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Journal of Power Sources 97–98 (2001) 644–648

JOURNAL OF
**POWER
SOURCES**

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Enhancement of ion transport in polymer electrolytes by addition of nanoscale inorganic oxides

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Received 20 June 2000; received in revised form 29 January 2001; accepted 4 February 2001

Abstract

The effect of addition of nanoparticle inorganic oxides to poly(ethylene oxide) (PEO) complexed with LiClO₄ on cation transport properties has been explored by electrochemical and ⁷Li nuclear magnetic resonance (NMR) methods. The presence of the nanoparticles generally increases the ionic conductivity and the cation transference number, the effect being greatest for TiO₂. The enhancement in cation transference number is directly correlated with increased Li diffusivity measured by NMR. The NMR results also demonstrate that the increased ionic conductivity is not attributable to a corresponding increase in polymer segmental motion, but more likely a weakening of the polyether-cation association induced by the nanoparticles. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Nanocomposite polymer electrolyte; Nuclear magnetic resonance; Enhanced cation transport

1. Introduction

In previous papers we have illustrated and discussed the transport properties of various types of nanocomposite polymer electrolytes formed by dispersing into a poly(ethylene oxide) PEO–LiX matrix selected types of ceramic powders having nanoparticle sizes [1–4].

The electrochemical investigation of these materials has clearly demonstrated that the ceramic fillers induce quite relevant effects, such as a consistent enhancement of the ionic conductivity, both below and above the PEO crystallization temperature. These effects have been interpreted by assuming that the role of the ceramic filler is that of inhibiting the PEO chain crystallization kinetics, as well as providing specific surface interactions with the electrolyte components [1,2].

In this work we attempt to refine the interpretation model and to confirm it with a series of specifically addressed electrochemical and nuclear magnetic resonance (NMR) measurements.

2. Experimental

The nanocomposite polymer electrolytes were obtained by combining PEO (either Aldrich Chemical Co. or BDH Polyox WSR-301), with LiClO₄ (Merck “Selectipur”, battery grade) and using TiO₂ (CISE, 11 nm), Al₂O₃ (Aldrich, 5.8 nm) or SiO₂ (Aldrich, 7 nm) respectively, as the ceramic filler. The LiClO₄/PEO concentration ratio was fixed to 1/8 or 1/30 concentration and the amount of added ceramic to 10% of the total PEO₈LiClO₄ weight. The preparation of the nanocomposite electrolyte samples involved first the dispersion of the selected ceramic powder and of the LiClO₄ lithium salt in acetonitrile, followed by the addition of the PEO polymer component and by a thorough mixing of the resulting slurry. The homogeneous slurry was then cast between two glass plates to yield mechanically stable membranes of average thickness of about 150 μm. The same casting procedure was also used to prepare ceramic-free PEO–LiClO₄ samples for comparison purpose.

The lithium transference number, T_{Li}^{+} , was evaluated using the method developed by Vincent and co-workers, in which ac and dc polarization pulses are applied to cells of the Li/electrolyte sample/Li type and the time evolution of the resulting current flow is monitored. [5] To improve the accuracy of the results, we have developed a special soft-

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ware capable of acquiring a very large number of current data per second immediately after the application of the voltage pulse.

For both NMR spectroscopic and diffusion measurements, about 500 mg of sample was packed into sealed 5 mm (o.d.) pyrex tubes. Prior to the measurements the samples were annealed at about 90°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 ^7Li resonance frequency of about 117 MHz. Variable temperature wide-line spectra were acquired with either single pulse ($\pi/2$ pulse width of about 2 μs) 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 π pulse width of 5 μs) sequence with a pair of square-shaped magnetic field gradient pulses of magnitude G and duration δ . The first is applied between the two rf pulses and a second identical gradient pulse is applied following the π pulse at a time Δ after the first gradient pulse. It can be shown [6] 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 γ the nuclear gyromagnetic ratio. Fitting Eq. (1) to the echo amplitudes for a series of gradient strengths G (0.2–1.4 Tm^{-1}), allows determination of D . Experimental parameters were Δ about 15 ms and δ around 10 ms.

3. Results

Fig. 1 shows in comparison the Arrhenius plots of two composites with that of a ceramic-free polymer electrolyte. The first effect which is evidenced from this figure is that the Arrhenius plots of the composites do not break at the PEO crystallization temperature (i.e. around 70°C), this giving them a much higher (i.e. about two orders of magnitudes) ambient temperature conductivity. This has been explained assuming that the nanosized ceramic filler, due to its large surface area, prevents local PEO chain reorganization with the result of locking in at ambient temperature a high degree of disorder which in turn favors fast ionic transport. Various experimental tests, including electrochemical impedance spectroscopy (EIS), differential scanning calorimetry (DSC) and energy dispersive X-ray diffraction (EDXD) analyses, have been carried out to support this part of the model, with the successful results extensively described in the previous papers [1,2].

