Effect of Filler Surface Group on Ionic Interactions in PEG−$LiClO_4$−Al_2O_3 Composite Polyether Electrolytes

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The effect of filler surface group on the conductivity, ion−ion, ion−polymer interactions, and microstructure of PEG−$LiClO_4$−Al_2O_3 composite polymer electrolytes is studied. It is shown that the addition of fillers results in an increase in ionic conductivity of polyether electrolytes observed in the narrow lithium salt concentration range. The position of conductivity maximum depends on the type of the surface groups of the filler and results from the Lewis acid−base type interactions between filler surface centers, ions, and ether oxygen base groups. These interactions are reflected by changes in the polymer chain flexibility observed by DSC and rheological experiments as well as microstructural changes due to polymer−filler−Li^+ interactions as revealed by FT-IR experiments. Finally, the addition of the filler results in the changes in ionic associations as studied by FT-IR and by applying the Fuoss−Kraus formalism to the salt concentration dependence of the molar conductivity of the composite electrolytes studied.

Introduction

Polymer electrolytes are widely investigated due to the possibility of their application in various electrochemical devices working from the subambient to moderate temperature range.[1] A number of methods for modification of the structure leading to the enhancement in ionic conductivity of polymer electrolytes have been realized to this end.[2,3] The addition of inorganic filler is one of the most commonly used and effective methods of modification.[4−17] It has been shown that the addition of fillers to semicrystalline PEO−alkali metal salt complexes leads to the decrease in the crystallinity of the electrolyte and hence an enhancement in ionic conductivity.[6] It has also been shown that the use of fillers improves mechanical stability and extends thermal stability range of polymer electrolytes.[7] Scrosati and co-workers demonstrate that the addition of various type fillers, like zeolites or aluminates, leads to an improvement in the electrochemical stability of polymer electrolytes and limits the formation of resistive passive layers at the alkali metal electrode−polymer electrolyte interface.[8,9] The same authors[10] as well as Kumar and co-workers[11] show that the addition of filler leads to an enhancement in the cation transport number of polymer electrolytes thus improving their performance in alkali metal batteries.

It has been described recently that similar benefits can be reached by the addition of inorganic filler to amorphous high or low molecular weight polyether based electrolytes.[12,13] However, the conductivity enhancement in the latter case is limited to the narrow salt concentration range.[13] Changes in the ionic conductivity and microstructure of composite polymer electrolytes result from the Lewis acid−base type interactions between variety of Lewis acid or base type species present in the system studied. This comprises acid Lewis centers of the filler, alkali metal cations (being hard acid according to Pearson classification),[14] anions (being weak Lewis bases), and base centers of polyether oxygens.

In the present paper this concept is proved by the use of fillers surface groups of various Lewis type acidity (basicity). Changes in the ionic conductivity as the function of $LiClO_4$ concentration are analyzed by impedance spectroscopy. Polymer chain flexibility is analyzed by DSC and rheological experiments whereas the ion−polymer interactions are additionally studied by FT-IR. Ion−ion interactions are studied by the Fuoss−Kraus formalism based on the analysis of salt concentration changes in molar conductivity as well as by FT-IR studies of the bands characteristic for ClO_4^- anions. Additionally, preliminary investigations of the effect of filler on the polymer electrolyte−lithium electrode interfacial stability are also reported.

Experimental Section

Sample Preparation. PEG (M_w = 350, Aldrich, monomethyl capped) was filtered and then dried on a vacuum line first at ∼60 °C for 72 h and then, under vacuum of 10^{-5} Torr, stringently freeze-dried using freeze−pump−thaw cycles. 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. Salt concentration varied from 10^{-6} to 5 mol/kg of polymer. Samples of the salt concentration from 5 mol/kg down to 0.5 mol/kg were prepared by the direct dissolution of salt in a polymer. Samples of the highest salt concentration were heated to 50 °C to facilitate the dissolution process. Samples of lower salt concentration were prepared by the successive dilution of a batch containing electrolyte with 0.5 mol/kg $LiClO_4$.

$LiClO_4$ (Aldrich, reagent grade) was dried under vacuum at 120 °C prior to the dissolution. The composite electrolytes were obtained by the dispersion of Al_2O_3 in a PEG−$LiClO_4$ solutions. The concentration of Al_2O_3 in the composite electrolytes was equal to 10 mass %. Al_2O_3 (Aldrich, reagent grade) fraction of grain size lower than 5 μm with the various type of surface

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TABLE 1: Characteristic of Al_2O_3 Filler Barring Different Type Surface Groups

type of the filler surface groups	fraction of grain size lower than 5 μm (%)	surface area (m^2/g)
neutral	∼100	132
basic	∼80	142
acidic	∼100	145
neutral[a]	>75	132

[a] After dispersion in PEG.

groups were dried under vacuum of 10^{-5} Torr at 150 °C for over 72 h prior to the addition to polymer−salt mixture.

