

Phase Structure and Conductivity of Polymer Ceramic Composite Electrolytes Studied by Solid-State NMR

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Abstract. The influences of nano- Al_2O_3 on the phase structure and conductivity of PEO/ LiCF_3SO_3 polymer electrolyte complex are discussed in this work. The addition amount of Al_2O_3 is 0-30wt%. The phase structure of the complex shows complicated changes with the addition of Al_2O_3 . The crystallinity of the complex first decreases when Al_2O_3 content less than 15wt% then increases when Al_2O_3 content more than 15wt%. As the addition amount of Al_2O_3 is 15wt%, the ^{13}C NMR signals from PEO/ LiCF_3SO_3 crystalline complex and neat crystalline PEO can hardly be seen. The complex obtains the highest ionic conductivity at room temperature when the content of Al_2O_3 is 15wt% (3.822×10^{-5} S/cm).

Keywords: polymer ceramic electrolytes, lithium-ion batteries, solid-state nuclear magnetic resonance.

1. Introduction

Lithium-ion batteries (LIBs) are the technology of choice for high energy density requirements today. [1] They are now used in most of the portable applications as well as electric vehicles. [1,2] In most of the commercial LIBs, a liquid solution of one lithium salt (such as LiCF_3SO_3) dissolving in organic solvent (mixture of linear and cyclic carbonates) is used as the dominant electrolyte. [3] The organic solvent can cause both environmental and safety problems. The commercial LIBs are not safety at elevated temperature. This problem becomes especially critical for large format batteries used for electric vehicles. To increase the safety and energy density of LIBs, solid polymer electrolytes (SPEs) consisting of one lithium salt associated with polar polymer matrix (such as PEO) without organic solvent have been suggested. [4-6] It is widely accepted that the conductivity of SPEs only occurs in the amorphous phase above the glass transition temperature T_g . [7-9] Although PEO-based SPEs have many specific features, it's impossible for PEO-based SPEs to have both high ionic conductivity and good mechanical stability. [10-12] To improve this problem, polymer-nanoparticle hybrid electrolytes are intensively studied as they can achieve high ionic conductivity and high mechanical strength. [12-14] Unfortunately, little is known about the phase structure of this hybrid electrolytes which are important for in-depth study over the conduction mechanism.

Solid-state high-resolution nuclear magnetic resonance (NMR) technique is a powerful tool for investigating the phase structure and chain dynamics of polymer. [15] In our previous work, we have demonstrated that the ^{13}C NMR spectra of SPEs based on PEO and lithium salts (LiCF_3SO_3 , LiClO_4 and LiPF_6) show very high resolution. [16-19] Such high resolution enables us to study the microstructure and ion mobility of SPEs at atomic scale. Based on these findings, the influences of nano- Al_2O_3 on the phase structure and conductivity of PEO/ LiCF_3SO_3 complex are discussed over detailed solid-state high-resolution ^{13}C NMR study and electrochemical characterization In this work.

2. Experiment section

2.1 Sample preparation

Polymer-ceramic composite complexes were prepared by solvent casting technique. PEO ($M_w=6000$ g/mol, 5000000 g/mol), Al_2O_3 and LiCF_3SO_3 were purchased from Aldrich. The average pore size of Al_2O_3 is 0.58 nm. The amount of Al_2O_3 is 0wt%, 5wt%, 10wt%, 15wt%, 20wt%, 25wt%,

30wt%, respectively. Stoichiometric amounts of PEO, Al_2O_3 and LiCF_3SO_3 were dissolved in acetonitrile and stirred continuously for 24 hours at room temperature. The solution was cast on a Teflon plate and the solvent was allowed to evaporate gradually in dry air. The formed samples were finally dried in a vacuum drying oven for one day at 65°C and kept in a desiccator at least for two weeks at room temperature before use.

2.2 X-ray Diffraction Measurements

X-ray diffraction (XRD) measurements were performed on Bruker D8 Avance X-ray diffractometer. The diffraction patterns of the sample were recorded from 3° to 40° (2θ) with a step rate of 0.02° .

2.3 Solid-state NMR Measurements

Solid-state NMR experiments were performed on Bruker AVNCE 400 spectrometer operating at 100.62 MHz for ^{13}C . The ^{13}C chemical shifts were determined from the carbonyl carbon signal of glycine (176.03 ppm). The ^{13}C cross polarization/magic angle spinning (CP/MAS) experiments were performed. The acquisition time was 50 ms. The spin rate was 3 kHz. The delay time was 5 s.

2.4 Electrochemical testing

The Electrochemical Impedance Spectroscopy (EIS) measurement of the films was conducted using CHI760E Impedance/Gain-Phase Analyzer in the frequency ranging from 0.01 Hz to 1×10^6 Hz. The thickness of the resulted electrolyte film was measured using micrometer screw gauge. The film was sandwiched between two stainless steel electrodes with diameter of 1.0 cm under spring pressure. The ionic conductivity of the sample (σ) was determined using equation (1):

$$\sigma = l/R_b A \quad (1)$$

where l is the thickness of the film and A is the effective film electrode contact area. The bulk resistance R_b is obtained from the complex impedance plot.

