Conductivity Studies of Solid Polymer Electrolytes Based on Polyethers and Polyphosphazene Blends

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ABSTRACT: In this work, electrical characteristics of several polymer electrolytes based on polyether and polyphosphazene blends are reported by means of complex impedance spectroscopy. In addition, a statistical analysis was conducted applying a mathematical model to a previously designed pattern to the purpose of gaining insight into the effect exerted on the conductivity of the electrolyte by the portion of each component in the blend. Evidence was obtained to prove that the dependence of conductivity on blend composition adjusts to a reduced cubic model, whose regression coefficients are determined in this work. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2181–2186, 1998

Key words: polyethylene oxide; polyphosphazene; poly(epichlorhydrine); ionic conductivity; polymer electrolytes; statistical analysis

INTRODUCTION

Major efforts are being made in academic and industrial research to produce lithium batteries with a polymer membrane, in view of the benefits that would be derived from the industrial manufacture of different sizes and shapes of such batteries, compared to the conventional ones presently in use. Significant advances are being made with different approaches. among which the development of new polymer systems with a high ion conductivity at room temperature should be especially highlighted,[1] the use of intercalary composites as electrodes,[2,3] and in some instances the use of graphite or coke electrodes[4] to replace lithium metal, as the former have been proved to be more efficient, less hazardous, and less polluting.

In this research several electrolytes based on polyethylene oxide (PEO), poly(octafluoropentoxytrifluoroethoxy)phosphazene (PPz), and poly-(epichlorhydrine) (PECH), obtained in our laboratory in previous work,[5,6] were characterized as to their electrical properties. In addition a statistical analysis was implemented applying a previously designed mathematical model, to the purpose of determining the influence of each of the components on the conductivity of the electrolyte. The benefit obtained from such statistical analysis is that it makes available the possibility of predicting the conductivity of any sample, only on the basis of its composition.

EXPERIMENTAL

Reagents and Materials Preparation

The following commercial polymers were used: polyethylene oxide (PEO) $(M_w = 5 \times 10^6)$ from the Aldrich Company; poly(octafluoropentoxytrifluoroethoxy)phosphazene (PPz) supplied by Firestone under the trade name PNF-200, and poly-(epichlorhydrine) (PECH) $(M_w = 7 \times 10^5)$ obtained from Aldrich. The lithium triflate salt
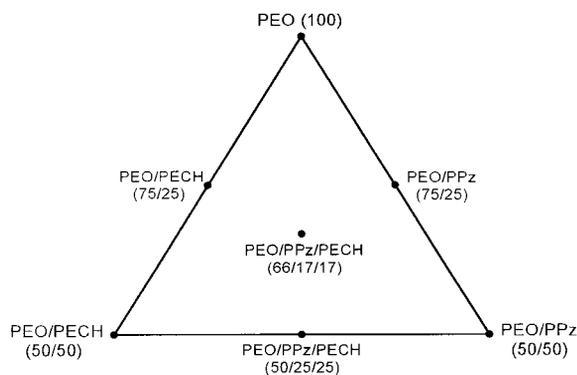
Figure 1 Composition of the different samples according to the experimental design.

LiCF$_3$SO$_3$ (LiTf) was also supplied by Aldrich, as well as the propylene carbonate (PC).

Seven polymer composites were prepared based on an experimental design as represented in the ternary diagram in Figure 1. As can be observed in the figure, the experimental sites are evenly distributed over the whole experimental range. Two different electrolyte families were prepared from these compositions: the first of these consisted of the polymer blends shown in Figure 1 and the lithium triflate salt at the ratio [O]/[Li] = 8, whereas the second type was composed of the same polymer blends at which 80% propylene carbonate (PC) was incorporated in regard to the total polymer mass. The blends were obtained dissolving the respective amounts of the components in acetonitrile and chloroform mixtures inside the glove box under controlled atmospheric conditions. Once the components had been dissolved, thin films of the different samples were obtained evaporating the solvent between two glass plates separated by a flat spacer that controled the thickness of the electrolyte membrane (≈0.02 cm) and mantained the samples under vacuum conditions until constant weight values were obtained.

