Role of Ionic Liquid and Tin (IV) Oxide Nanoparticles on the Ionic Conductivity of Biodegradable Solid Polymer Electrolyte

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Abstract: Solution casting technique is used to prepare solid polymer electrolyte (SPE) utilizing biodegradable hydroxyethyl cellulose (HEC) as host polymer and magnesium trifluoromethane sulfonate (MgTf2) salt as charge carrier. However, the performance of the SPE is hindered by its low ionic conductivity at room temperature. Thus, room temperature ionic liquid, 1-ethyl-3-methylimidazolium trifluoromethane sulfonate (EMIMTF) and tin (IV) oxide (SnO2) nanoparticles have been added into the SPE to overcome the shortcomings. As a result, the room temperature ionic conductivity improved to 9.28×10⁻² and 2.84×10⁻¹ S/cm upon addition of 40 wt.% EMIMTF ionic liquid and 2 wt.% of SnO₂ nanoparticles, respectively. The conductivity-temperature plot shows that the transportation of ions in these films obey Arrhenius theory. The improvement of the ionic conductivity at room temperature for HSn2 makes it attractive for application to electrochemical devices.

Key words: Hydroxyethyl cellulose, ionic liquids, nanoparticles, solid polymer electrolyte, energy storage device, electrochemical

INTRODUCTION

Ionic conductivity at room temperature is an essential parameter to determine the performance of solid polymer electrolyte in the fabrication of energy storage devices (Zhang et al., 2018). Therefore, researchers adopt various methods such as incorporation of nanoparticles and ionic liquids aside from preparation of blend polymers and copolymers to enhance the ambient ionic conductivity of the solid polymer electrolyte for almost one-third of the century (Chong et al., 2018; Pal and Ghosh, 2018). This is due to both solid and gel polymer electrolytes are still promising candidates to be applied in the energy storage devices owing to its distinct features such as leak proof, better flexibility and improve safety (Selvalakshmi et al., 2018).

Nanoparticles are used in numerous applications namely optoelectronics, sensors, catalysis, energy storage devices, medical, dye-sensitized solar cells and water treatment (Bulke and Modo, 2017; Chong et al., 2017; Yang et al., 2017; Zebardastan et al., 2017). The embedding of nanoparticles such as MgO, SiO₂, Al₂O₃, TiO₂, PbO and SnO₂ into the solid polymer electrolyte for energy storage devices is able to entrap the charge carriers on the polymer electrolyte (Choudhary and Sengwa, 2017; Yang et al., 2014). Hence, it improves the uptake of electrolyte which leads to the improvement in the ambient ionic conductivity, mechanical strength, thermal electrochemical and interfacial stability between electrode and electrolyte (Barik et al., 2017). As a result, tin (IV) oxide (SnO₂) has been chosen in this studies owing to its non-toxic in nature, cheap, high electron mobility, strong chemical and physical interactions with adsorbed species and strong thermal stability up to 500°C in air along with band gap of 3.6 eV and high degree of transparency across the electromagnetic spectrum (Al-Hamdi et al., 2015; Ivetic et al., 2016).

Ionic Liquid (IL) is used in numerous fields because IL possesses large electrochemical window, high ionic conductivity and excellent safety performances (Yang et al., 2018). In the preparation of solid polymer electrolyte, it improves the ionic
conductivity at room temperature by softens the polymer electrolyte through its tremendous plasticization effect (Turgut et al., 2017). Thus, 1-ethyl-3-methylimidazolium trifluoromethane-sulfonate has been a choice of ionic liquid in this studies.

Recently, the exploitation of fossil fuels motivates the researchers to prepare biodegradable solid polymer electrolyte to reduce the emission of pollutants. Du et al. (2017) states that cellulose is the most potential natural polymer besides starch, chitosan, collagen, soy protein and casein because it is easily available, inexpensive and its surface is rich with hydroxyl groups. Therefore, the cellulose derivatives (i.e., methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxypropyl methylcellulose, carboxymethyl cellulose, ethylcellulose, cellulose acetate, cyanomethyl cellulose, cellulose esters and cellulose phthalate) would be a promising candidate for solid polymer electrolyte. In hydroxyethyl cellulose, the hydroxylethyl group replaces the hydrogen atom in the cellulose as the residual group. Thus, hydroxyethyl cellulose owns physicochemical properties because its large amount of hydroxyl groups helps in the adsorption of charge carriers through ion-dipole interactions. Additionally, it is a green material with excellent biocompatibility, good solubility in water, easily available and cheap which is widely used in the pharmaceutical and food industries, zinc-carbon batteries (as an organic inhibitor), composites for relative-humidity sensors and polymer light-emitting diodes.

