Ionic Conductive Polymer Systems Based on Polyether and Polyphosphazene Blends

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SYNOPSIS

Several polymer electrolytes have been obtained, based on binary blends of polyethylene oxide (PEO), polypropylene oxide, and polyphosphazene by means of solvation with lithium triflate. The different samples were studied both as to their microstructure and for their electrical properties, either through the determination of their respective glass transition temperatures and melting enthalpies or by means of complex impedance spectroscopy. When comparing the results obtained for the synthesized binary systems with those known for PEO, the former systems prove to possess a better dimensional stability and a higher conductivity than PEO in itself. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

At present, there is increasing industrial and academic interest in the development of polymer-based lithium batteries. These batteries are known to be solid-state integrated systems that, in their most common form, combine a polymer membrane possessing ionic conduction with two reversible lithium electrodes. The polymer membrane acts as an ion conductor and as a separator between the electrodes. As a general rule, it is a high-molecular-weight polymer with heteroatoms in its backbone or lateral branches, in which a lithium salt has been dissolved. The anode commonly is a lithium film, and the cathode is based on a reversible lithium-intercalation compound.

After the discovery of the first solid-state reversible lithium battery with a polymeric electrolyte by Armand et al.,[1,2] a true race among scientists began toward the synthesis of polymer electrolytes with high ionic conductivity (10^{-3}–10^{-5} s · cm^{-1}) at temperatures approaching ambient and, in addition, possessing good dimensional stability to resist the physical dynamics occurring in electrodes during the charging and discharging periods.

The first polymer electrolyte described in the literature was a material resulting from dissolving a lithium salt (LiClO$_4$) in a polymer matrix with heteroatoms (ether groups) in its backbone (polyethylene oxide, which acts as a inmovile solvent). This material did not possess good conducting properties at room temperature, and this was the reason why research was extended to other polymeric materials to ensure not only good conducting properties but also better mechanical properties at room temperature. Thus, research was targeted in different directions,[3,4] such as synthesis of solvating polymers possessing slight or no crystallinity; addition of low-molecular-weight liquids, such as propylene carbonate or ethylene oxide oligomers; synthesis of new organometallic salts with low lattice energy, plasticizer ability, and a wide electrochemical stability window, and nonconventional polymer electrolytes based on polyacrylonitrile, polyvinylidene fluoride, and polyethyleneglycol-diethylether.

The objectives pursued by the synthesis routes described above, apart from obtaining materials that compatibilize excellent ion conductivity with an equally excellent chemical, thermal, and dimensional stability, aim at reducing the crystallinity and the glass transition temperature of the materials, that is, at minimizing the factors that are known to affect lithium ion transport through the material. On these lines, we study the preparation, thermal behavior, and electrical characterization of new

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polymer electrolytes based on binary systems of polyethylene oxide (PPE) and polypropylene oxide (PPO) or polyphosphazene (PPz).

EXPERIMENTAL

The following commercial polymers were used: PEO from Aldrich, PPO supplied by Zeon Chemical Inc., and poly(octofluoropentoxy trifluoroethoxy) phosphazene (PPz) from Firestone. All polymers were used as received; lithium triflate ($LiCF_3SO_3$) (TfLi) was the reagent grade supplied by Aldrich and used as received.

All polymer electrolytes were obtained by dissolving the appropriate polymers and TfLi in acetonitrile, ensuing solvent evaporation and the drying of the samples at high vacuum.

Glass transition temperatures were measured with a Mettler differential scanning calorimeter, model TA-4000. The samples were loaded in hermetical aluminum pans, held at 220°C for 5 minutes, and then annealed to −100°C. Finally, their thermograms were recorded at a rate of 10°C/min. The melting behavior of the samples was determined by recording the melting thermograms at a rate of 10°C/min.

Complex plane impedance and inductance analyses were conducted on an Impedance Analyzer (Hewlett Packard, model 4192 A), computer aided (HP Vectra) in the frequency range of $10-10^7$ Hz and in the temperature range between −170 and 110°C, applying a heating program geared through an Oxford Instruments ITC 4 temperature controller. The sample was placed in an Oxford Instruments DN 1710 cryostat provided with a liquid nitrogen chamber, specially designed for measurements at variable temperature. The surfaces of the samples were coated with a thin Ag film to ensure good contact between the sample surface and the measuring electrodes.

