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Thermal and Conduction Properties of a PCL-biodegradable Gel Polymer Electrolyte with $LiClO_4$, LiF_3CSO_3, and $LiBF_4$ Salts

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A biodegradable gel polymer electrolyte was prepared using Poly(ε-caprolactone) as a polymer host and its electrochemical performance was evaluated. The biodegradable gel polymer electrolyte was produced by casting through dissolution of PCL in tetrahydrofuran (THF) with 5, 10, and 15% wt. of the propylene carbonate and several salt concentrations of $LiClO_4$, LiF_3CSO_3, and $LiBF_4$. The thermal behavior of the gel polymer electrolytes has shown that the addition of propylene carbonate as a plasticizer agent in the PCL promotes an increase in the disorder of the crystalline phase, decreasing the crystallinity degree. The glass transition temperature increased as the concentration of lithium salts was increased. The ionic conductivities of the PCL/10% PC to $LiClO_4$, LiF_3CSO_3, and $LiBF_4$ with 12% wt at room temperature were about 2.26×10^{-4}, 4×10^{-5}, and 1.5×10^{-7} S cm^{-1}, respectively. The conductivity enhancement with temperature can be understood in terms of a free-volume model. The biodegradable gel polymer electrolyte was stable electrochemically up to 5.0 V vs Li/Li$^+$.

Keywords:

1. INTRODUCTION

The development of an electrochemical power source system is based on the insertion and removal of lithium ions into and from host compounds at both electrodes, the so-called lithium-ion cell. Lithium-ion technology can be considered the state-of-the-art for secondary batteries and it is an attractive candidate for automotive applications, due to their high energy and power density, as well as in the mini- and micro-systems that require miniaturized power sources (e.g. smart cards, sensors, miniature RF transmitters, biochips, implantable medical devices, and other devices[1-3].

There has been continuing interest in the development of cathode materials based on layered $LiCoO_2$, $LiNiO_2$, and mixed oxide with improved cycling stability[4-7]. The layered transition metal oxide, $LiCoO_2$ [8-10], is the most attractive and commercial cathode material for the rechargeable Li-ion battery, because it has high specific capacity, high operating cell voltage, and excellent rechargeability. One promising substitute material for $LiCoO_2$ is $LiMn_2O_4$ spinel [11-15], due to its economical and environmental advantages over the current $LiCoO_2$.

Nevertheless, such types of batteries are not being rapidly developed for electric vehicles due to the issue of the safety of the devices, because the use of a liquid electrolyte may result in some problems, i.e. leakage of a flammable electrolyte, production of gases upon overcharge or over discharge, as well as thermal runaway reaction when it is heated to high temperatures and due to the large volume of toxic and hazardous materials of the constituents [16-20].

An alternative substitute for the liquid electrolyte in the electrochemical device is the solid polymer electrolyte (SPE). SPEs are formed by the incorporation of lithium salt into polymer matrices. These materials show a lower ionic conductivity than the liquid electrolyte; however, they are less reactive with lithium, increasing the safety of battery. These materials can be used as the electrolyte, as the separator, or both. Moreover, it exhibits a high compliance, good mechanical stability up to its melting point, and an excellent processability for making thin films. The polymer more studied is the poly (ethylene oxide) (PEO) with inorganic salts dissolved in its matrix. However, the high degree of crystallinity of PEO restricts its use in battery, and it can be used only at temperatures above the melting point of the crystalline phase, which is approximately $60^{o}C$ [21,22].

Indeed, ambiental politics are being extremely rigid in the control of the use of materials that "attack" the environment. The battery industry represents one important and growing sector where the use of non-toxic and non-hazardous substitute materials has not rapidly developed. In 2004, the world-wide production of ion-lithium batteries was on the order of 700 million units. The consequence of the expansion of the market for these batteries will promote the increase in the technological garbage [23,24]. In the following, we report our investigation concerning the system gel polymer electrolyte based on poly (ε-caprolactone), a biodegradable polymer, with propylene carbonate as a plasticizer agent, with three different kinds of lithium salts. This proposal was based on the utilization of a biodegradable polymer electrolyte instead of a binder (glass fibre) soak with an organic liquid electrolyte as an alternative that is more ecologically correct.

