works have demonstrated that the feature of IR spectroscopy in C=O absorbance range is very useful in determining the number of interactions.^(17~20) In this article, we report the complex interaction behavior between PVP and LiClO₄ salt, which provides the direct evidence to support the proposed ionic interaction behavior in solid state. The ion interaction behavior of both Li⁺ and ClO₄⁻ within PVP polymer electrolyte will be discussed in detail in this article.



4-2 Experimental Section

4-2-1 Sample Preparations

The poly(vinyl pyrrolidone) (PVP) with M_n of 90,000, was obtained from the Aldrich.



The lithium perchlorate ($\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$) salt from Acros was treated in 190°C for 24 hrs in vacuum to eliminate crystal water and then stored under vacuum condition. 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 desired amount of the PVP and the vacuum-dried LiClO_4 salt in the anhydrous THF. After continuous stirring for 4 hr at room temperature, the solutions were allowed to stand at $40\sim 50^\circ\text{C}$ for 24 hr to facilitate the de-solvent, and then further dried under vacuum at room temperature for additional 12 hr. All these complexes were stored at N_2 atmosphere to avoid contact with moisture from air.

4-2-2 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 μs , 90° pulse angle, 3s pulse delay time, 30 ms acquisition time, 1ms contact time and 2048 number of 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.

4-2-3 Infrared spectra

Infrared spectra of polymer complex films were determined by using the conventional KBr disk method. The THF solution containing the complex was cast onto KBr 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 $\pm 0.1^\circ\text{C}$. All infrared spectra were obtained at a resolution of 2 cm^{-1} on a Nicolet AVATR 320 FTIR spectrometer at 140°C .

4-3 Result and Discussion

4-3-1 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. Extent of such field shift reflects the strength of the complex interaction.⁽²¹⁾ Figures 4-1a and 1b show 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 salt is added, shifts 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 ^{13}C 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 relative 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 LiClO_4 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 Figure 4-1(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 electron withdraw character of the *N*

atom would to be reduce some negativity. In addition, the resonances of C_b , and C_f are

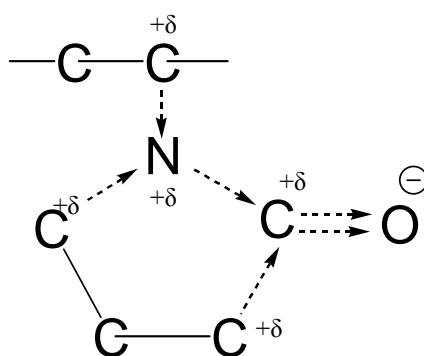
nearly independent of the [Li : O] equivalent ratio because both carbons are far

distance away from the active group.

Figure 4-2 shows the IR spectrum of the PVP— LiClO_4 ([Li : O] equivalent

ratio = 0.056) complex measured at 140 °C. The assignments for major bands are listed in Table 4-1. Figure 4-3 shows the FTIR spectra in the mid-IR region from 1350 to 1225 cm⁻¹ of various PVP—LiClO₄ 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 strength. Figure 4-3 (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 CH₂ wagging. These CH₂ peaks shift to higher frequencies gradually with the increase of the [Li : O] equivalent ratio, its electron surroundings have been deprived by the higher electro-negativity of *N* or/and C=O. It is reasonable to assume that the withdrawing group (*N* or/and C=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⁾

The dipole moment within the PVP chain induced by the LiClO₄ salt based on results from solid state NMR and FTIR spectra is depicted below:



Scheme I

4-3-2 The Interaction Behavior of Li⁺ Cation within PVP-LiClO₄ Complex

Measuring the degree of the complexed IR C=O stretching as function of blend composition is the most frequently employed method to quantify the relative fraction of “free”⁽²⁷⁾ and “complexed” C=O sites within the PVP chain.^(9, 28, 29) As shown in Figure 4-4, the band of C=O stretching is broadened gradually with the increase of the [Li : O] equivalent ratio. The fraction of the “free” and the complexed C=O group of compositions with different [Li : O] equivalent ratios can be measured by decomposing its C=O stretching band into three Gaussian peaks. Those peaks are composed of one “free” C=O absorptions (centered at ~1683 cm⁻¹ with the half width ($w_{1/2}$) of ~ 25 cm⁻¹) and two “complexed” C=O absorptions (centered at ~1657 cm⁻¹, respectively. The band of the “complexed” C=O group is actually composed of two Gaussian peaks; a narrower peak ($w_{1/2} \cong 25$ cm⁻¹) is assigned as primary complex; and the wider peak ($w_{1/2} \cong 65$ cm⁻¹) is assigned as the secondary complex with wider bond distance distribution within complex^(1, 30, 31), as shown in Figure 4-4(g). Table 4-2 and Figure 4-5 summarize the fractional area, width and location of the “free” and two the “complexed” C=O bands for comparison. The relative fraction of the “free” C=O group decreases exponentially with the increase of [Li : O] equivalent ratio. The fractions of the primary and secondary complexes of the Li⁺ ion increase with the increase of the [Li : 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 is evidenced 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; certain “free” $\text{C}=\text{O}$ groups are still present in the composition, even with high LiClO_4 salt concentration. In other words, the Li^+ ion involves equilibria with both ClO_4^- and $\text{C}=\text{O}$ simultaneously in the complex.

