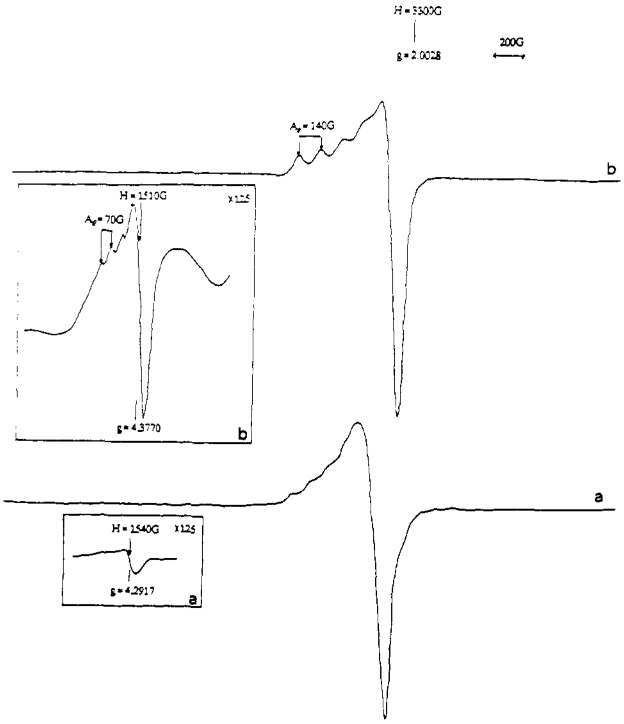

Figure 3. EPR signals (X-band) observed at room temperature with $Cu_{0.5}H_3PMo_{11}VO_{40}\cdot 13H_2O$: (a) signal obtained in the solid freshly prepared; (b) signal obtained after calcination of the solid at 373 K.

resolved. The splitting constant of the half-field signal has been measured as $A_{\parallel} = 70$ G. In this latter solid, the copper(II) ion pairs are more stable than in the $Cu_2PMo_{11}VO_{40}\cdot 21H_2O$ since the disappearance of the half-field signal occurs at 473 K and not at 373 K as in the first solid. This difference in the dimers stability can be correlated either to the copper concentration or to the number of H_2O molecules coordinated with the solid. Indeed, it has been demonstrated that the intensity of the copper(II) ion pairs signal in $Cu_{0.5}H_3PMo_{11}VO_{40}\cdot 13H_2O$ is weaker than in $Cu_2PMo_{11}VO_{40}\cdot 21H_2O$; also, the number of H_2O molecules is less.

Furthermore, since the $Cu_{0.5}H_3PMo_{11}VO_{40}\cdot 13H_2O$ spectrum (Figure 3) shows that the hyperfine splitting for the signal corresponding to monomers (140 G) is a factor 2 larger than for the half-field signal (70 G), the Cu^{2+} ion monomers must be the precursor of the copper(II) ion pairs in the solids.[20] Consequently the monomers and the dimers must have the same environment in the solids. Since in the case of $Cu_{0.5}H_3PMo_{11}VO_{40}\cdot 13H_2O$ the coordination number of ligands (H_2O molecules) in the surrounding of the copper(II) ion pairs is less than in $Cu_2PMo_{11}VO_{40}\cdot 21H_2O$, this phenomenon can explain why, in the first solid, the pairs are more stable than in the second one.

With the higher calcination temperature, the copper(II) ions corresponding to monomers also decrease and practically disappear at 573 K. The disappearance of Cu^{2+} ions, monomers, and dimers can be explained by the formation of clusters (wide EPR signal) and amorphous CuO (not detectable by EPR). Then, it appears that the formation of Cu^{2+} ion clusters or/and CuO amorphous oxides from $Cu_2PMo_{11}VO_{40}\cdot 21H_2O$ is more important. In the oxidative dehydrogenation of isobutyric acid into methacrylic acid, performed at 593 K, $Cu_2PMo_{11}VO_{40}\cdot 21H_2O$ is less active and less selective than $Cu_{0.5}H_3PMo_{11}VO_{40}\cdot 13H_2O$;[21] thus the existence of Cu^{2+} (monomers and dimers) localized between the Keggin units appears necessary to obtain a catalyst with rapid and reversible redox behavior.