PCL is one of the most promising synthetic polymers that can degrade in an aqueous medium or in contact with microorganisms, and thus it can be used to make compostable polymeric devices. In previous works, pure PCL/$LiClO_4$ was investigated as a biodegradable solid polymer electrolyte. This polymer showed a wide electrochemical stability window (5.5V *vs.* Li), good mechanical properties, and total biodegradation in soil compost at 60 days. However, it demonstrated a low ionic conductivity ($\approx 1 \times 10^{-6} S.cm^{-1}$) at room temperature [25].

2. EXPERIMENTAL PART

$LiClO_4$, LiF_3CSO_3, $LiBF_4$, and propylene carbonate were purchased from Aldrich and used as received. The Poly(ε-caprolactone) (PCL), for which the structural formula is shown in Figure 1, was obtained from Union Chemical Carbide Ltd., with an average molecular weight (M_w) of 80,000.

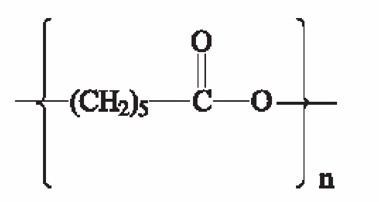

Figure 1. Sructural chemical formula of Poly(ε-caprolactone) (PCL).

The polymer was dissolved in tetrahydrofuran (THF) and was mixed with the PC solution of the lithium salt. The THF solvent of the polymer electrolyte solution was evaporated slowly and dried at high vacuum for 72 h. The salt concentrations were 2.0%, 6.0%, 10.0%, and 12% wt. of $LiClO_4$, LiF_3CSO_3, or $LiBF_4$.

Thermal behavior of the gel polymer electrolytes was analyzed using a differential scanning calorimeter (NETZSCH DSC 204). The samples were placed in aluminum pans under a nitrogen atmosphere, heated to 150 °C, cooled to -100 °C, and then heated to 250 °C. The thermograms were recorded at a rate of 10 °C min^{-1}. All DSC experiments were done in duplicate, and the thermograms shown in the next section refer to the final heating.

The electrochemical experiments were done using an AUTOLAB – PGSTAT30 FRA. The ionic conductivity of the blends was investigated by electrochemical impedance spectroscopy (EIS) in the frequency range of 1 to 10^5 Hz with an *AC* amplitude of 10 mV. To analyze the ionic conductivity of the blend at room temperature, the initial impedance spectra were obtained at room temperature. To analyze the ionic conducting mechanism and activation energy, the temperature was changed from 25 °C to 100 °C in steps of 10 °C, and the impedance spectra were measured after 60 min of stabilization at the desired temperature.

The electrochemical stability window was evaluated by cyclic voltammetry at a scan rate of 10 $mV.s^{-1}$ using a Li/polymer electrolyte/stainless steel (SS) cell, in which lithium was used as the counter and reference electrodes. All electrochemical experiments were carried out in a dry box under an argon atmosphere.

3. RESULTS AND DISCUSSION

Figure 1 shows the structural chemical formula of polyester Poly(ε-caprolactone) (PCL). PCL is one of the most promising synthetic biodegradable polymers presenting considerable degradation as in aqueous medium as in contact with microorganisms [1-4]. We demonstrate the possibility of developing a biodegradable polymer electrolyte (BPE) that can start the disposal of batteries, decreasing the environmental impact of these devices[25].

The effect of plasticizer addition on the conduction characteristics of the PCL system has been investigated. Propylene carbonate was chosen because of its high dielectric constant (ε=65 at 293K) and viscosity, which favors ionic dissociation of the solute and easy ion migration [5, 6].

The gel polymer electrolyte was blended homogeneously in 5, 10, and 15% PC as the plasticizer agent; above these percentages, phase separation was observed. The DSC traces of pure PCL and with different percentages of propilene carbonate are shown in Figure 2.

