Impedance spectroscopy of carbon nanotube/solid polymer electrolyte composites

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**A R T I C L E I N F O**

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**A B S T R A C T**

New composite polymer electrolytes (CPE) have been prepared by a solution-casting technique, using polyethylene oxide, lithium hexafluorophosphate (LiPF₆) as the doping salt, ethylene carbonate (EC) as the plasticizer and amorphous carbon nanotubes (αCNTs) as the filler. The crystallinity and ionic conductivity of the CPE are examined. Differential scanning calorimetry shows a decrease in melting temperature and crystallinity upon the addition of LiPF₆, EC and αCNTs to the polymer electrolyte system. The addition of salt increases the conductivity up to $10^{-5}$ S cm$^{-1}$. The incorporation of EC and αCNTs into the salted polymer shows a significant conductivity increase of $10^{-4}$ and $10^{-3}$ S cm$^{-1}$. The complexation process is examined using Fourier transform infrared spectroscopy. The Vogel–Tamman–Fulcher (VTF) plots suggest that the temperature dependence of conductivity is a thermally activated process.

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1. Introduction

Polymer electrolytes are of technological interest due to their possible applications in various electrochemical devices such as energy conversion units (batteries/fuel cells), electrochromic devices, photochemical solar cells, supercapacitors and sensors [1–3]. Among the various applications, the use of polymer electrolytes in lithium batteries has been most widely reported. Initial works on polymer electrolytes were mostly based on the complexes of poly(ethylen oxide) (PEO) with inorganic salts [4,5].

Poly(ethylene oxide) has been a popular choice of polymer matrix for lithium ion conductors [6]. LiPF₆ is the most common lithium salt employed in lithium-ion batteries as it offers good electrolyte conductivity and film forming. Studies have proved that in PEO based polymer electrolyte systems, conductivity will increase as the salt concentration increases [7–11].

Unfortunately, high lithium ion conductivity is not attainable at ambient temperature due to the pristine PEO matrix. Thus, considerable efforts have been devoted to improving the ionic conductivity of polymer electrolytes. A common approach is to add low molecular weight plasticizers to the polymer electrolyte system [12].

The plasticizers impart salt-salvating power and high ion mobility to the polymer electrolytes. However, plasticizers tend to decrease the mechanical strength of the electrolytes, particularly at a high degree of plasticization [13,14]. Alternatively, inorganic fillers are used to improve the electrochemical and mechanical properties [15]. The fillers affect the PEO dipole orientation by aligning dipole moments whereas the thermal history determines the flexibility of polymer chains for ion migration. Fillers generally improve the transport properties, resistance to crystallization and stability of the electrode/electrolyte interface. The conductivity enhancement depends on the filler type and size. The neural network model has been developed and it was successful to predict the role of salt, plasticizer and filler for the ionic conductivity enhancement in the nanocomposites polymer electrolyte system [16,17].

Carbon nanotubes (CNTs) are polymer composite materials which have been used as electrolytes in lithium-ion batteries and polymer electrolyte membrane fuel cells [18–20]. It is known that the introduction of CNTs in polymer improves the stability and conductivity. The highly flexible nature of CNTs in terms of their physical shape may improve the interaction and cross-linking between polymer molecules, which may significantly enhance the morphological and electrical properties of composite electrolytes [21]. CNTs will modify the polymer backbone and assist in moving more Li⁺ ion. To the best of the authors’ knowledge, there are a limited number of papers, if any, concerning the use of amorphous carbon nanotubes (αCNTs) as fillers. αCNTs that have been used here are pure samples and there is no functional group attached to αCNTs. In light of this, this paper
reports new polymer electrolyte films made from PEO, lithium hexafluoride (LiPF$_6$), ethylene carbonate (EC) and αCNTs, and their conductivity.

2. Experimental

PEO films were used as host polymer electrolytes and were prepared via standard solution-casting techniques. The materials used were PEO (MW = 600,000, Acros), lithium hexafluoride (Aldrich), ethylene carbonate (Alfa Aesar), and acetonitrile (Fisher). Amorphous carbon nanotubes were prepared via the chemical route at low temperatures [22]. Prior to use, PEO was dried at 50 °C for 48 h. All components were added accordingly and dissolved in acetonitrile. The solutions were stirred for 24 h at room temperature until homogeneous solutions were obtained. The solutions were cast onto Petri dishes and allowed to evaporate slowly to form films. The samples were prepared at room temperature and the films were stored under dry conditions.

