

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<sup>+</sup> 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<sub>4</sub> 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<sub>4</sub> blends possess a high degree of segmental motion over a wide range of LiClO<sub>4</sub> 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<sup>+</sup> 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<sub>4</sub> compatibilizes poly(ethylene oxide) and poly(2-vinylpyridine).

The PEO/P2VP/LiClO<sub>4</sub> system is an attractive material for potential use as a solid polymer electrolyte. While the conductivity value of  $6 \times 10^{-6} \text{ S cm}^{-1}$  at 30 °C is lower than the observed  $10^{-5}$ – $10^{-4} \text{ S cm}^{-1}$  values for some amorphous polymer salt systems,<sup>2,5,8</sup> 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.<sup>24-26</sup> In particular, this work demonstrates that a relatively easy process (i.e., blending) may be successfully utilized to prepare solid polymer electrolytes.

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- (24) Josowicz, M.; Janata, J. *Solid State Ionics* 1988, 28-30, 1625.  
 (25) Madou, M.; Otagawa, T. *Solid State Ionics* 1988, 28-30, 1653.  
 (26) Chao, S.; Wrighton, M. S. *J. Am. Chem. Soc.* 1987, 109, 2197.

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

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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<sup>1</sup> by showing that the addition of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> to

PEO-LiClO<sub>4</sub> 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,<sup>2</sup> we reported that the addition of fine powder  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> (and SiO<sub>2</sub>)-(PEO)NaI composite system were also found by Wiczorek<sup>3</sup> and, more recently, in our laboratory.<sup>4-6</sup> In particular, we have shown that the addition to the (PEO)<sub>8</sub>LiClO<sub>4</sub> complex of finely dispersed  $\gamma$ -LiAlO<sub>2</sub> ceramic powders with a grain size diameter of the order of 1  $\mu\text{m}$ , 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)<sub>8</sub>LiClO<sub>4</sub> electrolyte complex.

Indeed, we have shown<sup>5</sup> that, due to the cited dispersion action, the conductivity of composite electrolytes formed by the addition of  $\gamma$ -LiAlO<sub>2</sub>, 1- $\mu\text{m}$  grain size, powders to the (PEO)<sub>8</sub>LiClO<sub>4</sub> complex does increase to a maximum at a  $\gamma$ -LiAlO<sub>2</sub> 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)<sub>8</sub>LiClO<sub>4</sub> 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,<sup>7</sup> 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

(2) Liquan, C. In *Materials for Solid-State Batteries*, Chowdari, B. V., Radhakrishna, S., Eds.; World Scientific: Singapore, 1988; p 69.

(3) Wiczorek, K.; Such, K.; Plochanski, J.; Przulski, J. In *Second International Symposium on Polymer Electrolytes*; Scrosati, B., Ed.; Elsevier: Amsterdam, 1990; p 339.

(4) Croce, F.; Bonino, F.; Panero, S.; Scrosati, B. *Philos. Mag.* 1989, B.59 161.

(5) Capuano, F.; Croce, F.; Scrosati, B. *J. Electrochem. Soc.* 1991, 138, 1918.

(6) Brinkmann, D.; Gang, W.; Croce, F.; Scrosati, B. *Solid State Ionics* 1992, 53-56, 1202.

(7) *Polymer Electrolyte Reviews I*; MacCallum, J., Vincent, C. A., Eds.; Elsevier: London 1987.

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(1) Weston, J. E.; Steele, B. C. H. *Solid State Ionics* 1982, 7, 75.

appear as critical factors: a low particle size is essential to achieve a highly dispersed distribution of the ceramic additive while a controlled value of concentration is important to prevent phase discontinuity.

Undoubtedly, the concept of ceramic dispersion in polymer electrolytes has relevant implications not only on the basic understanding of the transport characteristics of the polymer ionic conductors but also on the practical application of these technologically important materials. Therefore, particular attention has been devoted lately in our laboratory to confirm and support the proposed structural model. In this work we report results obtained by thermal (differential scanning calorimetry), electrical (resistance changes), and spectroscopic (Raman) studies.

High molecular weight ( $MW = 4 \times 10^6$ ) poly(ethylene oxide) (PEO, pure BDH product),  $\text{LiClO}_4$  (Fluka fine reagent-grade product), acetonitrile (Aldrich, HPLC-grade glass-distilled, water content less than 0.003%), and end-capped poly(ethylene glycol) (PEG, Polysciences Inc.,  $MW = 4 \times 10^2$ ) were used as received. High surface area ( $8\text{--}12 \text{ m}^2 \text{ g}^{-1}$ )  $\text{LiAlO}_2$  (fine reagent-grade Foote Mineral Co.) powder was dried by annealing overnight at  $800^\circ\text{C}$ . This dried compound, with a phase composition of 95%  $\gamma\text{-LiAlO}_2$  and 5%  $\alpha\text{-LiAlO}_2$ , is composed of agglomerates ( $\approx 4\text{-}\mu\text{m}$  size) of fine powders with mean diameter  $<0.5 \mu\text{m}$ .

