Investigation of microstructure and conducting mechanism of nanocomposite polymeric electrolytes with rectorite clay by PALS

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Abstract. Polymeric electrolytes with different modified organic nanoretorite (OREC) content have been prepared. Measurements of the structural transition, the positron annihilation lifetime, free volume and ionic conductivity as a function of the OREC content and the temperature have been performed. According to the variations of the ortho-positronium (o-Ps) lifetimes with temperature, the glass transition temperatures have been determined. A direct relationship between the ionic conductivity and the fractional free volume has been established using based on free volume theory Williams-Landel-Ferry (WLF)equations, implying a free-volume transport mechanism. Our experimental results indicated that the segmental chain motion and ionic migration and diffusion could be explained by the free volume theory**.   .**

1. Introduction
As energy storage system and power source of various portable devices, electronic devices, the rechargeable lithium ion batteries have been widely used in our modern society. There has been increasing interest in development of solid polymer electrolytes due to their applications in solid state electrochemical device and particularly in solid rechargeable Lithium batteries. The study on the solid polymer electrolytes polyethylene oxide(PEO) has received more attention since the original work of Wright and Armand in 1973. PEO-based polymer electrolyte is the most attractive host because of its easy fabrication, light weight, low cost，high conductivity above melting temperature. However, high crystalline phase concentration limits the conductivity of PEO-based electrolyte, especially at room temperature. Many attempts have been made to overcome the drawbacks. Recent research has shown that these drawbacks may be particularly overcome by the incorporation of nano-scale fillers, such as nanoclay. The addition of nanoscale fillers not only improve the ionic conductivity，but also enhance the mechanical strength and stability of polymer electrolytes.

The aim of this study is to investigate the effect of nano-clay on the microstructure and conducting behaviour of nanocomposite electrolytes。

2. Experimental Section

2.1. Materials and sample preparation
Pristine rectorites, PEO(M_w=600 000), $LiClO_4 \cdot 3H_2O$ and Hexadecyl trimethyl ammonium bromide (CTAB) as the intercalation reagent to obtain the organophilic rectorite (OREC) were supplied by

Hubei Celebrities Technology Co. (Wuhan, China), Dadi Fine Chemical Co. Ltd, and Shanghai Zhanyun Chemical Co. Ltd (A.R.) respectively. The molar ratio of the ethylene oxide segments over the lithium ions was fixed at [EO]/[Li] =8. PLC0, PLC1, PLC3 and PLC6 are named to denote the nanocomposites with 0, 1, 3 and 6 wt.% OREC content, respectively. PLC is the abbreviation of PEO-LiClO$_4$ Clay. The detailed information on the preparation of OREC nanocomposites can be found elser where[1].

2.2. Characterization
The measurements of small angle X-ray diffraction (SXRD) and wide angle X-ray scattering(WAXS) were completed with a Bruker D8 Advance X-ray Diffractometer using Cu Kα radiation, 1.5406 Å wavelength, at a voltage of 40 KV, under 1°/min scanning rate respectively.

Electrical resistivity was measured by a conventional four-probe method, the detailed information can be found elsewhere[1].
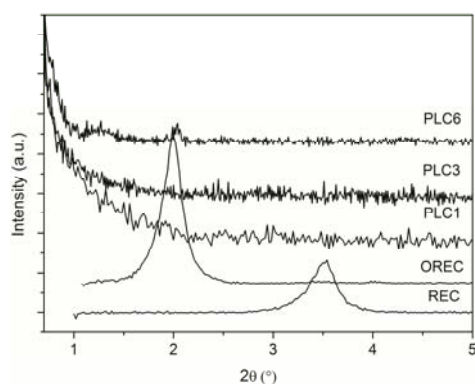
Positron lifetime measurements were carried out using a conventional fast- fast coincident spectrometer. A 15 Ci ^{22}Na source was sandwiched between two identical samples, each spectrum contained 1×10^6 counts for PATFIT analysis and 4×10^6 counts for MELT analysis respectively.
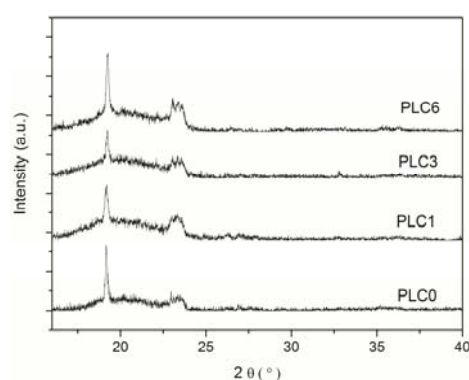
3.Results and Discussion

