Lithium Ion Motion in a Hybrid Polymer: Confirmation of a Decoupled Polyelectrolyte

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Ionic conductivity involving ion transport in polymer electrolytes has been a major focus of polymer battery research, and an important concept in understanding the mechanisms of ion transport in polymers is the issue of the coupling between ion motion and the relaxation of the polymer segmental chain.[1] This means that, in typical polymer electrolytes, ion transport is strongly coupled to the segmental motion of the polymer matrix. Therefore, significant conductivity is only observed above the glass-transition temperature of the system,[2] resulting in Vogel–Tamman–Fulcher behavior (VTF).[3–5] Research into polymer electrolytes has focused largely on enhancing the flexibility of the polymer matrix in order to promote ionic mobility.[6–8] This has met with success, but its disadvantage is that the conduction mechanism is dominated by ion–polymer interactions and the numbers of cations transported (vital for battery applications) can be very low.[9,10] New materials with unconventional conduction mechanisms are clearly needed.

However, a different class of polymer electrolytes has recently been reported, in which the ionic conductivity is not coupled to the segmental motion of the polymer chain, that is, in which the ions move independently of the viscous flow.[11–15] The approach used in the development of the segmental motion-decoupled polymer is the synthesis of a hard polymer (e.g., liquid-crystalline materials, polyesters, ordered polymers, and organic plastic crystals).[13,16–18] These materials represent an alternative way to increase ionic conductivity in polymer electrolytes.[19]

In a previous paper, we described the synthesis, thermal properties, and good ionic conductivity ($\sigma = 10^{-3} \Omega^{-1} \text{cm}^{-1}$ at room temperature) of a single-phase hybrid polyolethylene (SPHP). Arhenius behavior of the conductivity as a function of temperature was reported for the SPHP, suggesting that the ion motion is decoupled from the polymer segmental motion for temperatures above the glass-transition temperature $T_g$ (about 79°C).[10] This single-phase hybrid polyelectrolyte (SPHP) was synthesized by a derivative in situ polymerizable method (a nonhydrolytic sol–gel process) based on the formation of a complex of Si and citric acid (CA) that was subsequently polymerized by means of a polycondensation reaction with ethylene glycol (EG). The material became ionically conductive when Li$_2$CO$_3$ was dissolved in the structure during its synthesis. A transparent, amorphous solid hybrid was obtained after elimination of the solvent.[20]

The main goal herein is to understand the motion of the Li ions in an SPHP from a microscopic standpoint, and to identify the active sites, that is, the counterions of the hybrid polyelectrolyte matrix.

**Experimental Section**

The procedure used herein to obtain single-phase hybrid polyelectrolyte (SPHP) synthesis by a nonhydrolytic sol–gel process and has been described in greater detail elsewhere.[20] In a typical experiment, a CA/Si (molar) ratio of 2:1 and a Si–CA complex/EG mass ratio of 77:23 were used. Tetraethylorthosilicate (TEOS) was used as the Si source in the synthesis of the Si–CA complex. The Si-CA complexation and polymerization reaction performed in an ethanol solution at 40°C under constant magnetic stirring. The ionic conductivity arises from the addition of Li$_2$CO$_3$ during the synthesis. As discussed in ref.[20] only Li$^+$ is expected to be mobile in the inorganic–organic hybrid polyelectrolyte structure. It is believed that the anions are formed from the radical group present in the polymer network.[20] Consequently, SPHP is a single-ion conductor. It is important to point out that SPHP is fully amorphous at room temperature. In this work, the lithium concentration used was 10% wt in the SPHP systems. The SPHP was characterized structurally by FTIR measurements (Bruker Model EQUINOX 55), which were taken from 400 to 4000 cm$^{-1}$. From the gel-permeation chromatography (GPC) analysis we obtained the average molecular weight ($M_w = 2.6 \times 10^4$ g mol$^{-1}$) of the polymer and calculated the molar ratio [CCO]/[Li].[21] Based on the $M_w$ value, Li content, and monomer molecular weight (434.4 g mol$^{-1}$) the calculate value for the ratio was [CCO]/[Li] = 31.3.

A low [CCO]/[Li$^+$] ratio was use in this work to avoid possible ion cluster formation or phase segregation. The conductivity of the SPHP was obtained using an HP 4194 A capacitance voltage meter. In the present study, the measurements were taken in a temperature range of 25 to 60°C, while the frequency ranged from 100 Hz to 15 MHz with a perturbation amplitude voltage of 5 mV. The samples were sandwiched between two blocking platinum electrodes and placed in a temperature-controlled furnace.

