Chapter V Determination of the Interaction within Polyester-Based Solid Polymer Electrolyte Using FTIR Spectroscopy

5-1 Introduction

It has been a great concern about the energy problem that focuses on the highly efficient energy conversion and stable systems. The conventional organic sol gel electrolyte is expected to be replaced by solid polymer electrolytes (SPE) in the near future due to its dimensional stability, processability, flexibility, electrochemistry stability, safety, and long life. Especially, the SPE is more suitable for the large-scale batteries.⁽¹⁻³⁾ The interaction behavior of alkaline ion within SPE will determine their function and performance. However, the low Li⁺ ion conductivity of SPE is a principal drawback at ambient temperature. It is important to prompt the performance via understanding of the ionic interaction behavior within the polymeric electrolyte.

The application of Fourier Transform Infrared (FTIR) spectroscopic techniques to assess polymer interaction has been conducted for many years. FTIR spectroscopy has been proven as a powerful tool in characterizing the detailed structure and interaction of polymer solids with nondestructive and fast measurement. ^(4~12) The changes of interaction behavior can be characterized through the identification of the IR spectral features in intensity, bandwidth, and position. The success of IR method requires that the amount of sample in the infrared bean must remain constant and the extent of transformation from the "free" to "Li⁺ bonded" absorption is large to minimize error.

In this study, FTIR is used to identify and quantify the interaction between Li^+ and C=O in different linear solid polymer electrolytes within various $LiClO_4$ concentrations. There are two goals pursued: (1) calculating the absorptivity coefficient of "free/Li⁺ bonded C=O" from FTIR spectra; and (2) more important, calculating the interaction by varying content of lithium salt in different polymer electrolytes and sorts out their interaction behavior in quantitative manner.



5-2 Experimental Section

5-2-1 Materials

Poly(ethylene adipate) (PEA) with Mw of 10,000, m.p. = $58 \sim 62^{\circ}$ C



were purchased from Aldrich and used without purification. The lithium perchlorate (LiClO₄ \cdot 3H₂O) salt from Acros was treated in 190°C for 24 hrs in vacuum to eliminate crystal water and then stored under vacuum condition. Acetone, obtained from Aldrich, was refluxed at room temperature under N₂ atmosphere before used.

5-2-2 Beer-Lambert's Law

A single optical path was to study the interaction between Polyester and LiClO₄. All samples in the absorption range would obey the Beer-Lambert's law:

 $| I/cl | \lim_{C \to 0} = \varepsilon$ (A1)

Where I is the internsity of absorption; ε is absorptive coefficient; l is thickness of

sample; and *c* is the concentration of LiClO₄ in Polyester.

$$f_m^{CO} = I/\varepsilon cl \tag{A2}$$

 f_m^{CO} is the fraction of polyester containing "free" carbonyl group in Polyester/LiClO₄ blend.

5-2-3 Sample Preparation and Infrared Spectroscopy

Complexes of polyester – LiClO₄ were prepared by dissolving desired quantity of the polymer and anhydrous LiClO₄ in anhydrous acetone. After continuous stirring for 1 hr at room temperature, the solution was dropped on a KBr disk then placed the disk into the IR demountable cell which was pre-heated at 80°C to form a thin film. The measured temperature was controlled higher than T_m of the polymer to avoid polymer crystallization hindering the Li⁺ dissolution. ^(12~18) All infrared spectra were obtained at 32 scans with a resolution of 0.1 cm^{-1} on a Nicolet AVATAR 320 FTIR Spectrometer.

The film used in this study was sufficiently thin to obey the Beer–Lambert's law. IR spectra recorded at elevated temperatures were obtained by using a cell mounted inside the temperature-controlled compartment of the spectrometer. Temperature was controlled within ±0.1°C.

