Investigation of the free volume and ionic conducting mechanism of poly(ethylene oxide)-$LiClO_4$ polymeric electrolyte by positron annihilating lifetime spectroscopy*

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The positron annihilation lifetime and ionic conductivity are each measured as a function of organophilic rectorite (OREC) content and temperature in a range from 160 K to 300 K. According to the variation of ortho-positronium (o-Ps) lifetime with temperature, the glassy transition temperature is determined. The continuous maximum entropy lifetime (MELT) analysis clearly shows that the OREC and temperature have important effects on o-Ps lifetime and free volume distribution. The experimental results show that the temperature dependence of ionic conductivity obeys the Vogel–Tammann–Fulcher (VTF) and Williams–Landel–Ferry (WLF) equations, implying a free-volume transport mechanism. A linear least-squares procedure is used to evaluate the apparent activation energy related to the ionic transport in the VTF equation and several important parameters in the WLF equation. It is worthwhile to notice that a direct linear relationship between the ionic conductivity and free volume fraction is established using the WLF equation based on the free volume theory for nanocomposite electrolyte, which indicates that the segmental chain migration and ionic migration and diffusion could be explained by the free volume theory.

Keywords: positron, free volume, polymeric electrolyte, ionic conduction

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1. Introduction

The electrical properties of poly(ethylene oxide) (PEO) and its salt compounds have been extensively investigated due to its possible application in lithium ion batteries or in electrolyte fuel cells since lithium conductivity was studied.[1−3] However, the application of PEO solid electrolytes has been restricted due to the high crystallinity impeding the ion transport by limiting the segmental motion[4,5] and resulting in a relatively low ionic conductivity at ambient temperature. In order to overcome the drawback, the most common approach is to add liquid plasticizers, such as, low molecular weight polyethylene glycols or aprotic organic solvents, into the PEO matrix. However, the addition of liquid leads to the deterioration of the mechanical properties of electrolyte. Recently, the studies on the polymeric composite solid electrolytes with nano particle fillers have attracted considerable attention because the additional nanofiller not only reduces the crystallinity of the PEO and enhances the ionic conductivity, but also improves the mechanical stability and extends the thermal stability of PEO-based electrolytes.[6] Although significant progress has been made in developing the polymer nanocomposite solid electrolytes,[7] the micro-mechanism of the enhancement of the conductivity is not very clear and needs to be studied further. As is well known, significant ion transport requires the presence of a noncrystalline phase and the free volume, which indicates that the free volume plays an important role in determining ionic conductivity and mechanical property. However, the reports on direct experimental measurements of the free volume for polymer solid nanocomposite are very lacking, because the detection of the atomic scale free volume is very difficult for traditional experimental technologies, including TEM and XRD, etc.

Positron annihilating lifetime spectroscopy (PALS) is a very useful tool to probe the atomic scale

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free volume.[8,9] The principal advantage of PALS over other techniques is that the formation and annihilation characteristics of positronium (Ps), i.e., bound states of e^+ and e^-, strongly depend on an atomic-scale free volume hole. Therefore, PALS has been widely used in the study of polymeric materials for many years.[10−13]

In the present work, the effects of temperature and OREC on the atomic scale free volume and its distribution, and the ionic conductivity are systematically studied. The detailed analyses about the enhancing micro-mechanism of the ionic conductivity are presented.

2. Experiment

2.1. Materials

Pristine rectorites were supplied by Hubei Celebrities Technology Co. (Wuhan, China). Exchanging cation of rectorite is Ca^{2+}, and the cation exchange capacity is 44.9 mequiv/100 g. PEO was supplied by Dadi Fine Chemical Co. Ltd. (Changchun, China, $M_w = 6 \times 10^5$) $LiClO_4{\cdot}3H_2O$ was supplied by Shanghai Yingyuan Chemical Co. Ltd. (A.R.). Hexadecyl trimethyl ammonium bromide (CTAB) was supplied by Shanghai Zhanyun Chemical Co. Ltd. (A.R.).

