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Composite Polymeric Electrolytes from the PEODME−$LiClO_4$−SiO_2 System

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It is shown that the addition of fumed silica to polymer electrolytes results in the formation of gel-like polymer materials. Despite the quasi-solid structure of these composite systems, compared to the liquid base poly(ethylene oxide) dimethyl ether (PEODME)−$LiClO_4$ electrolyte, an increase in conductivity is observed for several salt concentrations of composite systems compared to that of the PEODME−$LiClO_4$ electrolytes. For other salt concentrations, the conductivities of the composite systems are slightly higher or at least comparable to that measured for the unmodified electrolyte. At the lowest salt concentrations (e.g., 10^{-5}−10^{-4} mol/kg PEODME), the conductivities of the PEODME−$LiClO_4$ electrolyte are higher. This increase in conductivity is related to the reduction in the fraction of ion pairs as revealed by FT-IR experiments and Fuoss−Kraus-type analyses of the salt concentration dependence of the ionic conductivity.

Introduction

Polymer electrolytes have been investigated over last two decades because of the possibility of their application in a variety of electrochemical devices working at ambient conditions.[1] To this end, high ionic conductivity, good electrochemical and chemical stabilities, compatibility with electrode materials, and a wide thermal stability range are of crucial importance. Despite various efforts to develop new polymeric matrixes, polyether-based electrolytes are still among the most intensively studied systems.[2] To improve polymer electrolytes, modified polyether−salt complexes have been studied.[3] Among the modifications tested, the introduction of inorganic fillers is one of the most successful.[4] The addition of fillers results in an increase in the ionic conductivity,[5] an extension of the thermal and mechanical stability ranges,[6] and a limiting of the formation of interfacial passive layers at the alkali metal electrode−polymer electrolyte interface.[7] Scrosati and co-workers demonstrated that the addition of fillers results in an increase in the cation transport numbers, which leads to an improvement of the electrolyte performance in primary and secondary batteries.[8]

Although the relation between the physical−chemical characteristics of composite polyether electrolytes and structural changes occurring upon the addition of fillers have been extensively studied by several research groups,[4] the microscopic mechanism of polymer−filler−salt interactions is still under discussion. An increase in conductivity is often related to a decrease in the fraction of the crystalline phase in semicrystalline PEO-based electrolytes[5] and changes in the polymer flexibility and ionic associations in the case of high- or low-molecular-weight amorphous polyether-based systems.[9,10] These changes result from Lewis acid−base reactions between the filler (being either Lewis acid or base), the base centers of the polyether oxygens, and Lewis acids (cations) or Lewis bases (anions).[11] The validity of the Lewis acid−base approach to describe ion−ion and ion−polymer interactions has recently been demonstrated for a variety of semicrystalline and amorphous systems.[9,11] However, there are problems regarding the effects of the end groups, the salt concentration, and the average size of the filler on the mechanism of polymer−filler−salt interactions.

To clarify these issues, a model system based on amorphous poly(ethylene oxide) dimethyl ether (PEODME) doped with $LiClO_4$ with dispersed nanosize fumed silica is investigated in the present work. The effect of the filler and salt concentrations on the conductivity and the ion−ion and ion−polymer interaction is analyzed by impedance spectroscopy, FT-IR spectroscopy, rheology, and DSC experiments. Similar

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systems utilizing low-molecular-weight PEG and silica fillers have been studied by Fan and co-workers,[12,13] but these authors concentrated on the electrochemical characteristics of the electrolytes and on a narrow salt concentration range.

Experimental Section

Sample Preparation. PEODME (M_w = 500, Aldrich) was filtered and dried on a vacuum line at ~60 °C for 72 h and then under a vacuum of 10^{-5} Torr. While still under vacuum, the polymer was transferred to an argon-filled drybox (moisture content lower than 2 ppm) where the salt was dissolved into the polymer using a magnetic stirrer. The salt concentration varied from 10^{-6} to 5 mol/kg of polymer (corresponding to an oxygen-to-lithium molar ratio that varied from $\sim 2.3 \times 10^6$ to 4.5). Samples with salt concentrations ranging from 5 to 0.5 mol/kg were prepared by the direct dissolution of salt into the polymer. Samples with the highest salt concentrations were heated to 50 °C to facilitate the dissolution process. Samples with lower salt concentrations were prepared by the successive dilution of a batch containing electrolyte with a concentration of 0.5 mol of $LiClO_4$/kg PEODME.