4-3-3 The Dissolved Behavior of the ClO_4^- Anion

The change of relative intensity or/and location of a particular band (ClO_4^- stretching) within the complex depends on the concentration of the LiClO_4 salt. Therefore, the interaction involving the ClO_4^- anion can be assigned to such change. Figure 4-6 gives the IR spectra of the neat PVP and various PVP/ LiClO_4 complexes showing the ClO_4^- stretching band ranging from 1200 to 950 cm^{-1} at 140 °C. There are a number of bands originating from the intermolecular interaction of the ClO_4^- anion; each component represents a different environment for the ClO_4^- anion (i.e. “free” anion and ion pair). The major band appears at 1092 cm^{-1} when small amount

of the LiClO_4 salt is added into the PVP resin (Figure 4-6 b). It is reasonable to assign this 1092 cm^{-1} band as the “free” ClO_4^- anti-symmetric stretching mode $\nu_{\text{as}}(\text{Cl—O})$. When the LiClO_4 salt is added incrementally, two new bands appear centered at 1112 cm^{-1} 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^+ --- ClO_4^-)) and the complexation with other position within PVP chain. 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 $[\text{Li} : \text{O}]$ equivalent ratio is greater than 0.281. This can be interpreted as the ClO_4^- anion interacts gradually with the Li^+ and the other position within PVP chain to form the cation---anion interaction with increasing the LiClO_4 salt concentration.

On the other hand, the increasing Li^+ ion concentration also induces the PVP chain to be more negatively charged, which prompts the electrostatic of PVP chain to pull the anion forming cation---anion interaction. The interaction of Li^+ ion is more complicated in concentrated ClO_4^- anion, when the primary complex converts into the secondary complex gradually, similar to the Figure 4-5.

4-3-4 The Formation of PVP-LiClO₄ Salt Complex

Summarizing results from the above solid-state NMR and IR spectra of the PVP—LiClO₄ complex, it is rationalized to assume that the Li⁺ cation is able to form 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 other position within PVP chain at concentrated LiClO₄ salt electrolyte. We can depict such multiple interactions and the related ionic interaction behavior of the PVP—LiClO₄ complex in Figure 4-7. When [Li:O]<0.025, the formation of complex is a simple Li⁺ interaction with C=O by the primary complex bond and the secondary complex bond. It is inferred that the Li⁺ cation can migrate through the 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. When [Li:O]>0.025, there formation of Li⁺---ClO₄⁻ and ClO₄⁻ interaction with other position within PVP chain is added into this system, as shown in Figure 4-7. 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 less negativity. It is reasonable to assume that the migration of the “free” ClO_4^- 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 ClO_4^- and the other position with PVP chain limits the mobility of the ClO_4^- anion in the electrolyte.

Further work is undergoing in order to obtain more relationships between conductivity and ionic interaction within PVP/ LiClO_4 electrolyte.



4-4 Conclusions

The present study describes in details the ionic interaction behavior within the PVP—LiClO₄ polymer electrolyte throughout solid-state NMR and FTIR techniques. The *N* atom 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 compartmented into two types of interactions. The primary and tight complex of Li⁺---C=O 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 0.225, and further increase on [Li : O] ratio results in more interaction with ClO₄⁻ anion. On the other hand, the ClO₄⁻ anion is essentially “free” in very dilute salt concentration. When the salt concentration is increased, the ClO₄⁻ anion begins to interact with Li⁺ cation and the other position with PVP. It implies that the solvated Li⁺ cation ion and the “free” ClO₄⁻ anion are favored in the diluted LiClO₄ salt electrolyte; whereas the solvation—shared ion pair is formed in the concentrated LiClO₄ salt electrolyte.

4-5 References and Notes

1. Scrosati, B. In "Polymer Electrolyte Reviews-I", MacCallum, J. R. and Vincent, C. A., Eds.; Elsevier Applied Science: New York, 1989, Vol 1, 315.
2. Scrosati, B. In "Applications of Electroactive polymers" Scrosati, B., Eds., Chapman and Hall: New York, 1993, p 251
3. Armand, M. B., Solid State Ionics 1983, 9~10, 745
4. Chao, S.; Wrighton, M. S., J. Am. Chem. Soc., 1987, 109, 2197
5. Armand, M. B., Anu, Rev. Mater. Sci. 1986, 16, 245
6. Ratner, M. A.; Shriver, D. F., Chem. Rev. 1988, 88, 109
7. Armand, M. B.; Sanchez, J. Y.; Gauthier, M.; Choquette, Y. In "Polymeric Materials for Lithium Batteries, in The Electrochemistry of Novel Materials"; Liplowski, J.; Ross, P. N., Eds.; VCH: New York, 1994, p65
8. Scrosati, B.; Neat, R. J. In "Applications of Electroactive Polymers"; Scrosati, B., Ed.; Chapman and Hall: London, 1993, p 182
9. Spindler R. and Shriver D. F., Macromolecules, 1986, 19, 347, 350
10. Blecher, L.; Lorenz, D. H.; Lowd, H. L.; Wood, A. S.; Wyman, D. P. In "Handbook of Water-Soluble Gums and Resins"; Davidson, R. L., Ed., McGraw-Hill: New York, 1980
11. Dissanayake M. A. K. L.; Frech R., Macromolecules, 1995, 28, 5312

