Probing the Interfacial Interaction of Polymeric PEO/Li-Al-MCM-41 Nanocomposite: A $^{27}$Al, $^{13}$C and $^{7}$Li Solid State MAS NMR Study

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Abstract

Interfacial interaction of poly(ethylene) oxide (PEO) and Li-Al-MCM-41 were studied by $^{13}$C, $^{7}$Li and $^{27}$Al solid state MAS NMR. In $^{27}$Al spectroscopy, it is found that Al in Li-Al-MCM-41 is in tetrahedral position, and generating AlO$_4^-$.$^{7}$Li spectroscopy confirmed that Li$^+$ electrostatically interacted with AlO$_4^-$ in the framework of Li-Al-MCM-41. When PEO was combined with Li-Al-MCM-41 by melt intercalation technique, the interaction of PEO oxygen-bridging atom with Li$^+$ was interpreted from $^{13}$C CP/MAS NMR spectroscopy in which case, the PEO peaks shifted downfield by ca. 2 ppm. A smaller linewidth of $^{13}$C CP/MAS NMR of PEO/Al-MCM-41 compared to free PEO suggested that PEO segments were distributed in preferred orientations, presumably in the pore channel of MCM-41. A distinct structural feature of the nanocomposite was shown by $^{7}$Li and $^{13}$C CP/MAS NMR of PEO/Li-Al-MCM-41 in comparison to Li-MCM-41. The results show that the presence Li$^+$ in Li-Al-MCM-41 does not produce any significant peak shifts in the $^{7}$Li spectra suggesting that Li$^+$ was strongly interacted with AlO$_4^-$.

Keywords: PEO/Li-Al-MCM-41, nanocomposite, $^{13}$C, $^{7}$Li and $^{27}$Al solid state MAS NMR.

Introduction

Poly(ethylene) oxide (PEO) is a leading candidate for the electrolyte in lithium polymer batteries. In practical applications, such systems are operated at temperatures above the glass–liquid transition but where sufficient interchain entanglement exists to form a rubbery material [1-3]. In polymer electrolytes, complete transport of charge by Li$^+$ is desired, but due to the mobility of the anions, experimentally determined transference numbers are low. A high Li$^+$ mobility in conducting polymer electrolyte can be obtained by immobilizing the PEO anions onto the pore of MCM-41 particles [4]. This is supported by the fact that molecular-level orientation can enhance electrical conductivity of conjugated polymers and it has more recently been demonstrated that this type of orientation can have effects on ionic conduction as well [5]. Research in this area is important since ionic conducting solids with anisotropic conductivity could be very important in future molecular electronic devices. The knowledge of the interaction characteristics of PEO in these nanocomposites is therefore a prerequisite to understanding the above-cited important property. Thus, a tunable interfacial molecular contact is necessary. Previously, PEO/Li-Al-MCM-41 nanocomposites were synthesized and characterized by XRD and FTIR [6]. However, the interfacial interaction between PEO and Li-Al-MCM-41 is not well understood. In this paper, we used $^{27}$Al, $^{7}$Li and $^{13}$C CP/MAS NMR to study their molecular interaction.
Materials and Methods

MCM-41 was synthesized according to the literature [6]. For the ion exchange with Li⁺, 1.0 g of the calcined Al-MCM-41 was dispersed in aqueous solutions of LiCl 1 M (50 ml) at 90°C in polypropylene bottles. The procedure was repeated three times to increase the ion exchange level, in order to obtain the Li⁺ form of AlMCM-41. After the treatment, the samples were filtered, washed with distilled water and dried at 100°C. Melt intercalation method was used for preparation of PEO/Li⁺-exchanged Al-MCM-41 nanocomposites. Appropriate amounts of poly(ethylene) oxide, (PEO) and Li⁺-exchanged Al-MCM-41 powders were weighed separately and then ground together in agate mortar and pestle. When a pellet of the mixture was required, the powder was spooned into a 13-mm diameter stainless steel die and pressed into pellets under 20 MPa pressure for 1 min at room temperature. The final pellet was about 2 mm thick. All samples were heated as required at 90°C in vacuum atmosphere, then cooled to room temperature.

The MAS NMR experiments were performed using Bruker Avance 400 MHz 9.4T spectrometer. The ³¹C CP/MAS NMR spectra were recorded with a recycle delay of 5.0 s, number of transient of 2000 and spinning rate of 7 kHz. The ⁷Li MAS NMR spectra were recorded at 155.50 MHz using 1.0 /ms radiofrequency pulses, a recycle delay of 2.0 s, number of transient of 600, and spinning rate of 7.0 kHz. The ⁷⁰Al MAS NMR spectra were recorded at 104.26 MHz using 2.0 /ms radiofrequency pulses, a recycle delay of 2.0 s, and spinning rate of 12.5 kHz. Chemical shifts for ³¹C, ⁷⁰Al and ⁷Li were referred to TMS, Al(H₂O)⁶⁺ and TMS, respectively.

