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# Nuclear magnetic resonance studies of nanocomposite polymer electrolytes

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## Abstract

The origin of the ionic conductivity enhancement in polymer electrolytes that occurs on adding inorganic oxide powders was explored by <sup>1</sup>H and <sup>7</sup>Li nuclear magnetic resonance. Ionic and molecular self-diffusion coefficients determined by pulsed field gradient spin-echo measurements demonstrate that lithium ionic diffusivity is enhanced in the composites, but this enhancement is not attributed to polymer segmental mobility. Two different systems were investigated: a high-molecular-mass poly(ethylene oxide)–LiClO<sub>4</sub> complex with nanoscale TiO<sub>2</sub>; and a low-molecular-mass poly(ethylene glycol)–LiClO<sub>4</sub> solution with Al<sub>2</sub>O<sub>3</sub>. In the latter case the effect of varying the alumina surface acidity or basicity was considered.

## 1. Introduction

Composite polymer electrolytes obtained by adding inorganic oxides with crystallite size several nanometres to poly(ethylene oxide) (PEO)–lithium salt complexes have received much recent attention [1–3]. The addition of the nanoparticles improves the dimensional stability at elevated temperatures, and often enhances the ionic conductivity. The latter effect has been attributed to several factors, including suppression of ion-transport-inhibiting crystalline phases characteristic of PEO–salt complexes. Most intriguing, however, are indications that surface interactions between the nanoparticles and ions can lead to a fundamentally different cation transport mechanism by reducing the cation–anion association or creating new conduction pathways near the nanoparticle surface [2].

Nuclear magnetic resonance (NMR) methods have been employed productively in studies of polymer electrolyte structure and ion transport for some two decades [4–8]—including more recent work on nanocomposite materials [9–11]. NMR owes its utility as an investigative tool for polymer electrolytes to several factors: nuclear (elemental) specificity; spectral parameters that depend critically on local structural arrangements via short-range interactions;

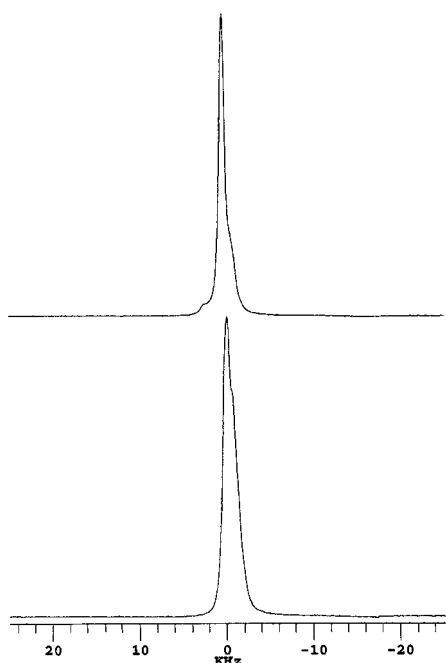
and sensitivity to both large- and small-scale motions spanning a dynamic range of some eight orders of magnitude. The most definitive early evidence that one of the most important factors that determine ionic mobility in polymer electrolytes is polymer segmental motion was derived from NMR line-narrowing studies [4]. A disadvantage of NMR is its requirement of relatively large samples, typically of the order of 100 mg, depending on the nucleus being studied and its concentration. This limitation on nuclear signal strength can be problematic when attempting to study surface as opposed to bulk phenomena, which is a principal goal in many battery materials investigations. On the other hand, well-dispersed nanoparticles in the material yield a large number, characteristic of the bulk phase, of surface interaction sites amenable to NMR study. An example of this can be found even without the presence of a polymer component. In particular, physical mixing of LiI and nanoscale  $\text{Al}_2\text{O}_3$  was found to enhance the ionic conductivity of the salt, and NMR measurements identified  $\text{Li}^+$  ions associated with alumina surface sites which were implicated in the increased ionic conductivity [12].

This communication describes further work on a recently reported study of nanoscale  $\text{TiO}_2$  added to high-molecular-mass PEO complexed with  $\text{LiClO}_4$  [11], and a new investigation of the effects of  $\text{Al}_2\text{O}_3$  added to low-molecular-mass poly(ethylene glycol) (PEG)– $\text{LiClO}_4$  solutions. End-capped PEG has long served as a low-molecular-mass analogue of PEO in studies of polymer electrolytes. An important aspect of the latter work is that the effect of varying the Lewis-type acidity or basicity of the  $\text{Al}_2\text{O}_3$  surface groups, while keeping the particle size constant, is explored for the first time [13]. By utilizing both  $^1\text{H}$  and  $^7\text{Li}$  NMR, we also attempt to address the relative importance of polymer segmental motion, which is related to the local viscosity (or macroscopic viscosity in the case of low-molecular-mass materials), and surface interactions with the inorganic particles, in determining the cationic mobility.

