

Determination of the interaction using FTIR within the composite gel polymer electrolyte

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ABSTRACT

In the previous research, the gel polymer electrolyte (GPE) which consisted of poly(methyl methacrylate) (PMMA) matrix, propylene carbonate (PC), LiClO₄ and OREC (Rectorite modified with dodecyl benzyl dimethyl ammonium chloride), achieved satisfactory properties. In the paper, the interaction between components was quantitatively determined. Characterization of interaction of C=O in PC and PMMA with Li⁺ and OH group on OREC surface has been thoroughly examined using FTIR, respectively. The quantitative analysis of FTIR shows that the absorptivity coefficient *a* of PMMA/LiClO₄, PC/LiClO₄, PC/OREC and PMMA/OREC is 0.902, 0.113, 0.430 and 0.753, respectively, which means that the Li⁺ or OH bonded C=O is more sensitive than the free C=O in FTIR spectra. The limit value of bonded C=O equivalent fraction of PMMA/LiClO₄, PC/LiClO₄, PC/OREC and PMMA/OREC is 17%, 94%, 57% and 20%, respectively, which implies that all the interaction within the components is reversible and the intensity of interaction is ordered as PC/LiClO₄, PC/OREC, PMMA/OREC and PMMA/LiClO₄.

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1. Introduction

Gel polymer electrolytes (GPEs) are reported to be suitable for electrochemical devices since their transport properties are quite exceptional and they have an ionic conductivity of the order of 10⁻³ S/cm, an electrochemical stability window exceeding 4.5 V and lithium ion transference number averaging 0.9 [1–13]. It is well recognized that the addition of inorganic fillers such as ceramic powder, alumina or silica into GPEs based on the polyether matrix will enhance not only the ionic conductivity but also the dimensional mechanical stability [14–21].

In previous research [22], we studied on the GPE consisted of PMMA (poly(methyl methacrylate)) matrix, PC (propylene carbonate) as a plasticizer and LiClO₄ as lithium ion producer and OREC (clay of rectorite modified with dodecyl benzyl dimethyl ammonium chloride) as filler. It was found that the maximum ionic conductivity was in the order of 10⁻³ S/cm, and OREC dispersed well in GPEs when its content was appropriate, which greatly increased ionic transport and solvent maintenance. In the GPE, there were four components which produced much complicated interaction. The existed interaction has been qualitatively determined [23], but for the further understand, the quantitative analysis of interaction was more important and necessary.

The application of FTIR (fourier transform infrared) spectroscopic techniques to quantitatively assess polymer interaction has been

conducted for many years. FTIR is a particularly suitable technique for investigating the specific intermolecular interaction [24–27]. The changes of interaction behavior can be characterized through the identification of the IR spectral features in intensity, bandwidth and position with which it allows to quantitatively study the interaction. Digar et al. [28] quantitatively studied the interaction of Li⁺ with segments of PUA with FTIR, and found that the deconvoluted FTIR spectra showed three kinds of C=O in PUA/LiClO₄ system. In addition, with the addition of lithium salt, three peaks were shifted to lower wave number, and the area of each peak also changed. Wu and Chang [27] also used FTIR to quantitatively study the interaction within polyester/LiClO₄ system, which clearly clarify the Li⁺ status in the polymer electrolyte. But until now, there have not been reports about FTIR quantitative research of GPE. In GPE systems, there are many components, so it is more necessary to quantitatively study the interaction between components.

In present research, we will focus on the quantitative determination of interaction between the components of PMMA, OREC, PC and LiClO₄ with FTIR spectrum, which will help us to understand the micro-interaction of GPEs modified with OREC.

2. Experimental

2.1. Material

The matrix of poly(methyl methacrylate) (PMMA) with $M_w = 6.5 \times 10^5$ g/mol was supplied from Xi'an Organic Glass

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Factory. The plasticizer was propylene carbonate (PC) from Shanghai Reagent Co. and acetone from Xi'an Chemical Reagent Co. was used as solvent. The PC and acetone were stored over molecular sieves (4 Å) in order to remove residual water traces, respectively. LiClO₄ was obtained from Xi'an Chemical Reagent Co. Sodium rectonite (Na-REC) was refined from clay minerals in Wuhan, China. The cation exchange capacity (CEC) is 45 meq/100 g, and the *d*-space is 2.22 nm. Dodecyl benzyl dimethyl ammonium chloride was supplied by Xi'an Chemistry Glass Station, China.

2.2. The preparation of OREC

Na-REC was screened with a sieve of 300-mesh in order to remove impurities. Certain amount of screened clay was suspended in deionized water in glass vessel using a glass-rod. Surfactant of dodecyl benzyl dimethyl ammonium chloride was dissolved in certain amount of water, and then added into the suspended clay-water solution, stirring vigorously for several minutes at room temperature. The mixture was transferred into three-necked flask, heated to 85 °C, and stirred for additional 8 h. Then the treated products were washed and filtered repeatedly in order to ensure a complete removal of chloride ions, and the filtrate was titrated with AgNO₃ until no AgCl precipitate was found. The product was then dried under vacuum at 90 °C for several hours, and the product, termed OREC, was obtained. In the modification experiment, weight of 30 g REC needed water of 1700 ml, while the molar of surfactant was about 75% of cation exchangeable capability (CEC).