In this research, both EMIMTTf and SnO2 nanoparticles are incorporated into the prepared solid polymer electrolyte (a mixture of hydroxyethyl cellulose as polymer backbone and magnesium trifluoromethane sulfonate salt as charge carrier) using solution casting method. The effect of ionic conductivity upon inclusion of ionic liquid and tin (IV) oxide nanoparticles into the prepared solid polymer electrolyte are investigated.

<table>
<thead>
<tr>
<th>Table 1: Compositions and designations for the SPE complexes</th>
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<tbody>
<tr>
<td>Composition of HEC: MgTTf (wt.%)</td>
</tr>
<tr>
<td>Designations</td>
</tr>
<tr>
<td>10:0:0 H0</td>
</tr>
<tr>
<td>9:1:10 H10</td>
</tr>
<tr>
<td>8:2:20 H20</td>
</tr>
<tr>
<td>7:3:30 H30</td>
</tr>
<tr>
<td>6:4:40 H40</td>
</tr>
<tr>
<td>Composition of HEC: MgTTf: EMIMTTf (wt.%)</td>
</tr>
<tr>
<td>Designations</td>
</tr>
<tr>
<td>8:0:20:0 H0</td>
</tr>
<tr>
<td>7:2:18:10 H10</td>
</tr>
<tr>
<td>6:4:16:20 H20</td>
</tr>
<tr>
<td>5:6:14:30 H30</td>
</tr>
<tr>
<td>4:8:12:40 H40</td>
</tr>
<tr>
<td>Composition of HEC: MgTTf: EMIMTTf: SnO2 (wt.%)</td>
</tr>
<tr>
<td>Designations</td>
</tr>
<tr>
<td>48:12:40:0 HSn0</td>
</tr>
<tr>
<td>47:2:11:8:40:1 HSn1</td>
</tr>
<tr>
<td>46:4:11:6:40:2 HSn2</td>
</tr>
<tr>
<td>45:6:11:4:40:3 HSn3</td>
</tr>
<tr>
<td>44:8:11:2:40:4 HSn4</td>
</tr>
</tbody>
</table>

Characterization: Mitutoyo micrometer screw gauge was used to measure the thickness of the film prior to the measurement of the ionic conductivity. The conductivity value of each thin film was measured three times by using HIOKI 3532-50 LCR HiTESTER, over a frequency range between 50 Hz and 5 MHz. Samples were sandwiched between two stainless steel blocking electrodes holder under spring pressure. The correlation between the conductivity and temperature was conducted in the temperature range of 25-120°C.

RESULTS AND DISCUSSION

Ionic conductivity of HEC-MgTTf, SPE: Figure 1 depicts the change in activation energy and ambient conductivities at different wt.% of salt. When the host polymer is free from MgTTf salt, the ionic conductivity of the SPE is 1.61×10-4 S/cm. It increases to 4.76×10-3 S/cm when 10 wt.% of MgTTf is added into it. Following this, when 20 wt.% of salt is added into the SPE, its ionic conductivity elevates to the maximum value of 6.71×10-7 S/cm because the number of available ions provided by the MgTTf salt is optimum. Subsequently, the ambient ionic conductivity decreases to 2.67×10-7 S/cm and 2.20×10-7 S/cm when 30 and 40 wt.% of MgTTf are added into the SPE, respectively. This is due to complexation of excessive amount of salt (Senevirathne et al., 2018).

Figure 2 portrays the change in log10 conductivities with the absolute temperature at different wt.% of salt. All
Fig. 1: The change in activation energy and ambient conductivities at different wt.% of salt

Fig. 2: The change in log_{10} conductivities with absolute temperature at different wt.% of salt

Fig. 3: The change in activation energy and ambient conductivities at different wt.% of ionic liquid

The solid polymer electrolytes achieve regression values (R²) values close to unity. It indicates the charge carriers receive sufficient energy to hop to vacant sites in the expanded host polymer at increasing temperature (Perumal et al., 2018). The charge carriers receive sufficient kinetic energy to overcome the barrier. Thus, H20 (the most conducting sample) achieves the lowest activation energy of 0.518 eV based on the Eq 1 and gradient in Fig. 2. This is because the mobile carriers in H20 which possess high kinetic energy are able to overcome the activation energy. Following this, H30, H40, H10 and H0 obtained activation energies of 0.562, 0.617, 0.621 and 0.780 eV, respectively (Wang et al., 2018) Eq 1:

\[ \sigma = \sigma_0 e^{-\frac{E_a}{kT}} \]

Where:
- \( \sigma \) = The ionic conductivity at different temperature
- \( \sigma_0 \) = The conductivity pre-exponential factor
- \( E_a \) = The activation energy
- \( T \) = The absolute temperature