$LiClO_4$ (Aldrich, reagent grade) was dried under vacuum at 120 °C prior to dissolution. The composite electrolytes were obtained by the dispersion of SiO_2 in a PEG−$LiClO_4$ solutions. The addition of the filler results in the formation of gel-like electrolytes. The concentration of SiO_2 in the composite electrolytes was 10 mass%.

Fumed SiO_2 (Aldrich, reagent grade; with an average grain size equal to 7 nm) was dried under a vacuum of 10^{-5} Torr at 180 °C for 72 h prior to addition to the polymer−salt mixture. It has been found from thermogravimetric experiments that, at temperatures up to ~180 °C, SiO_2 loses about 5% of its weight, which is most probably related to the loss of surface H_2O or OH groups. No further reduction in weight was observed up to 1000 °C.

DSC Studies. DSC data were obtained between −110 and 150 °C using a UNIPAN 605M scanning calorimeter with a low-temperature measuring head and a liquid-nitrogen-cooled heating element. Samples in aluminum pans were stabilized by slow cooling to −110 °C and then heated at 10 °C/min to 150 °C. An empty aluminum pan was used as a reference. The estimated experimental error in the determination of the glass transition temperature (T_g) is ±2 °C.

Conductivity Measurements. Ionic conductivity was determined by the complex impedance method in the temperature range from 20 to 90 °C. The samples were sandwiched between stainless steel blocking electrodes and placed in a temperature-controlled oven. Experiments were performed in a constant-volume cylindrical cell with an electrode diameter of 7.8 mm and a fixed electrolyte thickness of 1.6 mm. The impedance measurements were carried out on a computer-interfaced Solartron-Schlumberger 1255 impedance analyzer over the frequency range 1 Hz to 1 MHz. The reproducibility of the impedance spectroscopy results was checked by multiple experiments performed at room temperature. Results obtained for samples of the same composition did not differ by more than 10%.

FT-IR Experiments. Infrared absorption spectra were recorded on a computer-interfaced Perkin-Elmer 2000 FT-IR system with a wavenumber resolution of 2 cm^{-1}. FT-IR studies were performed at 25 °C. Electrolytes were sandwiched between NaCl plates and placed in a temperature-controlled cell; the accuracy of the temperature was estimated to be ±1 °C.

Rheological Experiments. Rheological experiments were conducted at 25 °C using a Bohlin Visco 88BV viscometer in a two-coaxial-cylinder geometry. The measurements were performed within a shear rate range of 24−1200 cm^{-1}. The estimated error in the rheological experiments is 10%.

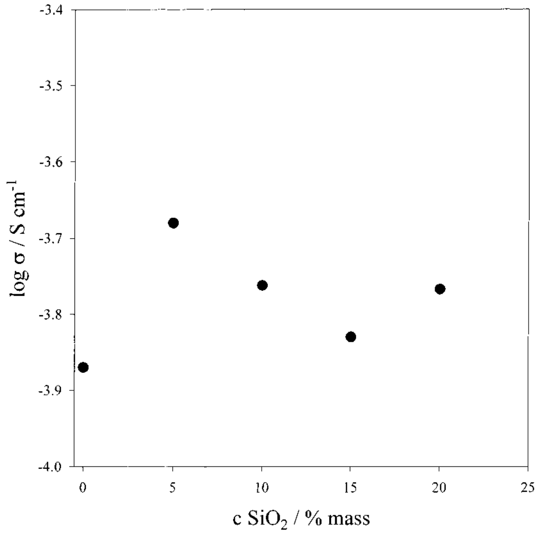

Figure 1. Isotherm of ionic conductivity of PEODME−$LiClO_4$ (1 mol/kg)−SiO_2 composite electrolytes measured at 25 °C as a function of SiO_2 concentration (error bars are within the size of the experimental points shown on the graph).