DSC Studies. DSC data were obtained between −110 and 150 °C using a UNIPAN 605M scanning calorimeter with a low-temperature measuring head and 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 of the determination of glass transition temperature (T_g) is equal to ±2 °C.

Conductivity Measurements. Ionic conductivity was determined using 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. The experiments were performed in a constant volume cylindrical cell of the electrode diameter equal to 7.8 mm and fixed electrolytes thickness equal to 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 impedance spectroscopy results was checked by multiple experiments performed at room temperature. All results obtained for samples of the same composition do not differ by more than 10%.

Ac Impedance Studies on Li/PEG−$LiClO_4$−Filler Electrolyte/Li Cells. For these studies electrolytes were soaked on polypropylene textile separator of 210 μm thickness. All types of electrolytes with and without Al_2O_3 fillers were used. Concentration of $LiClO_4$ in all electrolytes was equal to 2 mol/kg PEG. Prolonged ac impedance measurements (up to 250 h) in the 1MHz-1Hz frequency range with ac amplitude = 20 mV, were performed.

FT-IR. 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 two NaCl plates and placed in the FT-IR 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 two coaxial cylinders geometry. The measurements were performed within a shear rate range of 24−1200 cm^{-1}. The estimated error of rheological experiments is equal to 10%.

Results

Table 1 presents the filler characteristic for all three fillers barring different type surface groups. Grain size distribution and average surface area were measured for pure fillers as well as for dispersions of fillers in PEG using the Mastersizer S 2.19 Malvern Instrument with BET adjustment. Both grain size distribution and average surface area measured for the fillers are within 10% difference. Additionally, these features are unaffected by the dispersion of filler in PEG. Therefore, the differences in the interactions between fillers, alkali metal salts, and PEG should be attributed to the different surface groups of filler used.

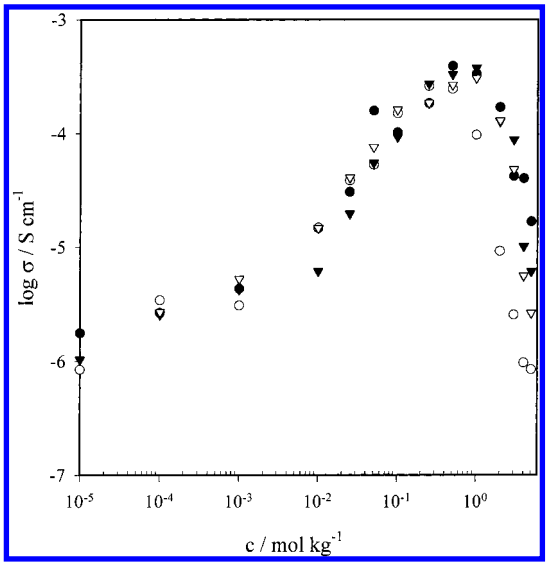

Figure 1. Changes in ionic conductivity as a function of salt concentration measured at 25 °C for (●) PEG−$LiClO_4$−Al_2O_3 neutral surface groups; (▼) PEG−$LiClO_4$−Al_2O_3 basic surface groups; (▽) PEG−$LiClO_4$−Al_2O_3 acidic surface groups; (○) PEG−$LiClO_4$ electrolytes.

Figure 1 presents the conductivity isotherms measured for the base PEG−$LiClO_4$ electrolyte and PEG−$LiClO_4$−Al_2O_3 electrolytes with various type of filler surface groups at 25 °C. Up to the salt concentration of ∼0.5 mol/kg PEG, conductivities measured for the base electrolyte are higher than or at least comparable to that obtained for systems with fillers. For higher salt concentrations, conductivities measured for composite electrolytes are higher. The conductivity maximum depends on the type of filler surface groups and is observed at 0.25 mol $LiClO_4$/kg PEG (base electrolyte), 1 mol $LiClO_4$/kg PEG (composite systems with basic filler surface groups), and 1 mol/kg (composite system with acidic filler surface groups). The highest conductivities are observed for systems with neutral filler surface group (conductivity maximum at 0.5 mol/kg PEG) whereas for the composite system with basic filler surface groups the conductivity enhancement extends for the widest salt concentration range.