2.2. Nanocomposite preparation

Na-rectorite (Na-REC) was successfully made through a cation exchanging reaction with alkylamine as follows:

$$\mathrm{REC} - \mathrm{Ca}^{2+} + \mathrm{Na}^{+} \rightleftharpoons \mathrm{REC} - \mathrm{Na}^{+} + \mathrm{Ca}^{2+}.$$

Then, hexadecyl trimethyl ammonium bromide (CTAB) was used as the intercalation reagent to obtain the OREC.

PEO and $LiClO_4{\cdot}\ 3H_2O$ were dried in a vacuum oven at 60 °C for 24 h and at 120 °C for 48 h, respectively, which were mixed according to the molar ratio of the ethylene oxide segments to the lithium ions as [EO]/[Li]=8. The preparation procedure of OREC nanocomposite was as follows: first, OREC was dissolved in anhydrous acetonitrile, and then dispersed on magnetic stirring apparatus for 30 min, followed by adding predetermined amounts of $LiClO_4$ and PEO. This mixed solution was stirred at room temperature for approximately 12 h until a homogeneous solution was formed. The resulting solution was cast on a teflon plate in a fume cupboard overnight to evaporate the solvent. Finally, the films were dried at 60 °C in a vacuum for 48 h. PLC0, PLC1, PLC3, and PLC6 denote the nanocomposites with 0, 1, 3, and 6 wt% OREC, respectively. PLC stands for PEO–$LiClO_4$–Clay.

2.3. Characterization

The small angle X-ray diffraction (SXRD) of modified clays and polymer-clay composites were measured with a Bruker D8 Advance X-ray Diffractometer using Cu Kα radiation, 1.5406 Å (1 Å=0.1 nm) wavelength, at a voltage of 40 kV, under a 1°/min scanning rate respectively.

Electrical resistivity was measured by a conventional four-probe method. The current was provided by a Keithley 2400 Sourcemeter. The voltage drop across the sample was measured by a Keithley 2182 Nanovoltmeter, and the temperature was controlled by a LakeShore 340 temperature controller.

Positron lifetime measurements were carried out using a conventional fast–fast coincident spectrometer. A 15-μCi ^{22}Na source was sandwiched between two identical samples, each spectrum contained 1×10^6 counts for PATFIT analysis.[14] To reduce artificial effects, all spectra were resolved using the same parameters. The temperature was controlled by a LakeShore 340 temperature controller.

3. Results and discussion

3.1. XRD results

Figure 1 shows the SXRD patterns of all samples. From Fig. 1, we can identify the intercalated structure with Bragg's law, $\lambda = 2d\sin\theta$, where λ is the wavelength of the X-ray radiation (1.5406 Å), d corresponds to the spacing between the (001) diffraction lattice plane in this study, and θ refers to the measured diffraction angle.

The pristine REC shows a d_{100} peak at $2\theta = 3.51°$, which corresponds to a d-spacing of 2.52 nm, while the OREC modified clay shows a d-spacing of 4.42 nm. This result reveals that the organic modification of the clay extends the d-spacing, which facilitates the PEO intercalating into the interlayers of

clay. In PLC1 and PLC3, there are found no apparent intercalated peaks of the clay, which means that an exfoliated structure is formed. However, a new peak is observed at a lower angle ($2\theta = 1.23°$) for PLC6 as shown in Fig. 1, suggesting that PEO chains are intercalated into the OREC layers, which makes the d-spacing increase up to 6.96 nm. We also find a d_{100} peak of modified clay, which implies that part of OREC aggregates in PLC6.