The ionic conductivities of the samples were measured at a temperature ranging from 298 to 373 K using HIOKI 3531 LCR Hi-Tester with a frequency range of 50 Hz–5 MHz. Infrared spectra were carried out using Fourier Transform Infrared (FTIR) Spectrum Nicolet IS 10 within the wave region of 4000–500 cm$^{-1}$. The morphology of αCNTs was observed using scanning electron microscope (SEM, Hitachi S-3400 W).

3. Results and discussion

3.1. Amorphous carbon nanotubes

Fig. 1 represents the scanning electron microscope (SEM) image of the amorphous carbon nanotubes (αCNTs). A mass of entangled αCNTs can be seen in this image, ranging from 70 to 100 nm in diameter, and about 6 μm in length. Dissanyake et al. [23] suggested that the conductivity enhancement increases with increasing specific surface area of the filler grain. The large surface area of the nanosized filler prevents local PEO chain reorganization. This results in “locking in” at ambient temperature and a high degree of disorder in the amorphous phase, which in turn favors high ionic transport [24–28]. In battery systems, the CNTs and CNT bundles were coated with an insulative polymer in such a way which prevents the charge from transferring from one CNT bundle to another [29]. The following chemical reaction equation have been proposed to explain how the αCNTs were synthesized [30]:

$$4(C_5H_4)Fe + O_2 + 4NH_4Cl \rightarrow 4(C_5H_4)_2FeCl + 4NH_3 + 2H_2O (1)$$

$$4(C_5H_4)FeCl + 3O_2 + 2NH_4Cl \rightarrow 10C + 4FeCl_3 + 2NH_3 + 6H_2O. (2)$$

3.2. Morphology of nanocomposite polymer electrolyte

Fig. 2 shows the SEM micrograph of salted plasticized polymer electrolytes with 5 wt% of αCNTs. The micrograph images reveal that αCNTs are well distributed in the polymer matrix [31]. The surface become smooth (using the casting technique) and it can be observed that the αCNTs is embedded within the nanocomposite polymer electrolyte.

3.3. Ionic conductivity

Fig. 3 shows the temperature dependence of conductivity for various electrolytes between 25 and 100 °C. It is evident that the room temperature conductivity increases with different chemical compositions. The results are summarized in Table 1. The conductivity increases by 5 orders of magnitude upon the addition of LiPF$_6$. 4 orders of magnitude upon the addition of EC and 3 orders of magnitude upon the addition of αCNTs. The sudden increase in conductivities is due to the role of lithium ions in the PEO and increase in flexibility of the polymer chains attributed to the EC and αCNTs on the polymer electrolytes.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Conductivity and activation energy values for composite polymer electrolytes.</th>
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<tbody>
<tr>
<td>Polymer electrolytes</td>
<td>$\sigma$ (S cm$^{-1}$) at 298 K</td>
</tr>
<tr>
<td>Pure PEO</td>
<td>$3.25 \times 10^{-3}$</td>
</tr>
<tr>
<td>PEO–20 wt% LiPF$_6$</td>
<td>$4.10 \times 10^{-3}$</td>
</tr>
<tr>
<td>PEO–20 wt% LiPF$_6$–15 wt% EC</td>
<td>$2.06 \times 10^{-4}$</td>
</tr>
<tr>
<td>PEO–20 wt% LiPF$_6$–15 wt% EC–5 wt% αCNT</td>
<td>$1.30 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

There is a sudden increase in conductivity for pure PEO electrolyte at 40–50 °C (Fig. 3a). However, the ionic conductivity increases linearly beyond 50 °C. Upon the addition of LiPF$_6$, EC and αCNTs, the thermal effects are clearly observed in Fig. 3b–d, which show a slight increase in conductivity within a wide temperature range. Polymer complex curvature in the plots shows that ionic conduction in the polymer electrolytes obeys the Vogel–Tamman–Fulcher (VTF) relation. This non-linearity plot of conductivity–temperature is generally observed for high viscous electrolytes or much amorphous polymeric systems [32,33]. Eq. (3) represents the Vogel equation:

$$\sigma = AT^{-1/2} \exp \left[-\beta/(T - T_0)\right]$$

where $\sigma$ is the conductivity; $\beta$ is the activation energy; $T$ is the temperature and $T_0$ is the ideal glass transition temperature. $A$ is proportional to the concentration of free ions, and $AT^{-1/2}$ is sometimes expressed as $\sigma_0$. $T_0$ is usually 30–50 °C lower than the experimentally determined $T_g$. As the salt concentration increases, $A$ should increase and the conductivity should also increase. However, as the salt concentration increases, the number of free coordinating sites decreases and thus the activation energy required increases, which lowers the conductivity. Additionally, as the salt concentration increases, the rigidity of the side chains increases, which increases the $T_g$ of the polymer, which also lowers the conductivity [34].