Figure 2 presents the same conductivity isotherms quoted in the molar conductivity vs square root of molar concentration coordinates. It is evident that the increase in conductivity of composite systems compared to the base PEG−$LiClO_4$ electrolyte is related to the region in which the high degree of ionic association is expected to occur and the lowering of molar conductivity is predominantly due to the increase in the viscosity of the electrolyte related to the decrease in the mobility of charge carriers.[19]

Figure 3 presents the changes in the T_g obtained from DSC experiments as a function of salt concentration for all sets of electrolytes studied. T_g values measured for composites with basic Al_2O_3 fillers are considerably lower than for other systems studied. For salt concentrations up to roughly 0.1 mol/kg PEG, T_g for other three sets of electrolytes are comparable. For higher salt concentrations, T_g for composites with neutral Al_2O_3 surface groups are lower than for PEG−acidic Al_2O_3 and base PEG−$LiClO_4$ electrolyte. At salt concentrations higher than 0.25 mol/kg, T_g for the base PEG−$LiClO_4$ electrolyte are the highest.

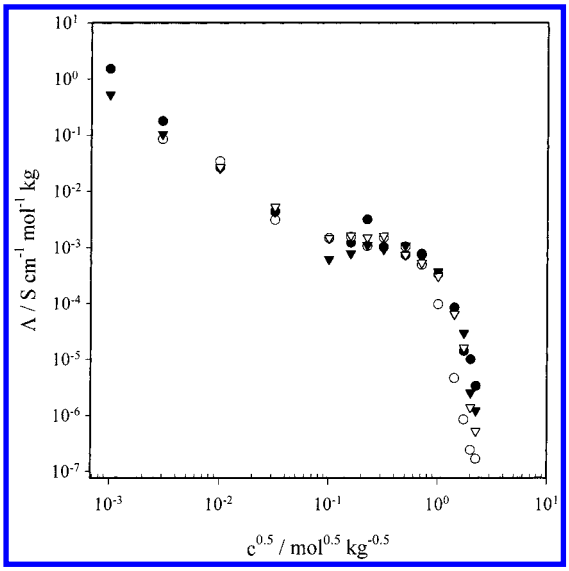

Figure 2. Changes in molar conductivity as a function of square root of molar concentration for (●), PEG−$LiClO_4$−Al_2O_3 neutral surface groups; (▼) PEG−$LiClO_4$−Al_2O_3 basic surface groups; (▽) PEG−$LiClO_4$−Al_2O_3 acidic surface groups; (○) PEG−$LiClO_4$ electrolytes.

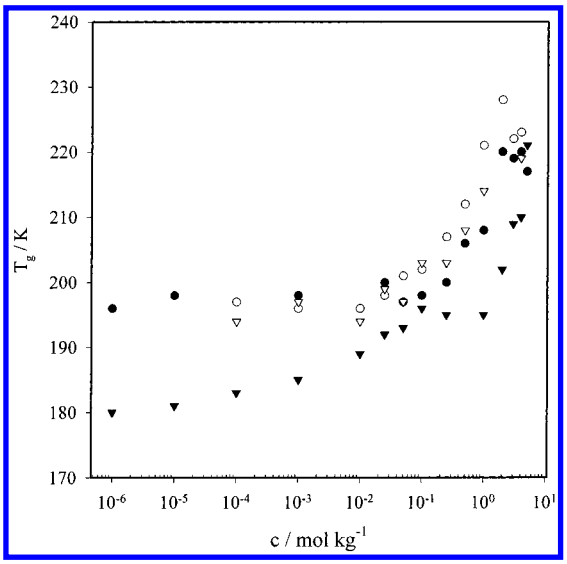

Figure 3. Changes in the T_g as a function of salt concentration. Data for (●) PEG−$LiClO_4$−Al_2O_3 neutral surface groups; (▼) PEG−$LiClO_4$−Al_2O_3 basic surface groups; (▽) PEG−$LiClO_4$−Al_2O_3 acidic surface groups; (○) PEG−$LiClO_4$ electrolytes.