A best fit of the experimental impedance data performed by a nonlinear least-square analysis program with a modified Levemberg–Marquardt algorithm (we adapted the Boukamp[5] EQIVCT original code) was used to obtain the equivalent circuit parameter values of the samples.

RESULTS AND DISCUSSION

Thermal Behavior

Taking into account that ionic conductivity in a polymer system takes place in the amorphous region of the system and that the complex formed by the metallic salt and the heteroatom in the polymer chain causes both the glass transition temperature and the melting temperature of the polymer to shift upward, it is vital to examine both magnitudes to find out whether this shift inhibits or favors ionic conduction at a given temperature. Hence, our approach is based on the study of thermal behavior, concretely speaking on the study of the glass transition temperature and the melting point. Table I compiles the glass transition temperature values, melting points, and melting enthalpies of the homopolymers, as well as those of their binary blends for the two TfLi concentrations used. These values show that the T_g of the homopolymers is shifted toward higher temperatures as a function of increasing TfLi content, except that of PPz, whose T_g remains invariable independent of TfLi concentration. This supports the assumption that the coordinating reaction between the TfLi and the heteroatom (ether group) of the lateral branch of PPz has not taken place. In the case of PEO and PPO, the temperature rise is spectacular (approximately 80°C) for the higher lithium concentration. In the binary blends, a single glass transition is recorded that, independent of blend composition, salt concentration, or of the nature of the second polymer (PPO or PPz), remains practically unaltered (wherever it presents) around −60°C, indicating that either the system has become compatible as a consequence of the solvation reaction of the TfLi and the heteroatom in the polymeric chain and thus logically possesses but a single glass transition or else the transition of the second polymer has dropped below the experimental temperature range.

The results obtained for the melting behavior of the systems under study are also compiled in Table I, as well as in the thermograms shown in Figure 1, in which, by way of illustration, the thermal behavior in the melt of PEO in the absence of lithium is compared with that of PEO solvated with two different TfLi concentrations, as well as with that of the system PEO–PPO (80/20), solvated with the same TfLi percentages as PEO. As a result of this comparison two significant facts should be underlined. First, when comparing the thermogram of the unsolvated PEO with those corresponding to the solvated systems, these latter present two or more melting peaks, which is not the case for unsolvated PEO. The position of the first melting point remains practically invariable, independent of lithium concentration and coincides with the melting point recorded for unsolvated PEO (67–68°C). The position of the second peak appears at a considerably higher

temperature, that is, in the range of 150–190°C, and is assigned to the solvated complex TfLi–PEO.

Second, when comparing the two solvated systems to the two lithium concentrations used, the melting peak assigned to PEO is observed to become smaller (the enthalpy diminishes) with increasing salt concentration, whereas the second peak is shifted to higher temperatures for the higher lithium concentration, thus increasing the melting enthalpy. This phenomenon can be explained as a consequence of the fact that the higher the solvation grade, the higher the lithium content in the material, which implies a decrease in the degree of freedom of the PEO chains to melt. Hence, they melt at a higher temperature. Nevertheless, the formation of a new crystalline phase, consequential to the solvation reaction, is not to be discarded either, as pointed out by Wantabe et al.,[6] when studying other ionic conductor systems, where the same phenomenon had appeared.

We conclude that the T_g of the PEO-based binary polymer systems is not influenced by the TfLi concentration. Moreover, it is the crystalline phases of the complexes formed that are subject to its effects.

Ionic Conductivity

Systematic studies[7] of the electrical properties of the PEO-based polymer electrolytes have demonstrated that in this type of material, ion transport
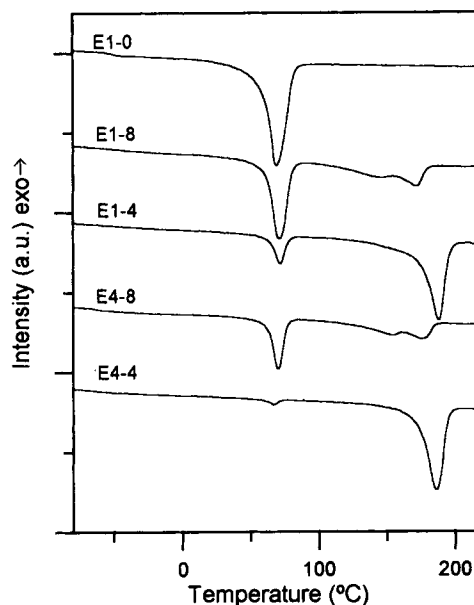