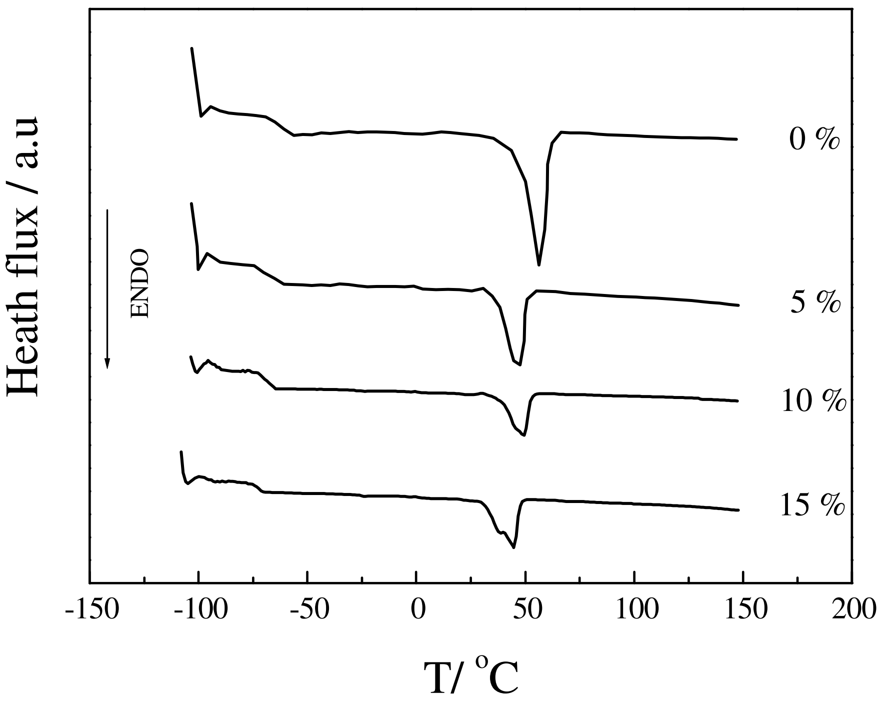

Figure 2. DSC curves for PCL containing different concentrations: 0, 5, 10, and 15% wt of carbonate propylene

The preparation of polymer electrolyte with a low glass transition temperature (*T*g) is one of the important factors for increasing conductivity. PCL showed a phase transition at –65°C, which was attributed to the glass transition temperature (T_g) and a melting process located between 40°C and 66°C with a $T_m = 55.7^oC$, related to a crystalline phase. For the gel polymer electrolyte, the increase in the percentages of PC for which Tg ≈-110°C [7] implies a decrease in the Tg of the PCL at lower temperatures as observed in Figure 2; the same behavior was observed by other authors [8,9]. In each curve, the endothermic process can be identified as the melting of the crystalline phase of the PCL. To sample with 15% PC shows a weak second minimum at a temperature lower than the main minimum at 44.5° C. This implies that there are two groups of structures in the crystalline phase of the samples. The literature has often reported [10] such cleaving of the melting minimum, attributing it to the melting of two different types of crystals, such as the perfect crystal and an imperfect crystal. The crystallinity of a policrystalline polymer is calculated from:

$$X_c = \frac{\Delta H_m}{\Delta H^o_{PCL}} \qquad [1]$$

where ΔHm is the enthalpy of melting of the sample and $\Delta H^o PCL$ is the enthalpy of melting of 100% crystalline PCL, namely 81.6 $J.g^{-1}$ [11]. Figure 3 presents the variation of the degree of crystallinity as a function of the percentage of PC in the polymer. The addition of PC as a plasticizer agent in the PCL promotes an increase in the disorder of the crystalline phase, decreasing the degree of crystallinity to 12.8 % for 10% of PC.