12. Chintapalli, S.; Frech R., *Macromolecules*, 1996, 29, 3499
13. Dong, J.; Ozaki, Y.; Nakashima, K., *Macromolecules*, 1997, 30, 1111
14. Zhang, X.; Takegoshi, K. Hikichi, K., *Macromolecules*, 1992, 25, 2336
15. Miyoshi, T.; Takegoshi, K. Hikichi, K., *Polymer*, 1996, 37, 1, 11
16. Bovey, F. A. and Mirau, P. A. "NMR of Polymers", Academic Press: New York,
Chap. 4, 1996
17. Painter, P. C.; Graf, J. F.; Coleman M. M.; *Macromolecules*, 1991, 24, 5630
18. Ma, C. C. M.; Wu H. D.; Lee C. T., *J. of Polymer Sci. Part. B-Polymer Physics*,
1998, 36, 10, 1721
19. Goldstein, M., *Macromolecules*, 1985, 18, 277
20. Luo, X., Goh, S. H., Lee, S. Y., *Macromolecules*, 1997, 30, 4934
21. Wu, H. D.; Ma, C. C. M.; Chang, F. C., *Macromolecules*, 1999, 32, 3097
22. March T., Ed., "Advanced Organic Chemistry—Reactions, Mechanism, and
Structure" 3rd, Chap. 1, p 14, John Wiley & Sons: New York, 1985
23. Bovey, F. A. and Mirau, P. A. "NMR of Polymers", Academic Press: New York,
Chap. 1, p .68, 1996
24. Cheung, M. K.; Zheng, S.; Mi, Y.; Guo, Q., *Polymer*, 1998, 39, 25, 6289

25. Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G., "Infrared and Raman Characteristic Frequencies of Organic Molecules; Academic Press: San Diego, 1991
26. Williamson, J. Am. Chem. Soc. 1963, 85, 516; Laszlo and Schkeyer, J. Am. Chem. Soc. 1963, 85, 2709
27. Here "free" identified as no coordination with Lithium ion.
28. Coleman, M. M.; Graf, J. F.; and Painter, P. C., "Specific Interactions and the Miscibility of Polymer Blends—Practical Guides for Prediction and Designing Miscible Polymer Mixtures", Technomic, Publishing Co. Inc.: Landcaster Basel, Pennsylvania, USA, 1991
29. Ma, C. C. M.; Wu, H. D.; and Tseng, H. T., *Macromolecules*, 1997, 30, 5443
30. Yang, T.P.; Peace, E.M.; Kwei, T.K., *Macromolecules*, 1989, 22, 1813
31. Lee, J.Y.; Painter, P.C.; Coleman, M.M., *Macromolecules*, 1988, 21, 954

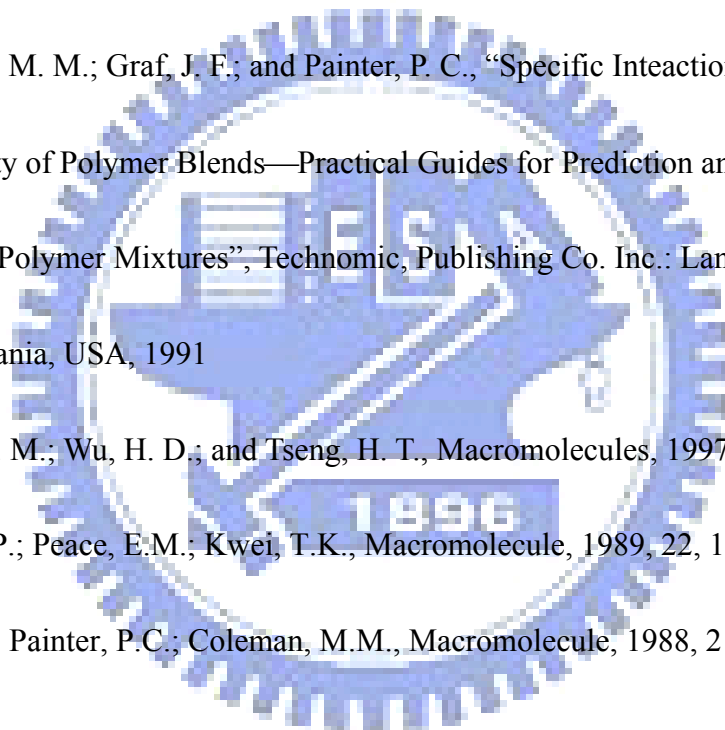


Table 4-1 Observed Frequencies and Assignments of Infrared Bands of PVP-LiClO₄ Complex, the [Li : O] = 0.056, in a Cast Film at 140 °C.⁽²⁵⁾