When EC was added into the system, more salts were dissociated into ions, which have a low viscosity and therefore increases ionic mobility. The addition of αCNTs increases the conductivity by inhibiting recrystallization of the PEO chains and providing a Li$^+$ conducting pathway at the filler surface [35]. The conduction of Li$^+$ ion in the polymer electrolyte is pictorially shown in Fig. 4. Under the influence of a potential gradient, the coordination spheres of the Li$^+$ ions keep changing to adjacent locations and this is assisted by the segmental motion of the polymer chain. The polymer chain undergoes reorganization.
Fig. 2. SEM images of nanocomposite polymer electrolytes.

Fig. 3. Conductivity dependence of temperature for nanocomposite polymer electrolytes at various compositions (a) PEO (b) PEO–20 wt% LiPF$_6$; (c) PEO–20 wt% LiPF$_6$–15 wt% EC (d) PEO–20 wt% LiPF$_6$–15 wt% EC–5 wt% αCNT.

Fig. 4. Schematic view of chain mobility, change of coordination sphere and chain reorganization during CNT. Nanosize αCNT are shown as closed circles and oxygen of the PEO chain as open circles.

during the continuous breaking and reforming of coordination sphere for Li-ions [36].

As the doping salt has not yet reached to saturation level, the ions are predominantly coupled to the segmental motions of the host polymer. The ion transport in polymer electrolytes is improved with segmental motions of the polymer host [37]. The conductivity behavior obeys the VTF equation. The migration of Li ion depends mainly on the segmental movement of the polymer chain in the amorphous region. The decrease in segmental mobility arises from virtual cross-linking and has an obvious signature in the increased glass transition temperatures. The free volume model is very useful for discussing the ion transport mechanism and for understanding the polymer segment mobility [10]. It states that as temperature increases, the expansivity of the material produces local empty space, free volume, into which ions, solvated molecules or polymer segments themselves can move. The overall mobility of the material is determined by the amount of free volume present in the material. As temperature increases, the amount of free volume increases, leading to increase of ion mobility and segment mobility.

The electrical conduction, on increasing the plasticizer concentration, extends to the low temperature region similar to as observed by Pradhan et al. [38]. This can be explained by considering the preferential interaction of the plasticizer with crystalline PEO increasing thereby the amorphous content [39]. When the plasticizer is increased, the ions would transport mainly in the plasticizer-rich phase and the transport mechanism here could be governed by the free-volume related characteristic of the plasticizer-rich phase, which would be responsible for the VTF relation [40].

When the organic filler was added into the polymer electrolytes, αCNTs/polymer spherulite interfaces are formed with the filler surface. This provides more effective paths for the migration of conductivity ions. Moreover, the nanosized αCNTs improve the conduction of mobile ions due to their extremely high surface energy [41–46]. This prevents local PEO chain re-organization which results in freezing at ambient temperature and a high degree of disorder. This in turn, favors fast ionic transport. As the αCNTs’ concentration increases, the conductivity also increase due to an increase in mobile ion transport within the polymer electrolytes. Generally, it is well known that the addition of nano-fillers in the polymer improves the transport properties, recrystallization and ionic conductivity due to enlargement of the amorphous phase in the polymer network [19,47]. In addition, a high degree of crystallinity is unfavorable for ion conduction of polymer electrolyte [19].

3.4. Complex impedance analyses

Fig. 5 shows the complex impedance spectra for various electrolytes at low and high temperatures. The semicircle in Fig. 5 represents the ionic resistance of the polymer electrolyte within a high frequency range and an inclined line at lower ones. It shows a typical blocking electrode capacitive behavior. The slopes of the inclined lines do not strongly depend on the components’ molar ratios at high temperatures. This indicates that the resistance of the inclined line is mainly against ion passage at the electrolyte/electrode interface. However, it is a different case for low temperatures, in which the inclined lines are strongly dependent on the components’ molar ratios. The semicircle shrinks and decays due to shifting towards higher frequencies which is
attributed to a decrease in ionic resistance of the electrolyte at high temperatures. The arc’s intercept on the real axis gives the value of the bulk resistance, which decreases with increasing temperature.