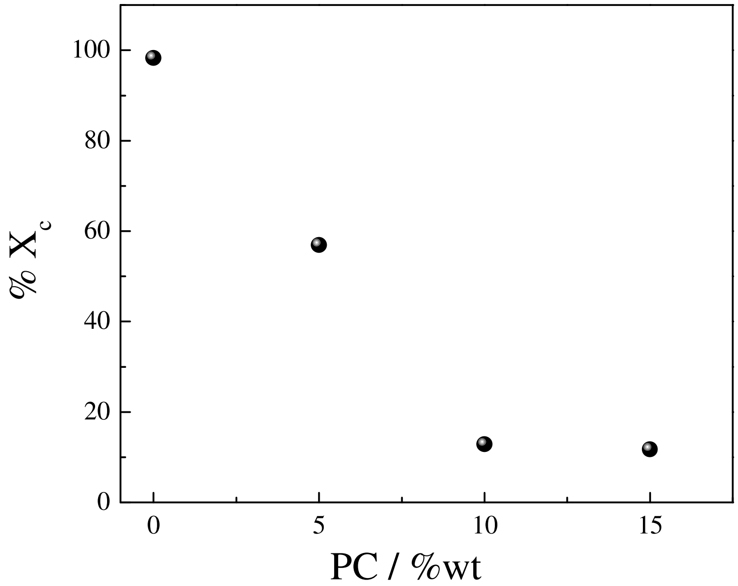

Figure 3. Variation in the degree crystallinity (%X_c) as a function of PC concentration.

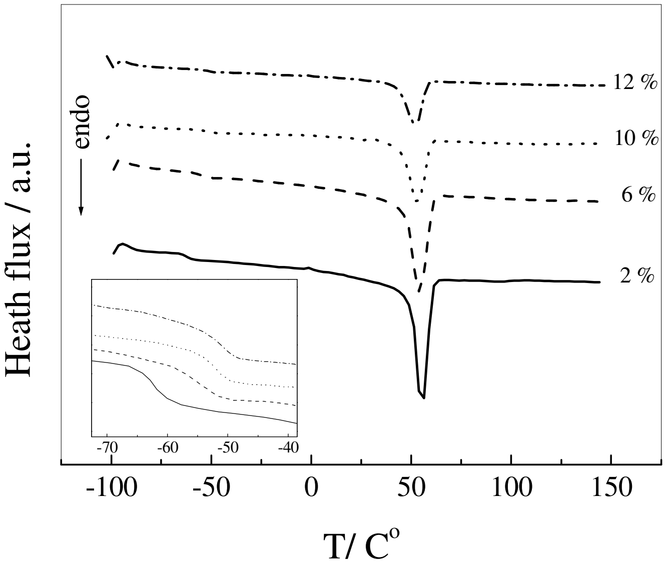

Figure 4. DSC curves for PCL/10%PC with 2.0, 6.0, 10.0, and 12% wt. of LiF_3CSO_3. The inset shows the glass transition temperature (T_g) respectively.

The dimensional stability of the prepared gel polymer electrolyte depended on the content of the liquid electrolyte. A self-supportive film was obtained up to 10 wt.% of PC.

The DSC curves of PCL/10%PC systems with different lithium salts have the same presented profile. Figure 4 presents the curves of DSC to PCL /10% PC with 2.0, 6.0, 10.0, and 12% wt. of LiF_3CSO_3 as example for the other DSC curves of PCL/10%PC systems with $LiClO_4$ and $LiBF_4$. The ionic conductivity of the polymer electrolyte is closely related to the ion mobility, which in turn is the segmental motion of the polymer chain. Thermal parameters, such as the glass transition temperature

(*T*g), degree of crystallinity, and melting temperature obtained during the second heating process, are shown in Figures 5, 6, and 7, respectively.

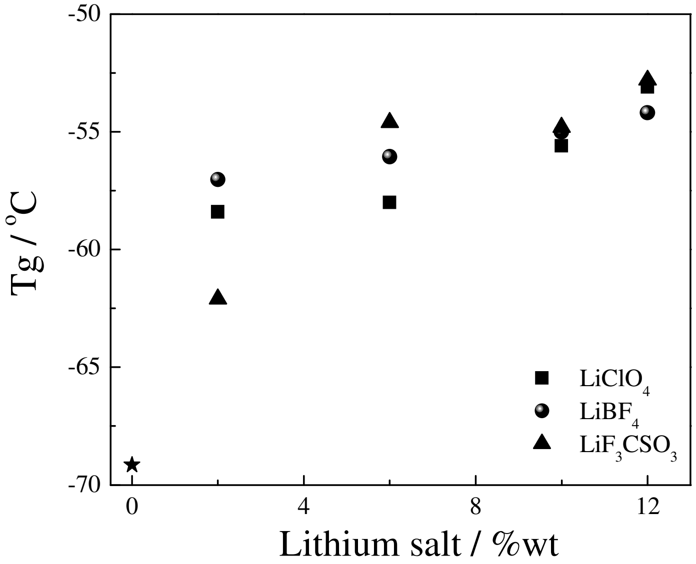

Figure 5. Variation in the glass transition temperature (T_g) as a function of salt concentration.