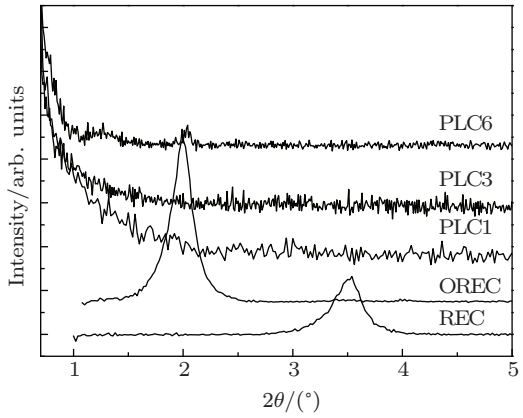


Fig. 1. SXRD patterns of pristine rectorite (REC), organophilic rectorite (OREC), and PEO/Li^+/clay composites with different values of clay content.

3.2. Effect of clay content on the conductivity

In order to study the effect of free volume on conductivity of polymeric electrolyte, a relatively free volume fraction f_r is calculated based on the following equations:[15]

$$\tau_3 = \frac{1}{2}\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]^{-1}, \quad (1)$$

$$V_f = 4\pi R^3/3, \quad (2)$$

$$f_r = V_f I_3, \quad (3)$$

where R is the radius of the free volume cavity and $\Delta R = 1.656$ Å[16] is derived from fitting the observed o-Ps lifetime in a molecular solid with a known cavity size.

The variations of the fractional free volume and the conductivities of PLC composites with clay content at room temperature are shown in Fig. 2.

From Fig. 2, it is obvious that the conductivity increases rapidly with the OREC content, increasing up to 3 wt% at which the conductivity reaches a maximum value, then it decreases drastically with a further increase in clay content, which is consistent with previous reports.[17,18]

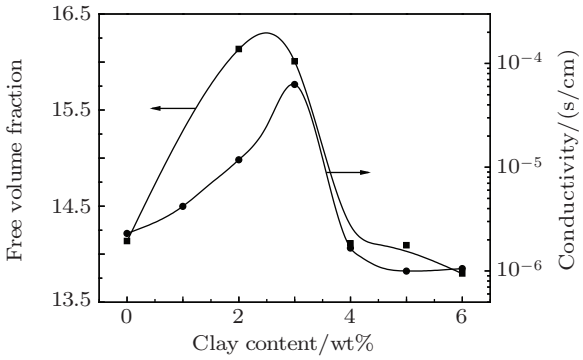


Fig. 2. Free volume fraction and conductivity versus clay content.

From Fig. 2, it is obvious that the variation trend of the fractional free volume with OREC content is similar to the conductivity variation with OREC content. The experimental results can be explained. According to the Nernst–Einstein equation,[19] the ionic conductivity σ can be expressed as[20]

$$\sigma = \frac{q^2 n D}{kT}, \quad (4)$$

where n and q are the concentration and charge of the charge carriers respectively, k is the Boltzmann constant, and T refers to the absolute temperature. The diffusion coefficient D can be rewritten as

$$D = g a^* u \exp\left[-\frac{\gamma V^*}{V_f}\right], \quad (5)$$

where g is a geometrical factor, a^* is the molecular diameter, u is the average speed of the molecules and is proportional to $T^{1/2}$, γ is a numerical factor, and V^* is the critical volume just large enough to permit another molecule to jump in after the displacement. The ionic conductivity σ can also be written as

$$\sigma = \frac{C}{T^{1/2}} \exp(-\gamma V^*/V_f), \quad (6)$$

where C is a fitting parameter including the change carrier number.[10] Therefore, at the same temperature, the ionic conductivity σ is closely related to the free volume. The increase of fractional free volume can directly lead to the increase of the ionic conductivity.

When the OREC was added into the PEO matrix, the changes in the segmental chain configurations were induced. The PEO molecular segments were partly disarranged due to the interaction between the nano-rectorite and polymer matrix, leading to the increase in free volume.[21–23] In the pure PEO matrix, the Li^+ and PEO chains can form complex I as shown in Fig. 3.[17,24] The additional OREC nanosheets can destroy part of these complexes and release more "free" ions. Moreover, the nanosheets

can create a higher interfacial area between the polymer matrix and the clay. According to the reported results in Ref. [25], the "free" lithium ion can transport through the surface of the nanosheet, which can effectively enhance the conductivity of nanocomposite. However, when the clay content exceeds 3 wt%, the excess clay may lead to the formation of two types of complexes (complex II and complex III) with the lithium ion as shown in Fig. 3,[17,24] which restricts the mobility of the lithium ion, leading to a decrease in the ionic conductivity. When the filler content exceeds 3 wt%, the fractional free volume decreases significantly. Maybe this is attributed to the coordination of the Li^+ ions with solvating sites in the polymer.[26,27]