Results

Figure 1 presents the conductivity isotherm obtained at 20 °C for PEODME−$LiClO_4$ (1 mol/kg)−SiO_2 electrolytes as a function of mass percent of the filler. The addition of filler results in an increase in the ionic conductivity, which is the highest for the sample containing 5 mass % of SiO_2. For higher filler concentrations, the conductivity decreases, but it remains higher than that of the PEODME−$LiClO_4$ system that does not contain SiO_2 filler. Because the sample with 5 mass % of SiO_2 is still liquidlike, the quasi-solid PEODME−$LiClO_4$−SiO_2 (10 mass %) system was used to investigate the effect of salt concentration on the conductivity of the studied electrolytes.

Figure 2 presents a comparison of the conductivity isotherms obtained as functions of the salt concentration for PEODME−$LiClO_4$ and PEODME−$LiClO_4$−SiO_2 electrolytes at 25 °C. At the lowest salt concentration (e.g., 10^{-5}−10^{-4} mol/kg PEODME), the conductivities measured for the PEODME−$LiClO_4$ electrolytes are higher than those of the composite systems. At other salt concentrations, the conductivities for the two systems are comparable, with the conductivities for the composite systems being higher at 1×10^{-3} and 1×10^{-2} mol/kg. The observed differences are roughly 5 times for the 1×10^{-3} mol/kg salt concentration and 3 times for the 1×10^{-2} mol/kg salt concentration and are much higher than the estimated experimental error of the experiments (10% as mentioned in the Experimental Section). For the other salt concentrations, differences in the conductivities of the composite electrolytes and the base PEODME−$LiClO_4$ system are not higher than 50%.

Figure 3 presents the same conductivity isotherm as shown in Figure 2 expressed in terms of molar conductivity versus square root of molar concentration. Three characteristic regions can be distinguished: a decrease in conductivity occurs at low salt concentration, due to

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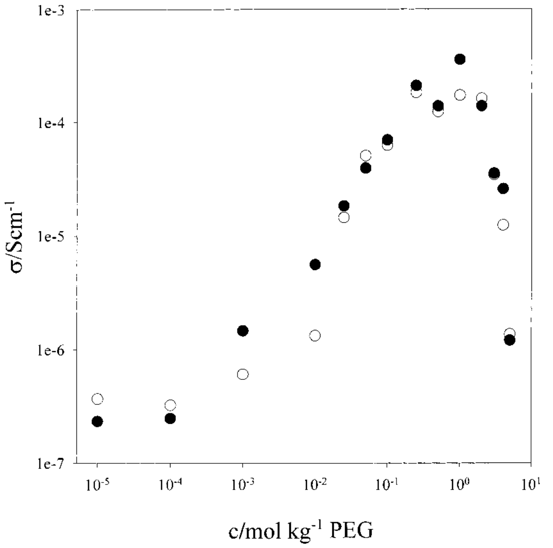

Figure 2. Changes in ionic conductivity as a function of salt concentration measured at 25 °C for the (●) PEODME–$LiClO_4$–SiO_2 and (○) PEODME–$LiClO_4$ electrolytes (error bars are within the size of the experimental points shown on the graph).

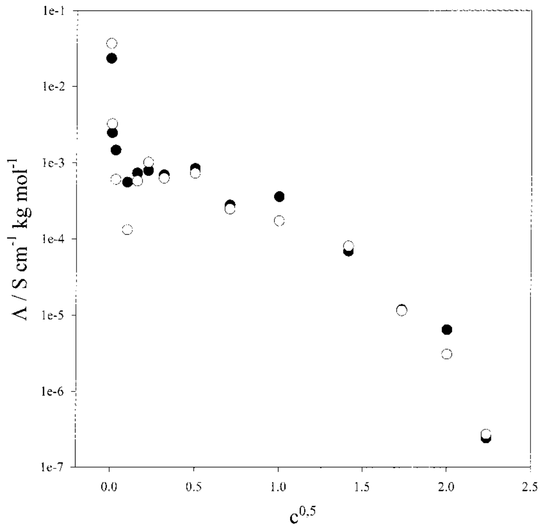

Figure 3. Changes in molar conductivity as a function of the square root of the molar concentration for the (●) PEODME–$LiClO_4$–SiO_2 and (○) PEODME–$LiClO_4$ electrolytes (error bars are within the size of the experimental points shown on the graph).