However, the conductivity enhancement in the composite polymer electrolytes cannot be solely attributed to the retention of the amorphous phase caused by the steric

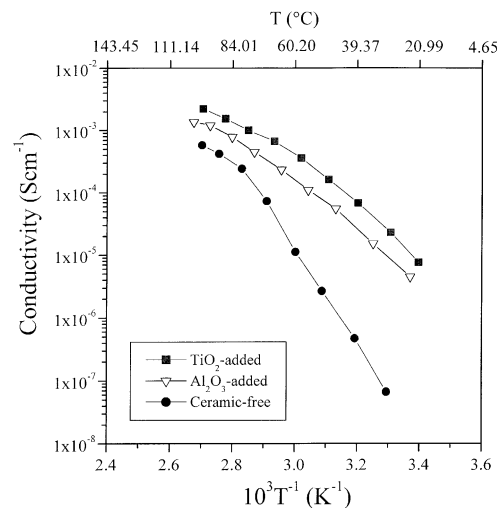


Fig. 1. Arrhenius plots of the electrical conductivity of nanocomposite polymer electrolytes formed by dispersing in a $\text{P}(\text{EO})_8\text{LiClO}_4$ matrix 10 w/o of TiO_2 and Al_2O_3 , respectively. The plot of the ceramic-free $\text{P}(\text{EO})_8\text{LiClO}_4$ polymer electrolyte is also reported for comparison purposes. Data obtained from impedance spectroscopy.

hindrance effect of the nanometric inorganic filler. Indeed, this argument does not hold for the conductivity enhancement observed above 70°C (see Fig. 1) where the polymer electrolyte is amorphous by its own nature. Therefore, the model must be extended to consider other ceramics' effects for accounting for the overall enhanced transport properties of the nanocomposite electrolytes. These may involve specific interactions between the surface groups of the ceramic particles and both the PEO segments and the lithium salt anions.

This specific role of the filler may be further interpreted in terms of Lewis acid–base interactions. In this fashion the Lewis acid groups of the added ceramics (e.g. the $-\text{OH}$ groups on the SiO_2 surface) may quite likely compete with the Lewis-acid lithium cations for the formation of complexes with the PEO chains, as well as with the anions of the added LiX salt.

According to this model, two structural modifications occurs at the ceramics surface, namely

- Ceramic surface groups provide cross-linking centers for the PEO segments and for the X^- anions, thus lowering the PEO reorganization tendency and thereby promoting structural modifications of the polymer chains. This, in turn, establishes Li^+ conducting pathways at the ceramic surface;
- Lewis acid–base interactions between the polar surface groups of the inorganic filler and the electrolyte ionic species, which yields salt dissociation via “ion-ceramic complex” formation.

The two effects may indeed account for the observed enhancement of the conductivity of the nanocomposites over a large temperature range. Thus, our task is here that of

Table 1

Li⁺ transference numbers of PEO–LiX composite and for comparison, of ceramic-free, electrolytes at 70, 90 and 100°C

Sample	T_+
P(EO) ₃₀ LiClO ₄ ($t = 100^\circ\text{C}$)	0.18–0.19
P(EO) ₈ LiClO ₄ ($t = 90^\circ\text{C}$)	0.19–0.20
P(EO) ₈ LiClO ₄ + 10 w/o TiO ₂ ($t = 90^\circ\text{C}$)	0.50–0.60
P(EO) ₈ LiClO ₄ + 10 w/o Al ₂ O ₃ ($t = 90^\circ\text{C}$)	0.31–0.33
P(EO) ₃₀ LiClO ₄ + 10 w/o SiO ₂ ($t = 100^\circ\text{C}$)	0.22–0.23

confirming the model by carrying out additional analytical measurements. These include electrochemical tests, i.e. the determination of the lithium ion transference number and of the conductivity of various samples differing in the type and the nature of the ceramic filler and/or of the anion of the LiX salt, as well as NMR measurements.

Table 1 lists the lithium transference numbers of various nanocomposite samples. The results are consistent in confirming the model, i.e. by demonstrating a difference in T_{Li^+} when passing from the ceramic-free to the composite polymer electrolytes. In addition, the T_{Li^+} values consistently vary according to the Lewis acid character of the added ceramic. For the most acidic type, i.e. the TiO₂ one, the transference number value increases up to 0.5–0.6 in the 45–90°C temperature range, i.e. to our knowledge, the highest value so far obtained for PEO-based electrolytes. This value, however, is consistent with the effect (i) of the transport model above proposed, according to which the action of the ceramic filler is that of promoting surface conducting pathways as a result of its Lewis acid type interactions with the PEO chains. Lithium ions are expected to move freely along these ceramic surface pathways and thus, under these

conditions, a consistent enhancement of the cation transference number is logically expected.

