

Solid Electrolytes Based on the Poly(epichlorohydrin-co-ethylene oxide)/Poly(ethylene oxide) blend

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Introduction

When Wright (1975) reported that the complexes of poly(ethylene oxide), PEO, and lithium salts have good ionic conductivity at room temperature, the study of solid ionic conducting polymers increased considerably. Polymer electrolytes received extended attention as solid electrolyte materials in advanced applications such as: electrochromic devices, solid state batteries, electrochemical supercapacitors and photoelectrochemical cells (MacCallum and Vincent, 1987). Many of the systems described nowadays are based on polymers carrying ethylene oxide groups in the main or side chain. Their high crystallinity, however, decreases the ionic conductivity to a level too low for room temperature applications. Ionic conductivity in semicrystalline polymer electrolytes is mainly achieved through the amorphous phase (Tonge and Shriver, 1989). Thus, the chemical structure of the polymer matrix is often modified in order to reduce the crystallinity to obtain high conductivities at room temperature (Zoppi *et al.*, 1996).

Polycapichlorohydrin elastomers, PECH, and [P(ECH-co-EO)] have been investigated as polymer electrolytes. It was verified that the ionic conductivity is ca. $10^{-5} \text{S}\cdot\text{cm}^{-1}$ at room temperature when a plasticizer is added (Munichandraiah *et al.*, 1994)

Silva *et al.* (1994) observed that the addition of poly(epichlorohydrin-co-ethylene oxide), [P(ECH-co-EO)] in a matrix of PEO decrease the crystallinity of the PEO phase. In this work we have prepared polymer electrolytes based on the [P(ECH-co-EO)]/PEO blend containing LiClO_4 . The solid electrolytes were characterized by electrochemical spectroscopy impedance and cyclic voltammetry.

Experimental

Polymer electrolytes were prepared by dissolving LiClO_4 in a blend solution (5% in chloroform) with [P(ECH-co-EO)]/PEO 1/4 ratio. The mixture was placed on a Teflon plate and the solvent was evaporated at room temperature and under vacuum for 24h. Transparent films with 2, 5, 10, 15, 25 wt% LiClO_4 were obtained, the thickness was ca 0.01mm.

The conductivity was evaluated by electrochemical spectroscopy impedance, with blocking electrode cells inside a dry box (humidity < 5ppm) under argon, using a Schlumberger Solartron frequency response analyzer connected to a 273A PAR potentiostat which were interfaced to a 286 IBM-PC/AT computer. The range of analyzed frequencies was 1 to 10^5Hz . Each sample was allowed to equilibrate for 1h at each temperature before measurement, the temperature range was 25 to 95°C .

The electrochemical stability was analyzed by cyclic voltammetry in the range from -1.0 to 4.0V vs Li^0 at $0.020 \text{V}\cdot\text{s}^{-1}$ and 80°C inside the dry box. The electrodes were a stainless steel and a Li^0 sheet and packed in a disk cell with an area of 0.785cm^2 .

Results and Discussion

Intercalation host materials based on V_2O_5 and TiS_2 are used for high-energy and high-density secondary batteries. These need an electrolyte with a voltage stability window in the range of 3.0V (Sequeira *et al.*, 1984). The use of solid-state polymer electrolytes will also improve these systems

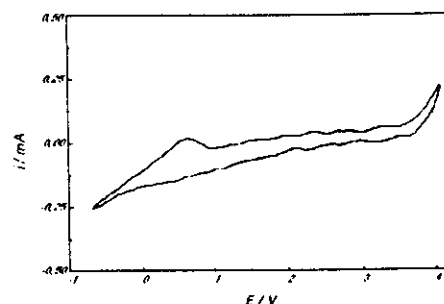


Figure 1. Cyclic voltammogram of [P(ECH-co-EO)]/PEO/ LiClO_4 solid electrolyte (15%).

Figure 1 shows the cyclic voltammetry of the stainless steel/polymer electrolyte/ Li^0 system at 80°C under argon. This indicates an electrochemical stability window of ca. 3.5V vs Li^0 . The stability of the polymer to reduction is limited by the pseudo reversible lithium deposition process. The cyclic voltammogram (Fig. 1) shows clearly the anodic limit due to the anion oxidation process (MacCallum and Vincent, 1987).