Figure 1 Thermal behavior in the melting of the samples.

takes place in the amorphous zone of the polymers and that electrical conductivity of polymer electrolytes is measured in a cell with the following configuration: electrode–electrolyte–electrode. The conductivity of all synthesized electrolytes, whose compositions are listed in Table I, was determined by means of complex plane impedance spectroscopy

Table I   Composition and Melting Behavior of the Samples

	Composition		Melting Behavior				
Samples	PEO–PPO–PPz	O/Li	T_g (°C)	$T_m, 1$ (°C)	ΔH_{m1} (J/g)	$T_m, 2$ (°C)	ΔH_{m2} (J/g)
E1-0	100/0/0	0	−51.7	68.4	130.2	—	—
E1-8	100/0/0	8	−34.7	68.3	63.2	154.0	35.9
E1-4	100/0/0	4	24.7	57.1	11.7	183.8	73.5
E2-0	0/100/0	0	−60.5	—	—	—	—
E2-8	0/100/0	8	−14.6	—	—	—	—
E2-4	0/100/0	4	22.6	—	—	—	—
E3-0	0/0/100	0	−61.7	—	—	—	—
E3-8	0/0/100	8	−61.0	—	—	—	—
E3-4	0/0/100	4	−62.5	—	—	—	—
E4-8	80/20/0	8	−64.4	67.3	27.2	163.4	42.0
E4-4	80/20/0	4	—	—	—	185.3	73.0
E5-8	50/50/0	8	−60.6	67.5	1.9	178.8	42.3
E5-4	50/50/0	4	13.0	—	—	189.1	43.0
E6-8	80/0/20	8	—	67.3	28.3	159.5	30.9
E6-4	80/0/20	4	—	—	—	188.0	63.4
E7-8	50/0/50	8	−62.4	68.3	24.6	156.6	24.4
E7-4	50/0/50	4	—	—	—	185.3	52.9

and by using nickel in the cell as a blocking electrode. The ion conductivity of each of the samples is a function both of temperature and frequency, as is demonstrated below.

Figure 2 shows a representation of all samples, i.e., the complex plane impedance spectra of the system PEO–PPz (80/20) ($x = 8$) at four sequential temperatures, which allow the evolution of the impedance to be followed as a function of temperature. At temperatures below 60°C, the sample is observed to have a different response from the one recorded for the same sample at higher temperatures. Below 60°C, the conductivities obtained are relatively low; there are arcs and circles, some of which are not closed. Above 60°C, conductivity becomes increasingly higher. A straight line appears at low frequency due to the diffusion impedance at the electrode–electrolyte interface, followed by a circle with a Y-intercept in the higher frequency range. This latter response is what characterizes

polymer electrolytes with significant ionic conductivity. Such spectra represent an equivalent circuit in which the capacitance of the electrode is placed in a serial array, with a parallel combination of a capacitance and an electrolytic resistance. In Figure 3, the effect of temperature and frequency on the impedance of sample PEO–PPz (80 : 20) ($x = 8$) can be seen more distinctly. At the lowest experimental temperature (10°C) and as of 10^a Hz, the impedance is practically independent of frequency. At higher temperatures, the threshold frequency constantly increases, until, at 60–70°C the frequency, at which the sample becomes independent of the impedance, surpasses 10 Hz, a circumstance that, apart from being closely related to the ion conduction mechanism, is one of the distinctive characteristics of these systems.