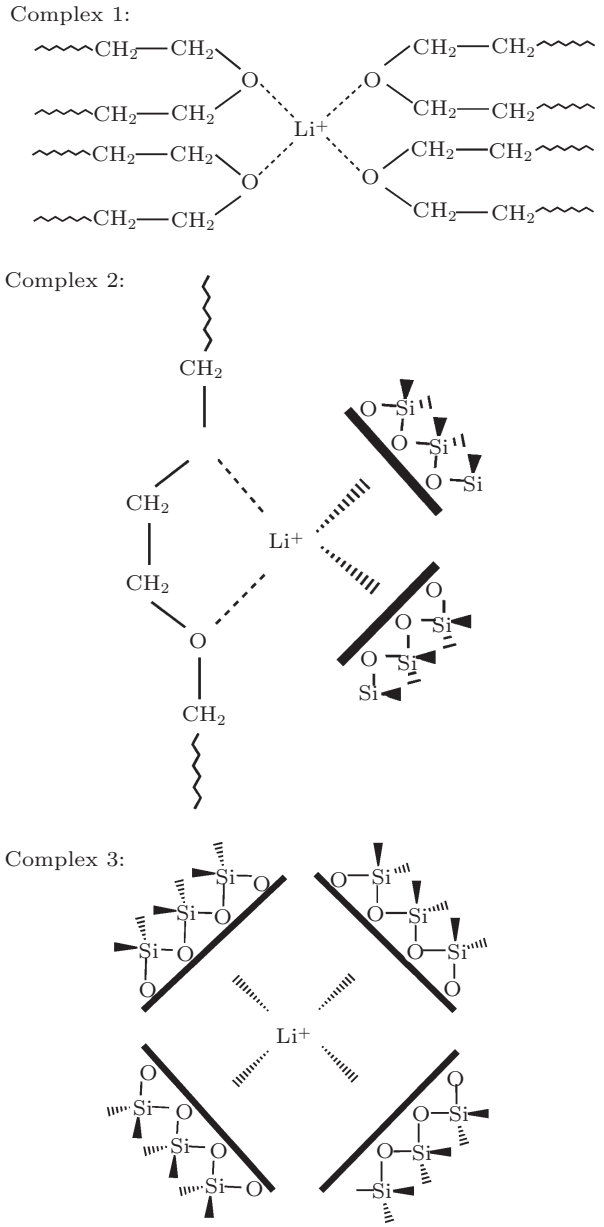


Fig. 3. Schematic structure of the complex formed by Li^+ cation with polymer chains (complex I), polymer and silicate layers (complex II), and silicate layers (complex III).

3.3. Free volume analysis of the conductivity dependence on temperature

3.3.1. Structural transition and free volume distribution

The most important structural transition for a polymer is a glassy transition, because there are dramatic changes in the properties of a polymer at the glassy transition temperature, such as heat capacity, thermal expansion coefficient, etc. One of the most widely used methods of demonstrating the glassy transition and determining T_g is to measure the specific volume of a polymer as a function of temperature. Recent research indicated that the o-Ps annihilation lifetime is very sensitive to the change in the free volume with temperature.[28,29] As is well known, one of the most useful approaches to the analysis of the glass transition is to use the concept of free volume. The temperature dependences of the o-Ps lifetime and the free volume for composites with different values of clay content are shown in Fig. 4.