3.1. XRD Results.
The results of small angle x-ray diffraction are shown in figure.1. Using the SXRD results, the intercalated structures can be identified with Bragg's law: with Bragg's law, $\lambda = 2dsin\theta$, where λ is the wavelength of the X-ray radiation (1.5406 Å), d corresponds to the spacing between the (001) diffraction lattice plane and refers to measured diffraction angle. From this figure, we can see that the interlayer spacing has been extended up to 4.42nm for organic OREC, which is much wider than 2.52 nm of pristine rectorite. On the other hand, for nanocomposites samples with 1wt% and 3wt% clay content, no obvious peaks were observed, which means that the clays were exfoliated.

The WAXS measurements were conducted as shown in figure 2. From this figure，we can see that the intensities of the characteristic peaks of 1wt% and 3wt% clay content samples are lower than that of pure PEO, which means that the small quantity of OREC added into PEO matrix can effectively decrease the crystallinity of PEO matrix[2]. Because polymer intercalation disrupted the normal, three dimensional structure to suppress polymer crystallization[3]. However, the sample with 6% clay content has small effect due to the aggration of clay
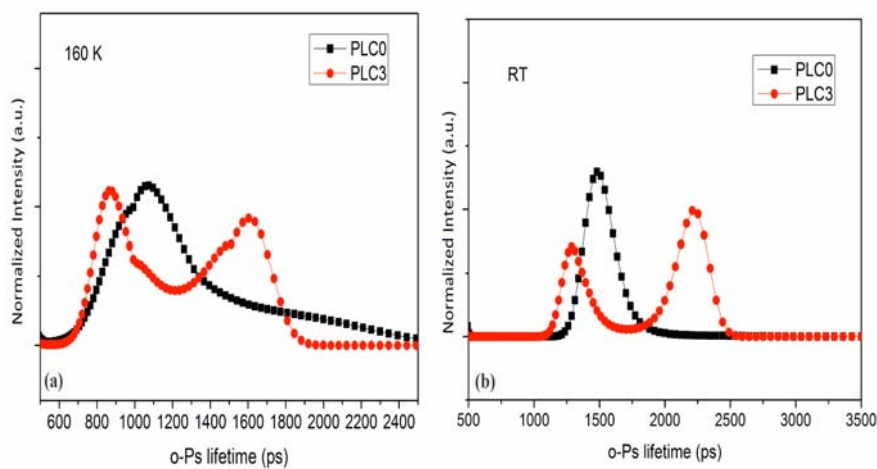

Figure 1. SXRD patterns of pristine rectorite (REC), organophilic rectorite (OREC) and PEO/ Li$^+$/ clay composites with different clay contents.

Figure 2. WXRD patterns of PEO/ Li$^+$/ clay composites with different clay contents.

3.2.Free volume distributions
In order to deeply discern the influence of clay on the free volume distribution, positronium lifetime distributions with temperature and OREC content were measured as shown in figure 3. From figure 3, it is very clear that the values of peaks shift to higher values with increasing temperature due to the free volume thermal expansion. On the other hand, comparing the positronium lifetime distribution between PLC0 and PLC3, an interesting phenomenon was observed that peaks of sample with 3wt% OREC content were spitted into two sub peaks, which suggest that the two different kinds of the free volumes exist. According to the reports, we think that shorter o-Ps lifetime is attributed to the o-Ps annihilation in the free volume at interfacial regions between the polymer matrix and nanoclays and in the interstital free volumes in crystalline region due to the change in the chain packing density induced by nanoclays[3-4]. The longest o-Ps lifetime is attributed to the o-Ps annihilation in the free volume in the amorphous region.