Fig. 2 is an Arrhenius plot of the ⁷Li NMR central ($\pm 1/2$) transition linewidth in PEO₈LiClO₄, both with and without TiO₂. Although, the linewidth temperature dependences for both materials are quite similar, the linewidth of the ceramic-containing electrolyte is slightly higher throughout the entire temperature range. Earlier ⁷Li NMR studies of polymer electrolytes have established that the leading contribution to the central transition linewidth arises from the ⁷Li–¹H heteronuclear dipole–dipole interaction due to polyether protons. [7,8] Two possible explanations for the modest linewidth increase in the ceramic-containing system are: (i) there is less segmental motion (which tends to average the dipole–dipole interaction) than in the ceramic-free material; (ii) the average Li–H separation is smaller in the ceramic composite. Because it is difficult to envision a mechanism whereby the TiO₂ nanoparticles engender a tighter helical winding of the PEO units around the cations (effectively decreasing the Li–proton distance), we attribute the result shown in Fig. 2 to decreased segmental motion in the composite electrolyte.

Fig. 3 displays NMR spectra of both samples acquired at comparable temperatures (23°C for the composite and 20°C for the ceramic-free material). The composite sample exhibits a rigid baseline with clear evidence of distributed nuclear quadrupole satellite transitions. [7,8] Close examination of this spectrum reveals a small relatively narrow mobile Li component superimposed on the rigid line, but it is nevertheless appropriate to conclude that most of the Li⁺ ions are immobile at room temperature. The rigid environment of the Li⁺ ions may be partly attributable to close association with the nanoparticle surface (i.e. the second of

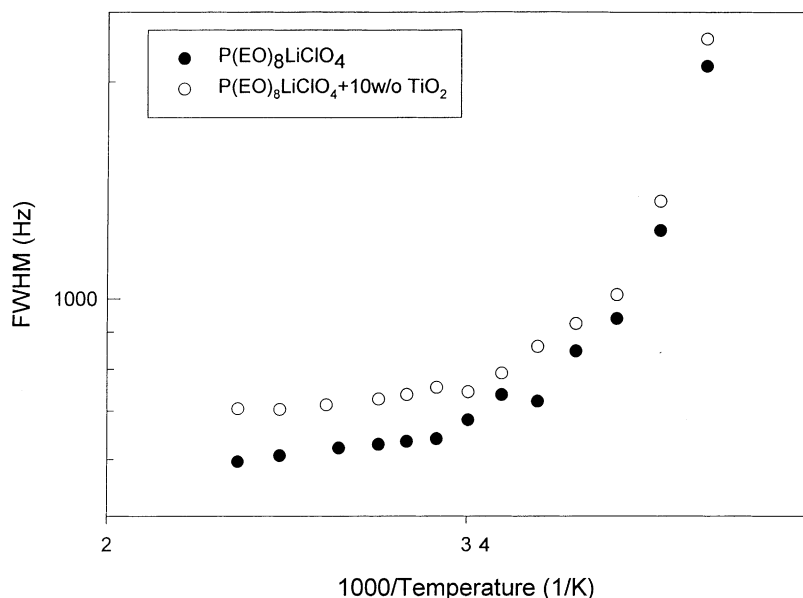


Fig. 2. Arrhenius plot of ⁷Li NMR line widths of PEO₈LiClO₄.

