Conductivity, thermal and infrared studies on plasticized polymer electrolytes with carbon nanotubes as filler

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1. Introduction

Polymer electrolytes have now become truly interdisciplinary materials. From their origins in the polymer community [1,2] they were quickly adopted by the electrochemical community who recognized the potential of a flexible, plastic ion-transporting medium in vital applications such as energy storage [3] and electrochemical displays [4]. It shall be noted that much initial work on polymer electrolytes was focused on the complexes of poly (ethylene oxide) (PEO) with inorganic salts [5,6].

Poly (ethylene) oxide (PEO) has been a popular choice of polymer matrix for lithium-ion conductors [7]. LiPF$_6$ is the most common lithium salt employed in lithium-ion batteries because it offers good electrolyte conductivity and film-forming due to its excellent solubility and high conductivity in various solvents [8]. Many salts, including those containing di- and trivalent cations, have been combined with a variety of polymers in order to form polymer electrolytes [9–11]. Studies have proven that in PEO based polymer electrolyte systems, the conductivity increases as the salt concentration increases [12–16]. Unfortunately, high lithium ionic conductivity cannot be attained at ambient temperatures with the pristine PEO matrix. Thus, considerable efforts have been devoted to improve the ionic conductivity of polymer electrolytes. A common approach is to add low molecular weight plasticizers to the polymer electrolyte systems [17]. There has been significant work carried out on the pristine and plasticized PEO–lithium salt systems [18–21]. The plasticizers impart salt-solvating 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 [22,23]. Alternatively, inorganic fillers are used to improve the electrochemical and mechanical properties [24]. The fillers affect the PEO dipole orientation by their ability to align dipole moments, while the thermal history determines the flexibility of the polymer chains for ion migration. They generally improve the transport properties, the resistance to crystallization and the stability of the electrode/electrolyte interface. The conductivity enhancement depends on the type of filler and size. In 1999, the addition of carbon to improve the conductivity and stability of polymer electrolytes was proposed by Appetecchi and Passerini [25]. However, the room temperature conductivities for various weight percent of carbon are within the range of $10^{-3}$ S cm$^{-1}$. Neural network models have been developed, which were successful to predict the role of salt, plasticizer and filler for the ionic conductivity enhancement in nanocomposite polymer electrolyte systems [26,27]. This paper presents a new kind of composite polymer electrolyte prepared by our group using amorphous carbon nanotube (αCNTs) as filler. By adding αCNTs, the electrical and thermal properties of solid polymer electrolytes are increased. This study shows that the conductivity increases to $10^{-3}$ S cm$^{-1}$ when αCNTs are added into plasticized polymer. Several works have reported CNT dispersion in polymer matrix [28–31]. However, to the best of our knowledge,
2. Experimental

PEO was used as host polymer electrolytes and PEO films were prepared by standard solution-casting technique. The materials used in this work were PEO (MW = 600,000, Acros), lithium hexafluorophosphate (LiPF₆) (Aldrich), ethylene carbonate (EC) (Alfa Aesar), and acetonitrile (Fisher). The αCNTs were synthesized via chemical approach. Ferrocene (2 g) and ammonium chloride (4 g) were added into a 30 ml crucible. The sample was covered and heated to 200 °C for 30 min, followed by cooling to room temperature. Two purification methods were developed to produce clean αCNTs. During acid purification, the sample was filtered and washed with hydrochloric acid and deionized water in sequence, and dried at 50 °C for 24 h. Microwave purification was accomplished by placing the sample into a closed vessel with deionized water for 30 min, followed by cooling to room temperature.

Prior to use, PEO was dried at 50 °C for 48 h. All components were added and dissolved in acetonitrile. The solutions were stirred for 24 h at room temperature until homogeneous solutions were obtained. The solutions were cast onto glass petri dishes and were added and dissolved in acetonitrile. The solutions were stirred for 24 h at room temperature until homogeneous solutions were obtained. The solutions were cast onto glass petri dishes and were left to evaporate slowly to form films. All samples were prepared at room temperature and stored under dry conditions. The average thickness for the films was 0.76 mm.