The PEO- $\text{LiClO}_4$  films with a concentration ratio of ether oxygen to lithium (O:Li) of 8:1 and the composite  $(\text{PEO})_8\text{-LiClO}_4\text{-}\gamma\text{-LiAlO}_2\text{-LiClO}_4$  films, were prepared using the standard casting technique from acetonitrile solutions. Particular care was taken in the preparation of the PEO- $\text{LiClO}_4\text{-}\gamma\text{-LiAlO}_2$  composite electrolyte films. The appropriate weight of  $\text{LiClO}_4$  and PEO to give on O:Li ratio of 8:1 were dissolved in acetonitrile, and the solution was stirred for 20 h at room temperature in a stopped flask. A known amount of  $\text{LiAlO}_2$  powder was then added, and the solution was stirred continuously by a high-intensity ultrasonic finger directly immersed into the solution in order to break down the particulates and facilitate the PEO solubilization. When complete homogenization had occurred, the mixture was cast on a flat polytetrafluoroethylene sheet and covered to allow slow evaporation of the acetonitrile. With this procedure homogeneous polymer films were obtained about  $75 \mu\text{m}$  thick with no evidence of powder agglomeration. All further manipulations of these films were carried out in an argon-filled glovebox having less than 10 ppm water content.

The differential scanning calorimetry tests were performed using a Perkin-Elmer DSC-2 instrument. The samples, sealed in aluminum pans, were scanned between 25 and  $250^\circ\text{C}$  with a programmed rate of  $10 \text{ deg min}^{-1}$ . Dry  $\text{N}_2$  (99.99%) was used as purge gas.

The recrystallization rates were determined by monitoring the time evolution of the resistance of cells formed by sandwiching between two stainless-steel electrodes films of pure  $(\text{PEO})_8\text{LiClO}_4$  and of composite  $(\text{PEO})_8\text{LiClO}_4\text{-}10 \text{ wt}\% \gamma\text{-LiAlO}_2$ , respectively. The experiment was carried out by annealing the cells at  $100^\circ\text{C}$  in a Buchi Model T-10 oven, quenching them at  $30^\circ\text{C}$ , and then following the resistance by ac impedance spectroscopy using a Solartron 1250 frequency analyzer and a Solartron 1286 electrochemical interface, both coupled to a HP-Vectra computer.

Raman measurements were performed at room temperature using a standard apparatus. Spectra were excited by the  $514.5\text{-nm}$  line of a Spectra Physics (Model 166)  $\text{Ar}^+$  ion laser (output power about 400 mW) and the scattered light was observed at  $90^\circ$  with respect to excitation. A double Raman monochromator Jobin-Yvon (Ramanor HG2-S) equipped with homographic gratings (1800

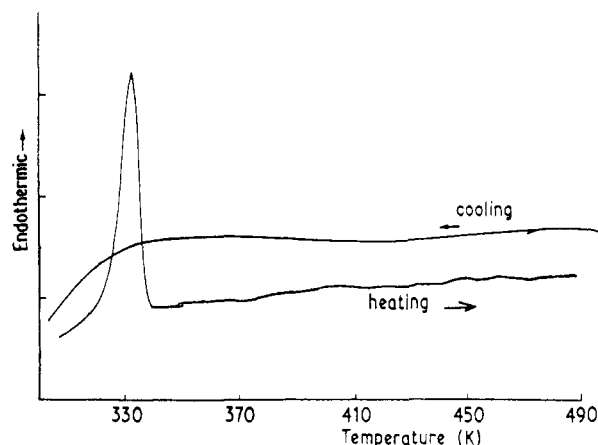
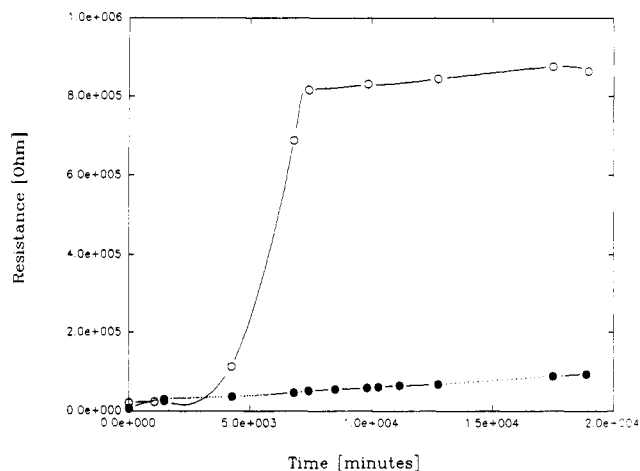


