

Morphology, Crystallinity, and Electrochemical Properties of *In Situ* Formed Poly(ethylene oxide)/TiO₂ Nanocomposite Polymer Electrolytes

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ABSTRACT: A method to produce nanocomposite polymer electrolytes consisting of poly(ethylene oxide) (PEO) as the polymer matrix, lithium tetrafluoroborate (LiBF₄) as the lithium salt, and TiO₂ as the inert ceramic filler is described. The ceramic filler, TiO₂, was synthesized *in situ* by a sol-gel process. The morphology and crystallinity of the nanocomposite polymer electrolytes were examined by scanning electron microscopy and differential scanning calorimetry, respectively. The electrochemical properties of interest to battery applications, such as ionic conductivity, Li⁺ transference number, and stability window were investi-

gated. The room-temperature ionic conductivity of these polymer electrolytes was an order of magnitude higher than that of the TiO₂ free sample. A high Li⁺ transference number of 0.51 was recorded, and the nanocomposite electrolyte was found to be electrochemically stable up to 4.5 V versus Li⁺/Li. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2815–2822, 2003

Key words: electrochemistry; morphology; nanocomposites; matrix; conducting polymers

INTRODUCTION

Lithium ions conducting solid electrolytes, particularly those of polymer origin, are increasingly used in the design of high energy density batteries, electrochromic devices, and chemical sensors because of the relative ease in fabricating compact and lightweight devices with enhanced safety.^{1,2} An exemplary solid polymer electrolyte is the poly(ethylene oxide) (PEO) system containing a lithium salt. It is widely accepted that ion conduction occurs in the amorphous phase above the glass-transition temperature (T_g) by a liquidlike motion of the Li cations associated with the segmental reorientations of the neighboring polymer strands.³ However, the polymers in such systems tend to crystallize, resulting in low room temperature ionic conductivity ($\sigma < 10^{-7}$ S cm⁻² at 25°C) and Li⁺ transference number (0.1–0.3).

Two approaches have been developed to address this problem, resulting in two different classes of polymer electrolytes known as gel and composite electrolytes, respectively. Gel electrolytes are usually obtained by incorporating a large amount of liquid plasticizer in a polymeric host capable of forming a stable gel.⁴ The ionic conductivities of such systems are often found to be close to those of liquid electrolytes.^{5–7}

However, the enhancement in conductivity is achieved at the expense of compactness, stability, and mechanical strength. Furthermore, the presence of a liquid component in the polymer electrolyte compromises safety and the reliability of the device. Therefore, the composite electrolyte approach remains an attractive alternative.^{8–10} Such composite systems are commonly obtained by dispersing an inert ceramic fine powder into the conventional polymer electrolyte system. The ceramic filler would bring about the formation of amorphous polymer phases at the surface of ceramic particles. Another role of the filler is to ensure solid structure at temperatures higher than the softening point of the polymer.

Various materials, such as γ -LiAlO₂,¹¹ Al₂O₃,¹² and SiO₂,¹³ have been used to produce polymer-ceramic nanocomposites and their implications over the electrochemical properties have been explored. The results generally show improvements in both the ionic conductivity and mechanical properties. It is the prevailing opinion that the increase in ionic conductivity is attributed to an enlarged amorphous phase in the PEO matrix. In addition, ceramic fillers with different surface properties^{14,15} and particle size¹⁶ have also been investigated. Relentless efforts on similar systems have shown that the electrochemical properties of the electrolytes increase with decreasing size of the ceramic fillers.^{14,17,18} From the work of Chung et al.¹⁹ on the effects of nanosized ceramic fillers TiO₂, Al₂O₃, and SiO₂ in PEO-LiClO₄, TiO₂ was identified as the

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ceramic filler that improved the ionic conductivity and cation transference number mostly because of the weakening of polyether oxygen–Li⁺ interactions. Of late, Best and coworkers²⁰ have shown that nanosize TiO₂ influences the ionic conductivity only at high lithium salt concentrations. In their opinion, the addition of TiO₂ increases the conductivity by lowering the degree of ion aggregation within the polymer–salt mixture attributed to the interactions between cations, anions, and fillers.