Acknowledgment. ATOCHEM and the CNRS are gratefully acknowledged for the financial support of this work. We thank Gilbert Hervé, Michel Fournier, Emmanuel Cadot, and André Tézé for valuable discussions.

Registry No. $Cu_2PM_{011}VO_{40}\cdot 21H_2O$, 143123-52-8.

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Poly(ethylene oxide)/(Poly(2-vinylpyridine)/Lithium Perchlorate Blends. New Materials for Solid Polymer Electrolytes

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Received April 9, 1992
Revised Manuscript Received August 17, 1992

Considerable effort has been devoted to the development of solid polymer electrolytes with high ionic conductivity at room temperature.[1-7] Because it is generally accepted that the mechanism of ion transport through a solid polymer matrix is by a liquidlike motion through the amorphous (low T_g) phase, a number of oligo(oxyethylene)-based amorphous polymers with low glass transition temperatures have been examined.[2,5,8] For example, poly(siloxane)s with pendant oligo(oxyethylene) side chains[2,8] and poly[bis((methoxyethoxy)ethoxy)phosphazene] complexed with Li^+ salts exhibit high ionic conductivity at room temperature.[5] A major drawback of such amorphous polymer/salt complexes is the lack of dimensional stability and/or mechanical strength. These problems may be overcome by the preparation of cross-linked networks or the synthesis of block copolymers where the low T_g ionic conductive block is reinforced by a high T_g nonconductive block.[2,9-12] While these new polymer electrolytes are promising materials, the fact that their preparation requires nontrivial synthetic and/or cross-linking processes is a drawback. Therefore, the preparation of solid polymer electrolytes which exhibit high ionic conductivity by an easier process is desirable. In this communication we report on a novel polymer electrolyte, poly(ethylene oxide)/poly(2-vinylpyridine)/lithium per-

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Table I. Glass Transition Temperature (T_g), Recrystallization Temperature (T_c), Melting Temperature (T_m), and Ionic Conductivity of Polymer/Salt Complexes

polymer system		T_g (°C)	T_c (°C)	T_m (°C)	T_m (°C)	σ^a (S cm^{-1})
PEO/$LiClO_4$	EO/Li = 6	−17				1.0×10^{-7}
	EO/Li = 8	−23				5.4×10^{-7}
	EO/Li = 10	−23	37	60		2.1×10^{-6}
	EO/Li = 12	−34	20	60		8.0×10^{-7}
	EO/Li = 15	−37	11	63		2.3×10^{-7}
Blend/$LiClO_4$	EO/Li = 2	−48			123	6.0×10^{-6}
	EO/Li = 5	−35			122	3.6×10^{-6}
	EO/Li = 10	−41	10	43	125	1.1×10^{-6}
	EO/Li = 15	−35	20	62		6.5×10^{-7}
	EO/Li = 20	−34	6	65		2.0×10^{-7}
	EO/Li = 25	−40	−11	66		4.8×10^{-8}

[a] Conductivities were obtained at 30 °C.

chlorate (PEO/P2VP/$LiClO_4$) blend. To the best of our knowledge, this is the first report of a solid polymer electrolyte obtained by the solution blending of two high molecular weight commercial polymers and $LiClO_4$.[13,14]

Blends of poly(ethylene oxide) (PEO), poly(2-vinylpyridine) (P2VP), and $LiClO_4$ were prepared by dissolving PEO (MW 600 000) and P2VP (MW 200 000), in CH_2Cl_2, followed by the addition of a solution of $LiClO_4$/THF with vigorous stirring for 3 h at ambient temperature. The $LiClO_4$ salt used was dried in vacuum at 50 °C and stored in a desiccator; poly(ethylene oxide) and poly(2-vinylpyridine) were used as received. The solvent was removed by evaporation under a N_2 stream at room temperature. The blends were dried in a vacuum oven for at least two days at 50 °C. PEO/$LiClO_4$ complexes were prepared in similar manner to that used for the preparation of PEO/P2VP/$LiClO_4$. All samples were stored in a desiccator and dried again overnight in a vacuum oven at 60 °C before conductivity measurements were undertaken. Conductivity measurements were carried out on polymer disks (1.25 cm in diameter) held between copper plates under a dried N_2 stream, using a Hewlett-Packard 4192A impedance analyzer over the range of 5 Hz–13 MHz. Bulk resistance was determined by plotting the real versus the imaginary part of the impedance. Bulk resistance was derived from such a plot where the imaginary impedance is zero.[15,16] Conductivity was calculated from the bulk resistance according to following equation:

$$\sigma = D/AR_b$$

where σ is conductivity, D is the thickness of sample, A is section area of the sample, and R_b is bulk resistance. Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSC-4 with a heating rate 20 °C min^{-1}.