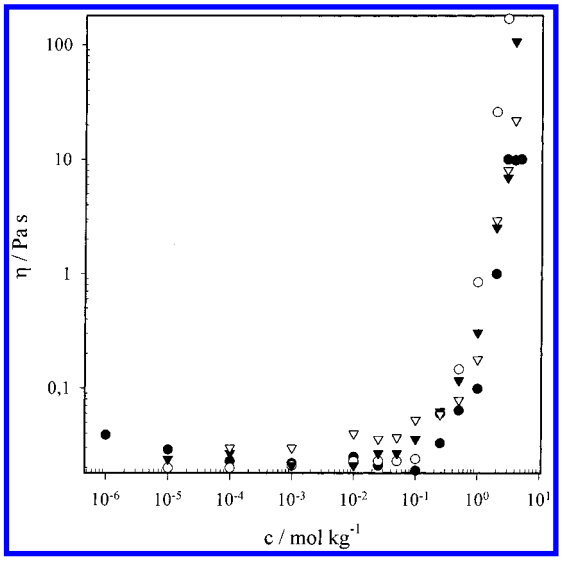

Figure 4. Viscosity as a function of salt concentration. Data obtained at 25 °C for (●) PEG−$LiClO_4$−Al_2O_3 neutral surface groups; (▼) PEG−$LiClO_4$−Al_2O_3 basic surface groups; (▽, PEG−$LiClO_4$−Al_2O_3 acidic surface groups; (○) PEG−$LiClO_4$ electrolytes.

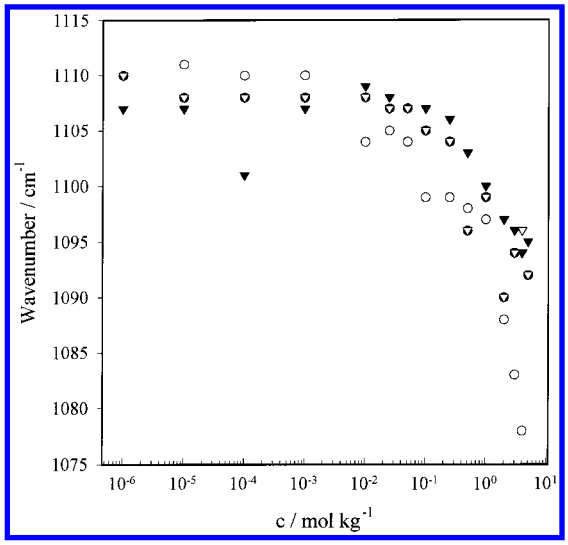

Figure 5. Changes in the maximum of the C−O−C stretching mode as a function of salt concentration. Data for (●) PEG−$LiClO_4$−Al_2O_3 neutral surface groups; (▼) PEG−$LiClO_4$−Al_2O_3 basic surface groups; (▽) PEG−$LiClO_4$−Al_2O_3 acidic surface groups; (○) PEG-$LiClO_4$ electrolytes.

Figure 4 presents changes in the viscosity measured at 25 °C for all four sets of electrolytes as the function of salt concentrations. Up to 0.5 mol/kg PEG viscosities measured for composite electrolytes with Al_2O_3 barring acidic surface groups are the highest. Viscosities for base PEG−$LiClO_4$ electrolyte and PEG−$LiClO_4$−Al_2O_3 (neutral or base surface groups) are similar in this salt concentration range. For salt concentrations higher than 0.5 mol/kg PEG viscosities of the base PEG−$LiClO_4$ are the highest.

Two-region of IR spectra, e.g., first C−O−C stretch (at ∼1100 cm^{-1}) the position of the maximum of which is connected with the intensity of polymer−salt interaction) and the $\gamma(ClO_4^-)$ envelope (at ∼620 cm^{-1}) which is used to study ion−ion interactions are of interest in our studies. Figure 5 shows the position of the maximum of C−O−C stretch measured at 25 °C for all four sets of electrolytes. Up to the salt concentration of 5×10^{-2} mol/kg PEG position of this maximum does not differ by more than the experimental error for each of the electrolyte type studied. For higher concentrations, the maximum of the C−O−C stretch for the base PEG−$LiClO_4$ electrolyte is at lower frequences than for composite systems whereas the position of this maximum measured for PEG−$LiClO_4$−Al_2O_3 (base surface group) usually occurs at slightly higher frequences than for two other composite systems.

Figure 6 shows the fraction of ion pairs obtained from the FT-IR experiments. The fraction of ion pairs was calculated on the basis of the separation of $\nu_{ClO_4^-}$ envelope for the peaks characteristic for spectroscopically free anions and contact ion pairs using the previously described procedure.[13] For all sets of composite electrolytes fraction of contact ion pairs is lower than for pure PEG−$LiClO_4$ electrolyte.