As a general rule, polymer electrolyte conductivity increases proportionally to temperature, as indicated by the Arrhenius equation:
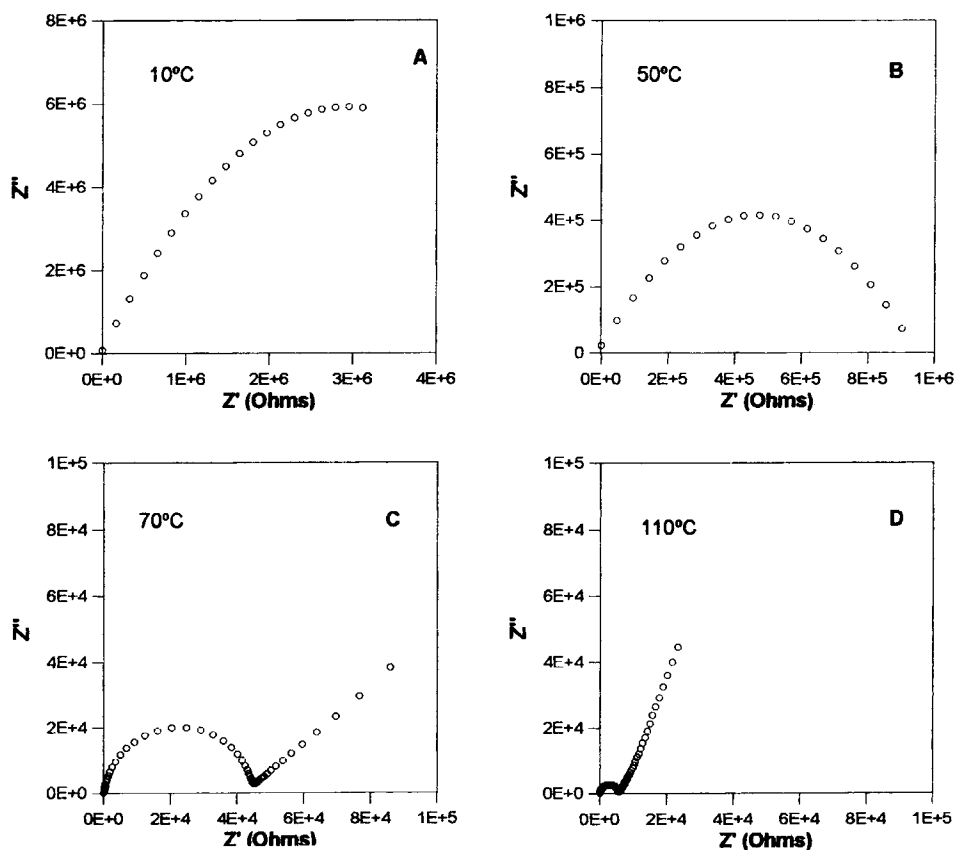

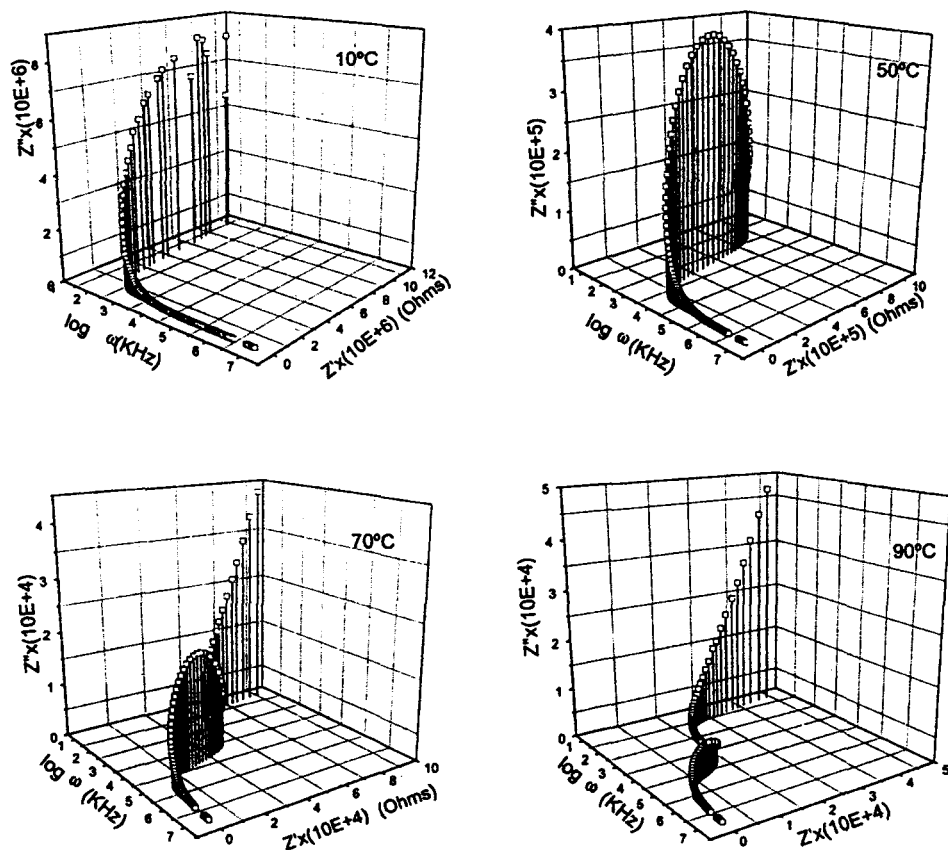**Figure 2** Complex plane impedance spectra of PEO–PPz (80/20) ($x = 8$) sample at four sequential temperatures.