3. Results and discussion

3.1 Influence of Al_2O_3 on phase structure

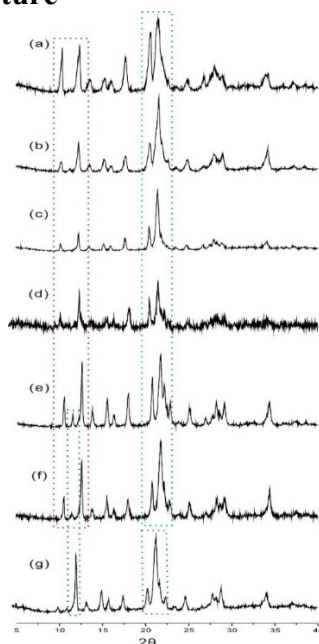


Figure 1: XRD patterns of the $\text{PEO}_3/\text{LiCF}_3\text{SO}_3$ - $n\text{Al}_2\text{O}_3$ complexes: (a) $n=0\text{wt}\%$; (b) $n=5\text{wt}\%$; (c) $n=10\text{wt}\%$; (d) $n=15\text{wt}\%$; (e) $n=20\text{wt}\%$; (f) $n=25\text{wt}\%$; (g) $n=30\text{wt}\%$.

Figure 1 is the XRD patterns of the PEO/LiCF₃SO₃ complexes with different Al₂O₃ content, denoted as PEO₃/LiCF₃SO₃-nAl₂O₃ (n=0-30wt%). The average molecular weight of PEO is 6000 g/mol. The O:Li⁺ mole ratio is 3:1. Figure 1a is the XRD pattern of the PEO₃/LiCF₃SO₃ complex. The diffraction peaks at 10° and 12° (red region) come from the PEO₃/LiCF₃SO₃ crystalline complex. The diffraction peaks at 20° and 22° (blue region) come from neat crystalline PEO phase. [20] The diffraction peaks of PEO₃/LiCF₃SO₃ crystalline complex and neat crystalline PEO still exist in figure 1b. There are no diffraction peaks of Al₂O₃ in figure 1b, because the amount of Al₂O₃ is too low to be observed. The diffraction peaks in figure 1c are the same as figure 1b, but the intensity of the diffraction peaks of crystalline region is lower. As the addition amount of Al₂O₃ reaches to 15wt%, the intensity of the diffraction peaks of PEO₃/LiCF₃SO₃ crystalline complex and neat crystalline PEO extremely decreases (figure 1d). As Al₂O₃ content increases to 20wt%, the diffraction peaks of PEO₃/LiCF₃SO₃ crystalline complex and neat crystalline PEO still exist and the peak intensity increases (figure 1e). The diffraction peaks of Al₂O₃ (green region) can be observed in figure 1e, however the intensity of these peaks is very weak. In figure 1f, the diffraction peaks of PEO₃/LiCF₃SO₃ crystalline complex and neat crystalline PEO still appear and the diffraction peaks of Al₂O₃ are more obvious. In figure 1g, the diffraction peaks of PEO₃/LiCF₃SO₃ crystalline complex, neat crystalline PEO and Al₂O₃ all can be observed. The intensity of the diffraction peaks of Al₂O₃ is very intensive.

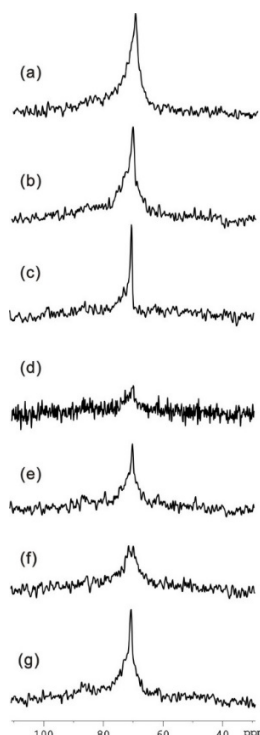


Figure 2: ¹³C CPMAS spectra of the PEO₃/LiCF₃SO₃-nAl₂O₃ complexes: (a) n=0wt%; (b) n=5wt%; (c) n=10wt%; (d) n=15wt%; (e) n=20wt%; (f) n=25wt%; (g) n=30wt%.

Figure 2 is the ¹³C CPMAS spectra of the PEO₃/LiCF₃SO₃-nAl₂O₃ complexes (n=0-30wt%). The contact time used here is 3 ms, only the signals from crystalline region are selected. There appears a sharp peak at 70 ppm in figure 2a, this peak comes from neat crystalline PEO phase. [17] This peak at 70 ppm also appears in figure 2b and 2c. The intensity of this peak decreases as the addition amount of Al₂O₃ increases. In figure 2d, as the addition amount of Al₂O₃ reaches to 15wt%, the peak at 70 ppm hardly can be observed. As the addition amount of Al₂O₃ increases (figure 2e-2g), the peak at 70 ppm appears again, and the intensity of this peak increases as the Al₂O₃ content increases. This implies as the addition amount of Al₂O₃ is 15wt% the sample reaches the lowest crystallinity. This results are the same as the XRD results.