An extensive literature survey reveals that almost all polymer–ceramic nanocomposites were prepared through mechanical blending of nanosize TiO₂ particles, polymer, and salt in a compatible solvent. Aggregation of these particles stemming from their high surface energy is a perennial problem that undermines the efficacy of the ceramic fillers. A simple and effective method to overcome such a problem is the sol–gel process, wherein the nanosized ceramic fillers are precipitated *in situ* in the polymer matrix through a series of hydrolysis and condensation reactions of suitable precursors. Thus the ceramic fillers are uniformly distributed in the polymer and exhibit excellent properties. The successful implementation of this versatile process in the synthesis of siloxane-derived composite polymer electrolytes has appeared in several recent reports.^{21–23} These organic–inorganic hybrids are generally classified into two broad families: in type I nanocomposites the interactions between the hosting matrix and the entrapped species are weak and based on hydrogen bonds and van der Waals forces; whereas in type II nanocomposites the organic and inorganic components are connected through stronger chemical bonds.

In this study we report a sol–gel process to prepare PEO/TiO₂ nanocomposite polymer electrolytes to obtain a uniform dispersion of TiO₂ particles in the polymer matrix. To the best of our knowledge, this is the first report on using *in-situ* formed TiO₂ for PEO-based polymer electrolytes. TiO₂ was chosen because it is more surface active than SiO₂. The sol–gel process involves the hydrolysis and condensation reaction of titanium (IV) ethoxide [Ti(OC₂H₅)₄] in the presence of high MW PEO. The morphology and the crystallinity of the nanocomposites were examined by scanning electron microscopy (SEM) and differential scanning calorimetry (DSC), respectively. Electrochemical properties such as ionic conductivity, Li⁺ transference number, and electrochemical stability windows were measured by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV).

EXPERIMENTAL

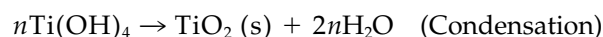
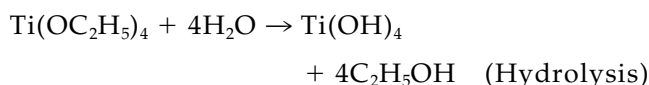
Materials

High molecular weight polyethylene oxide (PEO, MW = 900,000) was obtained from Aldrich Chemicals (Mil-

waukee, WI). PEO was dried at 50°C for 48 h under vacuum in a SalvisLAB vacuum oven (Rotkreuz, Switzerland) before use. Acetonitrile (gradient grade) from Merck (Darmstadt, Germany) was used as the solvent in the film-casting process. Titanium ethoxide [Ti(OC₂H₅)₄] and battery-grade LiBF₄ obtained from Gelest (Morrisville, PA) and Aldrich, respectively, were used without further purification.

Preparation of nanocomposite polymer electrolytes

All procedures including film casting were carried out in an MBraun Ar-filled glove box (Garching, Germany) with moisture and oxygen concentrations below 1 ppm each. PEO and appropriate amounts of LiBF₄ were dissolved in acetonitrile and the mixture was stirred at 40°C for 3 h to obtain a homogeneous solution. The concentration of PEO in acetonitrile was maintained at 5% for all solutions. The ratio of EO : Li was fixed at 20 : 1 for all the samples. A calculated amount of titanium ethoxide was added into the solution under continuous stirring. The TiO₂ contents of the nanocomposite polymer electrolytes were calculated by assuming complete conversion of titanium ethoxide into TiO₂. The residual water in acetonitrile (determined to be 0.5% w/w by a Mettler (Toledo, OH) Karl Fischer titrator) was adequate for hydrolysis, and no water was deliberately added to the mixture. The hydrolysis and condensation reactions of titanium ethoxide could be represented categorically by the following equations:



The solution was vigorously stirred for another 3 h before it was transferred to a Teflon petri dish to allow the solvents to evaporate. This process resulted in homogeneous, freestanding, and flexible membranes with thickness in the range of 50–150 μm. These nanocomposite membranes were further dried at 50°C under vacuum for 2 days to completely remove any trace amount of the residual solvent, moisture, and ethanol.