**Results and Discussion**

**Ionic Conductivity**

In order to show the influence of the Li$^+$ addition on the transport mechanism of the SPHP, we performed impedance spectroscopy (IS) characterization of this polymer with and without Li$^+$. The SPHP without Li$^+$ presented a high resistivity, suggesting a very low ionic conductivity, as shown in Figure 1. Figure 2a depicts the IS characterization of the SPHP with [CCO]/[Li$^+$] = 31.3 as a function of temperature ($T > T_g$). The semicircle observed (Figure 2a) by the complex-plane impedance, in the Cole–Cole plot ($Z'' = Z' + iZ''$), was attributed to the intrinsic properties of the SPHP with Li$^+$. The semicircle (related to an equivalent AC parallel circuit) is the expected behavior of the polymer with Li$^+$ due to the experimental condi-
tions used in our study, that is, blocking electrodes and the chosen frequency range. Therefore, our electrical measurements (Figures 1 and 2a) clearly confirm that only Li$^+$ appears to be mobile in the structure of the SPHP. In addition, the conductivity ($\sigma_o$) and the characteristic relaxation frequency ($\omega_o$) were extracted from these data. Note the displacements of $\omega_o$ and $\sigma_o$ with the temperature, suggesting that both parameters are thermally activated. The characteristic relaxation frequency ($\omega_o$) can also be observed in the curve of $\log(\omega_{/Hz})$ versus $1/T$, where the part of the curve at high frequency corresponds to a material relaxation phenomenon and the plateau regions are related to $\sigma_o$.

It is important to emphasize that the $\sigma_o$ and $\omega_o$ of all the samples showed an Arrhenius-type dependence on temperature (as indicated in Figure 3). This behavior served as the basis for calculating the activation energy, according to Equation (1):

$$\sigma_o, \omega_o = C_o \exp(-E/kT)$$  \hspace{1cm} (1)

where $C_o$ is a pre-exponential factor, $E$ is related to the activation energy for ion conduction ($E_{\sigma_o}$) or the activation energy for charge-carrier migration ($E_{\omega_o}$)\cite{22} and $k$ is the Boltzmann constant. Equation (1) was used to fit the experimental results of $\sigma_o$ (where $\sigma_o$ was extracted from Figure 1a) to $1/T$ and $\omega_o$ (where $\omega_o$ was extracted from Figures 2a and 2b) and $1/T$ shown in Figure 3. The values of $E_{\sigma_o}$ and $E_{\omega_o}$ obtained from these calculations are summarized in Table 1. The values of the activation energy obtained for $\sigma_o$ and $\omega_o$ were found to be approximately the same, indicating that the dispersive conductivity, $\sigma(\omega)$, originates from ion hopping\cite{22}. It is important to point out that this behavior (the ion-hopping mechanism) has been reported for conventional polymer electrolytes only at low temperature\cite{12}, that is, $T < T_g$ or in rigid polymers (with $T_g$ higher than room temperature), which can provide pathways for ion hopping\cite{13,14}. Another interesting characteristic ob-

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**Figure 1.** $Z'$ versus $Z''$ impedance complex-plane plot for the SPHP without Li$^+$ (at room temperature)

**Figure 2.** a) $Z'$ versus $Z''$ impedance complex-plane plots; b) the imaginary part of the impedance complex ($Z''$) as a function of frequency (log-frequency) is associated with the relaxation process for the SPHP with [CCO]/[Li$^+$]=31.3 at different temperatures.

**Figure 3.** Log $\sigma_o$ (●) and Log $\omega_o$ (○) as a function of inverse temperature for a single-phase hybrid polyelectrolyte (SPHP) with [CCO]/[Li$^+$]=31.3. The solid lines represent fits of Equation (1) to the experimental data.
served in the SPHP is the low conduction activation energy, suggesting a fast transport mechanism. The activation energy reported for this material is considerably lower than that found in conventional polymer electrolytes. Imrie and co-authors reported activation energy of 0.36 eV for a decoupled liquid-crystalline polyelectrolyte.