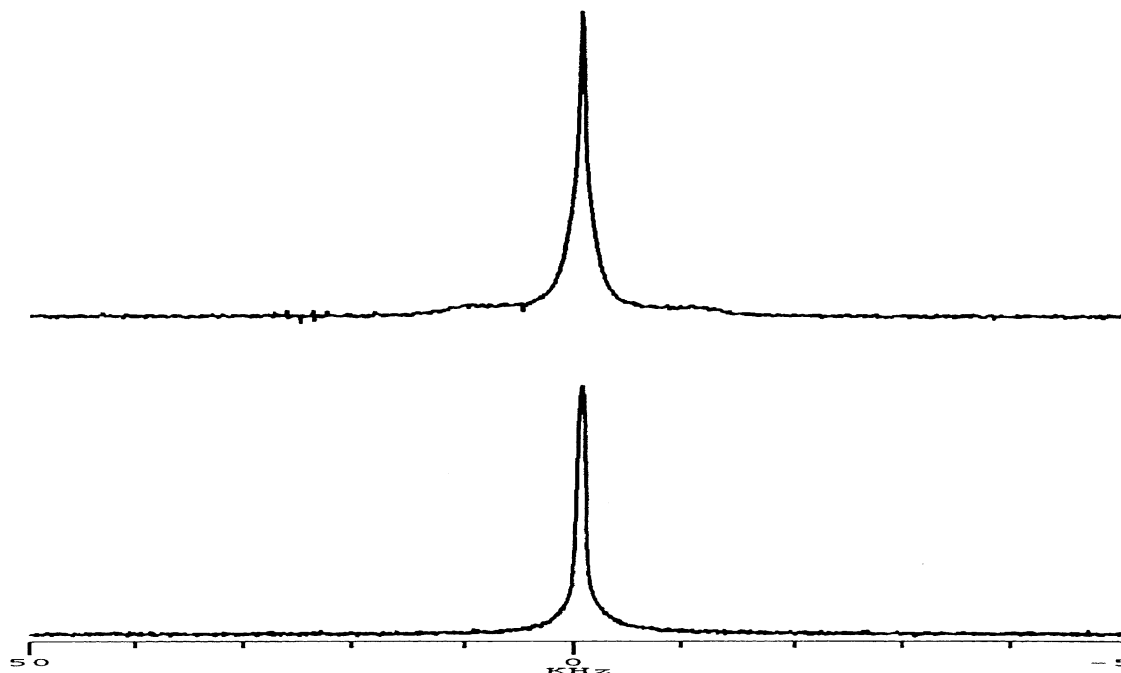


Fig. 3. Lithium-7 solid state NMR spectra of $\text{PEO}_8\text{LiClO}_4$. Top: 10 w/o TiO_2 at 23°C . Bottom: no TiO_2 at 20°C .

the two structural modifications postulated earlier), but this hypothesis requires further study involving comparison of low temperature (well below room temperature) spectra of the ceramic-free and composite electrolytes.

At first glance, the enhanced segmental motion of the ceramic-free system, is at odds with its lower conductivity, compared to the TiO_2 — containing sample. However, segmental motion in and of itself is not sufficient for cation transport. The transference number results in Table 1 imply that there are additional important factors, in particular a weakening of the normally strong cation polyether oxygen coupling due to the presence of the nanoparticles. The nanoparticle enhancement of cation transference numbers

is consistent with the results of ^7Li diffusivity, shown in Fig. 4, which is a plot of spin echo decay in the PGSE method for both samples. The combination of NMR line-width, short spin–spin relaxation times, and low diffusivity at ambient temperature precludes the determination of the self-diffusion coefficient by NMR methods, hence the data in Fig. 4 were obtained at 65°C . The D-values deduced from the echo decays are 6.6×10^{-7} and $8.3 \times 10^{-8} \text{ cm}^2/\text{s}$ ($\pm 10\%$) for polymer electrolyte with and without TiO_2 , respectively. Thus even with slightly enhanced segmental motion in the ceramic-free material (not only at ambient temperature, but also at 65°C), the Li^+ ion diffusivity is nearly an order of magnitude higher in the composite material, again consistent with the transference number results.

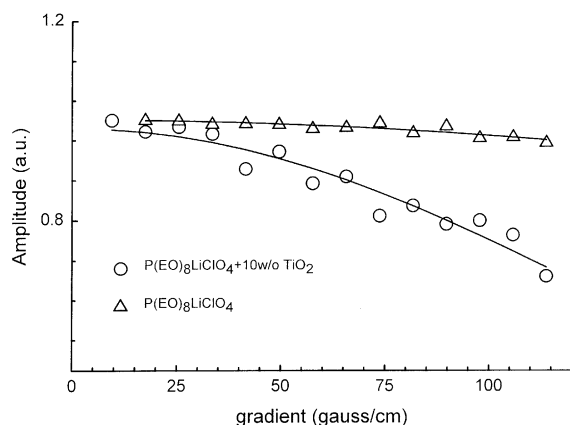


Fig. 4. Pulsed field gradient spin echo decay profiles for $\text{PEO}_8\text{LiClO}_4$ with and without TiO_2 . Diffusion coefficients calculated from decays are 6.6×10^{-7} and $8.3 \times 10^{-8} \text{ cm}^2/\text{s}$ for polymer electrolyte with and without TiO_2 , respectively.

4. Conclusions

The addition of nanoscale inorganic oxides increases the ionic conductivity and cation transference number of $\text{PEO}:\text{LiClO}_4$ polymer electrolytes. This improvement appears to be greatest for TiO_2 , and is not directly related to polymer segmental motion, but more likely to a weakening of the polyether oxygen–cation interaction. Enhanced cation diffusivity in the nanocomposite electrolyte is observed directly by PGSE NMR methods.

Acknowledgements

This work has been carried out with the financial support of the US Army European Research Office, under Contract

N. 68171-99-M-6040, and the US Department of Energy, Division of Basic Energy Sciences.

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