PVP-LiClO ₄ complex (cm ⁻¹)	Assignments (.)
2949, 2918, 2881	CH ₂ or CH stretching
~1680 (strong and board)	C=O stretching
1314, 1283, 1229	CH ₂ deformation
1166	C—CH ₂ stretching
1093	Cl—O stretching (free ClO ₄ ⁻)
1111, 1068 (shoulder of 1093)	Cl—O (ion pair)

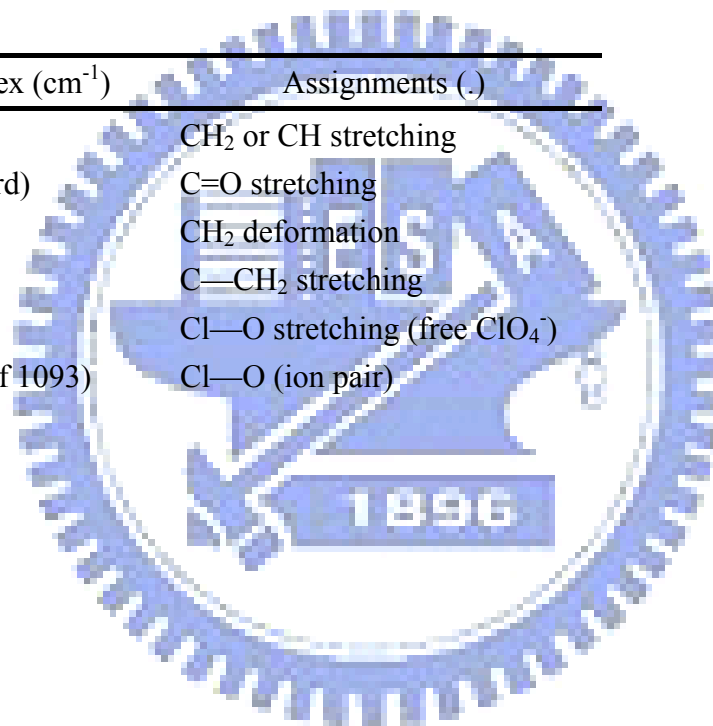


Table 4-2 Curve-Fitting Data of Infrared Spectra of C=O Stretching Region of PVP/LiClO₄ Complexes with Various Compositions at 140

°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

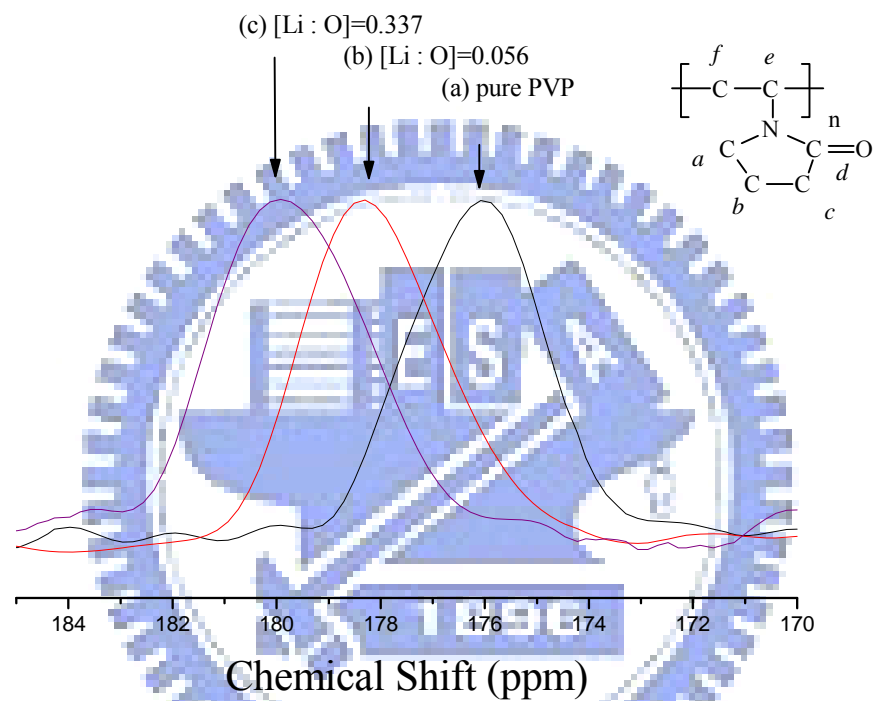


Figure 4-1 (a) Scaled ^{13}C CP/MAS NMR spectra region of LiClO_4 -PVP complex ranging from 185 to 170 ppm, the $[\text{Li} : \text{O}]$ equivalent ratio (a) = 0; (b) = 0.056; (c) = 0.337.