The ionic conductivities of the samples were measured within a temperature range of 298 to 373 K using HIOKI 3531 LCR Hi-Tester with a frequency range of 50 Hz to 5 MHz. Differential Scanning Calorimetry (DSC) thermographs were obtained using DSC 820 fitted with 56 thermocouples. Infrared studies were carried out using FTIR Spectrum Nicolet IS 10 in the wave region of 4000 to 500 cm⁻¹. The morphologies of αCNTs and nanocomposite polymer electrolytes were observed through scanning electron microscope (SEM, Hitachi S-3400W).

3. Results

Fig. 1 represents the TEM image of amorphous carbon nanotubes (αCNTs). The sample prepared by microwave-assisted purification method is in bundle form and shows presence of carbonaceous impurities around nanotubes. Hydrochloric acid removes the amorphous carbon and iron particles on the nanotubes’ surface by oxidation and dissolves into acid solution [32]. A mass of entangled αCNTs can be seen in this image, ranging in diameter from 70 to 100 nm, and about 6 μm in length. The αCNTs are successfully produced in nanometre size.

Fig. 2 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 conductivity values at room temperature are summarized in Table 1. The polymer complexes’ curvature in the plots shows that ionic conduction in the polymer electrolytes obeys the Vogel-Tamman–Fulcher (VTF) relation. The conductivity increases by 4 orders of magnitude with the addition of EC. Further addition of αCNTs increases conductivity by 3 orders of magnitude. There is a sudden increase in conductivity for pure PEO electrolyte at 40–50 °C (Fig. 2(a)). However, the ionic conductivity increases linearly beyond 50 °C.

Fig. 3 shows the complex impedance spectra for various electrolytes at low and high temperatures. The semicircle in Fig. 3 represents the ionic resistance of the polymer electrolytes in the higher frequency range and an inclined line at lower ones. This indicates a typical blocking electrode capacitive behavior. Typical impedance plots (Z’ vs. Z”) for all the polymer electrolytes at 298 K and 373 K are given in Fig. 3. The plots show 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-frequency, the impedance plot should exhibit a straight line parallel with the imaginary axis, but the double-layer at the blocking electrodes causes the curvature [33]. The low-frequency intercept on the Z’ axis gives the bulk electrical resistance (Rb) value. The bulk resistance decreases upon the addition of EC and αCNTs in the polymer electrolytes.

Fig. 4 shows the temperature dependence of conductivity for 2 different ratios of αCNTs, which is 1 wt.% and 5 wt.%. It is evident that the room temperature conductivity increases with different ratio of αCNTs. The conductivity at room temperature is 2.20×10⁻³ S cm⁻¹ and 1.07×10⁻³ S cm⁻¹ for 1 wt.% and 5 wt.% αCNTs, respectively. The conductivity slightly increases when temperature increases to 100 °C, whereby the values are 1.37×10⁻² S cm⁻¹ and 2.78×10⁻³ S cm⁻¹ for 1 wt.% and 5 wt.% αCNTs, respectively.

Fig. 5 shows the differential scanning calorimetry (DSC) curves for various electrolytes over the temperature range of 30 to 100 °C. The results for melting temperature (Tm) and % crystallinity (Xc) are summarized in Table 1. All polymer electrolytes exhibit endothermic peaks between 50 and 70 °C, suggesting the presence of a crystallization phase, based on the melting point for PEO (60–75 °C). The curves show that the addition of salt, plasticizer and filler on polymer electrolyte influences the melting transition temperature Tm. During the heating process, a sharp endothermic peak is observed near 65 °C for the melting of pure PEO, as shown in Fig. 5(a). The calculated values of Xc are summarized in Table 1. It is evident from the results that overall, there is a marked decrease in Tm and Xc during heating as a result of the addition of salt, plasticizer and filler.
500 cm⁻¹. The spectra exhibit band characteristic of stretching and bending vibrations of the films, and are listed in Table 2.

The SEM of PEO shows the features of spherulites. The SEM image for pure PEO, as shown in Fig. 8a, demonstrates clear spherulite structure at room temperature [38]. The optical microscopy, XRD and DSC investigations suggest a lower degree of crystallinity and smaller lamellae size with the addition of Li salt into the PEO [38]. For PEO-LiPF₆ films with high EC content, microporous structures are observed, as shown in Fig. 8c. The observed pore size for high EC content is obtained for plasticized polymer electrolytes. The same phenomenon was observed by Song [39], where the pore size was obtained to be above 1 μm for PVdF-HFP-EC films with high EC content. Upon addition of αCNTs, the surface becomes smooth by using casting technique. This is shown in Fig. 8d.