Arrhenius conductivity plots for a PEO/P2VP (75/25 wt/wt) blend with different $LiClO_4$ concentration are presented in Figure 1. These plots indicate that ionic conductivity increases as the salt content is increased. The blend with an ethylene oxide/Li$^+$ mole ratio of 2 exhibits a conductivity value of 6×10^{-6} S cm^{-1} and displays elastomeric properties at 30 °C. These properties make these blends potentially useful as solid polymer electrolytes. The observed increase in conductivity with increasing salt content for the PEO/P2VP/$LiClO_4$ blend is in contrast to that observed for the PEO/$LiClO_4$ system. A plot of log σ versus ethylene oxide/Li$^+$ mole ratio for PEO/$LiClO_4$ and PEO/P2VP/$LiClO_4$ are shown in Figure 2.[17] The conductivity values at 30 °C, T_g, T_c, and T_m of

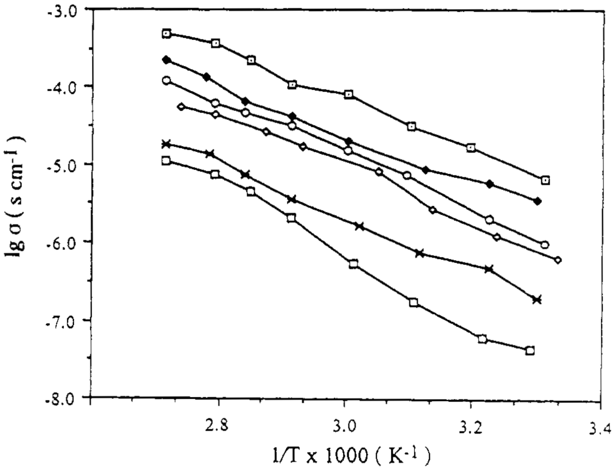

Figure 1. Arrhenius conductivity plots of poly(ethylene oxide)/poly(2-vinylpyridine)/$LiClO_4$ complexes (PEO/P2VP = 75/25 wt/wt): (⊡) EO/Li = 2; (◆) EO/Li = 5; (○) EO/Li = 10; (◇) EO/Li = 15; (✱) EO/Li = 20; (□) EO/Li = 25.

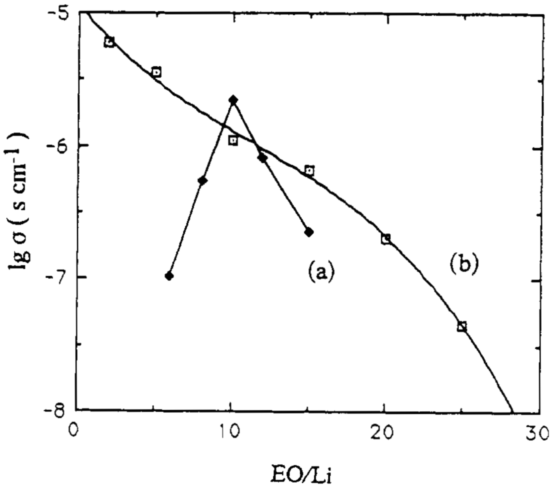

Figure 2. (a) log σ vs ethylene oxide/Li$^+$ mole ratio plot for poly(ethylene oxide)/$LiClO_4$ complexes at 30 °C; (b) log σ vs ethylene oxide/Li$^+$ mole ratio plot for poly(ethylene oxide)/poly(2-vinylpyridine)/$LiClO_4$ complexes at 30 °C.

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[13] Previously high molecular weight noncommercial poly(methacrylic acid), low molecular weight (400 and 6000) poly(ethylene oxide) and $LiClO_4$ blends have been examined. The maximum room temperature conductivity for a blend system using poly(ethylene oxide) of molecular weight 6000 is 1.2×10^{-7} S cm^{-1}. See: Tsuchida, E.; Ohno, H.; Tsunemi, K.; Kobayshi, N. *Solid State Ionics* **1983**, *11*, 227.