Electrical Evaluation

Complex impedance spectroscopy was carried out using a Hewlett Packard impedance analyzer, model 4192A. The frequency range used was 0.01–10,000 kHz, and the measuring temperatures ranged from 0 to 110°C, following a heating schedule monitored by an Oxford Instruments temperature controller ITC4. The sample was placed in an Oxford Instruments cryostate, DN 1710, equipped with a liquid nitrogen chamber especially designed for measurements at variable

temperature. Temperature was controlled by means of a Pt sensor, electrically connected to the outside temperature control device. During experiments each sample was kept at the specified temperature for 1 h before recording AC spectrum. The samples were thin film slabs, 0.6 cm in diameter and a thickness of approximately 0.02 cm. They were placed between two nickel electrodes in a swagelock™ constructed cell fitted at the inside of a glove box under controlled atmospheric conditions.

Each polymer electrolyte was run twice, results being reproducible in all cases.

From the complex impedance data obtained, the respective equivalent circuits were computed, using a mathematical software proposed by Boukamp.[7]

Mathematical Evaluation

To determine the influence of component proportion in a blend on a certain physical property (in our case it was ionic conductivity), the reduced cubic model was taken as valid, as it takes into account the potential component interactions, according to the following expression:

$$\text{Parámetro} = a_1 \text{PEO} + a_2 \text{PECH} + a_3 \text{PPz}$$
$$+ a_{12} \text{PEO·PECH} + a_{13} \text{PEO·PPz}$$
$$+ a_{23} \text{PECH·PPz} + a_{123} \text{PEO·PECH·PPz} \quad (1)$$

where PEO, PPz, and PECH are the respective component portions in the different blends. To select the terms of the reduced cubic model represented by eq. (1) and to estimate the values of the respective regression coefficients, stepwise regression analysis was applied. The ensuing computing processes were conducted using the statistical software package BMDP[8] and the SYSTAT program.[9]

RESULTS AND DISCUSSION

Electrical Study

The impedance spectra of the different plasticized and untreated samples are shown in Figure 2 as representative of the two families. They describe a semicircle whose center is not situated on the x-axis, and which describes the conductive behaviour inside the electrolyte, adjusting to a straight line with a slightly steeper or flatter slope in the
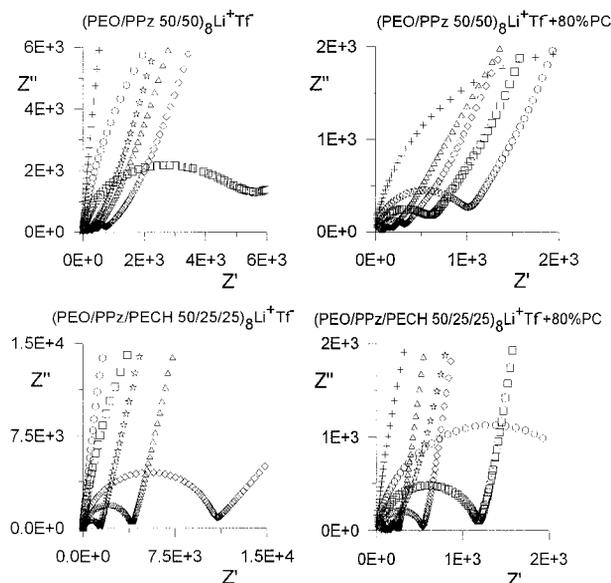
Figure 2 Impedance graphs at different temperatures: (+) 0°C, (○) 30°C, (□) 50°C, (◇) 70°C, (△) 90°C, and (&☆) 110°C.