3.2 Influence of Al₂O₃ on conductivity

Table 1: Conductivity of the PEO₃/LiCF₃SO₃-nAl₂O₃ complexes (n=0-30wt%)

Al ₂ O ₃ content	R _b (Ω)	σ (s/cm)	Lgσ
0%	/	/	/
5%	1800000	2.213E-06	-5.67
10%	450000	8.493E-06	-5.07
15%	100000	3.822E-05	-4.41
20%	500000	7.643E-06	-5.11
25%	600000	6.369E-06	-5.19
30%	700000	5.459E-06	-5.26

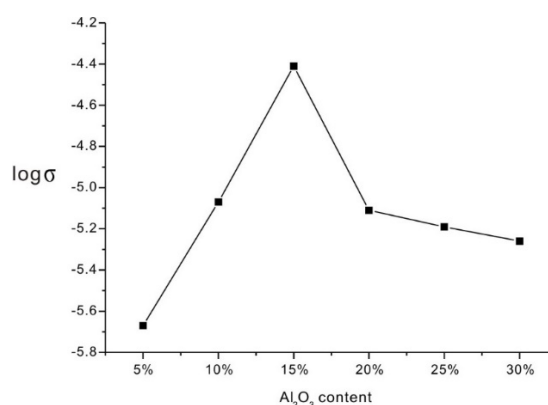


Figure 3: The conductivity of the PEO₃/LiCF₃SO₃-nAl₂O₃ complexes at room temperature

Table 1 and figure 3 show the conductivity of the PEO₁₀/LiCF₃SO₃-nAl₂O₃ complexes (n=0-30wt%) at room temperature. The average molecular weight of PEO used here is 5000000 g/mol. The O:Li⁺ mole ratio is 10:1. When there is no Al₂O₃ addition, the conductivity of the sample is too low to be detected at room temperature (<10⁻⁸ S/cm). When the addition amount of Al₂O₃ is 5wt%, the conductivity of the sample is 2.213x10⁻⁶ S/cm. This shows the addition of nano-Al₂O₃ can improve the ionic conductivity of PEO/LiCF₃SO₃ complex. As the addition amount of Al₂O₃ increases to 10wt%, the conductivity of the sample increases to 8.493x10⁻⁶ S/cm. The conductivity reaches the highest (3.822x10⁻⁵ S/cm) when the amount of Al₂O₃ is 15wt%. As the Al₂O₃ content reaches to 20wt%, the conductivity of the sample decrease to 7.643x10⁻⁶ S/cm. When Al₂O₃ content is 25wt%, the conductivity of the sample is 6.396x10⁻⁶ S/cm. When Al₂O₃ content reaches to 30wt%, the conductivity of the sample is 5.459x10⁻⁶ S/cm. The conductivity first increases as the amount of Al₂O₃ increases, as Al₂O₃ content is 15%, the sample reaches the highest conductivity of 3.822x10⁻⁵ S/cm. When the Al₂O₃ amount exceeds 15wt%, the conductivity drops rapidly and then decline slowly.

As discussed above, the addition of Al₂O₃ can affect the crystallinity and conductivity of the PEO/LiCF₃SO₃ complex. The amount of the crystalline region decreases first then increases with the addition of Al₂O₃. The conductivity increases then decrease with the addition of Al₂O₃. When the addition amount of Al₂O₃ is 15wt%, the content of crystalline region is the lowest, which has the highest conductivity. This implies the conductivity mainly comes from the amorphous region, which is the same with the previous studies. When the Al₂O₃ content is too low (<15wt%), the effect of Al₂O₃ is negligible on the formation of PEO₃/LiCF₃SO₃ crystalline complex. When the Al₂O₃ content is too high (>15wt%), the agglomeration of Al₂O₃ appears. When the agglomeration of Al₂O₃

becomes more and more obvious, the content of crystalline region increases. Only as the Al_2O_3 content is 15wt%, the nano- Al_2O_3 powder disperses uniformly. In this case, the crystallization of PEO and $\text{PEO}_3/\text{LiCF}_3\text{SO}_3$ complex is prevented, which leads to the highest conductivity.

4. Conclusion

The influences of nano- Al_2O_3 on the phase structure and conductivity of the $\text{PEO}/\text{LiCF}_3\text{O}_3$ complex are discussed in this work. The results show that the phase structure and conductivity of the $\text{PEO}/\text{LiCF}_3\text{O}_3$ -n Al_2O_3 complex show complicated changes with the addition of Al_2O_3 . The amount of crystalline region and conductivity first decrease then increase with the addition of Al_2O_3 . When the Al_2O_3 content is too low (<15wt%), the effect of Al_2O_3 is negligible on the formation of $\text{PEO}_3/\text{LiCF}_3\text{SO}_3$ crystalline complex. When the Al_2O_3 content is too high (>15wt%), the agglomeration of Al_2O_3 appears. Only as the Al_2O_3 content is 15wt%, the nano- Al_2O_3 powder disperses uniformly. In this case, the crystallization of PEO and $\text{PEO}_3/\text{LiCF}_3\text{SO}_3$ complex is prevented, which leads to the highest conductivity.

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