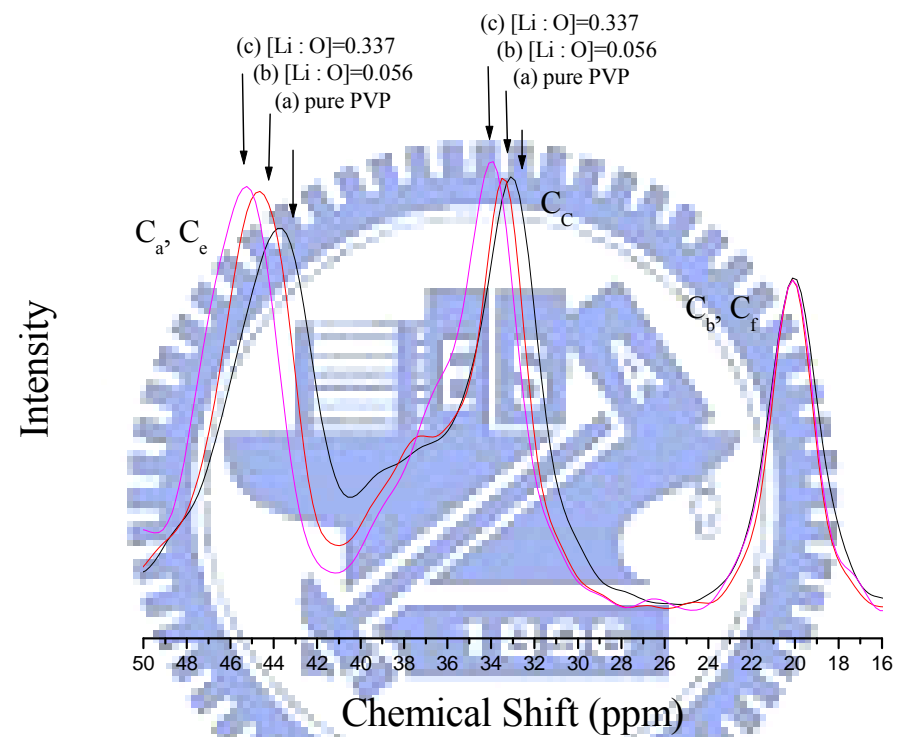


Figure 4-1 (b) Scaled ^{13}C CP/MAS NMR spectra region of LiClO_4 -PVP complex ranging from 50 to 16 ppm, the [Li : O] equivalent ratio

(a) = 0; (b) = 0.056; (c) = 0.337.

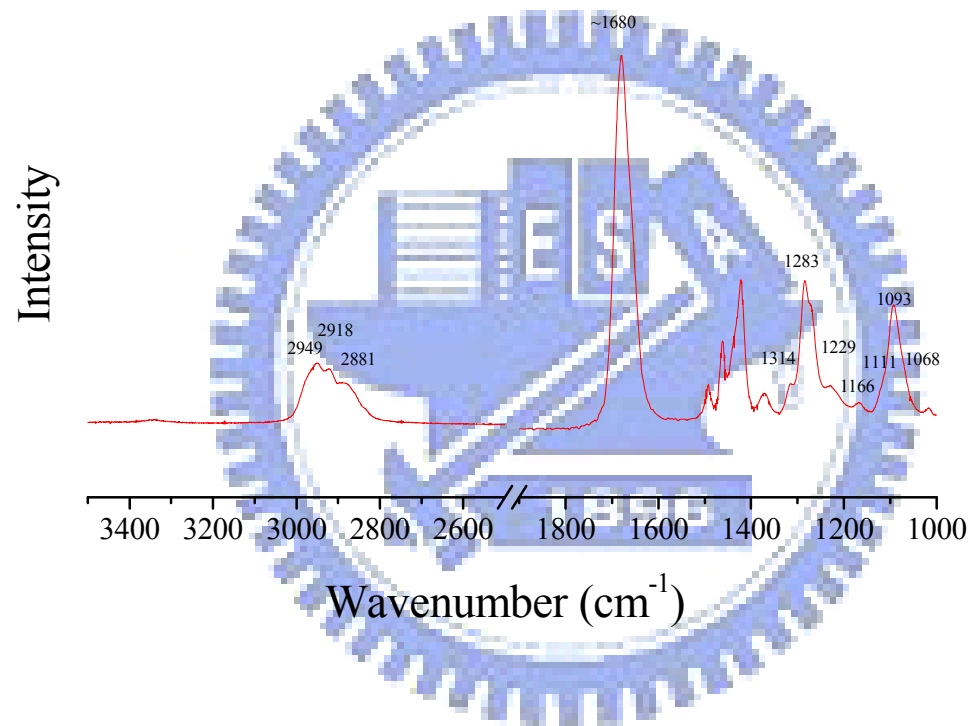


Figure 4-2 Infrared spectrum of PVP/LiClO₄ ([Li : O] equivalent ratio = 0.056) complex in the spectral region between 3500 and 1000 cm⁻¹ at 140 °C.