Figure 3   Effect of temperature and frequency on the impedance of PEO–PPz (80/20) (x = 8) sample.
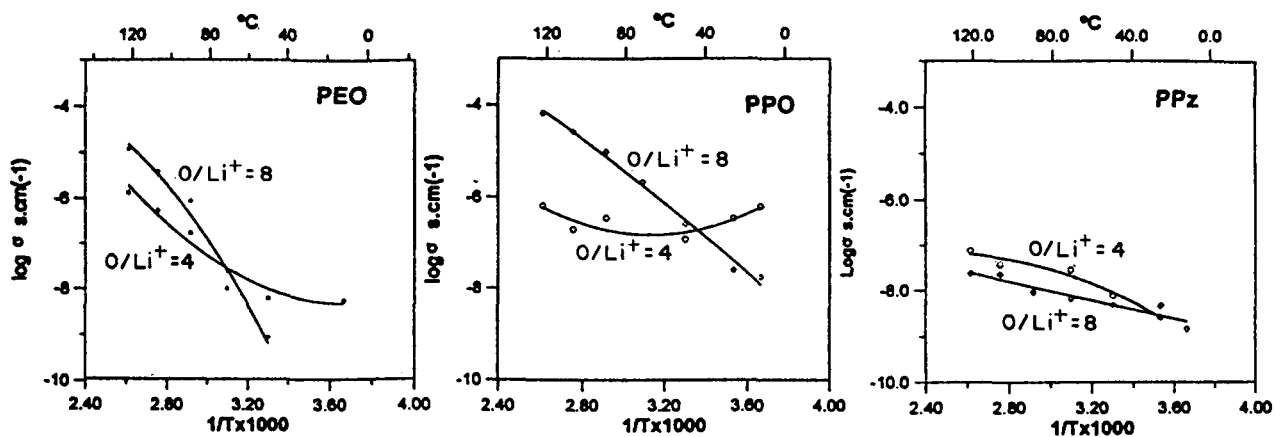

Figure 4   Conductivity versus reciprocal temperature for the samples solvated with different O/Li^+ ratios.
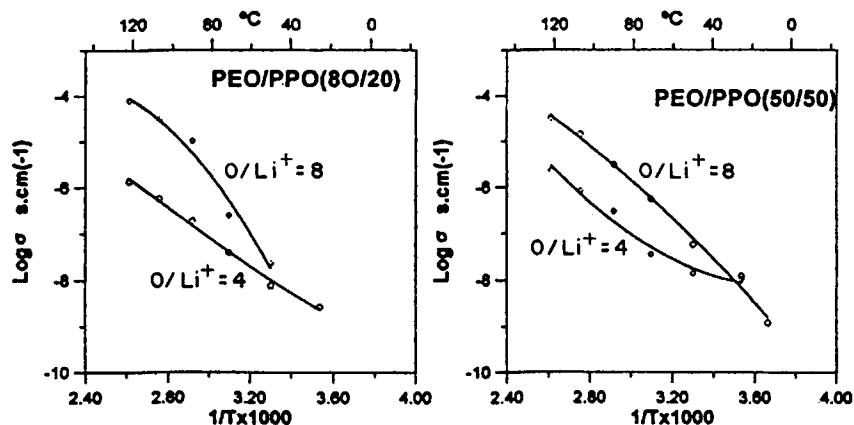
Figure 5   Conductivity versus reciprocal temperature for the samples solvated with different O/Li⁺ ratios.

$$\sigma = \sigma_0 \exp(-E/KT) \qquad (1)$$

where E is the activation energy. Figures 4–6 show the plots of conductivity against $1/T$ for all the synthesized samples, having achieved in all cases good agreement between the graph and the experimental items.