Morphology and crystallinity of nanocomposite polymer electrolytes

The morphology of the nanocomposites was examined by a JEOL 6320 scanning electron microscope (JEOL, Peabody, MA) at 15 kV. The cast polymer electrolyte membranes were affixed to the sample holder by double-sided adhesive tape and shadowed with Pt before the SEM measurements. The crystallinity of the nanocomposites was determined by DSC by use of a Netzsch DSC 200 analyzer (Bayern, Germany).

About 10 mg of samples were sealed in standard aluminum cans and heated in a nitrogen atmosphere from -100 to 200°C at the rate of $10^{\circ}\text{C}/\text{min}$.

Measurements of ionic conductivities and transference numbers

A sample membrane disc was sandwiched between two stainless steel electrodes and assembled into a tightly sealed test cell. The cell was thermostated so that its temperature could be varied from 30 to 70°C . The electrochemical impedance of the cell was measured between 1 Hz and 1 MHz by use of an Eco Chemie PGSTAT 30 potentiostat/galvanostat (Utrecht, The Netherlands) equipped with a frequency-response analyzer module. Ionic conductivity was calculated from the impedance response according to established procedures.^{24,25} For the measurement of the Li^{+} transference numbers, lithium metal was used for both electrodes to constitute a symmetric test cell with the structure of $\text{Li}/\text{nanocomposite polymer electrolyte}/\text{Li}$. The cell assembly was thermostated at 70°C , which could be maintained within $\pm 1^{\circ}\text{C}$. The electrochemical impedance was first measured before a dc bias of 20 mV was applied to the cell. The current response of the cell was monitored over time until a steady state was reached. Another measurement of the cell impedance was then made to complete the procedure.

Cyclic voltammetry measurements

The electrochemical stability window of the PEO/TiO₂ nanocomposite polymer electrolyte was evaluated in a test cell with stainless steel as the working electrode, and lithium metal as both counter and reference electrodes. The test cell was equilibrated at 70°C for 1 day before the measurements. Cyclic voltammetry measurements were carried out on the Eco Chemie PGSTAT 30 potentiostat by use of a potential range of 2.5 to 5.5 V and a scanning rate of 1 mV/s.

RESULTS AND DISCUSSION

Morphology of nanocomposite polymer electrolytes

The morphologies of three nanocomposite polymer electrolytes of different TiO₂ loadings [0% (a), 10% (b), and 20% (c)] are shown in Figure 1. Despite some discontinuity in the image, which is apparent only in the sample with the highest TiO₂ content, there are no large particles detected in (b) and (c), or any clear sign of phase separation into pure PEO and a TiO₂-rich phase. The relatively featureless micrographs are taken as evidence of the excellent mixing between TiO₂ and the PEO phases,²⁶ which was a consequence of the uniform precipitation of TiO₂ in the polymer matrix by sol-gel reactions.