As we observed in the results of ionic conductivity, the Arrhenius-type behavior exhibited by SPHP at temperatures exceeding \( T_g \) is known to characterize an ion transport mechanism that is independent of the polymer’s segmental motion. In conventional electrolyte (low-\( T_g \)) ion transport is generally facilitated by segmental motion, so the bent behavior is more appropriate to the VTF model. Another important characteristic to emphasize about the Arrhenius-type behavior observed here is that the SPHP under study presented a single transport mechanism in the temperature range applied (25–60 °C). This was expected, inasmuch as the counterions are provided by the hybrid organic–inorganic polymer chains and Li\(^+\) is expected to be the only ion moving through the polymer structure. This is a characteristic required in many applications.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>( E_s ) [eV]</th>
<th>( R^* )</th>
<th>( E_w ) [eV]</th>
<th>( R^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPHP</td>
<td>0.23</td>
<td>0.99962</td>
<td>0.22</td>
<td>0.99936</td>
</tr>
</tbody>
</table>

\( R^* \) is the parameter of the fit represented by the solid line in Figure 3.

**Fourier-Transform Infrared Studies**

In a previous paper, we discussed and identified the absorption peaks in full FTIR spectra; however, our main focus here is to understand the effect of Li and determine what polyelectrolyte counterion was developed. Figures 4a and 4b present the experimental and deconvoluted FTIR spectra (using a Gaussian function and the respective values of maximum intensity position, full width at half height, and normalized intensity) of the SPHP with Li\(^+\) ([CCO]/[Li\(^+\)] = 31.3) and without Li\(^+\). Since the major modification in the FTIR spectra observed after the addition of Li\(^+\) was in the region 500–1100 cm\(^{-1}\), we concentrated our analysis on this region of the spectrum. The peak in the region around 1070–1080 cm\(^{-1}\) was used as the reference (indicated in Figures 4a and 4b).

The FTIR spectra of the SPHP without lithium salt (shown in Figure 4a) reveal a well-defined peak at around 1020 cm\(^{-1}\) related to the C–O stretching vibration mode. When 10% wt lithium was added, a shoulder became visible at around 1040 cm\(^{-1}\), indicating that the lithium ion interacted with this organic group, as clearly illustrated in Figure 4b. We believe that this region, attributed to an alkoxide, is the active site of the hybrid polyelectrolyte, that is, the counterion of the hybrid polyelectrolyte. The C–O stretching vibrations of esters actually consist of two asymmetric coupled vibrations: C–C(=O)–O and O–C–C, with the former being more important. These bands occur in the region 1300–1000 cm\(^{-1}\). We found an O–C–C band of the molecule (alcohol carbon–oxygen stretching) that could be assigned to the primary, secondary, or tertiary structure of an alcohol and that occurred at around 1064–1031 cm\(^{-1}\). The O–C–C stretching vibration was attributed to tertiary binding, as indicated in Scheme 1a. Our electrical measurements clearly showed movement of the lithium ion independently of the viscous flow of the hybrid polymer chain, with the transport mechanism governed by migration of the ion (i.e., ion hopping). Based, on the FTIR results we identified the counterion as the (Li\(^+\))/[CCO]/[Li\(^+\)] = 31.3 and Scheme 1b. The solid line represents the experimental curve and the discontinuous lines are the deconvoluted fits by the Gaussian function.
In summary, the Conclusions Single-phase hybrid polyelectrolyte (SPHP) a) without and b) with lithium salt.

**Conclusions**

In summary, the $\alpha_s$ and $\omega_s$ of the SPHP materials shows an Arrhenius-type dependence on temperature ($T > T_g$) and the activation energy values obtained for $\alpha_s$ and $\omega_s$ are approximately the same ($\approx 0.23$ eV). Based on these results, it can be concluded that, in the temperature range studied here, the conductivity appears to be governed by hopping of the Li$^+$ ions. These results are very interesting, considering that the literature reports some materials with a decoupled transport mechanism that is governed by ion hopping, but these materials usually present a $T_g$ above room temperature. Moreover, ion hopping is expected when materials are at a low temperature, that is, if the material has a rigid structure (at low temperatures the structure is frozen). Furthermore, from our results it is clear that the single-ion conductor has an ion transport mechanism that is independent of the segmental motion of the hybrid polyelectrolyte, that is, it is a decoupled system. Based on the FTIR spectra, we identify the counterions or active sites and gain an understanding of the pathways lithium ions use to migrate in this hybrid matrix.

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**Keywords:** conducting materials · ion conductor · lithium · polyelectrolyte · polymers

[21] The [CCO]/Li$^+$ ratio is important because the CCO$^-$ was identified as the counterion in this study.

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