low-frequency range, which shows the behavior of the electrode–electrolyte interface. When applying the Boukamp[7] software, the spectra are found
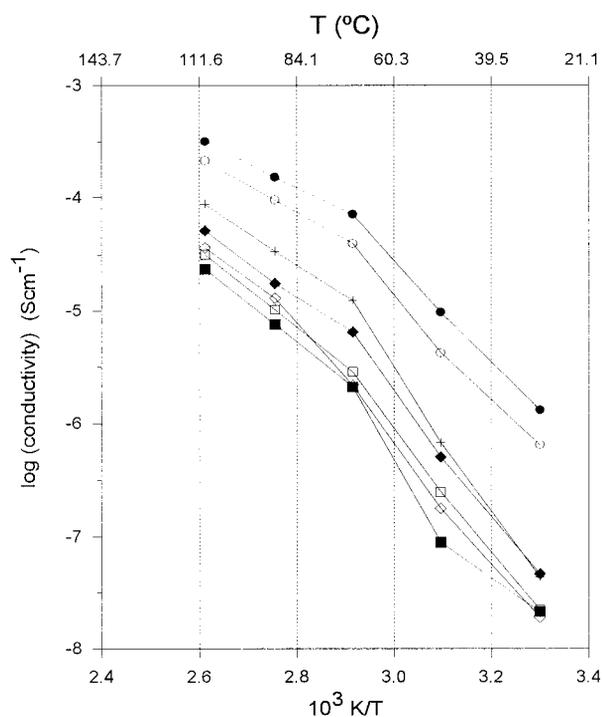

Figure 3 Arrhenius plots of polymer electrolytes without PC: (+) PEO; PEO/PPz (○) 75/25, (●) 50/50; PEO/PECH (□) 75/25, (■) 50/50; PEO/PPz/PECH (◇) 66/17/17, and (◆) 50/25/25.
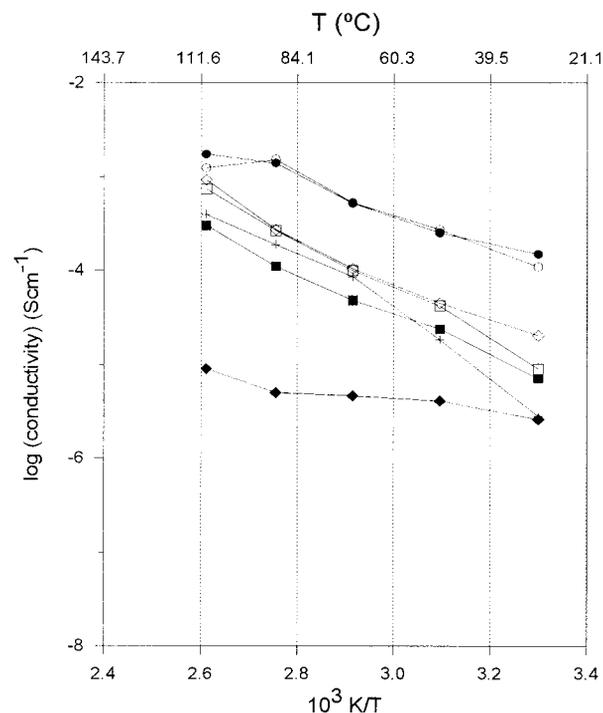

Figure 4 Arrhenius plots of polymer electrolytes with 80% of PC: (+) PEO; PEO/PPz (○) 75/25, (●) 0/50; PEO/PECH (□) 75/25, (■) 50/50; PEO/PPz/PECH (◇) 66/17/17, and (◆) 50/25/25.

to be equivalent to a serially arranged circuit consisting of a "Constant Phase Element" (CPE), which corresponds to the electrode–electrolyte interface with a parallel combination of the resistance and the CPE of the electrolyte.

Taking into account that the conductivity the electrolytes ought to possess to qualify for application in rechargeable solid state batteries must be above 10^{-5} S-cm^{-1}, it is clear that the only electrolytes to comply with this requirement are the plasticized ones (at room temperature) and the nonplasticized electrolytes as of 60°, which limits these latter to be used in battery applications at temperatures above 60°C. Figures 3 and 4 show conductivity plotted against temperature for all the samples of the nonplasticized and the plasticized families, respectively, according to the Arrhenius coordinates. Several aspects should be pointed out: first, that for all samples conductivity increases as a function of temperature; second, that the conductivities of the plasticized series are higher than those of the nonplasticized systems over the whole temperature range, the most significant differences presenting in the low temperature range; third, the conductivity of the nonplasticized samples is shown to undergo a wide rise in the 30–70°C environment, indicative of the

Table I   Values of the Regression Coefficients Obtained from Stepwise Regression, Coefficients of Determination (R^2), and Residual Standard Deviation (s) for the Conductivity Values (log σ_T) at Different Temperatures