## 2. Experimental details

Preparation of the PEO ( $5 \times 10^6 M_m$ )  $\text{LiClO}_4$  complexes has been described elsewhere [2, 11]. The samples investigated by means of NMR were  $\text{PEO}_8\text{LiClO}_4$  (meaning an ether oxygen:Li ratio of 8:1), both with and without 10 nm particles of  $\text{TiO}_2$ , the former constituting 10 mass% of the sample. For the low-molecular-mass analogues, PEG ( $M_m = 350$ , monomethyl capped) was mixed with  $\text{LiClO}_4$  over a concentration range of 0.5–5 mol  $\text{kg}^{-1}$ . Composite electrolytes were prepared by adding 10 mass%  $\text{Al}_2\text{O}_3$  of average grain size around 1  $\mu\text{m}$ . In order to compare the effects of surface activity, the alumina particles were chosen with different surface groups in terms of their Lewis acidity: composite samples were made with neutral, acidic, and basic alumina. Complete details concerning sample preparation are published elsewhere [13]. Because of the low molecular mass of the PEG and relatively large alumina grain size, some alumina sedimentation was observed. It is estimated that only about half of the  $\text{Al}_2\text{O}_3$  in the samples participates in formation of the composite.

For both NMR spectroscopic and diffusion measurements, about 500 mg of sample was packed into sealed 5 mm (OD) Pyrex tubes. Prior to the measurements the PEO composite samples were annealed at about 110 °C for about 1 h and then quenched to 0 °C, in order to ensure that they were in the amorphous phase (the recrystallization kinetics of even the ceramic-free compounds are much slower than the time necessary to complete the NMR measurements). Lithium-7 NMR measurements were conducted on a Chemagnetics CMX 300 spectrometer operating at a  $^7\text{Li}$  resonance frequency of about 117 MHz. Variable-temperature wide-line spectra were acquired with either single-pulse ( $\pi/2$  pulse; width of about 2  $\mu\text{s}$ ) or quadrupole echo ( $[\pi/2]_x-\tau-[\pi/2]_y$ ) sequences. The pulsed gradient spin-echo (PGSE) diffusion measurements were conducted with a Nalorac Z-Spec gradient probe, using a Hahn spin-echo ( $\pi/2-\tau-\pi$ ; typical  $\pi$  pulse width of 5  $\mu\text{s}$ ) sequence with a pair of square-shaped



**Figure 1.** Proton NMR spectra of PEO<sub>8</sub>LiClO<sub>4</sub> at 80 °C, with TiO<sub>2</sub> (top) and without TiO<sub>2</sub> (bottom).

magnetic field gradient pulses of magnitude  $G$  and duration  $\delta$ . The first is applied between the two rf pulses and a second identical gradient pulse is applied following the  $\pi$  pulse at a time  $\Delta$  after the first gradient pulse. It can be shown [11] that the attenuation of the echo amplitude is given by

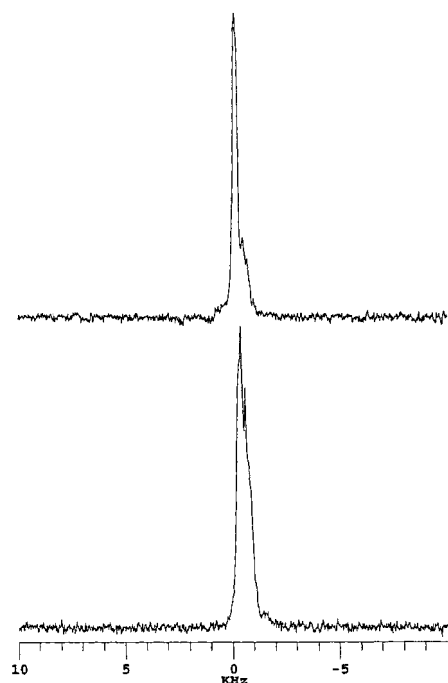
$$A(G) = \exp[-\gamma^2 D G^2 \delta^2 (\Delta - \delta/3)] \quad (1)$$

where  $D$  is the self-diffusion coefficient and  $\gamma$  is the nuclear gyromagnetic ratio. Fitting equation (1) to the echo amplitudes for a series of gradient strengths  $G$  (0.2–1.4 T m<sup>-1</sup>) allows determination of  $D$ . The experimental parameters were  $\Delta$ , about 15 ms, and  $\delta$ , around 10 ms.