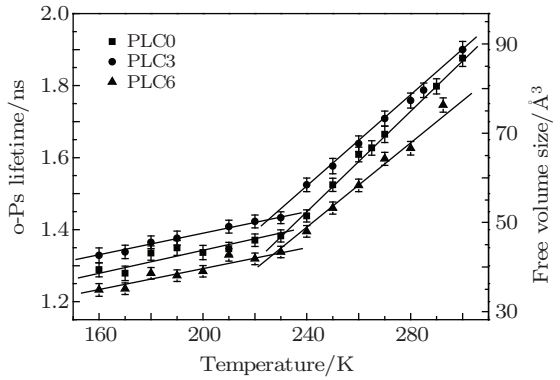


Fig. 4. Temperature dependences of the o-Ps lifetime for PEO–$LiClO_4$–clay composites.

From Fig. 4, it is obvious that the o-Ps lifetime and the free volume all increase with temperature. However, in different temperature ranges, these curves have different slopes dv/dT or $d\tau_3/dT$, which indicates the existence of structural transition. In order to determine the glassy transition temperature, a least-squares linear fitting program is used to fit the two regions. The temperature corresponding to the intersection of the two straight lines is identified as the glassy transition temperature T_g as shown in Fig. 4. Below T_g, the motion of the main chains is frozen,

only the short-range diffusion of the chains and motion of branch chains can occur, which leads to slow increases in o-Ps lifetime and free volume. Above T_g, the motion of the main chains is activated, which brings about sharp increases in the o-Ps lifetime and the free volume.

In order to inspect the effects of temperature and the OREC content on o-Ps lifetime and free volume distributions, the lifetime spectrum containing approximately 4×10^6 counts for the continuous maximum entropy lifetime (MELT) analysis has been measured,[22] as shown in Fig. 5.

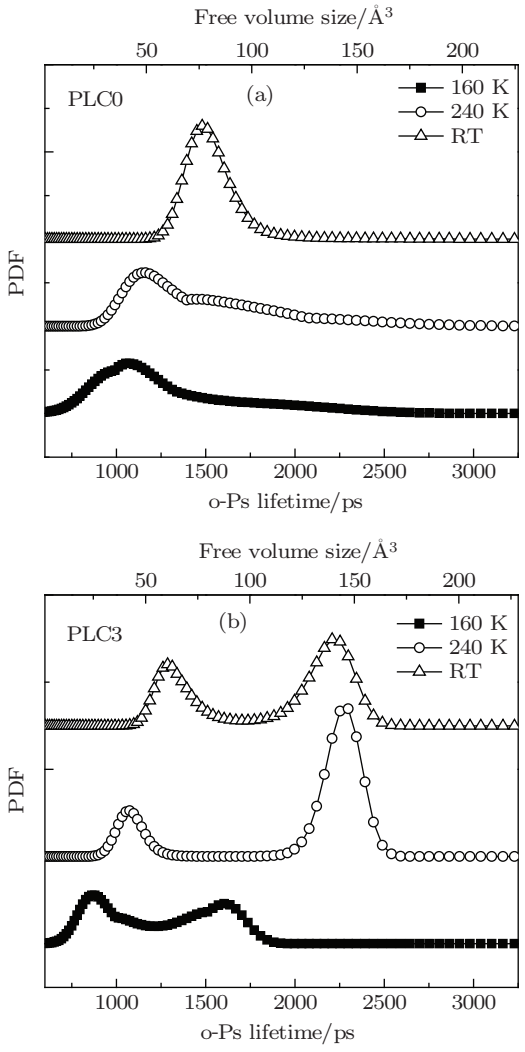


Fig. 5. Variations of probability density function (PDF) with o-Ps lifetime for (a) PLC0 and (b) PLC3 at different temperatures.