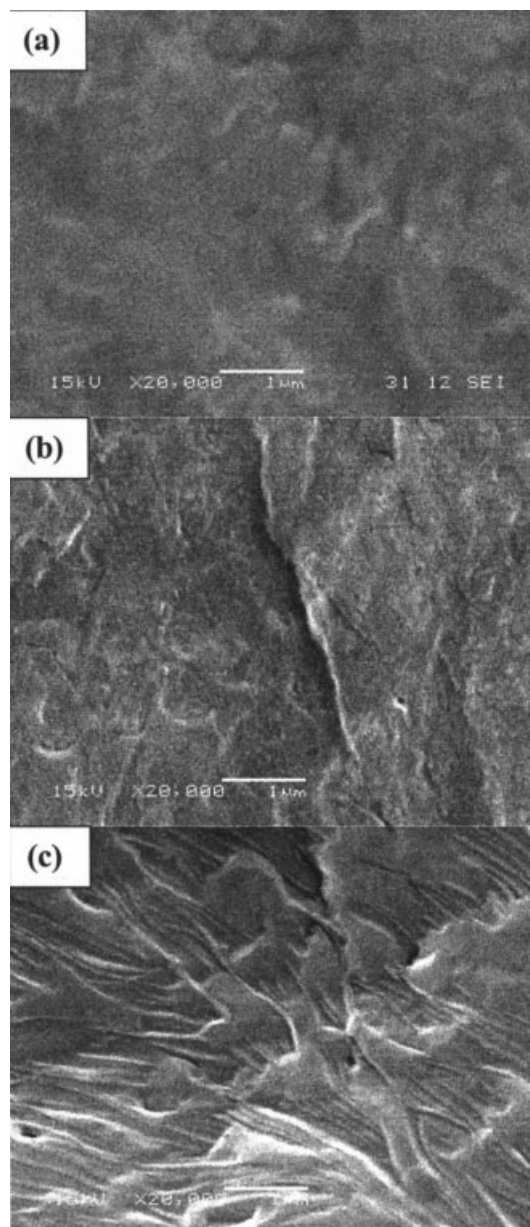


Figure 1 SEM images of PEO-TiO₂ nanocomposite polymer electrolytes at different TiO₂ loadings: (a) without TiO₂, (b) 10% TiO₂, and (c) 20% TiO₂.

For the system studied herein, titanium ethoxide was converted into TiO₂ through a sol-gel process taking place within a polymer host. The presence of high molecular weight PEO in the solution would substantially lower the mobility of hydrolyzed precursor molecules because of steric hindrance and the increased viscosity of the reaction medium. As a result, the probability of the resulting sol nuclei meeting one another to grow into large particles or an extensive three-dimensional network structure was greatly reduced. The mobility of growing particles was further reduced during film casting,²⁷ where solvent evaporation further escalated the system viscosity, fa-

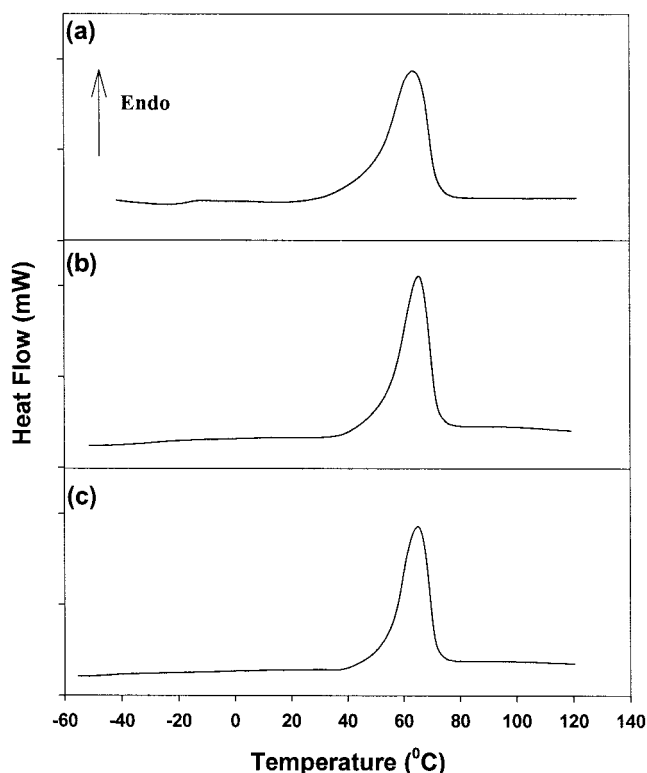


Figure 2 DSC measurements of PEO-TiO₂ nanocomposite polymer electrolytes at different TiO₂ loadings: (a) without TiO₂, (b) 10% TiO₂, and (c) 20% TiO₂.

vor the solidification of all phases into a composite. Under such conditions, only a limited number of sol particles were able to undergo gelation to form larger assemblies, and most TiO₂ should exist as isolated nanoscale particles uniformly dispersed in the polymer matrix. With the increase in TiO₂ loadings, a rapid expansion of TiO₂ particle number in a given matrix makes each PEO chain interact with numerous particles, which creates mechanical stress in the matrix. This is reflected by the appearance of some discontinuous boundaries in Figure 1(c). Such boundaries are believed to be detrimental to ion conduction.²¹

Crystallinity of nanocomposite polymer electrolytes

Changes in the crystallinity of the polymer electrolytes as a result of ceramic particle addition can be revealed by DSC. The DSC traces in Figure 2, which all show the endothermic peak centered about 65°C generally assigned to the melting of the crystalline region of PEO, indicate that the ceramic addition has not led to the total amorphization of PEO, and PEO remains at least partially crystalline in the nanocomposites. On the other hand, there are significant differences in the glass-transition temperature between the three samples. The important parameters obtained from DSC measurements are summarized in Table I.