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The plot of the ionic conductivity as a function of salt concentration (Fig. 2) shows a maximum for electrolytes containing 15 wt% LiClO_4 .

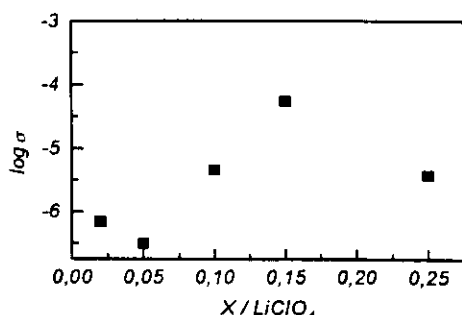


Figure 2. Dependence of conductivity on %wt LiClO_4 of $[\text{P}(\text{ECH-co-EO})]/\text{PEO}/\text{LiClO}_4$ solid electrolyte in the room temperature.

The conductivities decrease above a certain concentration has been reported in the literature of polymer electrolytes (Takeoka *et al.*, 1984 and Fang *et al.*, 1991) and has been interpreted as two opposite effects. In the low salt concentration region, the increasing of ionic conductivity was assigned to the increase in the number of charge carriers. In the high salt concentration region, the ionic conductivity decreases due to a lowering in charge carrier mobility caused by the complex formation acting as crosslink nodes.

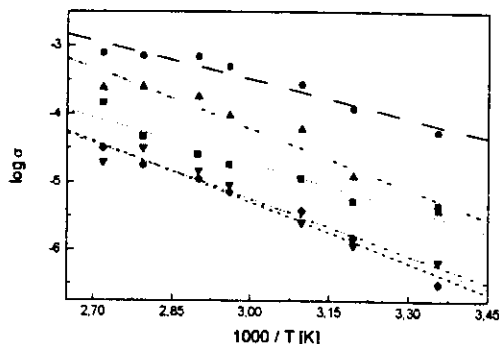


Figure 3. Arrhenius plot of conductivity for $[\text{P}(\text{ECH-co-EO})]/\text{PEO}/\text{LiClO}_4 / \text{LiClO}_4$ solid electrolyte. ∇ , \blacklozenge , \blacksquare , \bullet 2, 5, 10, 15 and \blacktriangle 25 wt% LiClO_4 .

Figure 3 shows the variation of the $\log \sigma$ as a function of inverse of temperature. In all cases the conductivity is correlated to the temperature by the Arrhenius equation fitting.

The calculated activation energies were plotted as a function of salt concentration (fig. 4) showing an increasing tendency. This was related to the mobility of the ions in the polymeric chain. The values obtained were comparable to those described in the literature (Tonge and Shriver, 1989 and Goulart *et al.*, 1996) and were lower indicating that $[\text{P}(\text{ECH-co-EO})]/\text{PEO}$ is a better solvent for LiClO_4 .

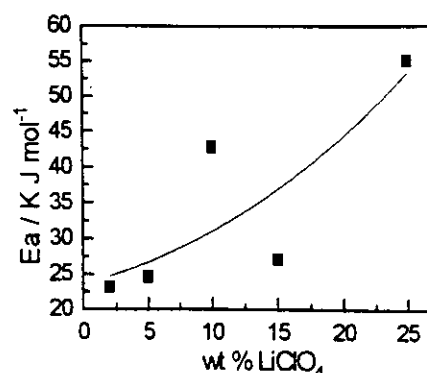


Figure 4. Activation energy vs %wt LiClO_4 of $[\text{P}(\text{ECH-co-EO})]/\text{PEO}/\text{LiClO}_4$ solid electrolyte.

Conclusions

Polymer electrolytes based on $[\text{P}(\text{ECH-co-EO})]/\text{PEO}/\text{LiClO}_4$ show conductivity values of the order of $10^{-4} \text{ S.cm}^{-1}$ for films with 15 wt% LiClO_4 at room temperature, one order of magnitude higher than $[\text{P}(\text{ECH-co-EO})]$ electrolytes. This blend/ LiClO_4 complex present an electrochemical stability window of 3.5V. The high ionic conductivity of these polymer electrolytes and the good electrochemical stability window enables its practical application in electrochemical devices. Investigation of the electrochemical performances of these electrolytes is in progress.

Acknowledgements

C.N.P.F. thanks fellowships from CNPq. The authors also thank FAPESP for financial support (94/2493-1).

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