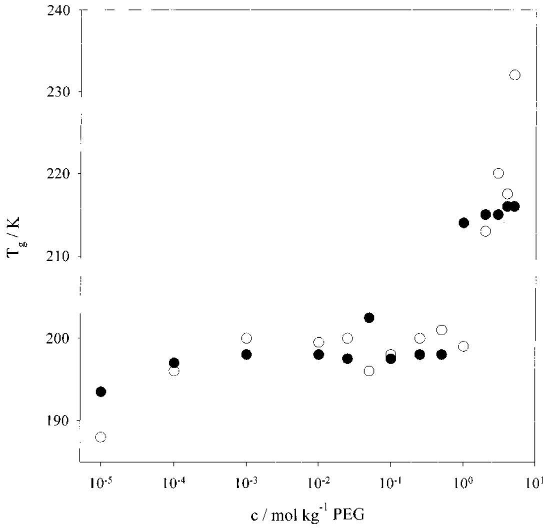

Figure 4. Changes in T_g as a function of salt concentration. Data for the (●) PEODME–$LiClO_4$–SiO_2 and (○) PEODME–$LiClO_4$ electrolytes.

the formation of ion pairs, followed by an increase in conductivity resulting from the formation of charged triplets (or redissociation of ion pairs) and finally a decrease in conductivity due to the rise in the viscosity for high salt concentrations.[14] The increase in conductivity was originally assigned to the formation of charged triplets.[14] According to recent suggestions based on electrochemical[15] as well as spectroscopic[16] experiments, this increase in conductivity can be associated with the redissociation of ion pairs due to an increase in the system permittivity or dipole–dipole-type interactions. The minimum in the conductivity due to the formation of ion pairs is lower for PEODME–$LiClO_4$ where the maximum due to the formation of charged triplets or redissociation of ion pairs has a narrow salt concentration range. The increase in conductivity observed for the composite electrolyte compared to the PEODME–$LiClO_4$ electrolyte corresponds to the region of conductivity minimum in which the highest concentration of ion pairs should be expected in both systems.

Figure 4 presents a comparison of the changes in T_g as a function of the salt concentration for both sets of electrolytes. Up to a salt concentration of roughly 0.5–1 mol/kg PEODME, the T_g values for the two sets of electrolytes do not differ significantly and are within the 190–200K range. At about 1 mol/kg PEODME, a rise in T_g of about 20–35 K is observed for both sets of electrolytes. At higher salt concentrations, the T_g values for the PEODME–$LiClO_4$–SiO_2 system are roughly constant (214–216 K), whereas the T_g values for the PEODME–$LiClO_4$ system increase from 213 to 232 K for the system with the highest salt concentration.

Figure 5 presents the change in the position of the maximum of C–O–C stretch for both sets of electrolytes. Up to a salt concentration of roughly 0.1 mol/kg PEODME, the maximum of the C–O–C stretch is at 1105–1100 cm^{-1} for both electrolyte systems. For higher salt concentrations, a decrease in the maximum is observed, but the values measured for the PEODME–$LiClO_4$ and PEODME–$LiClO_4$–SiO_2 electrolytes do not differ by more than the experimental error for samples of the same salt concentration.

Figure 6 presents the fraction of contact ion pairs calculated from analysis of the ν_4 ClO_4^- mode using the procedure described previously.[9] In the salt concentration range studied, the fraction of contact ion pairs calculated for the composite electrolytes is much smaller than that for the PEODME–$LiClO_4$ system.