It should perhaps be recalled that the T_g for the PEO-LiBF₄ system is -20.2°C, which is higher than the T_g of pure PEO.^{28,29} The high T_g is attributed to the formation of complexes between Li⁺ and the ether oxygen atoms, which reduces the degree of freedom in polymer chain movements. The addition of a ceramic component often shifts the T_g toward lower temperatures, with the extent of the shift increasing with the increase in the ceramic content. The lowering of T_g is therefore an indication of an enlarged amorphous domain in the nanocomposite electrolytes. The heat of fusion (ΔH) values, which are proportional to the weight fractions of crystalline PEO,^{30,31} provide further evidence of suppressed crystallization after the addition of TiO₂. The suppression of crystallization with TiO₂ content could be understood in terms of the steric hindrance presented by the ceramic component toward the repacking of the polymer chains into a more orderly structure. Furthermore, hydroxyl groups on the particle surface may also form hydrogen bonding with the ether oxygen atoms in the polymer chains. The effect of this interaction is twofold: (1) it weakened the complexation between Li⁺ and these ether oxygen atoms, facilitating the migration of Li⁺; and (2) it perturbed the PEO chain conformation and therefore introduced additional free space among the polymer segments, thus yielding a lower T_g . The resulting overall decrease in polymer crystallinity is desirable for ionic transport, because of the known higher ionic conductivity in the amorphous phase of PEO.³²

Ionic conductivities

For conductivity measurements that use two blocking electrodes to sandwich the polymer electrolyte, the following equation may be used:

$$\sigma = d / (R_b r^2 \pi)$$

where d and r represent the thickness and the radius of the sample membrane discs, respectively. R_b is the bulk resistance of the nanocomposite electrolyte from complex impedance measurements. It is widely accepted that R_b could be obtained from the intercept on

TABLE I
Comparison of DSC Parameters

Sample	T_g^a (°C)	T_m^b (°C)	ΔH^c (J/g)
PEO-LiBF ₄	-20.2	63.6	150.1
PEO-LiBF ₄ -10% TiO ₂	-38.8	65.6	136.1
PEO-LiBF ₄ -20% TiO ₂	-51.4	65.0	114.7

^a Glass-transition temperature, taken at the onset of the transition.

^b Melting temperature, taken at the peak maximum.

^c Heat of fusion, calculated as the area under the peak.

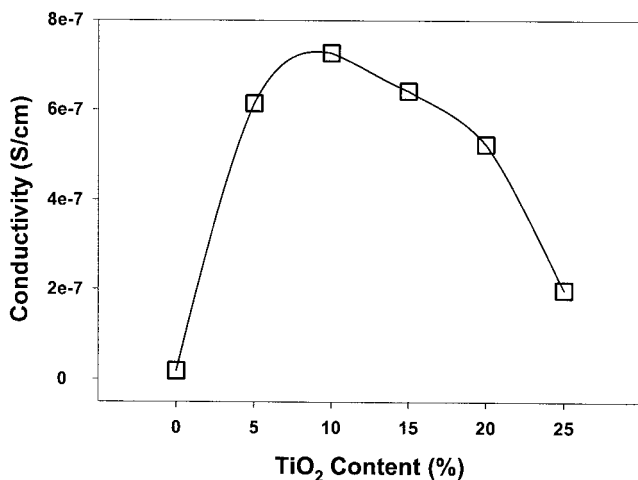


Figure 3 Ionic conductivities of PEO-TiO₂ nanocomposite polymer electrolytes at different TiO₂ contents.

the real axis at the high frequency end of the Nyquist plot of complex impedance.^{7,24}

The relationship between ionic conductivity at 30°C and the TiO₂ content in PEO/TiO₂ nanocomposite electrolytes is shown in Figure 3. A maximum value is obtained at 10% TiO₂ loading with a conductivity of 7×10^{-7} S/cm, which is over an order of magnitude higher than that of PEO-Li salt polymer electrolytes without TiO₂. These data are also favorably compared with similar systems based on mechanically mixed TiO₂, which is around 1×10^{-7} S/cm without extensive heat treatment.^{18,33} The existence of the maximum value indicates that there are two opposing effects in ionic conductivity^{11,14,16}; one is the enlargement of the polymer amorphous phase, which increases conductivity, and the other is the increase in discontinuity through the introduction of foreign matter (the ceramic particles), which decreases conductivity.

