

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231235790>

Composite polymeric electrolytes from the pEODME-LiClO₄-SiO₂ system

ARTICLE *in* CHEMISTRY OF MATERIALS · MARCH 2001

Impact Factor: 8.35 · DOI: 10.1021/cm001178n

CITATIONS

43

READS

40

3 AUTHORS, INCLUDING:



Dariusz Świerczyński

Institut Charles Gerhardt

40 PUBLICATIONS 947 CITATIONS

SEE PROFILE



W. Wiczorek

Warsaw University of Technology

101 PUBLICATIONS 2,531 CITATIONS

SEE PROFILE

Composite Polymeric Electrolytes from the PEODME–LiClO₄–SiO₂ System

D. Świerczyński, A. Zalewska, and W. Wieczorek*

Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3,
00-664 Warszawa, Poland

Received September 22, 2000. Revised Manuscript Received February 5, 2001

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)–LiClO₄ electrolyte, an increase in conductivity is observed for several salt concentrations of composite systems compared to that of the PEODME–LiClO₄ 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–LiClO₄ 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 electrolytes⁵ 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 LiClO₄ 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

* All correspondence regarding this paper should be addressed to Dr. Władysław Wieczorek, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warszawa, Poland. Tel. +48 22 6607572; fax +48 22 628 2741; e-mail wladek@ch.pw.edu.pl.

(1) *Applications of Electroactive Polymers*; Scrosati, B., Ed.; Chapman and Hall: London, 1993.

(2) *Solid State Electrochemistry*; Bruce, P. G., Ed.; Cambridge University Press: Cambridge, U.K., 1995.

(3) Gray, F. M. *Solid Polymer Electrolytes—Fundamentals and Technological Applications*; VCH: Weinheim, Germany, 1991.

(4) Quartarone, E.; Mustarelli, P.; Magistris, A. *Solid State Ionics* **1998**, *110*, 1.

(5) Wieczorek, W.; Such, K.; Plocharski, J.; Wycislik, H. *Solid State Ionics* **1989**, *36*, 255.

(6) Weston, J.; Steele, B. C. H. *Solid State Ionics* **1982**, *7*, 81.

(7) Croce, F.; Curini, R.; Martinello, A. Persi, L.; Ronci, F.; Scrosati, B.; Caminiti, R. *J. Phys. Chem.* **1999**, *103*, 10632.

(8) Croce, G. B.; Appetechi, L.; Perci, B.; Scrosati, B. *Nature* **1998**, *394*, 456.

(9) Wieczorek, W.; Lipka, P.; Żukowska, G.; Wycislik, H. *J. Phys. Chem. B* **1998**, *102*, 6968.

(10) Best, A. S.; Ferry, A.; MacFarlane, D. R. Forsyth, M. *Solid State Ionics* **1999**, *126*, 269.

(11) Wieczorek, W.; Florjańczyk, Z.; Stevens, J. R. *Electrochim. Acta* **1995**, *40*, 2251.

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 $\sim 60^\circ\text{C}$ 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 LiClO₄/kg PEODME.

LiClO₄ (Aldrich, reagent grade) was dried under vacuum at 120°C prior to dissolution. The composite electrolytes were obtained by the dispersion of SiO₂ in a PEG–LiClO₄ solutions. The addition of the filler results in the formation of gel-like electrolytes. The concentration of SiO₂ in the composite electrolytes was 10 mass%.

Fumed SiO₂ (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 $\sim 180^\circ\text{C}$, SiO₂ loses about 5% of its weight, which is most probably related to the loss of surface H₂O 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 $10^\circ\text{C}/\text{min}$ 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 $\pm 2^\circ\text{C}$.

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 $\pm 1^\circ\text{C}$.