Figure 1. Heating and cooling DSC traces for the composite  $(\text{PEO})_8\text{LiClO}_4\text{-}10 \text{ wt}\% \text{LiClO}_4$  electrolyte. Scan rate  $10^\circ\text{C}/\text{min}$ .

lines/mm) was used to resolve the spectra. The scattered light was detected by a cooled photomultiplier (RCA-31034A-02) operated at  $-35^\circ\text{C}$  in photon-counting mode. The signal was then stored in a multichannel analyzer, which was interfaced to an Olivetti M-240 personal computer. The samples of PEO salt complexes used for the Raman measurements were solid films of about  $1 \text{ cm}^2$  area and  $\approx 100\text{-}\mu\text{m}$  thickness. To prevent any contamination by the ambient moisture, the samples were assembled in a drybox by placing them between two very thin glass plates whose edges were then sealed with an epoxy cement. During the measurements the glass surface was oriented to form an angle of about  $55^\circ$  with the horizontal incident beam. This orientation was found to minimize the spectral contribution due the glass window which was characterized by an asymmetric broad band occurring in the region  $250\text{--}550 \text{ cm}^{-1}$ . On the other hand, PEO salt complexes yielded good Raman spectra up to  $1500 \text{ cm}^{-1}$  which were sometimes superimposed on nearly flat continuum luminescence background of comparable intensity as the Raman signal. The PEG solution was a perfectly transparent and homogeneous liquid, and the spectra were taken directly from sample cells as originally prepared. In this case, there was no scattering contribution from the glass walls, due to large diameter (7 mm) of the cell. This sample yielded high-quality Raman spectra with a small flat luminescence background.

Figure 1 illustrates the differential scanning calorimetry (DSC) traces of a  $(\text{PEO})_8\text{LiClO}_4\text{-}10 \text{ wt}\% \gamma\text{-LiAlO}_2$  electrolyte sample. It may be clearly noticed that in the heating scan a large endothermic peak related to the melting of PEO is revealed at about  $60^\circ\text{C}$ . On the other hand, no peaks are observed in the cooling trace, suggesting that the sample retains a high degree of amorphicity at low temperature. However, the DSC evidence is not conclusive since all polymer systems, including the pure PEO-LiX complexes, exhibit slow recrystallization kinetics, a fact which could lead to erroneous interpretation of the real steady-state structural properties.

To avoid this possible source of error, we have directly compared the recrystallization rate of a pure  $(\text{PEO})_8\text{LiClO}_4$  with that of a  $(\text{PEO})_8\text{LiClO}_4\text{-}10 \text{ wt}\% \gamma\text{-LiAlO}_2$  composite electrolyte. Since ionic transport in polymer electrolytes is directly connected to their degree of amorphicity, the changes in resistance can be directly related to changes in structure. The experiment has been performed by examining two identical conductivity cells (stainless steel electrodes) containing the pure and the composite samples, respectively.<sup>5</sup> The two cells were annealed overnight at  $100^\circ\text{C}$  to promote homogeneous amorphous phases and



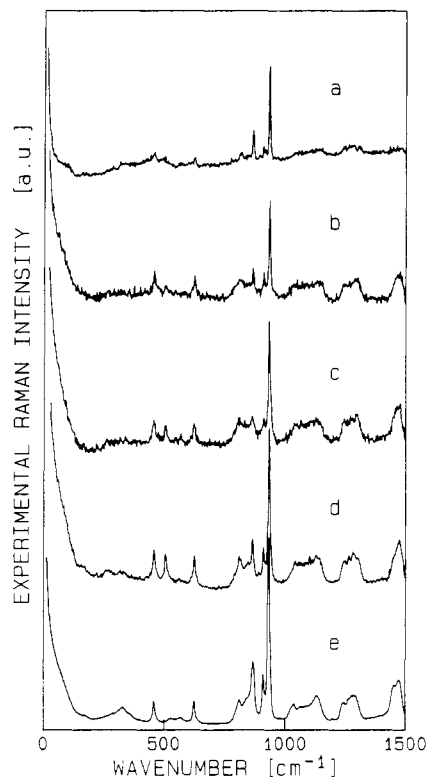
**Figure 2.** Resistance versus time at 30 °C of quenched pure  $(\text{PEO})_8\text{LiClO}_4$  (○) and of a composite  $(\text{PEO})_8\text{LiClO}_4$ -10 wt %  $\gamma\text{-LiAlO}_2$  (●) sample.

then quenched to 30 °C, after which the resistance of the two cells was monitored versus time.