A general characteristic found in all the synthesized polymer electrolytes was that conductivity was lower for the highest TfLi concentration than for the minimum lithium dose, a circumstance that is easy to explain from a structural point of view, taking into account that TfLi has an ordering and stiffening effect on the chains when solvation with the ether group occurs, causing the glass transition temperature to rise and crystallinity to increase, and hence ion transport through the material is constrained. Thus, it is not surprising that at a given temperature, a system solvated with a greater

amount of TfLi should present a lesser conductivity than when solvated with smaller quantities.

Figure 4 compiles the effects of temperature, expressed in terms of the Arrhenius coordinates, on the three homopolymers at the two experimental TfLi concentrations. Regarding these graphs, the following points should be stressed. First, ion conductivity of PPz is practically independent of temperature; in all cases the conductivities reached are very low, even at very high temperatures. As stated above, this is indicative of the fact that the solvation reaction has not taken place between the lithium salt and the ether groups positioned in the lateral branches of the PPz backbone and hence there does not occur any dissociation of the salt, which accounts for the low conductivity values. Second, PPO reaches slightly higher conductivity values than PPz at the highest temperature, but at medium and low temperatures the values remain below those of PEO,
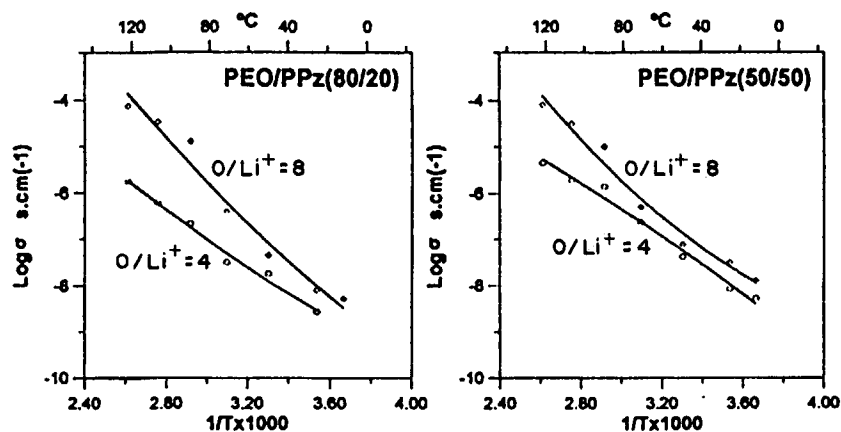

Figure 6   Conductivity versus reciprocal temperature for the samples solvated with different O/Li⁺ ratios.

which shows evidence that ion transport through a polymeric matrix is more favorable with a stronger polar chemical structure (PPO) than a less polarly structured material (PEO). In addition, at comparatively lower temperatures, the lithium ion encounters greater difficulties in moving through a PPO matrix due to other causes, such as the extraordinarily high viscosity of the medium in the lower temperature range.

The fact that log σ versus $1/T$ lines of O/Li^+ = 4 crosses the line with O/Li^+ = 8 is explained in terms that different materials, probably with a different solvation mechanism, and different behavior versus temperature can be expected. Figures 5 and 6 show the variations in conductivity of the binary systems PEO–PPO and PEO–PPz versus reciprocal temperatures. One or the other system may be considered as equivalent from a conductivity point of view, that is, both systems independent of their original chemical composition reach similar conductivity values, which are relatively better than those recorded for the unblended homopolymers PEO and PPO at the same temperatures. This supports the statement that blending does anything but deteriorate their conducting properties; on the contrary, it enhances them.

Conclusions

In the light of the results obtained, it is legitimate to conclude that in the experimental temperature range, the polymer electrolytes prepared on the basis of PEO–PPz and PEO–PPO achieve a higher degree of ion conductivity than unblended PEO, with the additional advantage that the synthesized binary systems have the ability of forming less stiff films than PEO, presenting good dimensional stability, apart from excellent mechanical properties. Research to further improve the conductivity of these binary systems at room temperature by means of the incorporation of a third component (plasticizer) is underway at our laboratories, as well as an exhaustive electrochemical study, which includes electrochemical stability measurements.

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