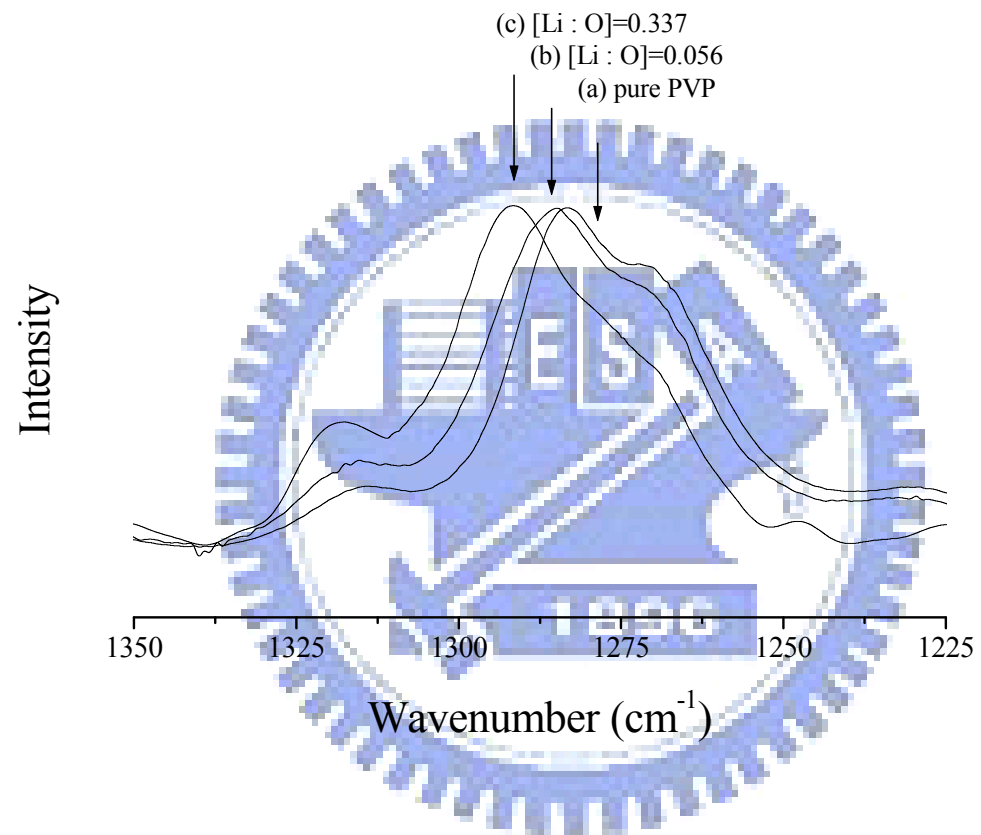


Figure 4-3 Mid-Infrared spectra region from 1350 to 1225 cm⁻¹ with various LiClO₄ salt concentration at 140 °C, the [Li : O] equivalent ratio (a) = 0; (b) = 0.056; (c) = 0.337.