The difference between the two samples is dramatic (Figure 2). The pure  $(\text{PEO})_8\text{LiClO}_4$  sample exhibits the expected response, namely, a progressive recrystallization to reach finally an equilibrium condition characterized by a moderately high resistance (ions blocked in their solvation sites within the rigid crystallized polymer structure). On the other hand, the resistance of the composite sample only slightly increases with no indication of reaching a steady value within the test period. Therefore, we confirm our previous observation<sup>5</sup> that the ceramic dispersoid prevents chain reorganization, possibly giving rise to a configuration which more resembles that of liquidlike, low molecular weight, PEG-LiX system than that typical of a high molecular weight, linear PEO-LiX system.

To obtain further credibility to this proposed model, it is essential to support the thermal and recrystallization results with some independent spectroscopic evidence. We have carried out a Raman investigation on the following samples: (a) a pure  $(\text{PEO})_8\text{LiClO}_4$  film; (b-d) composite  $(\text{PEO})_8\text{LiClO}_4$ - $x$  wt %  $\gamma\text{-LiAlO}_2$  (where  $x = 10, 20,$  and  $30$ , respectively) films; and (e) a  $(\text{PEG})_8\text{LiClO}_4$  solution. The objective was to obtain a direct comparison between the spectrum of the low molecular weight poly(ethylene glycol) system (which mimics a short-chain, amorphous polymer electrolyte) with those of the two high molecular weight, PEO-based systems.

Experimental Raman spectra obtained at room temperature in the region between 10 and 1500  $\text{cm}^{-1}$  from the different samples are reported in Figure 3. The spectra of all samples look quite complex with a large variety of peaks and bands above 850  $\text{cm}^{-1}$ . Since the  $\gamma\text{-LiAlO}_2$  Raman spectrum<sup>8</sup> is fully confined in the spectral region below 850  $\text{cm}^{-1}$ , these features have to be assigned to the vibrations of the polymer-salt complex. The spectral contribution from  $\gamma\text{-LiAlO}_2$  is relatively small for all samples (but yet recognizable even at its lowest content) and consists mainly of the peak observed at 505  $\text{cm}^{-1}$ , which is by far the strongest Raman feature in the pure  $\gamma\text{-LiAlO}_2$  phase.<sup>8</sup>



**Figure 3.** Room-temperature Raman spectra of a pure  $(\text{PEO})_8\text{LiClO}_4$  film (curve a), of composite  $(\text{PEO})_8\text{LiClO}_4$ - $x$  wt %  $\gamma\text{-LiAlO}_2$  ( $x = 10$  W%, curve b;  $x = 20$  W%, curve c; and  $x = 30$  W%, curve d) films, and of a  $(\text{PEG})_8\text{LiClO}_4$  (curve e).

A comparative analysis of the spectra of Figure 3 reveals that the most relevant changes in the spectral features due to the addition of the ceramic filler occurs in the region between 800 and 1500  $\text{cm}^{-1}$ . The intensity of the bands progressively increases with the concentration of the ceramic dispersoid (see curves b-d), while the resulting spectra evolve progressively toward that of the PEG-LiClO<sub>4</sub> solution (curve e). This spectral trend which reflects the structural rearrangement induced by the insertion of the ceramic filler indicates that the progressive addition of the ceramic dispersoid makes the PEO-based polymer films structurally similar to the short-chain PEG solution.

In conclusion, thermal, electrical and spectroscopic results all support a structural model which accounts for the effects exerted by finely dispersed ceramic additives on the transport properties of PEO-based polymer electrolytes. The addition of the dispersoid prevents the agglomeration of the polymer chain to form extended coiled crystalline clusters. While maintaining an overall rigid structure, these electrolytes assume structural and transport properties comparable to those of systems based on low-molecular weight poly(ethylene glycol)-lithium salt solutions, which are currently used to mimic low-crystallinity polymer electrolytes.

**Acknowledgment.** We are grateful to Dr. S. Panero for the preparation of the  $(\text{PEG})_8\text{LiClO}_4$  solution.

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(8) Mariotto G., unpublished results.