Figure 4 shows the temperature dependency of the

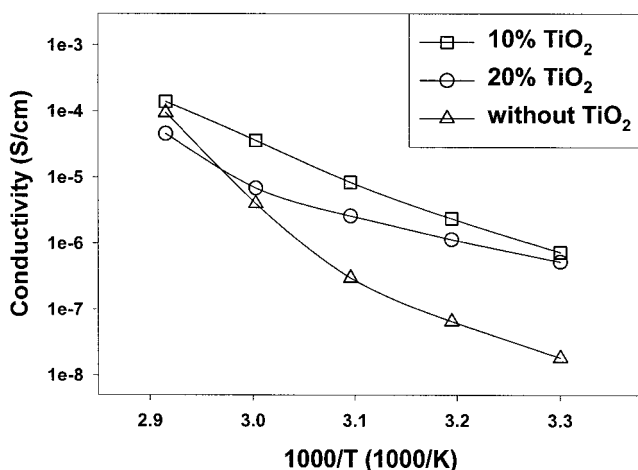


Figure 4 Temperature-dependent ionic conductivities of the PEO-TiO₂ nanocomposite polymer electrolyte system.

TABLE II
Activation Energies of Li Ion Conduction in Composite Electrolytes

Sample	E_a (kJ/mol)
PEO-LiBF ₄	181.6
PEO-LiBF ₄ -10% TiO ₂	114.2
PEO-LiBF ₄ -20% TiO ₂	92.0

ionic conductivities of PEO/TiO₂ for the three nanocomposite electrolytes. The plot of $\log \sigma$ versus $1000/T$ is approximately linear, suggesting the Arrhenius equation could be a good fit for the experimental data:

$$\sigma = \sigma_0 \exp(-E_0/RT)$$

The activation energies for the three nanocomposites are summarized in Table II.

The ionic conductivity of an electrolyte is determined by the product of the concentration of ionic charge carriers and their mobility:

$$\sigma = \sum n_i Z_i \mu_i$$

where Z_i is the charge on the ions, n_i is the number of charge carriers, and μ_i is the ionic mobility. Ionic conductivity enhancement could be realized by increasing either the charge carrier number or their mobility, or both. Table II shows clearly that TiO₂ addition has significantly influenced the conduction process. The decrease in activation energy indicates the increased mobility of the ions, given that lower energy is needed to overcome the barrier in ion movement. This could be understood in terms of the interactions between ceramic fillers, Li salt, and polymer chains. Such interactions, discussed in detail later, could weaken Li-ether oxygen interactions, leading to high Li ion mobility μ_i .

It is also generally believed that the addition of ceramic filler could suppress the polymer crystallization process and result in composite materials containing a high amorphous content of the polymer. Given that conductivity in the amorphous region is greater than that in the crystalline region because of the greater chain mobility in the amorphous region, the enlargement of amorphous phase could be considered as an increase in the "effective" charge carrier number n_i . Because both the ion mobility and the number of charge carrier are increased after the addition of TiO₂, the ionic conductivities are higher in the PEO/TiO₂ nanocomposite electrolytes. However, when the TiO₂ content in the nanocomposites is increased beyond 10%, the effect of phase discontinuity (as observed in Fig. 1) becomes increasingly dominant, resulting in conduction paths being blocked and subsequently an apparent reduction in the measured conductivities.

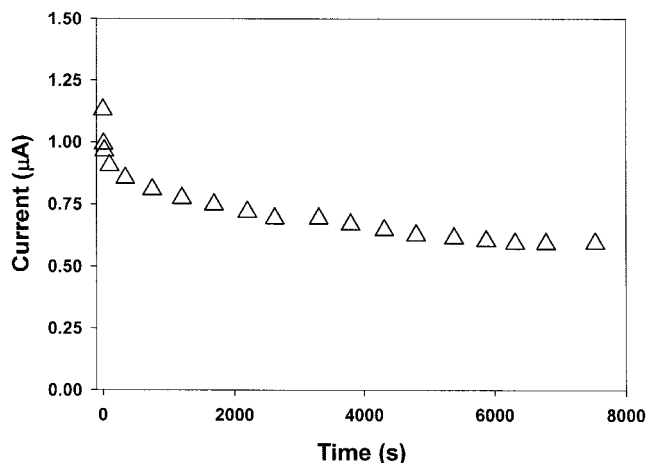


Figure 5 Current response of Li/PEO-TiO₂ nanocomposite electrolyte/Li assembly under a dc voltage (20 mV) as a function of time.