Parameter	T (°C)	Regression Coefficients				R^2	s
		a_1	a_2	a_3	a_{123}		
log σ_T							
log σ_{30}	30	−7.203	−8.006	−5.893	−21.021	0.904	0.339
log σ_{50}	50	−6.078	−7.150	−5.029	−20.227	0.971	0.177
log σ_{70}	70	−4.917	−5.852	−4.169	−20.456	0.952	0.190
log σ_{90}	90	−4.465	−5.275	−3.846	−11.206	0.936	0.179
log σ_{110}	110	−4.050	−4.757	−3.517	−10.355	0.943	0.146

fact that these samples being subject to a transition process, attributable to the melting of the free PEO portion (T_m^{PEO} = 69.7°C), which has not formed a complex with the lithium salt. Thermal properties of polymer blends have been reported in previous works.[5,6] In the plasticized electrolytes, however (Fig. 4), conductivity increases gradually as a function of temperature, without producing any prominent leaps. This is explained by the fact that PC exerts an effect on the microstructure of the polymer system favoring segmental movements. In addition, as organic solvent with high dielectric constant is involved, salt dissociation is favored that entails a decrease in ion–ion interactions and, hence, enhances ion mobility and improves the conductivity of the electrolyte.

In the plasticizer-free systems, as well as in the plasticized ones, the highest conductivity values are obtained for electrolytes based on binary PEO/PPz blends, conductivity being the higher the larger the PPz portion in the blend. This holds true within the concentration ceiling imposed by the mathematical design chosen, and hence, ex-

trapolation to other concentration ranges is not possible.

Regarding the remaining blends, the conductivity values obtained are similar to those obtained from the polymer electrolyte based on pure PEO, except for a slight trend towards improved values in the ternary systems. A certain trend towards lower conductivity values was found in the binary PEO/PECH blends. This behavior is quite logical and in full agreement with the findings of previous research[6] based on a statistical study of glass transition temperatures (T_g) as a function of composition. Those findings indicated that the T_g of the polymeric precursor systems of the electrolytes under study increases with increasing PECH portion. Hence, for these systems, lower conductivity values should be expected.

Mathematical Study

Tables I and II compile the results obtained when applying stepwise multiple regression in consecutive steps logσ_T and logσ_T^{PC}, respectively. This nomenclature corresponds to the experimental

Table II   Values of the Regression Coefficients Obtained from Stepwise Regression, Coefficients of Determination (R^2) and Residual Standard Deviation (s) for the Conductivity Values (log σ_T^{PC}) at Different Temperatures

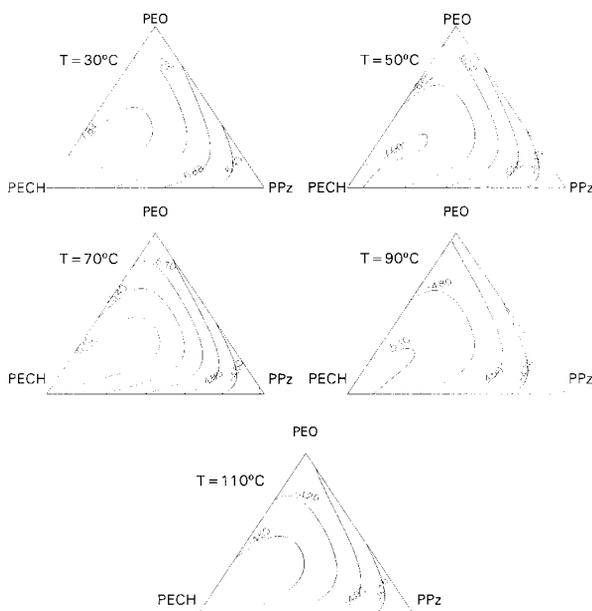| Parameter	T (°C)	Regression Coefficients				R^2	s
		a_1	a_2	a_3	a_{123}		
log σ_T^{PC}							
log $\sigma_{30}^{\mathrm{PC}}$	30	−5.223	−5.189	−3.701	−25.805	0.847	0.392
log $\sigma_{50}^{\mathrm{PC}}$	50	−4.442	−4.663	−3.521	−34.022	0.854	0.347
log $\sigma_{70}^{\mathrm{PC}}$	70	−3.872	−4.355	−3.242	−42.233	0.941	0.235
log $\sigma_{90}^{\mathrm{PC}}$	90	−3.489	−3.973	−2.790	−54.414	0.948	0.272
log $\sigma_{110}^{\mathrm{PC}}$	110	−3.263	−3.409	−2.711	−54.239	0.977	0.166