Results and Discussion

The ⁷⁰Al MAS NMR spectra of PEO/Li-Al-MCM-41 are shown in Fig. 1. Generally the spectra are broad with the main peak centered at -56 ppm corresponding to Al tetrahedral. No peak at 0 ppm confirming that no Al octahedral was present. This result suggested that tetrahedral Al (AlO₄) generated a negative charge in the framework and interacted with Li⁺ ion by means of electrostatic interaction.

![Fig. 1 ⁷⁰Al MAS NMR of PEO/Li-Al-MCM-41 with various Si/Al ratios; (a) Si/Al = 10, (b) Si/Al = 60, (c) Si/Al = 100. PEO content is 10 %wt.](image-url)
Si/Al ratios and PEO content is 10 %wt. The spectral signal of PEO/Li-Al-MCM-41 is sharpened in comparison to ‘free’ PEO. The degree of sharpening of the spectral signal might be due to the immobilization of PEO on the surface of Li-Al-MCM-41. A chemical shift, ca. 2 ppm, is also observed on PEO/Li-Al-MCM-41. The large low field chemical NMR shift of the signal at ca. 69 ppm can be explained by the interaction of the free electron pairs of the oxygen atoms of the PEO with a charged molecule on the surface of Li-Al-MCM-41 with PEO. There are two possibilities of interaction; with Li⁺ and/or silanol groups. These observations provide strong support for the conclusion that an interaction between PEO with Li-Al-MCM-41, presumably in internal pore, occurs in nanocomposite. This argument was supported by the fact that ¹³C peak of template surfactant (hexadecyltrimethylammonium bromide), as structure directing agent, of MCM-41 which is located inside the pore also

![Fig. 2 ¹³C CP/MAS NMR of (a) PEO, and PEO/Li-Al-MCM-41 with various Si/Al ratios; (b) Si/Al = 10, (c) Si/Al = 60, and (d) Si/Al = 100. PEO content is 10 %wt.](image-url)
showed a chemical shift to a lower magnetic field in comparison to free surfactant [7].

Fig. 3 shows the $^7$Li spectrum of PEO/Li-Al-MCM-41 compared to Li-Al-MCM-41. $^7$Li is a quadrupolar nucleus having spin I=3/2, a relatively low quadrupole moment and a high natural abundance of 93%, which renders the registration $^7$Li NMR spectra relatively easy. MAS $^7$Li NMR of a series PEO/Li-Al-MCM-41 with a different degree of Li exchange showed that a sharp singlet with linewidth of about 1 ppm was observed. It is clearly observed that a shoulder is observed for Li-Al-MCM-41 indicating that fully exchanged was achieved [8]. However, no significant chemical shift was observed in the spectrum. This might be only a weak electrostatic interaction of PEO and Li$^+$ was present. In addition, as shown in Fig. 3, it is seen that the $^7$Li NMR linewidth for PEO/Li-Al-MCM-41 is larger than that of Li-Al-MCM-41. This result reflects the broadening of the linewidth by segmental dynamics of PEO [9].

It was commonly accepted that the main driving force for the adsorption of PEO chain segments to MCM-41 surface groups was attributed to the acid-base interactions of the free electron pairs of the oxygen atoms of the PEO chain [hydrogen-bond accepting (HBA) groups] with the active hydrogen atoms of the silanol groups of the MCM-41 surface [hydrogen-bond donating (HBD) groups]. Of course, dispersion forces and specific interactions between siloxane bridges and the oxygen atoms of the PEO chain are also conceivable. Based on this consideration, as shown in Fig. 4, an interaction model is proposed. Since only weak interaction between Li$^+\leftrightarrow$PEO (a) was observed, the interaction of SiOH$\leftrightarrow$PEO (c) became dominant. This is supported by the fact that a strong Li$^+\leftrightarrow$AlO$_4^-$ (b) interaction also occurs, since fully Li-exchange was observed in $^7$Li spectra of Li-Al-MCM-41. The degree of the electrostatic interaction of SiOH$\leftrightarrow$PEO and AlO$_4^-$Li$^+$ is larger than Li$^+\leftrightarrow$PEO.

![Fig. 3 $^7$Li MAS NMR of (a) Li-Al-MCM-41 (Si/Al = 10) and PEO/Li-Al-MCM-41 with various Si/Al ratios; (b) Si/Al = 100, (c) Si/Al = 60, (d) Si/Al = 10. PEO content is 10 %wt.](image-url)
Conclusions

The effect of interaction of PEO and Li-Al-MCM-41 was demonstrated by by $^{13}$C, $^{7}$Li and $^{27}$Al solid state MAS NMR. The degree of the electrostatic interaction of SiOH$\leftrightarrow$PEO and Li$^+$,$\leftrightarrow$AlO$_4^-$ is larger than PEO$\leftrightarrow$L$^+$. 

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References