Figure 3. Positronium lifetime distribution with temperature((a):160K, (b)room temperature) and clay content.

3.3.Direct relationship between ionic conductivity and the fractional free volume
Positronium lifetimes with temperature and clay content were measured as shown in figure 4. Based on the infinite potential spherical well model, we can calculate the free volume V and the relative free volume fraction $f_r(T) = VI_3$, I_3 is the o-Ps intensity. Here, we can neglect the effect of the positronium annihilation in nanoclays because the nanoclay content is very small. From fig.4, we can see that o-Ps lifetimes of 3wt% clay sample are longer than those of pure PEO sample, whereas the lifetimes measured for the 6 wt. % sample are lower than those for the pure PEO. Maybe this results from the dispersion state of clay, which is consist with the WXRD results. In order to determine the glass transition temperature, a least-squares linear fitting program was used to fit the two regions. The temperature corresponding to the intersection of two straight lines is identified as the glass transition temperature Tg. Below Tg, polymer is in the glassy state, the chain motion is frozen, leading to small change in o-Ps lifetime. Above Tg, the matrix is in the rubber state, the motions of the segmental chains and all molecular motions are activated, resulting in marked increase in o-Ps lifetime.

In order to clarify the ionic conductivity mechanism, the WLF equation[5] based on the free volume theory was used to obtain a direct relationship between the ionic conductivity and the fractional free volume fr(T)as follows:

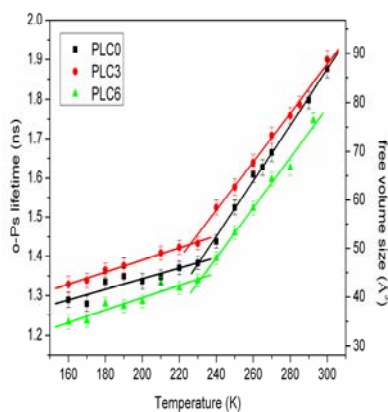$$\log \frac{\sigma(T)}{\sigma(T_g)} = \frac{C_1(T - T_g)}{C_2 + (T - T_g)} \tag{1}$$

$$C_2 = f_r(T_g)/\alpha = T_g - T_0 \qquad (2)$$
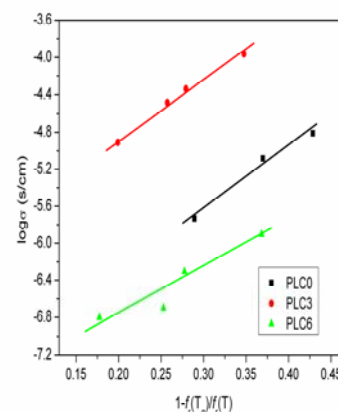
$$f_r(T) = f_r(T_g) + \alpha(T - T_g) \qquad (3)$$

Combining equations(1-3), we obtain

$$\log_{10}\sigma(T) = \log_{10}\sigma(T_g) + C_1\left[1 - \frac{f_r(T_g)}{f_r(T)}\right] \quad (R^2 = 0.968) \qquad (4)$$

Where C_1 and C_2 are a constant, α is the thermal expansion coefficient of the free volume, $f_r(T_g)$ is the fractional free volume at Tg, T_0 is a reference temperature at which the free volume vanishes and the ionic mobility goes to zero. Figure 5 shows a good linear relationship between the ionic conductivity and the fractional free volume, which suggests that polymer chain mobility, ionic migration and diffusion, and conductivity mechanism could be explained by the free volume theory .

Figure 4. Temperature dependence of o-Ps lifetime for PEO-LiClO$_4$-clay composites.

Figure 5. logσ versus 1-$f_r(T_g)/f_r(T)$ for PEO-LiClO$_4$-clay composites.

4.Conclusion
The free volume and structural transition, and the ionic conductivity have been investigated for PEO/LiClO$_4$/clay nanocomposite electrolytes. Experimental results found that the addition of a small quantity of OREC can effectively effect on the microstructure of PEO. A direct relationship between the ionic conductivity and the fractional free volume has been obtained using WLF equation based on the free volume theory. The conducting mechanics can be explained in terms of free-volume theory.

3. References
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