5-3 Results and Discussions

5-3-1 Infrared Spectra of the C=O Absorption Ranging from 1800 to 1650 cm⁻¹

The C=O absorption ranging from 1800 to 1650 cm⁻¹ is highly sensitive to interaction behavior, such as hydrogen bonding. The absorption of C=O group in IR spectroscopy can be separated into two bands — "free" and "hydrogen-bonded" when the C=O group interacting with other proton donating groups such as –NH, –OH,... etc. The newborn band corresponding to the absorption of "hydrogen-bonded" C=O appears at relatively lower wavenumber position from that of the "free" C=O in FTIR spectroscopy. The behavior of "Li⁺ bonded C=O" absorption formation is similar to the "hydrogen-bonded" C=O absorption formation. Figure 5-1 exhibits infrared spectra ranging from 1800~1650 cm⁻¹ at 80 °C of various solid polymer electrolytes. Figure 5-1a shows one characteristic infrared band of the pure PEA at 1730 cm⁻¹,

corresponding to the "free" C=O absorption. Figure 5-1b shows a newborn band appearing at 1705 cm⁻¹ of the PEA blended with 5 wt% LiClO₄, corresponding to the "Li⁺ bonded C=O". Figures 5-1c, 5-1d and 5-1e show the FTIR spectra ranging from $1800 \sim 1650 \text{ cm}^{-1}$ of PBA, PHA, and PCL polymer electrolytes blended with 5 wt% LiClO₄, respectively. Essentially, all show a new "Li⁺ bonded" C=O absorption band, implying that the lithium salt (LiClO₄) is soluble in the these polymer electrolyte concluded from the existence of interaction between C=O and Li⁺ ion. The characteristic peak of the "free" C=O group is at 1730 cm⁻¹, while the characteristic peak of the "Li⁺ bonded" C=O is located at ~1705 cm⁻¹ (shifted from 1730 cm⁻¹), respectively.

5-3-2 Quantitative Measurement of Interaction Behavior on Polymer

Electrolyte

The characteristic "Li⁺ bonded C=O becomes more evident with the increase of the LiClO₄ content in the PEA polymer electrolyte. Figure 5-2 shows the FTIR spectra at 80 °C ranging from 1800 to 1650 cm⁻¹ of LiClO₄/PEA blends with 1, 2, and 3 wt% LiClO₄ contents. By adding the LiClO₄, portion of the C=O group is able to interact with Li⁺ ion to form the "Li⁺ bonded" C=O. Therefore, the "Li⁺ bonded" C=O group of the polymer electrolyte is increased, while the "free" C=O group is decreased as would be expected. Figure 5-3 shows the FTIR of spectra PEA/LiClO₄, PBA/ LiClO₄, PHA/LiClO₄ and PCL/LiClO₄ blends by increasing LiClO₄ content with 1, 3, and 5wt%. The C=O stretching band is broadened gradually with the increase of the LiClO₄ concentration. It is found that the 1705 cm⁻¹ peak intensity (corresponding to "Li⁺ bonded" C=O) increases at the expense of the 1730 cm⁻¹ peak intensities (corresponding to "free" C=O) in these four series polymer electrolyte systems observed from Figure 5-2 and Figure 5-3.

Curving fitting ranging between 1800 and 1650 cm⁻¹ shows two Gaussian peaks that provides an adequate fit for the LiClO₄/PEA blend as dash-lines of Figure 5-2c. An unique method can be used to determine the absorptivity coefficient of respective absorbances of "free"/"Li⁺ bonded" C=O. This approach is based on the fact that certain fraction of the 1730 cm⁻¹ "free" peak has transformed into the 1705 cm⁻¹ peak after adding LiClO₄ into PEA, PBA, PHA, and PCL polymer electrolytes, respectively. Hence the following equation 1 can used to determine these "free/Li⁺ bonded" C=O absorptivity coefficient. $\alpha = \frac{A_{1730} \times M_2}{A_{1705} \times (M_1 - M_2)}$Eq.(5-1)

where α is the absorptivity coefficient of the "free"/"Li⁺ bonded" C=O group. A_{1730} and A_{1705} represents area fractions of "free" C=O and "Li⁺ bonded" C=O stretching absorption areas after adding lithium salt (LiClO₄) into the polymer electrolyte, respectively. M_1 and M_2 represents the equivalent fraction of C=O and Li⁺ in polymer electrolyte blend, respectively.