[14] Blends of high molecular weight poly(ethylene oxide) and low molecular weight amorphous polymers have been examined. In these instances the low molecular weight material acts as a plasticizing agent. See, for example, ref 2.

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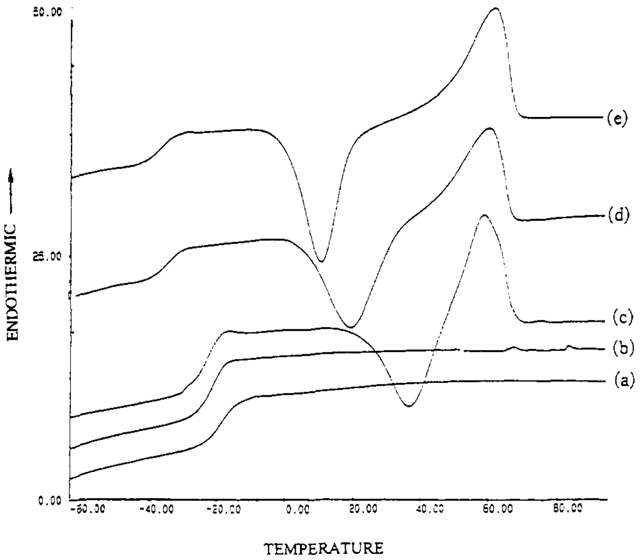


Figure 3. DSC thermograph of poly(ethylene oxide)/$LiClO_4$ complexes, (a) EO/Li = 6; (b) EO/Li = 8; (c) EO/Li = 10; (d) EO/Li = 12; (e) EO/Li = 15.

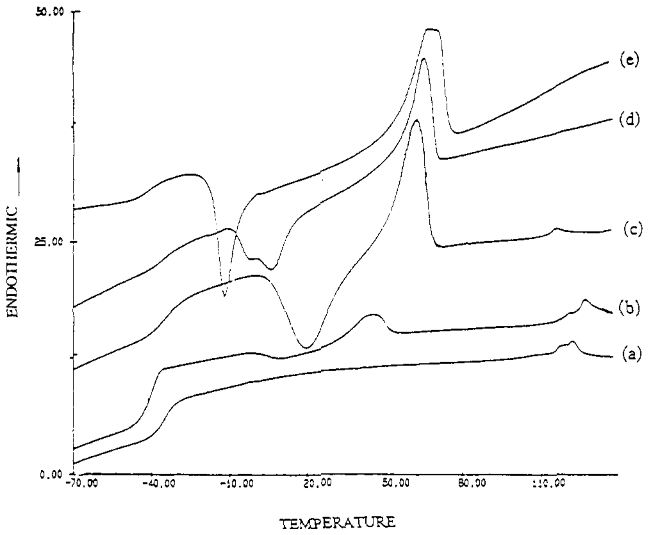
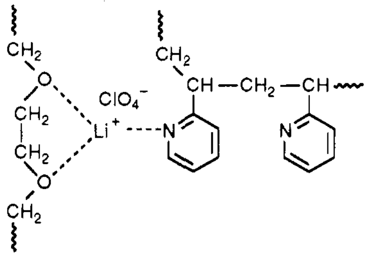


Figure 4. DSC thermograph of poly(ethylene oxide)/poly(2-vinylpyridine)/$LiClO_4$ complexes: (a) EO/Li = 5; (b) EO/Li = 10; (c) EO/Li = 15; (d) EO/Li = 20; (e) EO/Li = 25.

these two polymer/salt systems are given in Table I. The PEO/$LiClO_4$ conductivity initially increases with increasing salt content, reaches a maximum value at an ethylene oxide/Li^+ mole ratio of 10 and decreases as the $LiClO_4$ content is further increased. This conductivity behavior is consistent with the generally observed behavior of polymer salt electrolytes.[1] This phenomenon is attributed to an initial increase in the number of charge carriers followed by the formation of less mobile ionic aggregates as salt concentration is further increased.[18,19] The ionic aggregates results in the formation of a pseudo-cross-linked system with a simultaneous increase in T_g, indicating a decrease in the segmental motion of the polymer.[18,20] The decreased segmental motion results in lower ionic mobilities and hence lower conductivities. The DSC thermograms of the PEO/$LiClO_4$ as a function of $LiClO_4$ content are shown in Figure 3. These thermograms indicate that increasing salt content leads to higher T_g, indicating a decrease in segmental motion. The PEO/$LiClO_4$ system with ethylene oxide/Li^+ mole ratios of 10, 8, and 6 are amorphous at room temperature,[21] indicating that $LiClO_4$ impedes the crystallization process. At lower $LiClO_4$ concentration, for example, at ethylene oxide/Li^+ mole ratios of 12 and 15, the large T_m peak in the thermograms clearly indicate the presence of the crystalline phase at room temperature.