These results are confirmed by the studies of the concentration dependence of the conductivity using the Fuoss–Kraus formalism.[14] The details of the procedure used have been described previously. [9,17] The param-

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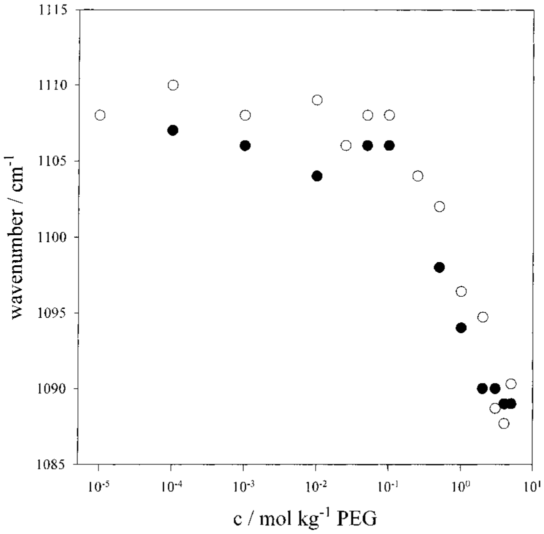

Figure 5. Changes in the maximum of the C−O−C stretching mode as a function of salt concentration. Data for the (●) PEODME−LiClO$_4$−SiO$_2$ and (○) PEODME−LiClO$_4$ electrolytes.

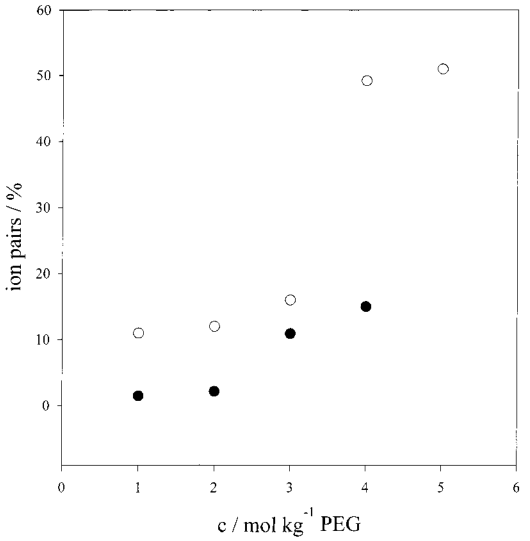

Figure 6. Changes in the fraction of Li$^+$ClO$_4^-$ contact ion pairs as a function of LiClO$_4$ concentration calculated on the basis of the IR analysis of $\nu_{ClO_4^-}$ band. Data are obtained at 25 °C in the 1−5 mol of LiClO$_4$/kg PEODME concentration range for the (●) PEODME−LiClO$_4$−SiO$_2$ and (○) PEODME−LiClO$_4$ electrolytes.

Table 1. Physicochemical Data Used for the Calculation of Ionic Association on the Basis of the Fuoss−Kraus Formalism[a]

	PEODME−LiClO$_4$	PEODME−LiClO$_4$−SiO$_2$
Λ_0^I (S cm^{-1} mol^{-1} kg)	0.00403	4.93×10^{-5}
λ_0^T (S cm^{-1} mol^{-1} kg)	0.00269	3.29×10^{-5}
d (g cm^{-1})	1.05[b]	1.205[b]
η (Pa)	0.016[c]	1.5[d]
K_I (mol^{-1} kg)	1.4×10^4	7.9
K_T (mol^{-1} kg)	127.9	252.2

[a] All Calculations are for 25 °C [b] Density of PEODME and PEODME − SiO$_2$ found from picnometric measurements. [c] Data for PEODME. [d] Data for PEODME − SiO$_2$.