We would like to find the absorptivity coefficient of "free/Li⁺ bonded" C=O

absorbance from low Li⁺ concentration region for further study. It is reasonable to assume that only simple interaction between Li⁺ ion and C=O group is presented and obey the Beer's law in low Li⁺ concentration blend. Curve fitting of PEA, PBA, PHA, and PCL systems were performed in low Li⁺ concentrations of 1, 2, and 3 wt%, respectively; and results of are given in Table 5-1. The "free/Li⁺ bonded" C=O absorptivity coefficient obtained "free" and "Li⁺ bonded" C=O equivalent fraction area were calculated from Eq. 5-1. The absorptivity coefficients of PEA, PBA, PHA, and PCL polymer electrolytes are 0.144 \pm 0.002, 0.145 \pm 0.008, 0.142 \pm 0.005 and 0.143 \pm 0.002, respectively. The average value of 0.144 \pm 0.005 is obtained. It implies that the absorptive sensitivity of the "Li⁺ bonded" C=O at 1705 cm⁻¹ is significantly higher than that of the "free" C=O at 1730 cm⁻¹.

The value of absorptivity coefficients (0.144) found in the Polyester/Li⁺ blend system is far less than that of (~0.65) in Polyester/H⁺ blend system that Painter and Coleman mentioned.⁽⁹⁾ It can be concluded that the stretching absorption of Li⁺ bonded C=O in IR spectroscopy is more sensitivity than that of Hydrogen bonded C=O.

The equivalent fraction of "free" C=O group in the solid polymer electrolyte can be obtained from the following equation:

$$f = \frac{A_{1730} \times \alpha}{A_{1730} \times \alpha + A_{1705}} \times 100\% \qquad \text{Eq. (5-2)}$$

where f represents the equivalent fraction of the "free" C=O in the solid polymer electrolyte and "1-f" is the equivalent fraction of the "Li⁺ bonded" C=O. A_{1730} and A_{1705} represents area fractions of "free" C=O and "Li⁺ bonded" C=O stretching absorption areas after adding lithium salt (LiClO₄) into the polymer electrolyte, respectively. A known infrared absorptivity coefficient is necessary in order to determine the true fractions of "free" and "Li⁺ bonded" C=O of any solid polymer electrolyte. Therefore, we can further study the Li⁺ ion interaction behavior within solid polymer electrolyte.

5-3-3 The Interaction between Li⁺ Ion and C=O of Polymer Electrolytes

Figure 5-4 shows FTIR spectra of PEA/LiClO₄, PBA/LiClO₄, PHA/LiClO₄ and PCL/LiClO₄ blends where the LiClO₄ content is increased from 10wt% to 45wt%. Two peaks corresponding to "free" and "Li⁺ bonded" C=O are clearly shown until the LiClO₄ content is greater than 35 wt%. The peak intensity of 1705 cm⁻¹ is increased continuously with the increase of the LiClO₄ concentration. The "free" C=O band of 1730 cm⁻¹ is nearly replaced by the 1705 cm⁻¹ band when the LiClO₄ concentration is more than 35 wt% in all four series of polymer electrolyte systems,

as shown in Figure 5-4. Table 5-2 summarizes curve fitting result of absorbance area fractions of "free" and "Li⁺ bonded" C=O of PEA/LiClO₄, PBA/LiClO₄,

PHA/LiClO₄, and PCL/LiClO₄ while the LiClO₄ ranging from 5 to 45 wt%. Table 5-3 summarizes the "Li⁺ bonded" C=O group equivalent fraction vs. LiClO₄ weight fraction where the equivalent fraction obtained from Table 5-1, 5-2 and Eq 5-2. Figure 5-5 shows the relation of "Li bonded" C=O equivalent fraction and LiClO₄ weight content of these four series polymer electrolyte blend systems, based on the result of Table 5-3. As would be expected, the "Li⁺ bonded" C=O equivalent fraction increased with increasing LiClO₄ content throughout whole range of these four series polymer electrolytes. It implies that interaction between the Li⁺ ion and C=O group within polymer electrolyte increases with the increase of the LiClO₄ content. The equivalent fraction of the "Li⁺ bonded" C=O closes to 80% when the LiClO₄ content is 10 wt% for all four series. There is a limit value of 95 % "Li⁺ bonded" C=O equivalent fraction, as shown in Figure 5-5. It implies that the efficiency of the Li⁺ ion interacting with C=O in lower concentration is greater than that in higher concentration. Furthermore, it is found apparently that the order of equivalent fraction of "Li⁺ bonded" C=O by the specific LiClO₄ weight contents is: PHA >PCL> PBA > PEA, as shown in Figure 5-5.