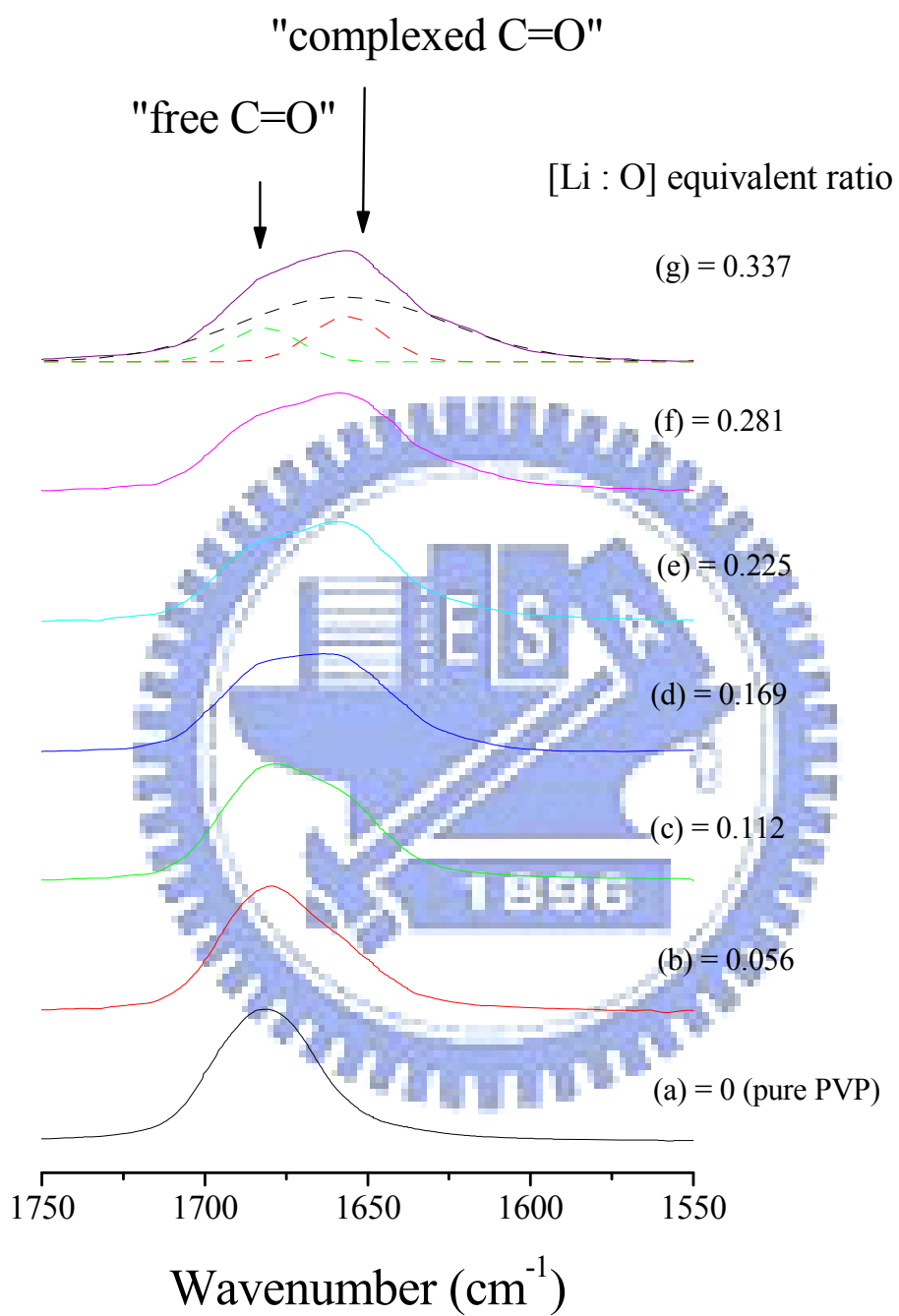


Figure 4-4 Infrared spectra of C=O stretching region of PVP/LiClO₄ complex at 140 °C, the [Li : O] equivalent ratio (a) = 0; (b) = 0.056; (c) = 0.112; (d) = 0.169; (e) = 0.225; (f) = 0.281; (g) = 0.337.

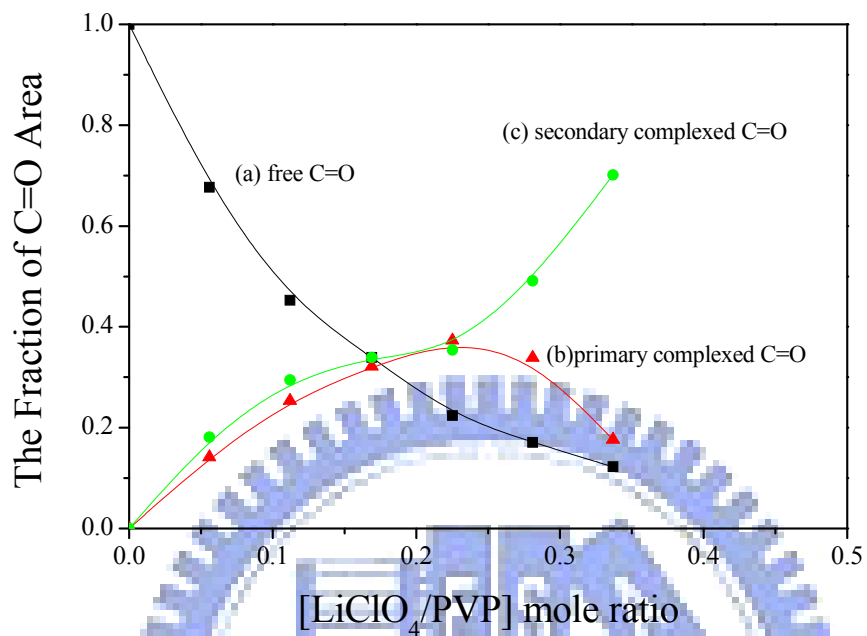


Fig. 4-5. The dependence of “free” and “complexed” C=O band on LiClO₄ salt concentration: (a) “free”; (b) the “primary complexed”; and (c) the “secondary complexed” C=O band.