Typical impedance plots ($Z_r$ versus $Z_i$) for all polymer electrolytes at 298 and 373 K are given in Fig. 5. The plots exhibit two well-defined regions, namely, a high frequency region semi-circle, which is due to the bulk effect of electrolytes, and a linear region in the low-frequency range which is attributed to the effect of blocking electrodes. At low frequencies, the impedance plots should exhibit a straight line parallel with the imaginary axis; however the double layer at the blocking electrodes causes the curvature [48]. The low-frequencies’ intercept on the $Z_r$ axis gives the bulk electrical resistance ($R_b$) value. The bulk resistance decreases upon the addition of EC and $\alpha$CNTs in the polymer electrolytes. The improved ionic conductivity is due to enhancement of the ionic mobility and number of carrier ions [49]. The salt content in the polymer is advantageous, which increases the number of charge carriers and results in increased conductivity. The addition of plasticizer reduces the glass transition temperature ($T_g$) of the polymer, increases the segmental mobility, and thus enhances the conductivity.

3.5. FTIR analyses

Figs. 6 and 7 depict the infrared (IR) transmittance spectra of the samples recorded at room temperature within the region of 4500–500 cm$^{-1}$. The vibration modes and wave numbers exhibited by PEO are CH$\_2$ rocking mode observed at 842 and 963 cm$^{-1}$, respectively. The strongest mode in the PEO is the antisymmetric bridge C–O–C stretching vibration at 1100 cm$^{-1}$ [50], asymmetric CH$\_2$ twisting at 1241 and 1280 cm$^{-1}$, and asymmetric CH$\_2$ at 1455 cm$^{-1}$. Other absorption bands are observed for symmetric and asymmetric C–H stretching vibrations, at 2800–3000 cm$^{-1}$ and 2700–3800 cm$^{-1}$, respectively [51].

When LiPF$_6$ was added into the PEO system, CH and C–O–C stretching modes are shifted from 1110 to 1100 cm$^{-1}$ and 2890 to 2886 cm$^{-1}$, respectively. A small shoulder appears at 1800 and 700 cm$^{-1}$ for the PEO–LiPF$_6$–EC system due to the reaction of EC with PEO. The fraction of “free” anions and “ion pairs” has been calculated as the ratio of the area corresponding to the peaks attributed to the free anions and ion pairs to the total area of the band corresponding to the envelope of $v_4$ ($PF_6^-$) mode [23]. The fractions of free anions and ion pairs have been found to be influenced substantially by the dispersion of filler particles within the polymer–salt complex matrices [23]. The peaks become more prominent when $\alpha$CNTs were added into the PEO–LiPF$_6$–EC system. When $\alpha$CNTs were added, the CH and C–O–C stretching modes are shifted from 2886 to 2885 cm$^{-1}$ and 1100 to 1099 cm$^{-1}$, respectively. These observations imply the existence of three interactions: (1) between the salt and polymer (2) between the salt, polymer and plasticizer (3) between the filler, salt, plasticizer and polymer.

4. Conclusions

New composite polymer electrolytes have been synthesized via solution-casting techniques. Conductivity analyses have been
carried out for the PEO–20 wt% LiPF$_6$–15 wt% EC–5 wt% αCNTs system. The PEO–LiPF$_6$ system exhibits a maximum conductivity of 10 from 10$^{-10}$ S cm$^{-1}$ at room temperature. The conductivity increases up to 10$^{-4}$ S cm$^{-1}$ upon the addition of EC into the PEO–LiPF$_6$ system. The addition of αCNTs gives a conductivity enhancement of 10$^{-3}$ S cm$^{-1}$. The addition of highly flexible αCNTs into the PEO networks improves the interaction and cross-linking between αCNTs and PEO molecules. The temperature dependence of ionic conductivity for these electrolytes obeys the VT relation. FTIR analyses provide strong evidence that there are bonding interactions for the PEO. The variations in intensity, shape and position of the peaks confirm the complexation of PEO blends with LiPF$_6$, EC and αCNTs. The SEM micrographs show a smooth surface when αCNTs were added into the polymer system.

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