Poly(ethylene oxide) and poly(2-vinylpyridine) and immiscible at weight ratios of 3 to 1. The fact that $LiClO_4$ acts as a compatibilizing agent is interesting. The exact mechanism by which $LiClO_4$ compatibilizes these two polymers is not clearly understood at the present time; however, it is most likely due to ion–dipole interactions. Mechanistically, the miscibility enhancement is probably because lithium ions interact simultaneously with oxygens of the poly(ethyleneoxide) and the nitrogen of the pyridine unit as depicted below:



Eisenberg and co-workers have previously demonstrated that ion–dipole interactions lead to miscibility enhancement in poly(styrene) ionomers and poly(alkylene oxide) systems.[22,23]

The contrasting ionic conductivity behavior, at the salt contents studied, of the PEO/P2VP/$LiClO_4$ and PEO/$LiClO_4$ systems is of considerable interest. At the higher salt concentrations the PEO/P2VP/$LiClO_4$ system displays higher conductivity values than the PEO/$LiClO_4$ system. The increasing conductivity of PEO/P2VP/$LiClO_4$ blends with increasing $LiClO_4$ content (Figures 1 and 2) is possibly because poly(2-vinylpyridine) effectively disperses the salt throughout the blend and impedes the aggregation process. This theory is consistent with the differential scanning calorimetry data exhibited by the blends. The thermograms of PEO/$LiClO_4$ and PEO/P2VP/$LiClO_4$ (Figures 3 and 4, respectively) at an ethylene oxide/Li^+ mole ratio of 10 show different thermal characteristics. The T_g of the PEO/P2VP/$LiClO_4$ blend is −41 °C, or 18 °C lower than the corresponding PEO/Li^+ system. This is in keeping with the theory that the $LiClO_4$ is better dispersed or less aggregated in the PEO/P2VP/$LiClO_4$ blend. Dispersed ion pairs are expected to have a smaller effect on the segmental motion than ion aggregates.[18,20] Furthermore, the T_c and T_m peak areas for the blend are significantly smaller and the T_m of PEO/P2VP/$LiClO_4$ blend has a maximum at 43 °C, or 17 °C lower than the corresponding PEO/Li^+ system. Therefore, the poly(ethylene oxide) crystallization process is further impeded by the presence of the poly(2-vinylpyridine) in

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(17) It has been suggested by a referee that the two systems may in fact be similar over a wider salt concentration, i.e., the PEO/P2VP/$LiClO_4$ system will reach a maximum conductivity at a specific salt concentration followed by a decrease in conductivity as the salt concentration is further increased.

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(21) The recrystallization temperature (T_c) for the PEO/$LiClO_4$ system at EO/Li^+ mole ratio of 10 is 40 °C and thus at ambient temperature the system does not have poly(ethylene oxide) crystalline domains as determinable by differential scanning calorimetry.

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the blend. Furthermore, increasing the salt content in the blend does not result in an increase in the T_g as observed for the PEO/Li^+ system. The T_g of the blends, at the salt contents studied, is -35 °C or lower. As the salt (i.e., charge carriers) content is increased in the PEO/P2VP/$LiClO_4$ blend the segmental motion, as indicated by the T_g of the blend, remains unchanged resulting in an increase in the conductivity. Thus, PEO/P2VP/$LiClO_4$ blends possess a high degree of segmental motion over a wide range of $LiClO_4$ concentration leading to the observed conductivity behavior. In these blends the poly(2-vinylpyridine) acts both as a polymer plasticizer and a reinforcing agent. The thermograms for the blend with ethylene oxide/Li^+ mole ratios of 5 and 10 show small melt peaks at approximately 122 °C. While the exact origin of the melt peak is not understood, it is possibly due to the decomplexation of the ion-dipole complex which enhances the miscibility of the polymers. Further work is required to understand the mechanism by which $LiClO_4$ compatibilizes poly(ethylene oxide) and poly(2-vinylpyridine).