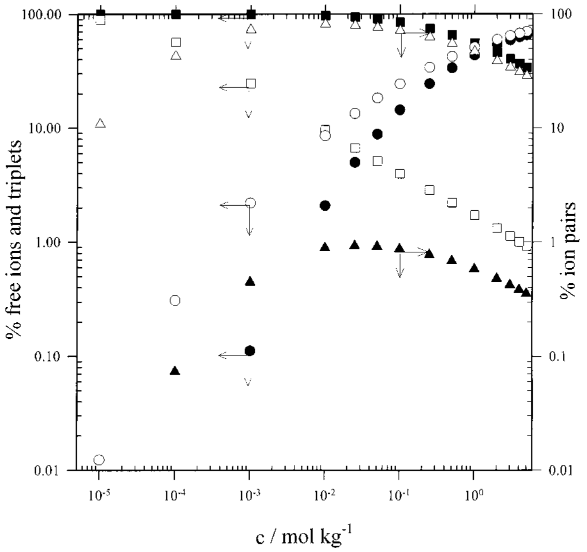

Figure 7. Changes in the fraction of "free ions" (□, ■); contact ion pairs (△, ▲), and charged triplets (○, ●) as a function of LiClO$_4$ concentrations calculated at 25 °C on the basis of the Fuoss−Kraus formalism for the PEODME−LiClO$_4$−SiO$_2$ (filled symbols) and PEODME−LiClO$_4$ electrolytes (open symbols).

eters used in the fitting procedure are given in Table 1. As can be seen from Figure 7, the fraction of free ions is higher for the composite system than for the PEODME−LiClO$_4$ electrolytes, whereas the fraction of ion pairs for the composite system is considerably lower over the entire salt concentration range studied.

Discussion

It has been shown that, for the majority of samples studied, the conductivities of the composite system containing nanosize silica fillers are comparable to these measured for PEODME−LiClO$_4$ electrolytes of the same salt concentration. The differencies are not higher than 50%. At the lowest salt concentration, the conductivities of unmodified polyether-based electrolytes are higher than those measured for composite systems because of their much lower viscosities (see data for PEODME and PEODME−SiO$_2$ systems in Table 1), which govern the long-range mobility of charge carriers. An increase in conductivity for composite electrolytes compared to PEODME−LiClO$_4$ systems is observed in the limited salt concentration range (10^{-3}−10^{-2} mol/kg) where the fraction of ion pairs in composites is considerably lower than that in the base PEODME−LiClO$_4$ electrolytes.

It can be assumed that, over the entire salt concentration range, the composite electrolytes display the physical−chemical characteristics of the PEODME−LiClO$_4$ system. This is confirmed by the similar T_g values (see Figure 4) and polymer−salt interactions [compared on the basis of the position of the maxima of the C−O−C mode (Figure 5)]. In terms of an acid−base approach to the mechanism of interactions in the polymer−salt−filler system, SiO$_2$ can be considered as a weak Lewis- and (or) Bronsted-type acid. Therefore, its interactions with the base centers on the polyether oxygens are weaker than those of Al$_2$O$_3$ filler and do not lead to a reduction of the transient cross-link density as in the case of Al$_2$O$_3$ fillers with acidic or neutral surface groups.[9,16] However, the interaction of the SiO$_2$ filler with ClO$_4^-$ anions leads to a reduction in the fraction of ionic associations, as revealed by FT-IR experiments (see Figure 6) as well as by studies of the salt concentration dependence of the molar conductivity using the Fuoss−Kraus formalism (see Figure 7). The effects described above are in agreement with our previous studies on high- and low-molecular-weight polyether-based electrolytes,[5,9,18,19] as well as recent findings of Scrosati and Best, who demonstrated an increase in the cation transport numbers and a reduction in the formation of ionic associations[8,10] upon the addition of fillers to polyether-based electrolytes. Most probably, the presence of SiO_2 fillers moves the $Li^+-ClO_4^-$ reaction equilibrium toward the redissociation of ion pairs. In the present studies, the highest increase in the conductivity was obtained for the salt concentration region in which high concentrations of ion pairs formed in the PEODME$-LiClO_4$ electrolytes but the fraction of free ions dominates in the composite systems.

It seems that the local segmental motions are more important for conduction than is the viscosity, which governs the long-range mobility of charge carriers. The reduction in the mobility of the polyether chains corresponds to the final drop of the conductivity, as can be concluded from a comparison of the results presented in Figure 2 (molar conductivity data), Figure 4 (T_g values), and Figure 5 (C−O−C maximum).

In conclusion, it has been shown that the addition of fumed nanosize silica can be a very effective method in the preparation of a new generation of gel-like electrolytes with conductivities exceeding 3×10^{-4} S/cm at ambient temperatures. These electrolytes, thanks to the reduction in the formation of ionic associates, are very promising materials for application in lithium batteries.

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