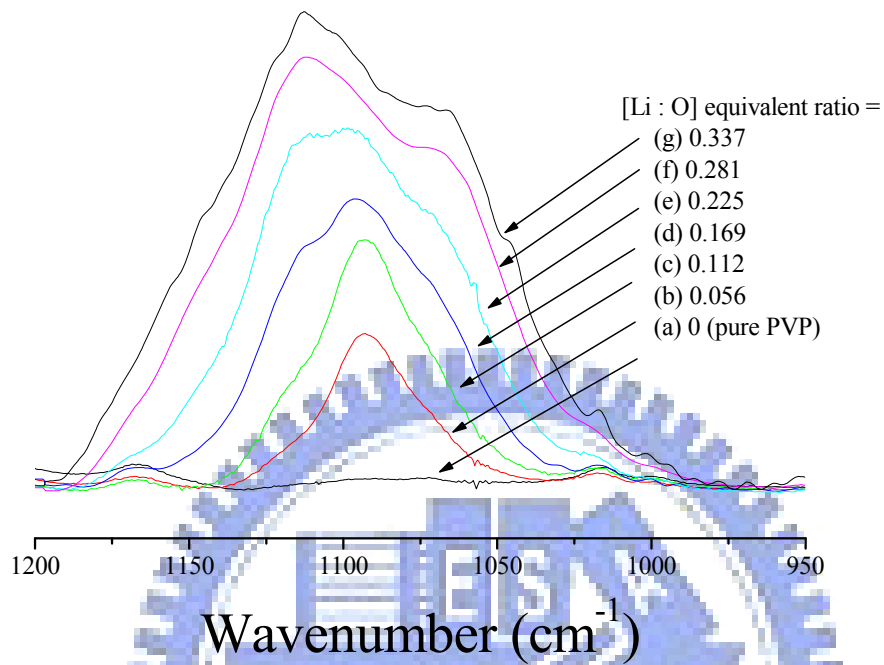


Figure 4-6 Mid-Infrared spectra region from 1200 to 950 cm^{-1} PVP/ LiClO_4 complex with various LiClO_4 salt concentration at 140 $^\circ\text{C}$, the [Li : O] equivalent ratio (a) = 0; (b) = 0.056; (c) = 0.112; (d) = 0.169; (e) = 0.225; (f) = 0.281; (g) = 0.337

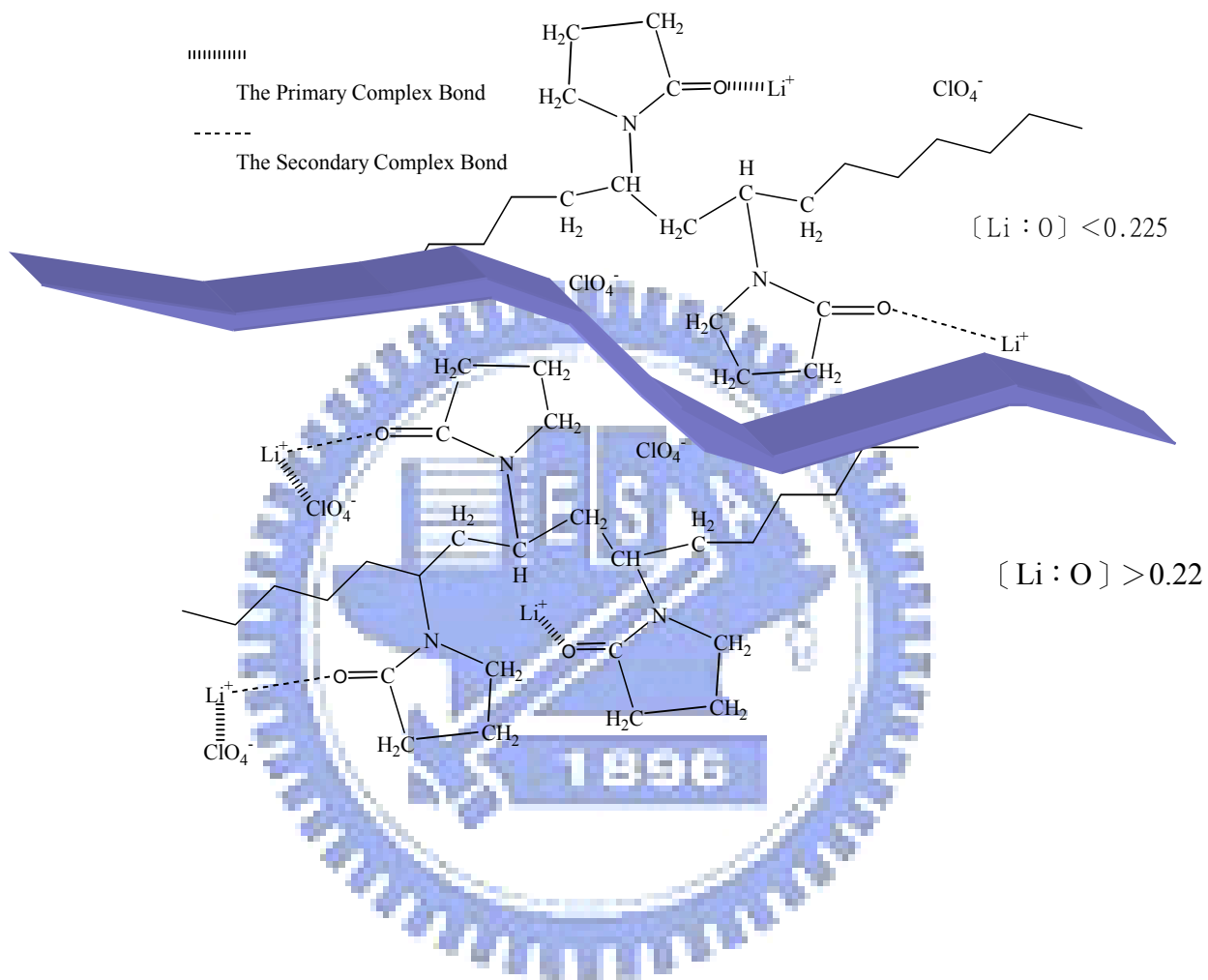


Figure 4-7 Schematic drawing of three types of the ionic association of polymer electrolytes—PVP/LiClO₄ complex.