Figure 7 presents the fraction of ion pairs calculated on the basis of the Fuoss−Kraus formalism for each type of the electrolyte studied. Details of the calculation procedure are described elsewhere.[13] The data used for calculation are included in Table 2. As can be seen from Figure 7, the fraction of ion

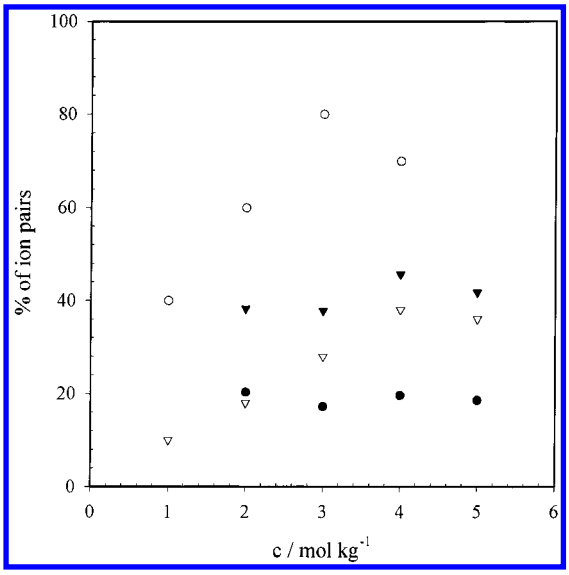

Figure 6. Changes in the fraction of $Li^+ClO_4^-$ contact ion pairs as a function of $LiClO_4$ concentration. Data are obtained at 25 °C in the 1−5 mol/kg $LiClO_4$ concentration range for (●) PEG−$LiClO_4$−Al_2O_3 neutral surface groups; (▼) PEG−$LiClO_4$−Al_2O_3 basic surface groups; (▽) PEG−$LiClO_4$−Al_2O_3 acidic surface groups; (○) PEG−$LiClO_4$ electrolytes.

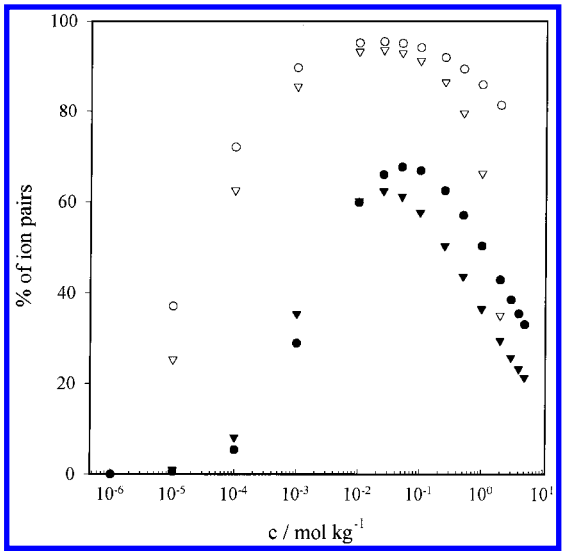

Figure 7. Changes in the fraction of contact-ion pairs as a function of $LiClO_4$ concentrations calculated at 25 °C on the basis of the Fuoss−Kraus formalism for (●) PEG−$LiClO_4$−Al_2O_3 neutral surface groups; (▼) PEG−$LiClO_4$−Al_2O_3 basic surface groups; (▽) PEG−$LiClO_4$−Al_2O_3 acidic surface groups; (○) PEG−$LiClO_4$ electrolytes.

TABLE 2: Physicochemical Data Used for the Calculation of Ionic Association on the Basis of the Fuoss−Kraus Formalism (All Calculations for 25 °C)

	PEG−$LiClO_4$	PEG−$LiClO_4$−Al_2O_3
Λ_0[1]/S cm^{-1} mol^{-1} kg	0.00336	0.00291
λ_0^T/S cm^{-1} mol^{-1} kg	0.00224	0.00194
d/g cm^{-1}	1.094[a]	1.282[a]
η/Pa s	0.020[b]	0.029[c]
K_I/mol^{-1} kg	9.4 × 104	611.3
K_T/mol^{-1} kg	48.8	21.2

[a] Density of PEG and PEG−$A1_2O_3$ found from picnometric determinations. [b] Data for PEG. [c] Data for PEG−Al_2O_3.

pairs decreases in the following order PEG−$LiClO_4$ > PEG−$LiClO_4$−Al_2O_3 (acidic surface groups) > PEG−$LiClO_4$−Al_2O_3 (neutral surface groups) > PEG−$LiClO_4$−Al_2O_3 (base surface groups). The differences in the fraction of ion pairs shown in Figures 6 and 7 result from the different quantities measured by IR and impedance spectroscopy method.