### 3. Results and discussion

In a previous investigation, it was reported that the ionic conductivity and lithium diffusivity were enhanced to nearly an order of magnitude higher in the composite PEO electrolyte compared to the ceramic-free material, in spite of the observation that the extents of segmental motion, as probed by NMR linewidth measurements, are comparable in the two samples [11]. This finding, as well as the observed improvement in cation transference number in the composite, support the view that the surface interactions in the vicinity of the TiO<sub>2</sub> particles reduce cation–anion pairing tendencies. Further evidence along these lines is presented below. Figures 1 and 2 display <sup>1</sup>H and <sup>7</sup>Li NMR spectra, respectively, of PEO<sub>8</sub>LiClO<sub>4</sub> at 80 °C, for both ceramic-free and TiO<sub>2</sub>-containing samples. The two samples exhibit comparable linewidths for both nuclei. In a previous study, room temperature linewidths for the TiO<sub>2</sub>-containing material were found to even be slightly larger than in the ceramic-free sample, despite the higher conductivity of the latter [11].

PGSE diffusion results for both samples and both nuclei are listed in table 1. The proton diffusion data reflect the similarity in polymer segmental mobilities of the composite and ceramic-free materials, as do the linewidth results, the latter being sensitive to motion over



**Figure 2.** Lithium-7 NMR spectra of PEO<sub>8</sub>LiClO<sub>4</sub> at 80 °C, with TiO<sub>2</sub> (top) and without TiO<sub>2</sub> (bottom).

**Table 1.** Self-diffusion coefficients for PEO<sub>8</sub>LiClO<sub>4</sub>, at 80 °C.

Sample	$D(^1\text{H})$ ( $10^{-7} \text{ cm}^2 \text{ s}^{-1}$ )	$D(^7\text{Li})$ ( $10^{-7} \text{ cm}^2 \text{ s}^{-1}$ )
Without TiO <sub>2</sub>	1.3	1.8
With TiO <sub>2</sub>	1.8	5.9

a shorter length scale. On the other hand, there is about a factor-of-three enhancement in lithium diffusivity in the composite material. Thus it is clear that factors other than exclusively segmental motion are responsible for the enhanced ionic conductivity and diffusivity of the composite. Early investigations of composite polymer electrolytes attributed conductivity enhancements to suppression of crystalline phases and, by implication, to enhancement of segmental motion. In the present study, care has been taken to ensure that the samples were entirely amorphous, at least during the experimental data acquisition, which has allowed a more in-depth view of the function of the ceramic nanoparticles to be obtained.

Composite PEG:LiClO<sub>4</sub> self-diffusion coefficients for both <sup>1</sup>H and <sup>7</sup>Li are listed in table 2. The proton self-diffusion largely reflects the solution viscosity; thus it is not surprising that the complexes with the highest salt concentrations (2 mol kg<sup>-1</sup>) exhibit the lowest diffusion coefficients for both nuclei. Due to the lack of precision associated with diffusion coefficients in the 10<sup>-8</sup> cm<sup>2</sup> s<sup>-1</sup> range (near the limit of instrument sensitivity), no conclusions can be drawn regarding the effect of alumina. For a much more salt-dilute composite (0.05 mol kg<sup>-1</sup>), some conclusions are apparent, and the table entries in bold type are the ones which we believe shed light on the effect of changing the Lewis acidity of the alumina particles. That is, the neutral alumina filler gives the highest Li diffusivity, while the corresponding proton diffusion does not follow this behaviour.

In a recent electrochemical and vibrational spectroscopic investigation of the above materials, it was determined that the presence of the filler enhances the ionic conductivity for the