Table 5-4 summarizes that the Li^+ equivalent fraction (M₂) Li^+ vs. "Li⁺ bonded" C=O equivalent fraction where the Li^+ equivalent fraction (M₂) is calculated from weight percent in Table 5-3.

Figure 5-6 shows the relation between "Li⁺ bonded" C=O equivalent fraction and LiClO₄ equivalent fraction for these four series polymer electrolyte blend systems, based on the results of Table 5-4. These four curves are essentially formatted a master curve as shown in Figure 5-6. It implies that the Li⁺ ion interacting with C=O group depends only on the concentration of C=O group in the polymer electrolyte system, independent of the molecular structure. The molecular structures of the four polyesters those with no side chain are not greatly different enough to provide the steric effect on Li⁺ ion coordination. Therefore, it is preferably to select a polymer with high C=O group density to prompt the higher "dissolve" efficiency of the LiClO₄ within the polymer electrolyte blend system.

Converting data from Figure 5-6 into semi-Log plot is shown in Figure 5-7. It is found that there is a simple semi-Log relation between the "Li⁺ bonded" C=O equivalent fraction and the LiClO₄ equivalent fraction. The turning point occurs at LiClO₄ equivalent fraction around 0.28 and the "Li⁺ bonded" C=O equivalent fraction is around 0.95. The saturation behavior is appeared when LiClO₄ equivalent fraction is more than 0.28. It means that the coordination behavior of Li^+ with C=O group would not be hindered until the equivalent is more than 0.28.

5-4 Conclusions

This study provides a method to study the interaction between Li⁺ ion and C=O group within polyester electrolyte with sufficient accuracy for the first time. The band corresponding to "Li⁺ bonded" C=O group (1705 cm⁻¹) is shifted from the band of "free" C=O group (1730 em⁻¹) in FTIR spectroscopy. The absorptivity coefficient of respective absorbances of "free/Li⁺ bonded" C=O is found to be 0.144 \pm 0.005. From the absorptivity coefficient, it is found that the sensitivity of "Li⁺ bonded" C=O group band in FTIR spectroscopy is significantly higher than that of the "free" C=O group.

The Li⁺ ion shows a strong interaction with C=O group within a polymer electrolyte, a limit value of 95% "Li⁺ bonded" C=O group is approached when the Li⁺ equivalent fraction is around 0.28. The molecular structure of polymer does not affect the interaction between Li⁺ ion and C=O group within a polymer electrolyte blend system. Selection of a polymer with high C=O density is able to prompt the high "dissolve" efficiency of the LiClO₄ within polymer electrolyte blend system.

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Table 5-1 : Curve fitting and	calculation results of FTI	R spectra of PEA	, PBA, PHA,
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Sample	"]	Free" C=0)	"Li ⁺	=O			Abo	
(weight	A ₁₇₃₀	Freq.	Width	A ₁₇₀₅	Freq.	Width	M_{I}	M_2	ADS.
fraction)	(Fraction)	(cm^{-1})	(cm^{-1})	(Fraction)	(cm^{-1})	(cm^{-1})			u
PEA 1wt%	0.945	1738	25	0.055	1705	15	0.992	0.008	0.142
PEA 2wt%	0.897	1738	26	0.103	1706	20	0.984	0.016	0.146
PEA 3wt%	0.848	1738	24	0.152	1708	22	0.976	0.024	0.143
Ave.						2.		0.1	44± 0.002
PBA 1wt%	0.938	1733	32	0.062	1700	20	0.991	0.009	0.145
PBA 2wt%	0.873	1733	32	0.127	1700	- 25	0.981	0.019	0.135
PBA 3wt%	0.837	1733	33	0.163	1696	22	0.972	0.028	0.155
Ave.	- 33	1		3 - 1 - 2	1.8			0.14	5 ± 0.008
PHA 1wt%	0.928	1734	24	0.072	1703	18	0.989	0.011	0.141
PHA 2wt%	0.869	1733	22	0.131	1704	19	0.979	0.021	0.148
PHA 3wt%	0.798	1733	21	0.202	1705	22	0.968	0.032	0.135
Ave.	1	λ.	10			- //		0.14	2 ± 0.005
PCL 1wt%	0.931	1733	23	0.069	1703	16	0.990	0.010	0.143
PCL 2wt%	0.908	1734	24	0.092	1703	15	0.986	0.014	0.141
PCL 3wt%	0.813	1733	24	0.187	1701	19	0.969	0.031	0.145
Ave.		19	100	Concession of the	100	×*		0.14	3 ± 0.002