**Ionic conductivity of HEC-MgTf₂-EMIMTf₂-SPE:** Figure 3 shows the change in activation energy and ambient conductivities at different wt.% of ionic liquid. The room temperature ionic conductivity of solid polymer electrolyte prior to the addition of IL is 6.71 × 10⁻⁴ S/cm. The ionic conductivity improves proportionally with the wt.% of ionic liquid because the IL enhances the transportation of charge carriers by improving the flexibility of the host polymer (Suatt et al., 2018). The presence of IL softens the polymer backbone through its plasticizing effect which resulted in rupturing of crystallinity of the host polymer and thus, more charge carriers are able to adsorb on it (Lu et al., 2008; Suleman et al., 2013). When 10 wt.% of IL is added into the solid polymer electrolyte, the ionic conductivity increases to 3.34 × 10⁻² S/cm. The ionic conductivity elevates to 1.92 × 10⁻³ S/cm and 5.64 × 10⁻³ S/cm upon inclusion of 20 and 30 wt.% of IL, respectively. It reaches the maximum ionic conductivity of polymer is 9.28 × 10⁻² S/cm when 40 wt.% of IL is added into it. At this point, H140 achieves the lowest activation energy of 0.302 eV because the charge carriers jump to vacant sites easily by overcoming the barrier (Shi et al., 2018). It is followed by 0.354, 0.356, 0.518 and 0.535 eV for H130, H120, H110 and H10, respectively. Nevertheless, the ionic conductivity at room temperature was not measured upon incorporation of 50 wt.% of IL because the preparation of free standing thin film was unsuccessful.

Figure 4 displays the relationship between log_{10} conductivities and absolute temperature at different wt.% of ionic liquid. All the SPEs fit Arrhenius theory because the R² values for H10, H110, H120, H130 and H140 are 0.98, 0.99, 0.99, 0.99 and 0.99, respectively (Manjuladevi et al., 2018).
Fig. 4: The change in \( \log_{10} \) conductivities with absolute temperature at different wt.% of ionic liquid.

Fig. 5: The change in activation energy and ambient conductivities at different wt.% of nanoparticles.

**Ionic conductivity of HEC-MgTf$_2$-EMIMTf$_2$-SnO$_2$ SPE:**

Figure 5 shows the change in activation energy and ambient conductivities at different wt.% of nanoparticles. HSn$_3$ achieves the maximum ionic conductivity at room temperature (2.86×10$^{-4}$ S/cm) along with the lowest activation energy (0.242 eV) because tin (IV) oxide nanoparticles have high affinity for adsorption of charge carriers (Chatterjee et al., 2016). This is because the nanoparticles are well dispersed on the host polymer due to their great Lewis-base interaction and small in size. Consequently, it promotes better interfacial contact between charge carriers and host polymer. Also, both the Sn$^4+$ and O$^{2-}$ ions on the nanoparticles will attract the Tf$^{-}$ and Mg$^{2+}$ ions, respectively through permanent dipole force which facilitate good transportation of ions

Fig. 6: The change in \( \log_{10} \) conductivities with absolute temperature at different wt.% of nanoparticles (Jeon et al., 2006; Sundaram et al., 2007). When excessive tin (IV) oxide nanoparticles (3 and 4 wt.%.) are incorporated into the solid polymer electrolyte, the ionic conductivity at room temperature were depressed to 1.44×10$^{-6}$ and 5.78×10$^{-7}$ S/cm, respectively. This is because the adsorption of charge carriers on the nanoparticles are blocked by clustering of the nanoparticles. It is worth to note that both HSn3 and HSn4 achieve high activation energy of 0.286 and 0.295 eV, respectively because these solid polymer electrolytes facing insufficient energy to overcome the barrier (Sil et al., 2015). On the other hand, when less amount of nanoparticles is added into the host polymer (1 wt.%), its ionic conductivity at room temperature is low (1.37×10$^{-4}$ S/cm) owing to less available sites for adsorption with charge carriers. As a result, HSn$_3$ requires more energy to overcome the high activation energy of (0.290 eV).

Figure 6 describes the relationship between \( \log_{10} \) conductivities and absolute temperature at different wt.% of nanoparticles. All the solid polymer electrolytes are activated by the increasing of temperature. The host polymer expands when heated, thus, the charge carriers are able to hop to the empty space (Karuppusamy et al., 2017).

**CONCLUSION**

The ambient ionic conductivity of the prepared solid polymer electrolytes by using solution casting technique was extensively improved by incorporating EMIMTf$_2$ ionic liquid and SnO$_2$ nanoparticles. The ionic conductivity at room temperature improved to 9.28×10$^{-4}$ and 2.86×10$^{-4}$ S/cm upon incorporation of ionic liquid and nanoparticles, respectively as compared to H2O (6.71×10$^{-4}$ S/cm). The plasticizing effect by the ionic liquid and extra adsorption...
sites in the nanoparticles assisted in the improvement of the ionic conductivity. Based on this study, all the prepared solid polymer electrolytes obeyed the Arrhenius theory.

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