From Fig. 5, we can see that as the temperature increases, the values of the peak shifts toward a higher value in both PLC0 and PLC3, resulting from the thermal expansion of free volume. Moreover, we also find that OREC has an important effect on the o-Ps lifetime and free volume distributions, i.e., in all temperature ranges, the peaks of the o-Ps lifetime distributions are split into two peaks due to the addition of nanoclay. Many polymeric composites show similar results.[28−30] This fact means the addition of nanoclay can induce an effective rearrangement of polymer chains. This phenomenon has been observed by Winberg *et al.*[22]

3.3.2. Relationship between ionic conductivity and temperature and free volume fraction

Figure 6 shows the temperature dependence of the ionic conductivity of PLC composites in the rubbery state. The conductivity shows a continuously curved Vogel–Tammann–Fulcher (VTF) type profile and increases with increasing temperature.

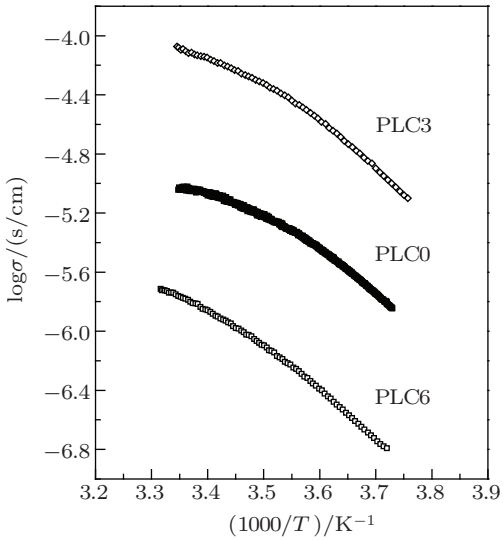


Fig. 6. Temperature dependence of conductivity of PEO-$LiClO_4$ complexes in a rubbery state.

As is well known, the ionic conduction depends strongly on the free volume and motion of polymer chains in the amorphous phase.[31] When the temperature is raised, the fractional free volume increases as shown in Fig. 4, which makes the motion of segmental chains more free and so brings about an increase in ionic conductivity.

The electrical conductivity temperature dependence can be well described by the VTF equation (7), especially for the ionic transport in the amorphous polymer electrolyte as[32,33]

$$\sigma = AT^{-1/2}\exp\left[-\frac{E_a}{k_b(T-T_0)}\right], \qquad (7)$$

where A is the pre-exponential factor, T_0 is the temperature at which the free volume vanishes and the

ionic mobility goes to zero. E_a is the apparent activation energy, which means the necessary energy required to move any chain segment for ion motion.[34] In order to calculate the value of E_a, equation (7) can be rewritten as

$$\log_{10}(\sigma T^{1/2}) = \log_{10} A - 0.43\frac{E_a}{k_b(T-T_0)}. \quad (8)$$

Figure 7 shows the dependences of $\log(\sigma T^{1/2})$ on temperature. A linear least-square procedure is used to evaluate the apparent activation energy E_a. Based on the equations of the fitting straight lines, we can obtain the values of E_a of PEO–$LiClO_4$–clay composites to be 4.07 kJ/mol (0.04 eV) for PLC0, 7.33 kJ/mol (0.07 eV) for PLC3, and 5.824 kJ/mol (0.06 eV) for PLC6. The values of E_a are quite close to the value of 0.076 eV found by Wright.[35] The temperature dependence of conductivity which obeys the VTF equation reveals that the conducting behaviour can be described by the free-volume ion transport mechanism and that the ionic mobility is affected by the micro-Brownian motion of the polymer segments. This fact indicates that ion transport occurs preferentially in an amorphous matrix.

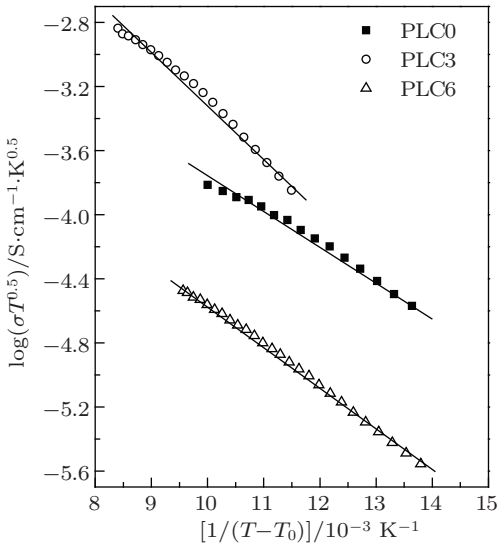


Fig. 7. Curves of $\log(\sigma T^{1/2})$ versus $1/(T-T_0)$ for PEO–$LiClO_4$–clay composites.