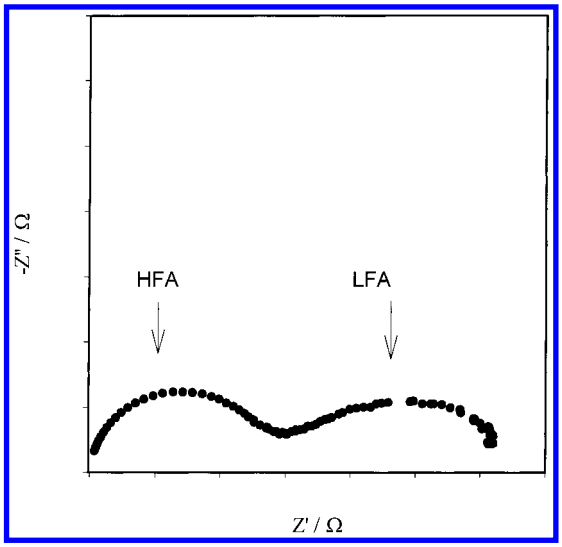

Figure 8. Exemplary impedance spectrum depicted at room temperature for PEG−$LiClO_4$−Al_2O_3 composite electrolytes. HFA and LFA present high- and low-frequency arc, respectively, corresponding to $RC_{parallel}$ subcircuit in series. Samples of metal concentration 2 mol/kg.

In addition, preliminary experiments on Li/electrolyte/Li symmetrical cells were performed and their results presented in Nyquist coordinates ($Z_{real}-Z_{imag}$) and analyzed by means of NLLS-fit technique (EQ program version 4.55).

Exemplary impedance spectrum consisting of low- and high-frequency arcs is shown in Figure 8. On the basis of our previous studies,[15] we attribute the high-frequency arc to the bulk properties of the electrolyte (bulk resistance (R_{HFA} and pseudo-geometrical capacity CPE_{HFA}) and low-frequency arc to the phenomena occurring at electrode−electrolyte interface (charge-transfer resistance R_{LFA} and pseudo-capacity of the double layer Q_{LFA}).

Changes of R or Q (CPE) parameters as a function of time are shown in Figures 9 and 10 for high- and low-frequency arc, respectively. In all sets of electrolytes the resistances start from low values, in the case of R_{HFA} corresponding to resistance of electrolyte measured in cells with blocking electrodes. Quick growth of both resistances is observed (see Figures 9a and 10a), but the rate of growth differ; the lowest rate for acidic filler. The values of both resistances stabilize with time, and the differences are not pronounced, although visible (lowest for acidic, highest for basic filler). The fast-growing charge transfer resistance stabilizes after a certain time, consistent with the stabilization of electrolyte resistance; the rate charge-transfer reaction Li^+-Li^0 is limited at some stage − possibly diffusion through the interfacial layer.

The values of Q_{LFA} range $10^{-6}-10^{-5}$ F/cm^2 (see Figure 10b) correspond with well-established values for double layer capacitance at solid electrodes and are fairly constant within the measurements cycle. On the other hand, CPE_{HFA} values decrease in time with the stabilization in the range $5 \times 10^{-10}-1 \times 10^{-9}$ F/cm^2.

Discussion

It is demonstrated that the addition of Al_2O_3 fillers to the PEG−$LiClO_4$ electrolyte leads to an enhancement of ionic conductivity in the limited concentration range (e.g., roughly for salt concentration higher than 0.5 mol/kg PEG). This increase is connected with the changes in ion−polymer and ion−ion