The PEO/P2VP/$LiClO_4$ system is an attractive material for potential use as a solid polymer electrolyte. While the conductivity value of 6×10^{-6} S cm^{-1} at 30 °C is lower than the observed 10^{-5}–10^{-4} S cm^{-1} values for some amorphous polymer salt systems,[2,5,8] the blend possess both requisite mechanical (i.e., elastomeric) properties and ionic conductivity values necessary to serve as solid polymer electrolyte in a variety of electrochemical devices e.g., sensors, transistors.[24-26] In particular, this work demonstrates that a relatively easy process (i.e., blending) may be successfully utilized to prepare solid polymer electrolytes.

Acknowledgment. We gratefully acknowledge the financial support of the work by the U.S. Army Research Office Grant No. DAAL03-89-G-0087. We thank Professor Adi Eisenberg and Dr. Attila Molnar of McGill University for valuable discussions.

Registry No. PEO, 25322-68-3; P2VP, 25014-15-7; $LiClO_4$, 7791-03-9.

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Electrochemical and Spectroscopic Study of the Transport Properties of Composite Polymer Electrolytes

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Received April 17, 1992
Revised Manuscript Received August 12, 1992

The idea of using inert fillers to increase the mechanical properties of polymer electrolytes in their conductive amorphous phase was initially demonstrated by Weston and Steele[1] by showing that the addition of α-Al_2O_3 to PEO–$LiClO_4$ complexes produced a significant improvement in the mechanical stability of the material at temperatures in excess of 100 °C. This improvement was explained assuming that the ceramic dispersoid acts as a filler providing a supporting matrix for the conductive amorphous polymer complex, so as to retain an overall solid structure even at high temperature.

The characteristics of these composite ceramic–polymer materials were further explored by Liquan,[2] we reported that the addition of fine powder γ-Al_2O_3 to the PEO–NaSCN complex not only improved the mechanical properties of the amorphous phase of the polymer electrolyte but also increased its conductivity. He suggested that the extent of the latter phenomenon depends critically on the filler's particle size.

Improvements of the conductivity in the Al_2O_3 (and SiO_2)–(PEO)NaI composite system were also found by Wieczorek[3] and, more recently, in our laboratory.[4-6] In particular, we have shown that the addition to the $(PEO)_8LiClO_4$ complex of finely dispersed γ-$LiAlO_2$ ceramic powders with a grain size diameter of the order of 1 μm, led to the formation of homogeneous composite membranes with a largely improved mechanical stability at temperatures above the crystalline-to-amorphous transition (i.e., around 60 °C) while still maintaining a conductivity comparable to or higher (depending on composition) than that of the pure $(PEO)_8LiClO_4$ electrolyte complex.

Indeed, we have shown[5] that, due to the cited dispersion action, the conductivity of composite electrolytes formed by the addition of γ-$LiAlO_2$, 1-μm grain size, powders to the $(PEO)_8LiClO_4$ complex does increase to a maximum at a γ-$LiAlO_2$ dispersoid composition of 10 wt %, beyond which the dilution effect becomes predominant and the conductivity decays. The interesting aspect is that, for the optimized composition, the conductivity of the composite electrolyte is higher than that of the pure $(PEO)_8LiClO_4$ complex.

The explanation of the enhancement in the transport properties is not immediate, since, as a first approach, one would expect that the addition of an electrically inert component would produce a consistent increase in the total resistance of the composite electrolyte. As a possible interpretation of the oppositely observed effect, we have suggested that the addition of small particle size ceramic powders, when maintained within certain composition limits, enhances the degree of amorphicity of the PEO–LiX complexes. A more refined explanation is that the ceramic filler, when highly dispersed in the polymer matrix, may affect the crystallization rate by preventing the agglomeration of the polymer chains. Fast ionic transport in PEO-based polymer electrolytes is an inherent property of the amorphous phase,[7] and thus the addition of a component which prevents polymer recrystallization is expected to reasonably produce a positive effect on the overall conductivity. On the basis of the proposed structural model, particle size and content of the dispersoid

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