Rheological Experiments. Rheological experiments were conducted at 25°C using a Bohlin Visco 88BV viscometer in a two-coaxial-cylinder geometry. The measurements were per-

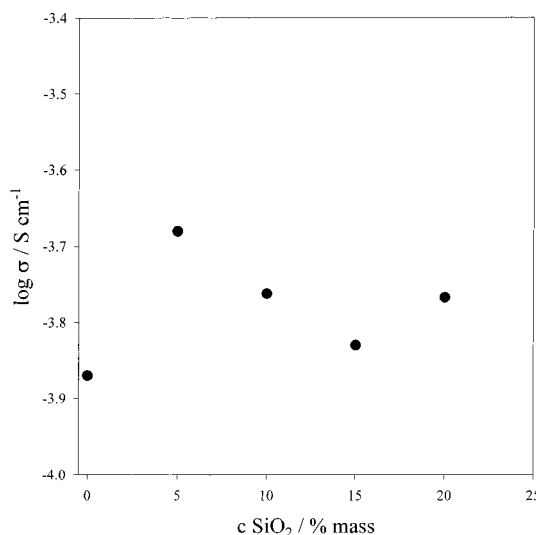


Figure 1. Isotherm of ionic conductivity of PEODME–LiClO₄ (1 mol/kg)–SiO₂ composite electrolytes measured at 25°C as a function of SiO₂ concentration (error bars are within the size of the experimental points shown on the graph).

formed within a shear rate range of $24\text{--}1200\text{ cm}^{-1}$. The estimated error in the rheological experiments is 10%.

Results

Figure 1 presents the conductivity isotherm obtained at 20°C for PEODME–LiClO₄ (1 mol/kg)–SiO₂ 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 SiO₂. For higher filler concentrations, the conductivity decreases, but it remains higher than that of the PEODME–LiClO₄ system that does not contain SiO₂ filler. Because the sample with 5 mass % of SiO₂ is still liquidlike, the quasi-solid PEODME–LiClO₄–SiO₂ (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–LiClO₄ and PEODME–LiClO₄–SiO₂ electrolytes at 25°C . At the lowest salt concentration (e.g., 10^{-5} – 10^{-4} mol/kg PEODME), the conductivities measured for the PEODME–LiClO₄ 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–LiClO₄ 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

(12) Fan, J.; Fedkiw, P. S. *J. Electrochem. Soc.* **1997**, *144*, 399.

(13) Walls, H. J.; Zhou, J.; Yeria, J. A.; Fedkiw, P. S.; Khan, S. A.; Stowe, M. K.; Baker, G. L. *J. Power Sources* **2000**, *89*, 156.

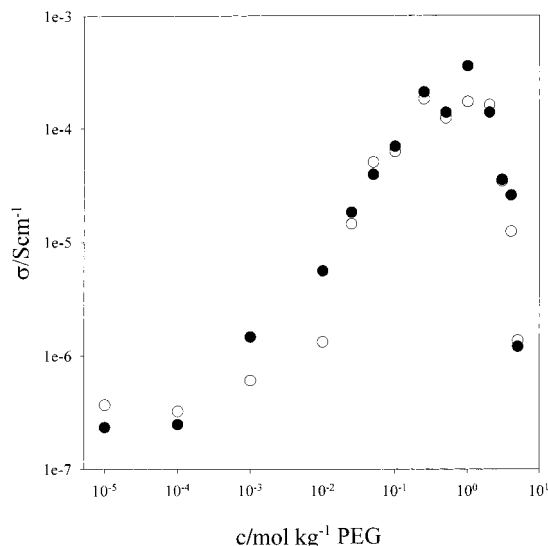


Figure 2. Changes in ionic conductivity as a function of salt concentration measured at 25 °C for the (●) PEODME-LiClO₄-SiO₂ and (○) PEODME-LiClO₄ electrolytes (error bars are within the size of the experimental points shown on the graph).