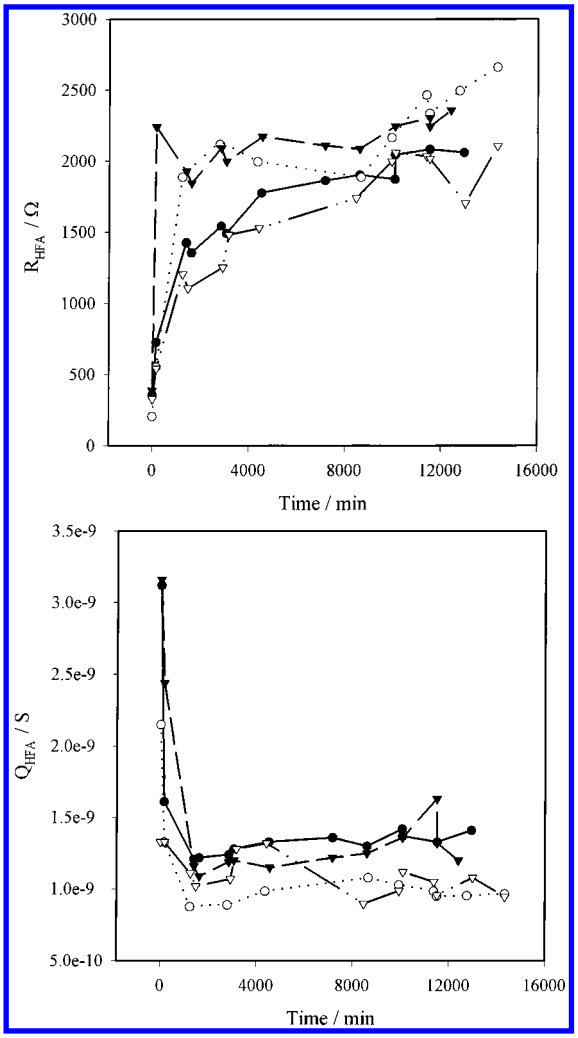

Figure 9. Changes of high-frequency resistance (R_{HFA}) and high-frequency capacitance (Q_{HFA}), respectively as a function of time (the starting point is the completion of the symmetrical lithium cell) measured at 25 °C for (●) PEG−$LiClO_4$−Al_2O_3 neutral surface groups; (▼) PEG−$LiClO_4$−Al_2O_3 basic surface groups; (▽) PEG−$LiClO_4$−Al_2O_3 acidic surface groups; (○) PEG−$LiClO_4$ electrolytes.

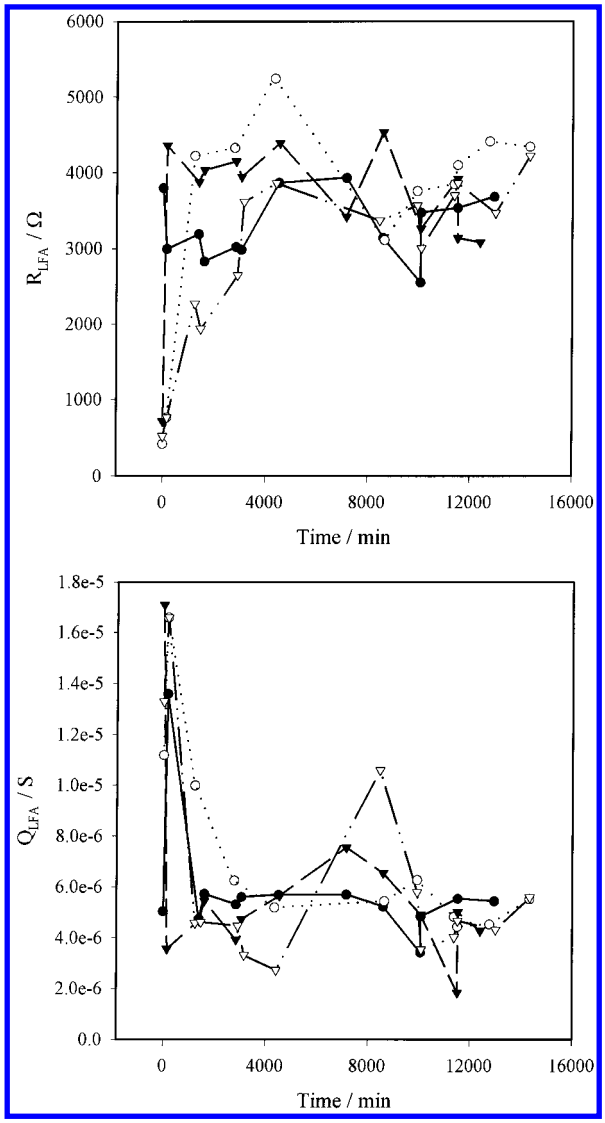

Figure 10. Changes of low-frequency resistance (R_{LFA}) and low-frequency capacitance (Q_{LFA}), respectively as a function of time measured at 25 °C for (●) PEG−$LiClO_4$−Al_2O_3 neutral surface groups; (▼) PEG−$LiClO_4$−Al_2O_3 basic surface groups; (▽) PEG−$LiClO_4$−Al_2O_3 acidic surface groups; (○) PEG−$LiClO_4$ electrolytes.