**Table 2.** Self-diffusion coefficients of PEG-based electrolytes ( $T = 24\text{ }^{\circ}\text{C}$ ).

Sample	Diffusion coefficient ( $\text{cm}^2\text{ s}^{-1}$ )	
	$^1\text{H}$	$^7\text{Li}$
PEG( $M_m = 350$ )–LiClO <sub>4</sub> (2 mol kg <sup>-1</sup> )—10 mass%. Al <sub>2</sub> O <sub>3</sub> acidic	$1.4 \times 10^{-8}(\pm 25\%)$	$1.4 \times 10^{-8}(\pm 25\%)$
PEG( $M_m = 350$ )–LiClO <sub>4</sub> (2 mol kg <sup>-1</sup> )—10 mass%. Al <sub>2</sub> O <sub>3</sub> neutral	$1.1 \times 10^{-8}(\pm 25\%)$	$1.6 \times 10^{-8}(\pm 25\%)$
PEG( $M_m = 350$ )–LiClO <sub>4</sub> (2 mol kg <sup>-1</sup> )—10 mass%. Al <sub>2</sub> O <sub>3</sub> basic	$1.2 \times 10^{-8}(\pm 25\%)$	—
PEG( $M_m = 350$ )–LiClO <sub>4</sub> (0.05 mol kg <sup>-1</sup> )—no filler	<b><math>2.9 \times 10^{-7}</math></b>	<b><math>2.5 \times 10^{-7}</math></b>
PEG( $M_m = 350$ )–LiClO <sub>4</sub> (0.05 mol kg <sup>-1</sup> )—10 mass%. Al <sub>2</sub> O <sub>3</sub> acidic	<b><math>2.54 \times 10^{-7}</math></b>	<b><math>2.40 \times 10^{-7}</math></b>
PEG( $M_m = 350$ )–LiClO <sub>4</sub> (0.05 mol kg <sup>-1</sup> )—10 mass%. Al <sub>2</sub> O <sub>3</sub> neutral	<b><math>2.21 \times 10^{-7}</math></b>	<b><math>2.96 \times 10^{-7}</math></b>
PEG( $M_m = 350$ )–LiClO <sub>4</sub> (0.05 mol kg <sup>-1</sup> )—10 mass%. Al <sub>2</sub> O <sub>3</sub> basic	<b><math>2.69 \times 10^{-7}</math></b>	<b><math>2.38 \times 10^{-7}</math></b>
PEG( $M_m = 350$ )–LiClO <sub>4</sub> (0.01 mol kg <sup>-1</sup> )—no filler	$2.70 \times 10^{-7}$	$3.20 \times 10^{-7}$
PEG( $M_m = 350$ )–LiClO <sub>4</sub> (0.01 mol kg <sup>-1</sup> )—10 mass%. Al <sub>2</sub> O <sub>3</sub> acidic	$2.88 \times 10^{-7}$	$2.22 \times 10^{-7}$
PEG( $M_m = 350$ )–LiClO <sub>4</sub> (0.01 mol kg <sup>-1</sup> )—10 mass%. Al <sub>2</sub> O <sub>3</sub> neutral	$3.17 \times 10^{-7}$	—
PEG( $M_m = 350$ )–LiClO <sub>4</sub> (0.01 mol kg <sup>-1</sup> )—10 mass%. Al <sub>2</sub> O <sub>3</sub> basic	$3.01 \times 10^{-7}$	—
PEG( $M_m = 350$ )–LiClO <sub>4</sub> ( $10^{-4}$ mol kg <sup>-1</sup> )—10 mass%. Al <sub>2</sub> O <sub>3</sub> acidic	$3.00 \times 10^{-7}$	—
PEG( $M_m = 350$ )–LiClO <sub>4</sub> ( $10^{-4}$ mol kg <sup>-1</sup> )—10 mass%. Al <sub>2</sub> O <sub>3</sub> neutral	$3.01 \times 10^{-7}$	—
PEG( $M_m = 350$ )–LiClO <sub>4</sub> ( $10^{-4}$ mol kg <sup>-1</sup> )—10 mass%. Al <sub>2</sub> O <sub>3</sub> basic	$3.14 \times 10^{-7}$	—

higher-salt-concentration (above 1 mol kg<sup>-1</sup>) samples [13]. The mechanisms responsible are the decrease in electrolyte viscosity attributed to a weakening of the polyether–salt interaction and the reduction of the fraction of ion pairs. The latter arises from Li<sup>+</sup> interactions with basic surface groups on the alumina particles and from ClO<sub>4</sub><sup>-</sup> interactions with acidic or neutral alumina surface groups [13]. At lower salt concentrations, in particular at the 0.05 mol kg<sup>-1</sup> grouping in table 2, where the filler concentration greatly exceeds the salt concentration, the effect of the filler is to decrease the ionic conductivity by increasing the solution viscosity. This is reflected in the  $^1\text{H}$  diffusion coefficients in table 2, which are highest for the electrolyte without filler. On the other hand the  $^7\text{Li}$  diffusivity is highest in the material with neutral filler. It is not understood at this time why the neutral filler enhances Li diffusivity better than the acidic filler—they both presumably interact with the anions in solution. Thus, as in the case of the solid PEO composites, factors other than segmental motion (i.e. related to viscosity in the low-molecular-mass analogues) of the host polymer are important in determining the ionic mobility. These factors are complicated functions of the various interactions between the inorganic particles and the ions and polymer. Unfortunately, the low signal-to-noise ratio characteristic of the samples in the 0.01 mol kg<sup>-1</sup> grouping (table 2), due to the low Li concentration, do not allow definitive comparison with the 0.05 mol kg<sup>-1</sup> grouping. It would be of great interest to be able to investigate the effects of variable surface acidity or basicity using nanoparticle additives, instead of the  $\sim\mu\text{m}$  scale employed in this work, because of the much larger surface area of the former.

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