and PCL in low Li^+ concentration of 1, 2 and 3 wt%.

 A_{1730} represents the area fraction of "free" C=O absorption.

 A_{1705} represents the area fraction of "Li⁺ bonded" C=O absorption.

 M_1 represents the equivalent fraction of C=O.

 M_2 represents the equivalent fraction of Li⁺.

 α represents the absorptivity coefficient of the "free/Li⁺ bonded" C=O group.

		Free C=C)	Li ⁺ bonded C=O			
Sample	A_{1730} (fraction)	Freq.(cm ⁻¹)	Width(cm ⁻¹)	A_{1705} (fraction)	Freq.(cm ⁻¹)	Width(cm ⁻¹)	
PEA 5wt%	0.811	1739	24	0.189	1709	21	
PEA 10wt%	0.668	1739	25	0.332	1708	25	
PEA 15wt%	0.573	1738	23	0.427	1708	25	
PEA 20wt%	0.469	1739	23	0.531	1709	28	
PEA 25wt%	0.377	1738	21	0.623	1709	27	
PEA 30wt%	0.282	1738	20	0.718	1709	30	
PEA 35wt%	0.236	1737	20	0.764	1710	31	
PEA 40wt%	0.187	1734	18	0.813	1710	27	
PEA 45wt%	0.205	1732	19	0.795	1710	26	
PBA 5wt%	0.779	1734	31	0.221	1701	22	
PBA 10wt%	0.643	1734	27	0.357	1700	26	
PBA 15wt%	0.526	1735	29	0.474	1700	31	
PBA 20wt%	0.414	1736	28	0.586	1702	34	
PBA 25wt%	0.317	1733	21	0.683	1704	29	
PBA 30wt%	0.254	1732	21	0.746	1705	30	
PBA 35wt%	0.202	1731	19	0.798	1705	28	
PBA 40wt%	0.165	1730	19	0.835	1706	29	
PBA 45wt%	0.132	1730	18	0.868	1706	30	
PHA 5wt%	0.756	1734	18	0.244	1707	22	
PHA 10wt%	0.601	1735	27	0.399	1703	25	
PHA 15wt%	0.477	1734	20	0.523	1705	26	
PHA 20wt%	0.351	1734	19	0.649	1705	28	
PHA 25wt%	0.292	1732	18	0.708	1705	25	
PHA 30wt%	0.253	1729	18	0.747	1705	25	
PHA 35wt%	0.204	1732	18	0.796	1706	29	
PHA 40wt%	0.153	1727	17	0.847	1706	25	
PHA 45wt%	0.138	1725	18	0.862	1705	26	
PCL 5wt%	0.775	1733	22	0.225	1703	20	
PCL 10wt%	0.595	1734	26	0.405	1702	25	
PCL 15wt%	0.486	1732	21	0.514	1702	25	
PCL 20wt%	0.364	1733	18	0.636	1704	27	
PCL 30wt%	0.197	1732	17	0.803	1704	30	
PCL 35wt%	0.160	1730	16	0.840	1705	30	
PCL 40wt%	0.180	1731	17	0.820	1705	29	
PCL 45wt%	0.169	1731	16	0.831	1705	29	

Table 5-2 : Curve fitting of FTIR spectra of PEA, PBA, PHA, and PCL blended with LiClO₄ from 5 wt% to 45 wt%.

 A_{1730} represents the area fraction of "free" C=O absorption.

 A_{1705} represents the area fraction of "Li⁺ bonded" C=O absorption.