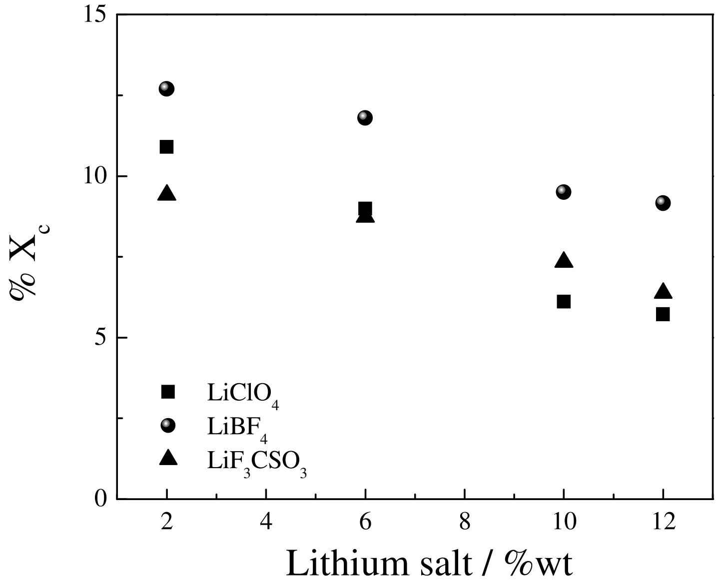

Figure 6. Variation in the degree of crystallinity (%X_c) as a function of salt concentration.

It was observed in Figure 5 that the glass transition temperature increased as the content of all lithium salt was increased. This behavior can be attributed to a reduction in polymer chain flexibility due to the interaction of ether oxygens in the polymer chain and Li^+ ions. This confirms the complexation between the polymer and the metal salt. Similar behaviors have been observed in other systems [12]. The polymer–salt interaction caused by the addition of salt causes disorder in the oriented crystalline-rich phase, decreasing the degree of crystallinity (Figure 5). This effect can also be observed in the reduction of the degree of crystallinity with the addition of the different lithium salt (Figure 6). The crystallinity reduces to a minimum of 9.2% for the $LiBF_4$, compared to 5.7% and 6.2% for $LiClO_4$ and $LiCF_3SO_3$, respectively. Figure 7 shows the variation of melting temperature as a function of % wt of lithium salt. The melting points of the complex polymer/lithium salts change at a lower temperature than PCL/10%PC without salt. This effect can also be associated with a reduction of the degree of crystallinity with the addition of the lithium salt. However, the salt increase in the polymeric matrix alters the melting temperature point a few degrees; this reflects the presence of crystalline regions at various degrees of perfection in the complexed samples[13].

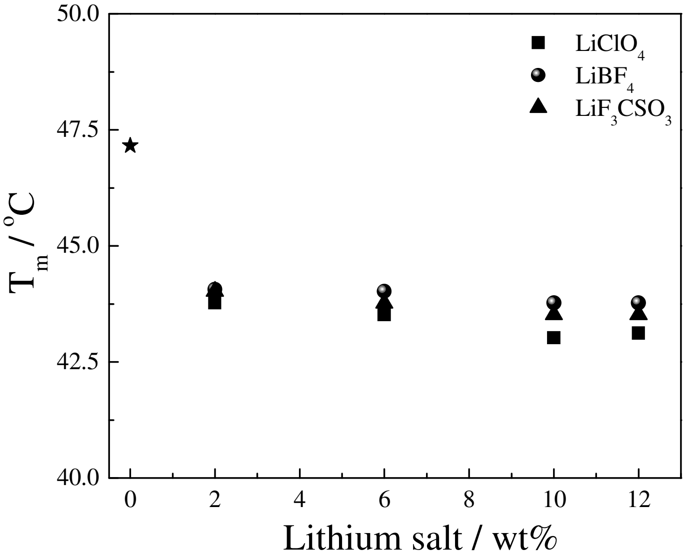

Figure 7. Variation in the melting temperature (T_m) as a function of salt concentration.