4. Discussion

4.1. Ionic conductivity analysis

The conductivity increment that occurs in salted polymer as shown in Fig. 2 is due to the polar and flexible PEO main chain dissociates LiPF₆ to generate carrier ions, and the migration of these ions through interchain and intrachain polymer segments in the amorphous region of the complex [40] is responsible for the increase in conductivity.

The polymer complexes’ curvature in the plots shows that ionic conduction in the polymer electrolytes obeys the Vogel–Tamman–Fulcher (VTF) relation. The non-linearity of the plots is generally observed for high viscous electrolytes or much amorphous polymeric systems [41,42]. Eq. (1) represents the Vogel equation:

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

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 \( \sigma_c \). 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.

![Complex impedance plot](image1)

![DSC thermograms](image2)
and thus the activation energy required increases as shown in Table 1, 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, and lowers the conductivity \[43\].

As the salt content increases, the conductivity increases because the density of mobile ions increases and therefore, the polymer segment’s motion is promoted \[44\]. The results agree well with the Rice and Roth model \[45,46\]:

\[
\sigma = \frac{2}{3} \left( \frac{Ze^2}{k_B T m} \right) \eta E_a \tau \exp \left( -\frac{E_a}{k_B T} \right)\]

(2)

where \( \sigma \), \( \eta \), \( Z \), \( E_a \), and \( m \) represent the conductivity, density, valency, activation energy, mass of the conducting ions, respectively. Furthermore, the parameters \( T \), \( k_B \), \( e \) and \( \tau \) represent the absolute temperature, Boltzman constant, electronic charge and time travel of ions between sites, respectively. From Eq. (2), it can be seen that conductivity increases when the density of mobile ions increases. Since the doping salt has not yet reached the 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 \[47\]. 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 crosslinking and has an obvious signature in the increased glass transition temperature. The free volume model is very useful for discussing the ion transport mechanism and for understanding the polymer segment mobility \[15\]. 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 increased ion mobility and segment mobility.

The conductivity increment on the plasticized salted polymer is due to the effects of the physicochemical properties of the individual plasticizers such as the high dielectric constant of EC \((\varepsilon_2 = 85.1)\) contribute significantly towards improving the conductivity performance \[48\]. The addition of plasticizer also decreases ion-pairing at higher salt concentration \[49\]. The high dielectric constant of EC effectively reduces the inter-ion Coulomb interactions; hence, more \( \text{Li}^+ \) contributed to the conductivity of the complexes. The addition of the plasticizer has been reported to reduce the crystallinity of the complexes, which leads to enhanced ionic conductivity \[50–52\]. The electrical conduction, on increasing the plasticizer concentration, extends to the low temperature region, as observed by Pradhan et al. \[53\]. This can be explained by considering the preferential interaction of the plasticizer with crystalline PEO, thereby increasing the amorphous content \[54\]. When the plasticizer is increased, the ions would transport mainly in the plasticizer-rich phase and the transport mechanism could be governed by the free-volume related characteristic of the plasticizer-rich phase, which would be responsible for the VTF relation \[55\].

The addition of \( \alpha \)CNTs increases the conductivity by inhibiting recrystallization of the PEO chains and providing \( \text{Li}^+ \) conducting pathway at the filler surface through Lewis acid–base interactions among different species in the electrolytes \[56\]. The addition of highly flexible \( \alpha \)CNTs into PEO networks improved the interaction and cross-linking between \( \alpha \)CNTs and PEO molecules, resulting in the increased ionic conductivity \[57\].