Table 5-3 : summarizes that LiClO₄ weight fraction vs. the equivalent fraction of

PEA		PBA		PHA		PCL	
(1-f)×100%	Wt%	(1-f)×100%	Wt%	(1-f)×100%	Wt%	(1-f)×100%	Wt%
28.71	1	31.49	1	33.92	1	35.68	1
43.68	2	50.19	2	51.25	2	41.41	2
55.47	3	57.37	3	63.77	3	63.59	3
58.06	4	59.99	4	62.31	4	66.77	4
63.08	5	68.48	5	69.11	5	65.45	5
77.59	10	78.38	10	82.16	10	81.89	10
84.66	15	85.92	15	84.78	15	88.38	15
88.99	20	90.71	20	92.07	20	92.12	20
92.37	25	93.69	25	94.12	25	94.36	25
94.56	30	95.44	30	95.80	30	96.34	30
96.25	35	96.33	35	96.89	35	97.06	35
96.81	40	97.04	40	97.47	40	97.34	40
96.49	45	97.69	45	97.61	45	96.94	45

"Telument

"Li⁺ bonded" C=O group results from Table 5-2 and Table 5-3 and Eq 5-2.

 $(1-f) \times 100\%$ represents the "Li⁺ bonded" C=O group equivalent fraction

Table 5-4 summarizes the Li^+ equivalent fraction (M₂) Li^+ vs. " Li^+ bonded" C=O

PEA		PBA		РНА		PCL	
(1-f)×100%	M_2	(1-f)×100%	M_2	(1-f)×100%	M_2	(1-f)×100%	M_2
28.71	0.008	31.49	0.009	33.92	0.011	35.68	0.01
43.68	0.016	50.19	0.019	51.25	0.021	41.41	0.014
55.47	0.024	57.37	0.028	63.77	0.032	63.59	0.031
58.06	0.033	59.99	0.038	62.31	0.043	66.77	0.043
63.08	0.041	68.48	0.047	69.11	0.054	65.45	0.053
77.59	0.082	78.38	0.095	82.16	0.107	81.89	0.107
84.66	0.125	85.92	0.142	84.78	0.159	88.38	0.159
88.99	0.168	90.71	0.19	92.07	0.212	92.12	0.212
92.37	0.212	93.69	0.239	94.12	0.263	94.36	0.263
94.56	0.258	95.44	0.287	95.80	0.315	96.34	0.315
96.25	0.303	96.33	0.336	96.89	0.366	97.06	0.366
96.81	0.35	97.04	0.386	-97.47	0.417	97.34	0.417
96.49	0.398	97.69	0.435	97.61	0.468	96.94	0.468

group equivalent fraction

(1-f)×100% represents the "Li⁺ bonded" C=O group equivalent fraction M_2 represent the equivalent fraction of Li⁺



Figure 5-1 : The characteristic infrared band of (a) pure PEA; and LiClO₄ 5wt% blend with (b) PEA; (c) PBA; (d) PHA; (e) PCL ranging from 1800~1650 cm⁻¹ at 80 °C.



Figure 5-2 : FTIR spectra of PEA/LiClO₄ blend ranging from 1800 to 1650 cm⁻¹
with various LiClO₄ content. (a) 1 wt%; (b) 2 wt%; (c) 3 wt% at 80 °C.
(Dash line: result of Figure 5-2c curve fitting ranging from 1800 to 1650 cm⁻¹)



Figure 5-3 : FTIR of spectra of (a) PEA/LiClO₄ (b) PBA/LiClO₄ (c) PHA/ LiClO₄ (d)

PCL/LiClO₄ ranging from 1800 to 1650 cm⁻¹ with increasing LiClO₄

content up to 5 wt%(1%, 3% and 5%) at 80 °C.



Figure 5-4 FTIR spectra of (a) PEA/LiClO₄, (b) PBA/ LiClO₄, (c) PHA/LiClO₄ and

(d) PCL/LiClO₄ blends ranging from 1800 to 1650 cm⁻¹ with the increase of LiClO₄ content ranging from 10 wt% to 45 wt% at 80 $^{\circ}$ C.





fraction for four series polymer electrolyte blends. (E: PEA; •: PBA;

▲: PHA; ▼: PCL)