Transference number

The transference numbers of the nanocomposite polymer electrolytes were determined using the method of Evans et al.³⁴ Figure 5 shows the current response with time of a test cell with the symmetric Li/nanocomposite electrolytes/Li configuration. The decrease in current from $t = 0$ until the steady state is the result of two concurrent processes: (1) the growth of passivation layers on the lithium electrode to a limiting thickness, and (2) the establishment of a concentration gradient in the electrolyte, which affects the motion of the ions. Taking these factors into consideration, the Li⁺ transference number in the electrolyte can be calculated from the following expression³⁴:

$$T_+ = I_s(\Delta V - I_0 R_0) / [I_0(\Delta V - I_s R_s)]$$

where ΔV is the value of the applied dc bias (20 mV); R_0 and R_s are the initial and steady-state resistance of the passivation layer, respectively, which can be obtained through complex impedance measurements; and I_0 and I_s are the initial and steady-state currents, respectively. The impedance response of the nanocomposite electrolytes as well as the simulated response from a simple equivalent circuit $R_b(R_i, Q)$ are shown in Figure 6. R_b and Q are the bulk resistance of the nanocomposite electrolyte and the Li/electrolyte interfacial double-layer capacitance, respectively, whereas R_i is the resistance of the Li/electrolyte interface. The exceedingly good fit justified the extraction of R_b and R_i values from the equivalent circuit model. The transference number so calculated was 0.51 and is in good agreement with those reported by others.^{19,35} This transference number is considerably higher than that of other PEO-based composite systems,¹⁹ as well as some gel electrolyte systems.^{36,37}

The high transference number in the TiO₂ system indicative of high cationic mobility is the result of increased interactions between Li⁺ ions, anions, ether oxygen atoms, and the surface of the ceramic filler. It is plausible to imagine that a few uncondensed, residual surface hydroxyl groups remain on the TiO₂ surface. The hydrogen atoms of these surface hydroxyl groups interact with the BF₄⁻ anion and/or the ether oxygen atoms of the polymeric strands. It is believed that these are weak and subtle interactions. Nevertheless, these interactions assist significantly in restricting the movement of the anions (whose unpaired electrons allow them to interact with the surface sites more strongly) and thereby cause an increase in the transference number of the Li cations. Additionally, it is expected that both the surface hydroxyl groups on

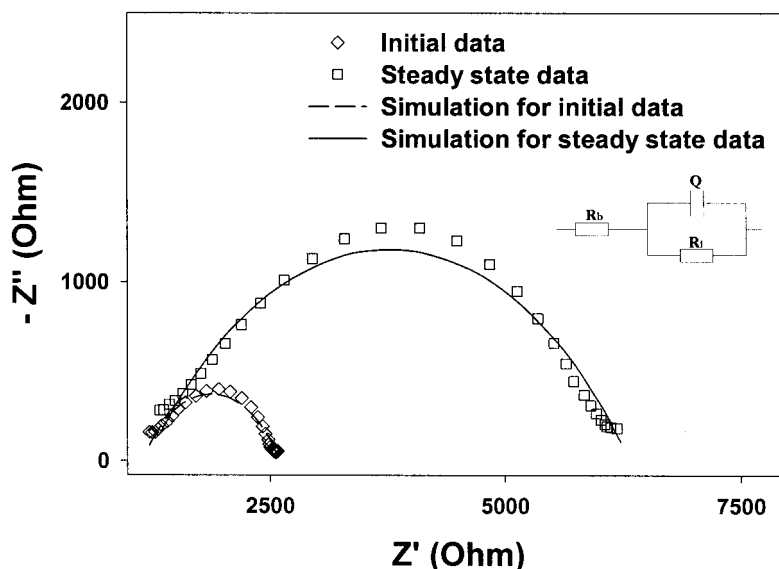


Figure 6 Initial and steady-state Nyquist plots of Li/PEO-TiO₂ nanocomposite electrolyte/Li assembly.