When the organic filler was added into the polymer electrolytes, \( \alpha \text{CNTs}/\text{polymer spherulite} \) interfaces are formed with the filler surface. This provides more effective paths for the migration of conductivity ions. Moreover, the nano-size \( \alpha \text{CNTs} \) improve the

### Table 2

<table>
<thead>
<tr>
<th>Material</th>
<th>Vibrational frequency (cm(^{-1}))</th>
<th>Band assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO</td>
<td>842, 963</td>
<td>CH(_2) twisting nagging [34]</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>Anti-symmetric bridge C – O – C stretching [34]</td>
</tr>
<tr>
<td></td>
<td>1241, 1280</td>
<td>Asymmetric C-H twisting [34]</td>
</tr>
<tr>
<td></td>
<td>1455</td>
<td>Asymmetric C-H [34]</td>
</tr>
<tr>
<td></td>
<td>2800–3000</td>
<td>Symmetric C – H stretching [34]</td>
</tr>
<tr>
<td></td>
<td>2700–2800</td>
<td>Asymmetric C – H stretching [34]</td>
</tr>
<tr>
<td>LiPF(_6)</td>
<td>651</td>
<td>( \nu(PF_6^-) ) [35]</td>
</tr>
<tr>
<td></td>
<td>837</td>
<td>( \nu(PF_6^-) ) [35]</td>
</tr>
<tr>
<td></td>
<td>1164</td>
<td>( \nu(PF_6^-) ) [35]</td>
</tr>
<tr>
<td>EC</td>
<td>718</td>
<td>C=O bending [36]</td>
</tr>
<tr>
<td></td>
<td>893</td>
<td>Ring breathing [36]</td>
</tr>
<tr>
<td></td>
<td>1774</td>
<td>C=O stretching bands [36]</td>
</tr>
<tr>
<td></td>
<td>1775</td>
<td>C=O stretching bands [36]</td>
</tr>
<tr>
<td>CNT</td>
<td>1635</td>
<td>H-bonded (C=O stretching) [37]</td>
</tr>
<tr>
<td></td>
<td>1708</td>
<td>C=O stretching bands [37]</td>
</tr>
<tr>
<td></td>
<td>3437</td>
<td>OH stretching [37]</td>
</tr>
</tbody>
</table>

Fig. 6. FTIR spectra of (a) PEO; (b) LiPF\(_6\); (c) PEO + LiPF\(_6\); (d) EC; (e) PEO + LiPF\(_6\) + EC; and (f) PEO + LiPF\(_6\) + EC + \( \alpha \)CNTs.

Fig. 7. FTIR spectra of \( \alpha \)CNTs.
conduction of mobile ions due to their extremely high surface energy [58–63]. 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 increases 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 [64,65]. In addition, a high degree of crystallinity is unfavorable for ion conduction of polymer electrolytes [65].

4.2. Complex impedance analysis

The semicircle in Fig. 3 represents the ionic resistance of the polymer electrolytes in the higher frequency range and an inclined line at lower ones. This indicates a typical blocking electrode capacitive behavior. The slopes of the inclined lines do not strongly depend on the components’ molar ratio at high temperatures. This indicates that the resistance on 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 ratio. The semicircle shrinks and decays as a result of shifting to higher frequencies due to the decrease in ionic resistance of the electrolytes at high temperatures. The arc’s intercept on the real axis gives the value of the bulk resistance, which decreases with increasing temperature.

The improved ionic conductivity is due to enhancement of the ionic mobility and number of carrier ions [66]. The salt content in polymer is advantageous to the increase in number of charge carriers, resulting in increased conductivity. The addition of plasticizer reduces $T_g$ of the polymer, increases the segmental mobility, and thus enhances the conductivity.

4.3. Conductivity analysis of various concentrations of carbon nanotubes

The introduction of CNTs into PEO matrix may sufficiently reduce the Ohmic contact to increase the electron exchange in the PEO network of electrolyte region [15]. The interaction between polymer and αCNTs can be explained by Lewis acid–base concept [13]. The mechanical properties and conductivity of polymer electrolytes are increased by adding carbon nanotubes [28]. Li$^+$ salt is the ion carrier in polymer electrolytes.

4.4. DSC analysis

Fig. 5 shows the differential scanning calorimetry (DSC) curves for various electrolytes over the temperature range of 30 to 100 °C. The addition of LiPF$_6$ salt causes a change in the shape of the endothermic peak, and the peak shifted towards lower temperature. This also indicates the complexation process between LiPF$_6$ and PEO. The $T_m$ continues to decrease with the addition of plasticizer (EC). The addition of filler (αCNTs) causes peak broadening. The peak slightly shifts to a lower temperature.
The relative crystallinity ($X_c$) was calculated using the relationship:

$$X_c = \frac{\Delta H_{m}^{\text{sample}} \times 100}{\Delta H_{m}^{\text{reference}}} \tag{3}$$