interactions as revealed from by the DSC, rheology, and FT-IR studies. The enhancement in the conductivity obtained for composite polymer electrolytes corresponds to the region in which lowering of the electrolyte viscosity (see Figure 4) and decrease in the fraction of ion pairs (see Figures 6 and 7) is observed compared to the base PEG−$LiClO_4$ system. In this salt concentration range the conductivity of the weak electrolytes is governed by the viscosity of the system according to the Fuoss−Kraus theory.[19] Fillers used differ from each other by the different surface groups of various Lewis acid−base type. Since the average grain size of fillers as well as the surface area of all three fillers does not differ significantly, the observed changes result mainly from the difference in the interaction of filler surface groups with Lewis base centers on polyether oxygen and ions. The interactions of base surface groups with Li^+ or positively charged triplets lead to the limitation of salt−polymer interaction. For the other two groups of electrolytes studied, the effect of the competition of acidic or neutral surface groups of the filler with Li^+ cations in the complexation of polyether oxygens is observed. All mentioned effects result in the decrease in the viscosity of the electrolyte and increase in the polyether chain flexibility (see Figures 3 and 4) in the salt concentration range in which the enhancement of the conductivity is observed. The weakening of polyether−salt interactions in this salt concentration range resulting from the presence of filler particles is additionally confirmed by changes in the position of the maximum of C−O−C stretch as revealed from FT-IR (see Figure 5).[2,3] For composite systems this maximum occurs at higher frequencies which confirms weaker interaction between base centers on polyether oxygens and Li^+ cations or positively charged triplets. In addition, interaction of base filler surface groups with Li^+ cations as well as neutral or acidic filler surface groups with ClO_4^- anions leads to the decrease of the fraction of ion pairs (see Figures 6 and 7), thus leading to an enhancement in the conductivity in the discussed salt concentration range.

For the lower salt concentration the concentration of the filler is much higher than the salt concentration. In this concentration range the presence of the filler decreases the ionic conductivity of the electrolyte. This is due to the increase in the viscosity of polyethers in the case of addition of fillers with acidic or neutral surface group (see Figure 4) and the immobilization of Li^+ cations for system containing fillers with base surface groups.

In PEG electrolytes in contact with lithium electrode, stable interfacial layers are formed regardless of the presence of Al_2O_3

fillers. With acidic filler the resistance parameters are most favorable from the point of view of battery application, although the advantage is not spectacular. The highest interfacial resistances measured for composite electrolytes containing filler with base surface groups confirm immobilization of cations and dominant anionic conduction leading to the formation of "anionic clouds" at the Li−polymer electrolyte interface thus increasing interfacial resistivity. With CPE_{HFA} attributed to pseudo-capacity of the bulk electrolyte, lowering of CPE_{HFA} with time is consistent with the concept of the formation of ionically conducting interface layer. The resistance of the electrolyte "absorbs" the additional resistance of the interfacial layer, which is accompanied by lowering of the electrolyte capacitance. Even if this capacitance consists of "true electrolyte" and "interfacial layer" components, and the geometry of such mixed capacitor is constant, the porous and strongly inhomogeneous layer results in lower dielectric constant. Such effect would produce measurable but not too pronounced lowering of the capacity which is the case in our measurements.

Based on the above discussion, it can be concluded that even if the trends in the changes of ionic conductivity observed upon the addition of fillers bearing different surface groups are similar, their origin results from different Lewis acid−base type interactions between filler particles, polyethers, and salt.

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References and Notes

(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, UK, 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.; Florjańczyk, Z.; Stevens, J. R. *Electrochim. Acta* **1995**, *40*, 2251.

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

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

(8) Scrosati, B.; Neat, R. *Applications of Electroactive Polymers*; Scrosati, B., Ed.; Chapman and Hall: London, 1993; Chapter 6.

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

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

(11) Kumar, B.; Scanlon, L. G. J. *Power Sources* **1994**, *52*, 261.

(12) Wieczorek, W.; Such, K.; Florjańczyk, Z.; Stevens, J. R. *J. Phys. Chem.* **1994**, *98*, 6840.

(13) Wieczorek, W.; Lipka, P.; Zukowska, G.; Wyciślik, H. *J. Phys. Chem. B* **1998**, *102*, 6968.

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

(15) 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.

(16) Kim, Y. W.; Lee, W.; Choi, B. K. *Electrochim. Acta* **2000**, *45*, 1473.

(17) Choi, B. K.; Kim, Y. W.; Shin, K. H. *J. Power Sources* **1997**, *68*, 357.

(18) Pearson, R. G.In *Survey of progress in chemistry—1*; Scott, A., Ed.; Academic Press: New York, 1969; Chapter 1.

(19) Fuoss, R. M.; Accascina, F. *Electrolytic Conductance*; Interscience New York, 1959.

(20) Borkowska, R.; Laskowski, J.; Plocharski, J.; Przyluski, J.; Wieczorek, W. *J. Appl. Electrochem.* **1993**, *23*, 991.

(21) Herr, R. *Electrochim. Acta* **1990**, *35*, 1257.