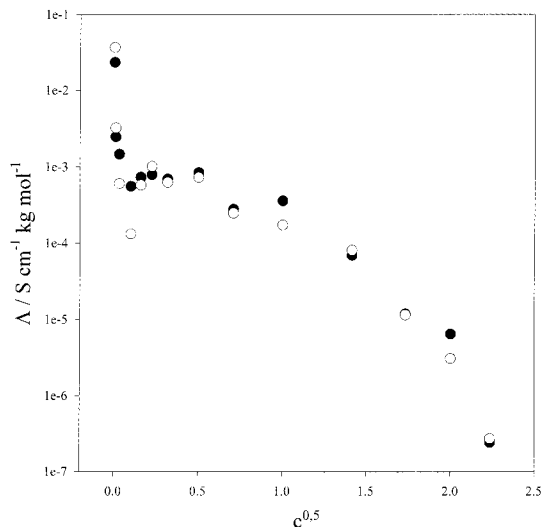


Figure 3. Changes in molar conductivity as a function of the square root of the molar concentration for the (●) PEODME-LiClO₄-SiO₂ and (○) PEODME-LiClO₄ electrolytes (error bars are within the size of the experimental points shown on the graph).

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 electrochemical¹⁵ as well as spectroscopic¹⁶ 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

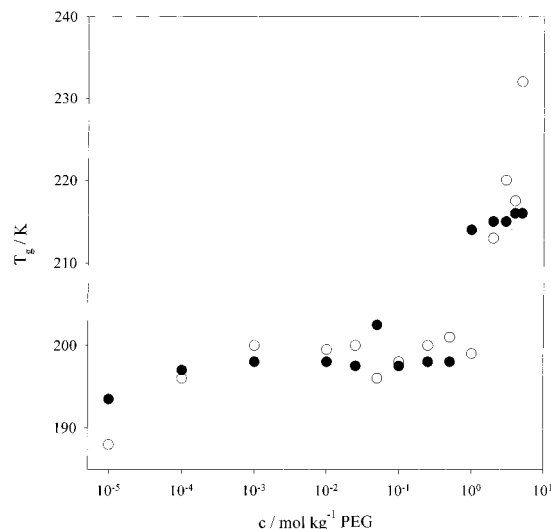


Figure 4. Changes in T_g as a function of salt concentration. Data for the (●) PEODME-LiClO₄-SiO₂ and (○) PEODME-LiClO₄ electrolytes.

formation of ion pairs is lower for PEODME-LiClO₄ 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-LiClO₄ 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 190–200 K 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-LiClO₄-SiO₂ system are roughly constant (214–216 K), whereas the T_g values for the PEODME-LiClO₄ 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-LiClO₄ and PEODME-LiClO₄-SiO₂ 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 ClO₄⁻ 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-LiClO₄ 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-

(14) Fuoss, R. M.; Accasina, F. *Electrolytic Conductance*; Interscience: New York, 1959.

(15) Petrucci, S.; Eyring, E. M. *J. Phys. Chem.* **1991**, *95*, 1731 and references therein.

(16) Ferry, A.; Orad, G.; Jacobsson, P. *Electrochim. Acta* **1998**, *43*, 1471.

(17) MacCallum, J. R.; Tomlin, A. S.; Vincent, C. A. *Eur. Polym. J.* **1986**, *22*, 787.

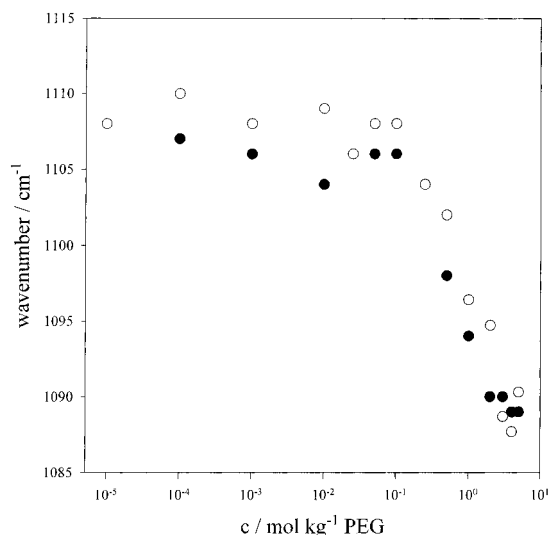


Figure 5. Changes in the maximum of the C-O-C stretching mode as a function of salt concentration. Data for the (●) PEODME-LiClO₄-SiO₂ and (○) PEODME-LiClO₄ electrolytes.