where $\Delta H_m$ is the melting enthalpy estimated experimentally and $\Delta H_{m}^{\text{reference}}$ is the melting enthalpy for 100% crystalline PEO (213.7 $\text{J g}^{-1}$) and is used as reference [67]. The calculated values of $X_c$ are summarized in Table 1. At room temperature, the polymer exists in crystalline phase and the atoms are bonded tightly to one another at the polymer chains. When the polymer reaches the melting point, the atoms begin to move (solid to liquid) and Li$^+$ ions react freely with O in PEO. When LiPF$_6$, EC and oCNtS are added into polymer complexes the $T_m$ reduces to lower temperature. Since lithium-ion conduction in PEO-based polymer electrolytes mainly takes place in the amorphous phase, low crystallinity should be favorable for ion conduction at low temperatures.

4.5. FTIR analysis

The vibration modes and wave numbers exhibited by PEO are CH$_2$ rocking mode observed at 842 and 963 cm$^{-1}$, respectively. The strongest interaction in PEO is the anti-symmetric bridge C–O–C stretching vibration at 1100 cm$^{-1}$ [68], symmetric 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 [69].

When LiPF$_6$ is added into the PEO system, CH and C–O–C stretching modes are shifted from 1110 to 1100 cm$^{-1}$ and 2890 to 2880 cm$^{-1}$, respectively. The intensity of this band implies the number of free ions from the addition of salt [70]. This explains why there is an increase in the conductivity value for PEO–LiPF$_6$ samples. This broadening and shifting indicate that there is a possible weak interaction between the polymer and the salt [71]. As shown in Fig. 3c, a small shoulder at 682 cm$^{-1}$ appears for PEO–LiPF$_6$ samples. This is possibly due to weak interactions between PEO and $\nu$(PF$_6^{1-}$) at 651 cm$^{-1}$. The shift in peak and decrease in intensity of CH$_2$ twisting at 961 cm$^{-1}$ prove the occurrence of interactions between PEO backbone and $\nu$(PF$_6^{1-}$) at 823 cm$^{-1}$ [72].

When EC is added to PEO–LiPF$_6$ system, the CH and C–O–C stretching modes at 2886 cm$^{-1}$ and 1100 cm$^{-1}$ remain unchanged. A small shoulder appears at 1780 cm$^{-1}$ for the PEO–LiPF$_6$–EC system due to the reaction of salted polymer with ethylene carbonate. The addition of EC leads to the formation of Li$^+$–EC complex [73]. The peaks shift from 1780 cm$^{-1}$ to 1800 cm$^{-1}$, and becomes more obvious when oCNtS are added into the PEO–LiPF$_6$–EC system, whereby the CH and C–O–C stretching modes remain unchanged. The intensity of OH peaks increase when Li$^+$ salt and EC plasticizer were added into polymer complex which is slightly effect on the ionic conductivity [74–78].

4.6. SEM analysis

A lower degree of crystallinity and smaller lamellae size in salted polymer signify that Li salt is well dissociated and affects the weak complexation of PEO, which leads to the disruption of continuous crystalline, and results in smaller lamellae dimension [38]. The increase in degree of roughness with increased LiPF$_6$ concentration indicates segregation of the dopant in the matrix [79]. The high salt categories having a salt content higher than 2–3 mol (x ≤ 20) are brittle with rough surfaces and are very hygroscopic [80]. The surface morphology of the high salt concentration system is rough compared with the low salt concentration samples, as shown in the SEM images in Fig. 8 [80].

5. Conclusion

Optimum solid polymer electrolyte (PEO–20wt.% LiPF$_6$–15wt.% EC–5wt.% oCNtS) system has been synthesized using solution-casting technique. It has been demonstrated in this paper that the addition of various weight percent of salt, plasticizer and filler into the PEO matrix enhances conductivity. It has also been shown that the temperature dependence conductivity is Arrhenius. It is found from the DSC curves that the addition of salt, plasticizer and filler into the PEO reduces the melting transition temperature ($T_m$) and crystallinity of the electrolytes. Analysis of the films by FTIR indicates that there exist interaction and complexation among the components. The SEM micrographs exhibit surface changes when LiPF$_6$, EC and oCNtS are added into the polymer system.

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