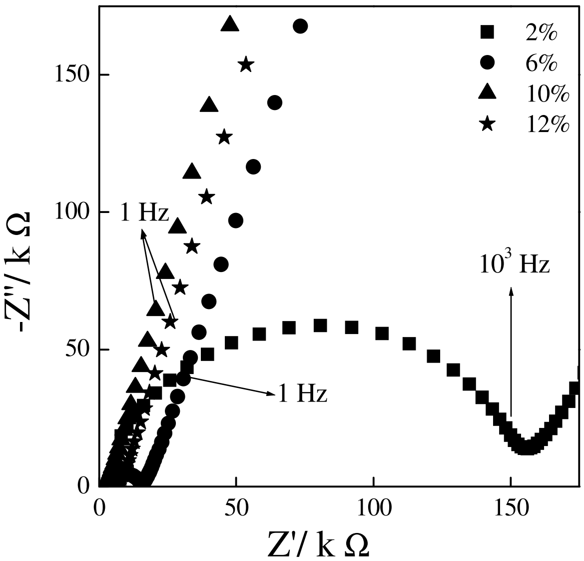

Figure 8. Impedance spectra for the PCL/10%PC containing different $LiClO_4$ concentrations.

Figure 8 shows impedance plots of PCL/10%PC with different concentrations of $LiCF_3SO_3$, at room temperature. A typical impedance plot for a polymeric electrolyte was observed in all polymer electrolyte compositions, where a depressed semicircle at high frequency was observed, followed by a straight line at the low frequency region. This semicircle was related to the relaxation process in the bulk of the electrolyte, whereas the straight line contains information regarding the electrode/electrolyte interface. With ideal blocking of the (inert) electrodes, the inclination of the straight line should be 90 °C, but some variation in this inclination was observed as a result of surface adsorption, or even unexpected electrochemical reactions at the interface may occur.

The electrolyte resistance was obtained by extrapolating the spike to the point of intersection with the *x*-axis. The electrolyte conductivity was obtained from the equation $\sigma = L\ /(R_b.A)$, where L is the thickness, R_b is the bulk resistance where it has been extracted in order to determine the conductivity, and A is the electrode area. With increasing of the salt concentration for all blends, the semicircle tended to disappear and shift to a lower resistance value, increasing the ionic conductivity.

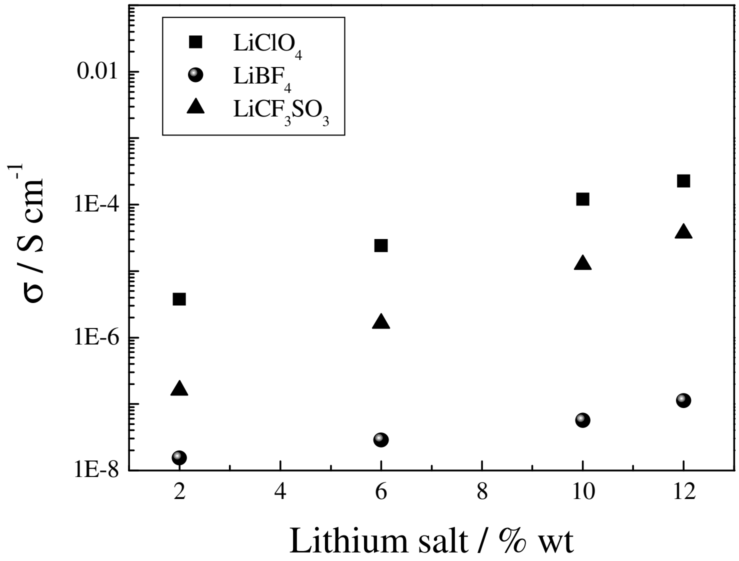

Figure 9. Ionic conductivity as a function of all salts studied at room temperature.

Figure 9 shows the ionic conductivity for all BPEs at room temperature. The increase in the ionic conductivity with the lithium salt concentration is very steep for all lithium salts investigated and does not reach a saturation value. This fact indicates an increase in the lithium salt dissociation due to the addition of plasticizer reducing crystalline phase and increasing the solvatation of the lithium salt. The salt, upon dissociation, provides free ions which promotes the ionic conduction [14].

