

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

^{1,2}Mee Yoke Chong, ¹Arshid Numan, ³YCY Evyan, ⁴WH Cheng,
⁴LS Wong, ²K. Ramesh and ²S. Ramesh

¹Centre for American Education, INTI International University,
Persiaran Bandar Baru Nilai, 71800 Nilai, Malaysia

²Centre for Ionics University of Malaya, Department of Physics,
University of Malaya, 50603 Kuala Lumpur, Malaysia

³Faculty of Science and Technology, Nilai University College,

⁴Department of Biotechnology, Faculty of Health and Life Sciences,
INTI International University, Persiaran Bandar Baru Nilai, 71800 Nilai, Malaysia

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^{-5} and 2.84×10^{-4} 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 (Bulte 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 Sb₂O₃ 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, hydroxypropylmethyl cellulose, carboxymethyl cellulose, ethylcellulose, cellulose acetate, cyanoethylated cellulose, cellulose esters and cellulose phthalate) would be a promising candidate for solid polymer electrolyte. In hydroxyethyl cellulose, the hydroxyethyl 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 EMIMTf 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.

MATERIALS AND METHODS

Preparation of SPE film: HEC and different wt.% of MgTf₂ procured from Sigma-Aldrich, USA were stirred in Deionized (DI) water. It was followed by constant stirring for 24 h at room temperature. Then, the homogenized solution was poured on a Teflon coated aluminium foil. The mixture was evaporated at 70°C. A thin and transparent film of solid polymer electrolyte was formed. The steps were repeated by varying different wt.% of EMIMTf and tin (IV) oxide nanoparticles purchased from Sigma-Aldrich, USA. Prior to use, the tin (IV) oxide

Table 1: Compositions and designations for the SPE complexes

Composition of HEC: MgTf ₂ (wt.%)	Designations
100:0	H0
90:10	H10
80:20	H20
70:30	H30
60:40	H40
Composition of HEC: MgTf ₂ : EMIMTf (wt.%)	Designations
80:20:0	HI0
72:18:10	HI10
64:16:20	HI20
56:14:30	HI30
48:12:40	HI40
Composition of HEC: MgTf ₂ : EMIMTf: SnO ₂ (wt.%)	Designations
48:12:40:0	HSn0
47.2:11.8:40:1	HSn1
46.4:11.6:40:2	HSn2
45.6:11.4:40:3	HSn3
44.8:11.2:40:4	HSn4

nanoparticles were activated to avoid any aggregation among them. The first step in the activation of nanoparticles was heating at 450°C for 2 h. Subsequently, the nanoparticles were cooled, suspended and sonicated in the water for 30 min (Taghizadeh and Seifi-Aghjekohal, 2015). The designations and compositions of the thin film formed is shown in Table 1.

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-MgTf₂ SPE: Figure 1 depicts the change in activation energy and ambient conductivities at different wt.% of salt. When the host polymer is free from MgTf₂ salt, the ionic conductivity of the SPE is 1.61 × 10⁻⁸ S/cm. It increases to 4.76 × 10⁻⁷ S/cm when 10 wt.% of MgTf₂ 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 MgTf₂ 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 MgTf₂ 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

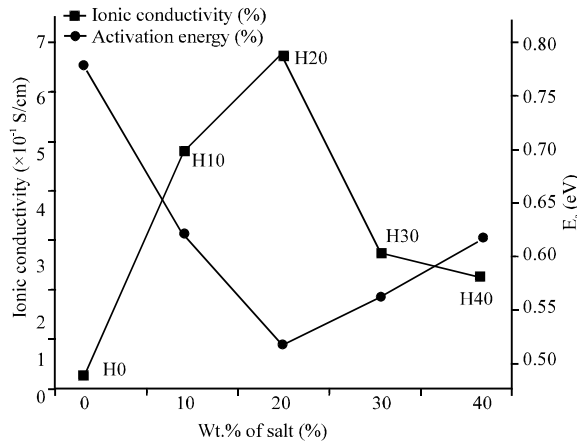


Fig. 1: The change in activation energy and ambient conductivities at different wt.% of salt