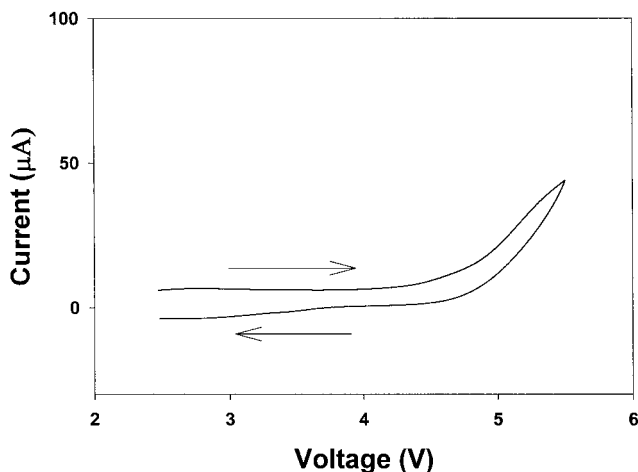


Figure 7 Cyclic voltammetric response of the PEO–TiO₂ nanocomposite polymer electrolyte (10% TiO₂ content) on stainless steel electrode at 70°C (lithium reference electrode, scan rate: 1 mV s⁻¹).

the TiO₂ and the Li cation may compete for binding with the oxygen atoms in the PEO polymer backbones.^{19,35} This competition, in all likelihood, reduces the interactions between the Li⁺ ions and the ether oxygen atoms on the polymer chains considerably, thus leaving the Li cations more loosely bound in the polymer matrix (when compared to other systems) and susceptible to ready displacement under an electric field. Furthermore, the surface hydroxyl groups on TiO₂ particles are also expected to bind with the ether oxygen atoms more readily than those on the SiO₂ particles because of their higher Lewis acidity. The effect of the Lewis acidity of the filler surface on the ion transport in composite electrolyte was also reported by others, reaching similar conclusions.^{38,39} Hence, the use of TiO₂ rather than SiO₂ would give rise to an enhanced lithium ion transport in the polymer.

Electrochemical stability window

Cyclic voltammetry was also used to assess the electrochemical stability window of the PEO/TiO₂ nanocomposite electrolytes. A typical response from a 10 wt % TiO₂/PEO nanocomposite at 70°C is shown in Figure 7. There is no indication of any oxidation reaction unless the potential is more anodic than 4.5 V, where the large increase in current is attributed to breakdown of the electrolyte. The electrochemical stability window is therefore as high as 4.5 V versus Li⁺/Li for the PEO/TiO₂ nanocomposite electrolytes prepared in this work. It should perhaps be emphasized that this stability window is not a thermodynamic one, but is dependent on the nature of the working electrode, which was stainless steel in this study. The wide electrochemical stability window is a

welcome feature for polymer electrolytes because it permits the use of the polymer electrolytes in high-voltage lithium battery applications.

CONCLUSIONS

Nanocomposite polymer electrolytes based on the PEO/LiBF₄ system were synthesized in which the ceramic filler, TiO₂, was formed *in situ* within the polymer host by a sol–gel process. Scanning electron microscopy (SEM) results showed that polymer and the ceramic fillers were uniformly mixed at the nanometer level. Differential scanning calorimetry confirmed the suppression of polymer crystallization in the presence of TiO₂. The nanocomposites displayed enhanced ionic conductivity, in part because of the increase in the number of “active” charge carriers, as well as higher Li ion mobility. The ionic conductivity reached its maximum value with 10% TiO₂ content. At 7×10^{-7} S/cm at 30°C, it is an order of magnitude higher than in the absence of TiO₂. A comparison of the activation energies for ion conduction showed enhanced Li⁺ ion mobility in the presence of TiO₂. The high transference number, on the other hand, is attributed to the interaction between ceramic fillers, anions, and polymer chains. Restricted anion motion and weakened polymer–lithium ion interaction both contributed to this increased transference number. The nanocomposite polymer electrolyte was also found to be electrochemically stable up to 4.5 V versus Li⁺/Li from cyclic voltammetric (CV) measurements.

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