The maximum ionic conductivity (σ=2.26 x 10^{-4} S cm^{-1}) was obtained with PCL/10% PC with 12 % wt. $LiClO_4$. This value is one order of magnitude higher than what is obtained from PCL without plasticizer, where the presence of a maximum conductivity of 1.2x10^{-6} S cm^{-1} at 10% wt. $LiClO_4$ was observed. The increase in conductivity caused by the addition of the plasticizer to produce a gelled biodegradable polymer electrolyte is due to two effects: increased ion mobility accorded by the decrease in Tg, and increased concentration of the charge carrier in the electrolyte because of the increase of the dissociation degree of the lithium salt.

For $LiCF_3SO_3$ and $LiBF_4$, the ionic conductivity maximum was also observed in 12% wt, σ= 3.6 x10^{-5} and 1.1 x10^{-7} S cm^{-1}, respectively. The discrepancy between the ionic conductivity maxima is probably related to the high value of the Tg for the salt $LiBF_4$ decreasing the segmental movement (Figure 5). The degree of crystallinity (Figure 6) showed also a small influence on the decrease of the crystalline phase with $LiBF_4$ addition.

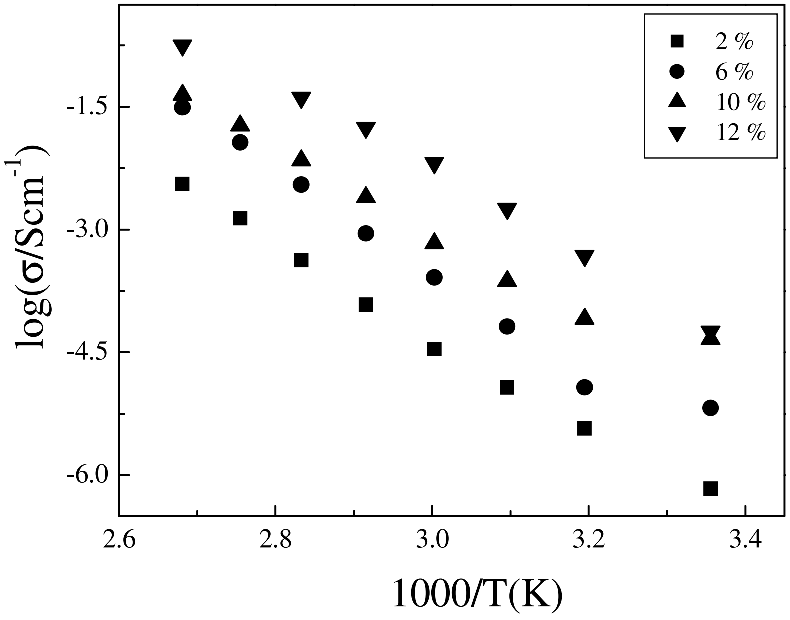

Figure 10. Ionic conductivity as a function of temperature for PCL/10%PC with 2, 6, 10, and 12% wt. $LiClO_4$.

Figure 10 shows the ionic conductivity variation of PCL/10%PC/ $LiClO_4$ as a function of temperature, with Arrhenius plots. The conductivity enhancement with temperature can be understood in terms of a free-volume model. According to the free volume theory, the ionic transport mechanism in the polymer electrolyte occurs due to the segmental motions that promote the ion motion through, making and breaking the coordination sphere of the solvated ion, and providing a space (free volume) into which the ions may diffuse under the influence of the electrical field [15]. The ions are transported by semi-random motion of short polymer segments and at temperatures below T_0, the free volume is assumed to vanish; if the temperature rises above T_0, the motion of ions and polymer segments is facilitated by creation of free volume. The pseudoactivation energy values of the polymer electrolyte (Figure 11) were obtained through fitting VTF from the Arrhenius plots (Figure 10). A pseudoactivation energy value was observed at 12 % wt. of all lithium salts on the order 10^{-3} eV. This value is one order of magnitude less than that of the several reported polymer electrolytes in the literature using a plasticizer agent [16-18]. This fact can be attributed to high power solvation of the biodegradable polymer with incorporation of propylene carbonate as the plasticizer, enhancing the amorphous phase of the polymeric matrix and also contributing to ionic conduction [19-22].