Figure 5   Isoresponse curves for the parameter $\log\sigma_T$ as a function of ternary composition.

conductivity data at different temperatures obtained for the polymer electrolytes in the absence and in the presence of the plasticizing agent, propylene carbonate (PC). The respective experimental data are shown in Figures 3 and 4. Tables I and II show the regression coefficients of the terms selected from the reduced cubic model specified in eq. (1), as well as the values of the fitting statistics [coefficient of determination (R^2) and residual standard deviation (s)], which assess the accuracy of the fit. It must be taken into account that the regression models for blends differ from the standard regression models, as the former lack the independent term and have one degree of freedom less in the sum of squares explained by the model. Thus, the regression coefficients for blend models should be lower than those determined for the standard models by means of multiple linear regression.[9]

Returning to Tables I and II, it is significant to note that the experimental data adjust accurately to the proposed model, the coefficients of determination (R^2) being greater than 0.85 in all cases and residual standard deviation (s) always below 0.39. On the other hand, both parameters $\log\sigma_T$ and $\log\sigma_T^{PC}$, prove to be predictable in all cases and for all temperatures as a function of the proportions of the individual components (PEO, PECH, and PPz) in the blend, even in the ternary composition. This fact allows determination of the variation of the regresion coefficients a_1 a_2 a_3 as a

function of temperature, which tend to increase when increasing the experimental temperature, both in the plasticized and the plasticizer-free systems (Tables I and II).

Finally, and with the aim of identifying the conductive behavior in terms of blend composition, Figures 5 and 6 show the isoresponse curves of the parameters $\log\sigma_T$ and $\log\sigma_T^{PC}$, respectively. In addition, these diagrams allow deriving the respective values of $\log\sigma_T$ and $\log\sigma_T^{PC}$ for a certain composition or else, inversely, to predict the blend composition that would give rise to a given value of these parameters.

Regarding the plasticizer-free family (Fig. 5), at any experimental temperature the highest conductivity values are consistently achieved by the electrolytes containing a major PPz portion, and preferably by those with the lowest PECH concentration. By the same token, the lower values of parameter $\log\sigma_T$ correspond to concentrations that approach the binary systems PEO/PECH with maximum PECH levels.

Figure 6 shows the isoresponse curves of the plasticized electrolytes. Here again, the higher $\log \sigma_T^{PC}$ values approach those of the binary polymer electrolytes based on a PEO/PPz blend with a major PPz portion. Nevertheless, and different from the findings recorded for the PC-free systems, in the plasticized electrolytes the lowest conductivities are recorded for the ternary systems, and among these, conductivity is lower for
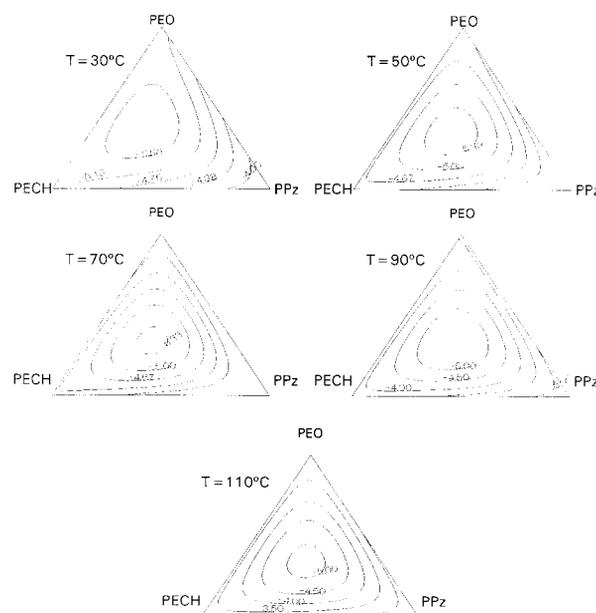

Figure 6   Isoresponse curves for the parameter $\log\sigma_T^{PC}$ as a function of ternary composition.

compositions positioned in the central area of the experimental triangle.

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