In order to clarify the ionic conductivity mechanism, the WLF equation based on the free volume theory is used to obtain a direct relationship between ionic conductivity σ and fractional free volume $f_r(T)$. This is because the free volume concept has been successfully used to describe solvent diffusion in a polymer, and it is logical that they may also be valuable in modeling the temperature dependence of the conductivity, that is, the evolution of the ionic conductivity with temperature also complies with the WLF equation,

$$\log\frac{\sigma(T)}{\sigma(T_g)} = \frac{C_1(T-T_g)}{C_2+(T-T_g)}, \quad (9)$$

where $C_1 = B/2.3(T_g - T_0)$ and $C_2 = T_g - T_0$, with T_0 being a reference temperature at which the free volume vanishes and the ionic mobility goes to zero. The variation of the fractional free volume as a functional of temperature above T_g can be described by the following equation

$$f_r(T) = f_r(T_g) + \alpha(T-T_g), \quad (10)$$

where α is the thermal expansion coefficient of the free volume hole. Combining Eqs. (9) and (10), we can obtain a good linear relationship between $\log_{10}\sigma$ and the fractional free volume as follows:

$$\log_{10}\sigma(T) = \log_{10}\sigma(T_g) + C_1\left[1 - \frac{f_r(T_g)}{f_r(T)}\right], \quad (11)$$

where $f_r(T_g)$ is the fractional free volume at the glass transition temperature of composites. Figure 8 shows the direct relationship between ionic conductivity and the free volume fraction.

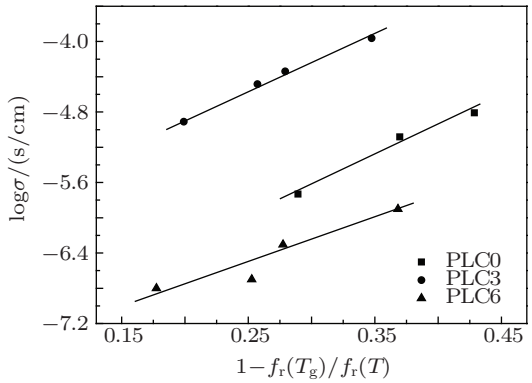


Fig. 8. Variations of $\log\sigma$ with $1-f_r(T_g)/f_r(T)$ for PEO–$LiClO_4$–clay composites.

From Fig. 8, it is very clear that the ionic conductivity increases with fractional free volume. From Fig. 8, the values of C_1 can be obtained for all samples to be 6.7±0.9 for PLC0, 6.4±0.4 for PLC3, and 4.9±1.2 for PLC6, which are lower than the universal constant value of 17.4. Maybe this is attributed to the fact that the critical volume for migration of the ions is less than the volume required to migrate the polymer segments.[32,36] This deviation may also result from the interaction between ions and polymeric chains, and it may be neglected in the WLF equation. In Fig. 8, the linear relationships between $\log\sigma$ and $1-f_r(T_g)/f_r(T)$ suggest that the segmental chain migration and ionic transmission and diffusion could be explained by the free volume theory.

4. Conclusion

The free volume, structural transition and ionic conduction are systematically investigated for PEO/$LiClO_4$/clay nanocomposite electrolytes. According to the change in the o-Ps lifetime with temperature, the glassy transition temperature is determined. Experimental results also show that a small amount of additional OREC can increase the ionic conductivity by nearly one order of magnitude compared with those of PEO–$LiClO_4$ composites. The apparent activation energy and several important parameters in the VTF and WLF equations are obtained. The conducting mechanism can be explained in terms of the free-volume theory.

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