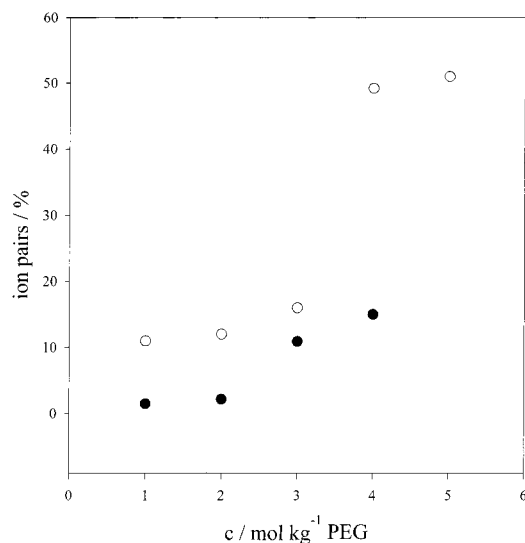


Figure 6. Changes in the fraction of Li⁺ClO₄⁻ contact ion pairs as a function of LiClO₄ concentration calculated on the basis of the IR analysis of $\nu_{\text{ClO}_4^-}$ band. Data are obtained at 25 °C in the 1–5 mol of LiClO₄/kg PEODME concentration range for the (●) PEODME-LiClO₄-SiO₂ and (○) PEODME-LiClO₄ 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^+ (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 - SiO₂ found from picnometric measurements. ^c Data for PEODME. ^d Data for PEODME - SiO₂.

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-LiClO₄ electrolytes, whereas the fraction of

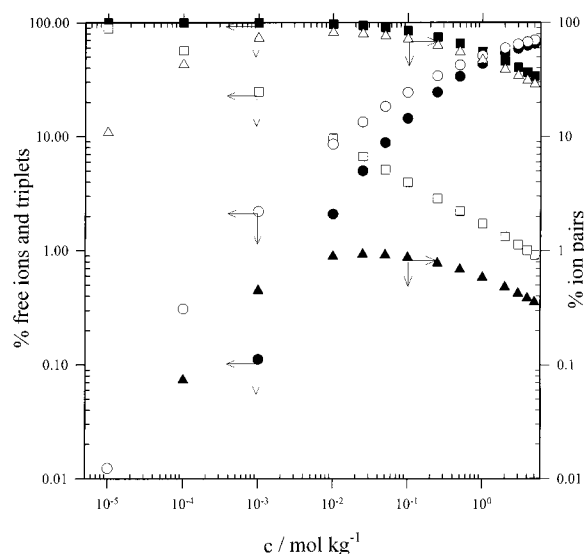


Figure 7. Changes in the fraction of "free ions" (□, ■); contact ion pairs (△, ▲), and charged triplets (○, ●) as a function of LiClO₄ concentrations calculated at 25 °C on the basis of the Fuoss-Kraus formalism for the PEODME-LiClO₄-SiO₂ (filled symbols) and PEODME-LiClO₄ electrolytes (open symbols).

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-LiClO₄ electrolytes of the same salt concentration. The differences 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-SiO₂ systems in Table 1), which govern the long-range mobility of charge carriers. An increase in conductivity for composite electrolytes compared to PEODME-LiClO₄ 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-LiClO₄ electrolytes.

It can be assumed that, over the entire salt concentration range, the composite electrolytes display the physical-chemical characteristics of the PEODME-LiClO₄ 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, SiO₂ 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 Al₂O₃ filler and do not lead to a reduction of the transient cross-link density as in the case of Al₂O₃ fillers with acidic or neutral surface groups.^{9,16} However, the interaction of the SiO₂ filler with ClO₄⁻ 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 SiO₂ fillers moves the Li⁺–ClO₄[–] 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–LiClO₄ 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.

Acknowledgment. This work was financially supported by the President of the Warsaw University of Technology through research grant 504/164/853/8.

CM001178N

(18) Marcinek, M.; Zalewska, A.; Żukowska, G.; Wieczorek, W. *Solid State Ionics* **2000**, 136&137, 1175.

(19) Przyłuski, J.; Such, K.; Wycislik, H.; Wieczorek, W.; Florjańczyk, Z. *Synth. Met.* **1990**, 35, 241.