2.3. Beer–Lambert's law

A single optical path was used to study the interaction within the GPE. All samples in the absorption range would obey the Beer–Lambert's law [27].

$$\left| \frac{I}{c} \right| \lim_{c \rightarrow 0} = \varepsilon \quad (1)$$

where *I* is the intensity of absorption; ε is absorption coefficient; *l* is thickness of sample and, *c* concentration.

2.4. Characterization

FTIR was performed on an infrared spectroscopy of WQF-310 in the wave number range of 4000–400 cm⁻¹. The sample dispersed in acetone was casted on KBr slice. Until the acetone was completely dropped out from the thin slice, the KBr slice with sample was placed in the meter for measurement. All infrared spectra were obtained at 16 scans with a resolution of 0.1 cm⁻¹ at room temperature. X-ray diffraction (XRD) measurements of REC and OREC were conducted with a Rigaku D/max-3C using nickel-filtered Cu K α ($\lambda = 0.154$ nm) radiation (40 kV, 40 mA) and a scan range of 1–10°.

3. Results and discussion

3.1. XRD analysis of REC and OREC

The analysis of X-ray diffraction (XRD) for natural clay and organic clays was shown in Fig. 1. We can obtain the *d*-spacing of the clay from their characteristic peaks based on Bragg equation. The *d*-spacing of OREC was 2.99 nm. It was larger than that of raw REC (2.22 nm), which indicated that cationic exchange reaction occurred between the clay and the surfactant, and the galleries in the REC were filled with the molecule of organic cation.

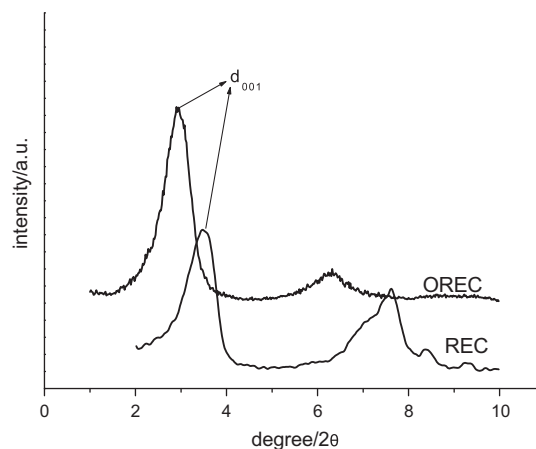


Fig. 1. Analysis of XRD of REC and OREC.

3.2. Determination of interaction

The C=O absorption 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 interacts with other proton donating groups such as –OH, and –NH. The new born band corresponding to the absorption of hydrogen-bonded C=O appears at relatively lower wave number position than that of the free C=O in FTIR spectroscopy [27]. The kind of interaction can reduce the electron density in C=O group, which make the vibration energy of C=O decrease, and that is to say the peak position of C=O shift to lower wave number in IR spectrum. The behavior of Li⁺ bonded C=O absorption formation is similar to the hydrogen-bonded C=O absorption formation.

A problem which arises in the quantitative analysis of FTIR spectra is the partial overlapping of both kinds of C=O stretching bands. A quantitative analysis of the observed profiles, including deconvolution and curve-fitting, is then really helpful in order to clarify the nature of both kinds of C=O. In order to separate both bands, we choose to fit the spectra with all the fitting parameters left free to vary upon iteration until converging solution is reached. Although the spectral decomposition procedures have no unique solution, we remark that the one we adopted here uses the minimum number of parameters and, at the same time, it furnishes extremely good fits to the data. The best-fit is, in fact, characterized by $r^2 \sim 0.9999$ for all the investigated systems.

3.2.1. Quantitative measurement of interaction for PMMA/LiClO₄ blends

Fig. 2 showed the FTIR spectra from 1800 to 1670 cm⁻¹ of PMMA/LiClO₄ blends with various lithium salt contents. It was obvious that with the increase of lithium salt content, the position of C=O in polymer shifted down to lower wave number.

By adding lithium salt, portion of C=O group interact with Li⁺ to form the Li⁺ bonded C=O. Therefore, the Li⁺ bonded C=O group of PMMA is increased, while the free C=O group is decreased. Curve fitting for C=O in polymer between 1750 and 1710 cm⁻¹ showed two Gaussian peaks, for example, Fig. 3 provided an adequate fit for the PMMA/LiClO₄ (5 wt%) blend as dashed line.

There are two kinds of C=O group in the PMMA/LiClO₄ blend, namely free and bonded C=O. Curve-fitting showed that two Gaussian peaks for C=O in PMMA was at 1731 and 1722 cm⁻¹, respectively. The results of area fraction (*A*₁, *A*₂) of peak obtained from the curve-fitting procedure were displayed in Table 1. The fol-

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