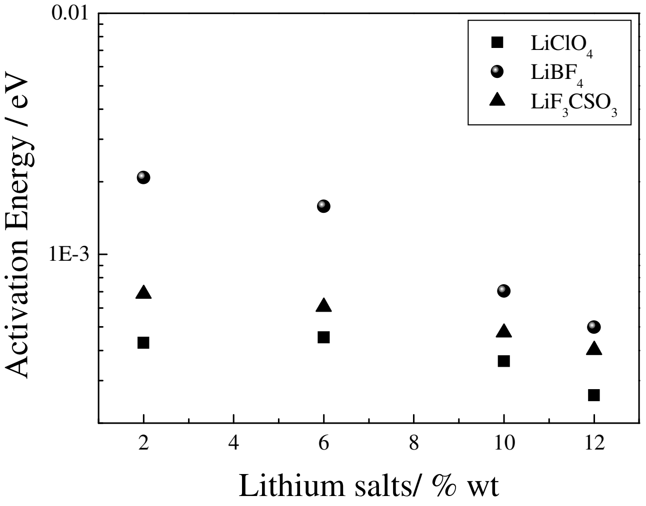

Figure 11. Activation energy for the PCL/10%PC as a function of all salt concentrations analyzed.

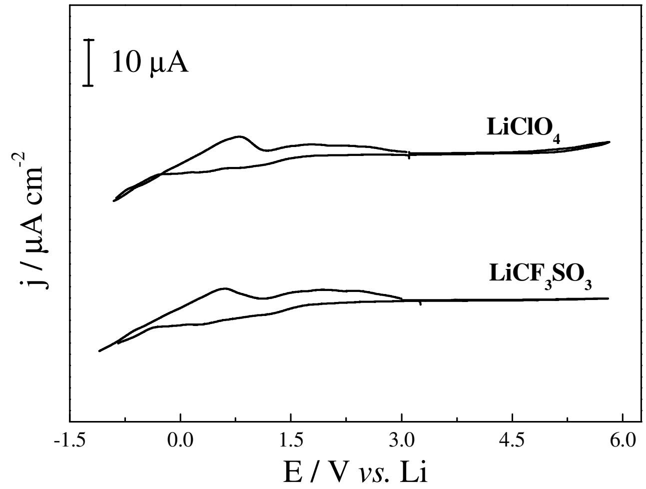

Figure 12. Electrochemical stability widows for the PCL/10%PC with 12% wt. $LiClO_4$ and $LiCF_3SO_3$.

The electrochemical stability window is an information essential for the success of any device, mainly the storage energy devices. For some electrochemical devices, such as lithium polymer batteries, the cell potential can approach values as high as 4.5 V vs. Li, implying that the polymer electrolyte should be electrochemically stable up to at least 4.5 V. Figure 12 shows the electrochemical stability window of the two systems that had presented better values of ionic conductivity: PCL/10% PC with $LiClO_4$ and $LiCF_3SO_3$. In the low voltage region, the deposition of lithium metal was observed at 0 V vs. Li^+/Li, whereas in the high voltage region, the process related to an anion oxidation process followed by a possible polymeric degradation was not observed [23,24] in the potential range studied. This fact indicates that the material shows an electrochemical stability window above 5.5 V. Therefore, it seems that the PCL/10%PC/ $LiClO_4$ or $LiCF_3SO_3$ system has enough electrochemical stability to apply for lithium secondary batteries.

4. CONCLUSIONS

Novel gel electrolytes based on a biodegradable polymer were prepared and studied. The gels studied contained 10 wt.% of plasticizer PC with three different lithium salts: $LiClO_4$, $LiCF_3SO_3$, and $LiBF_4$. Comparing the ionic conductivity of pure PCL (σ=1.2x10^{-6} S cm^{-1}) with a PCL based gel biodegradable polymer electrolyte (12 %wt $LiClO_4$ σ=2.26 x 10^{-4} S cm^{-1}) at room temperature, we conclude that higher conductivity in the PCL/10%PC could be attributed to the higher amorphicity and increased concentration of the charge carrier in the electrolyte, because of the increase of the degree of dissociation of the lithium salt due to the presence of plasticizer agent and polymer-salt complexation. The electrochemical stability window had a potential range of up to a potential of 5.5 V vs Li/Li^+. This novel gel electrolyte demonstrated the property of biodegradation, and it is a promising candidate to be one more component to green batteries.

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