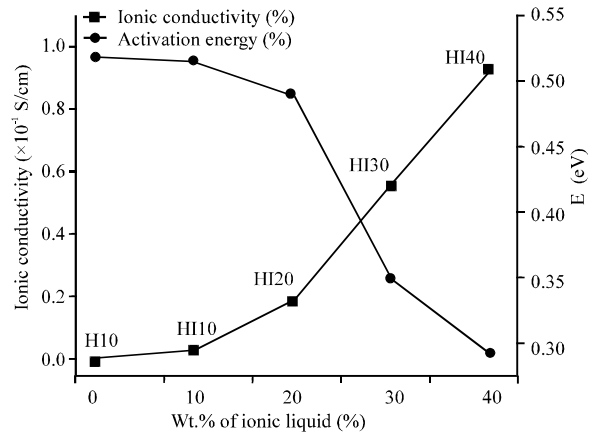


Fig. 3: The change in activation energy and ambient conductivities at different wt.% of ionic liquid

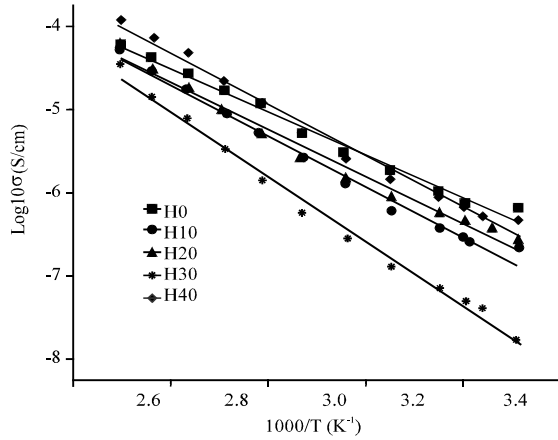


Fig. 2: The change in log₁₀ conductivities with absolute temperature at different wt.% of salt

the solid polymer electrolytes achieve regression values (R^2) 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:

$$\sigma = \sigma_0 e^{-\frac{E_a}{kT}} \quad (1)$$

Where:

- σ = The ionic conductivity at different temperature
- σ_0 = The conductivity pre-exponential factor

- k = The Boltzmann constant
- E_a = The activation energy
- T = The absolute temperature

Ionic conductivity of HEC-MgTf₂-EMIMTf 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^{-7} 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 (Suait *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^{-6} S/cm. The ionic conductivity elevates to 1.92×10^{-5} S/cm and 5.64×10^{-5} S/cm upon inclusion of 20 and 30 wt.% of IL, respectively. It reaches the maximum ionic conductivity of polymer is 9.28×10^{-5} S/cm when 40 wt.% of IL is added into it. At this point, HI40 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 HI30, HI20, HI10 and HI0, 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 log₁₀ conductivities and absolute temperature at different wt.% of ionic liquid. All the SPEs fit Arrhenius theory because the R^2 values for HI0, HI10, HI20, HI30 and HI40 are 0.98, 0.99, 0.99, 0.99 and 0.99, respectively (Manjuladevi *et al.*, 2018).

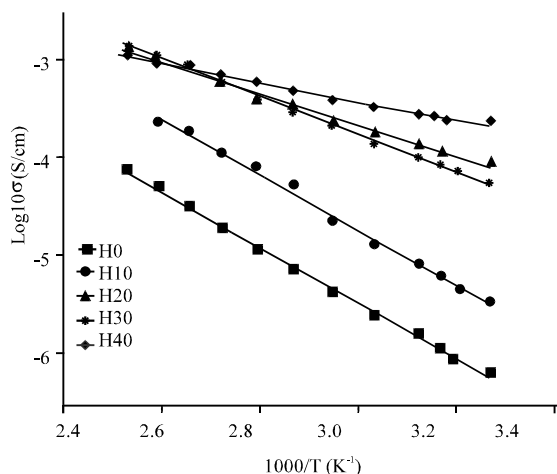


Fig. 4: The change in \log_{10} conductivities with absolute temperature at different wt.% of ionic liquid

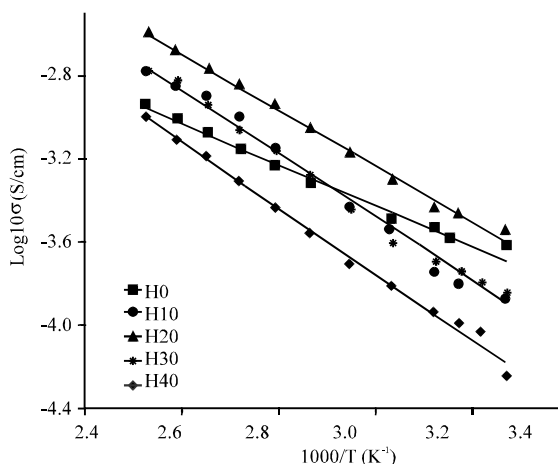


Fig. 6: The change in \log_{10} conductivities with absolute temperature at different wt.% of nanoparticles

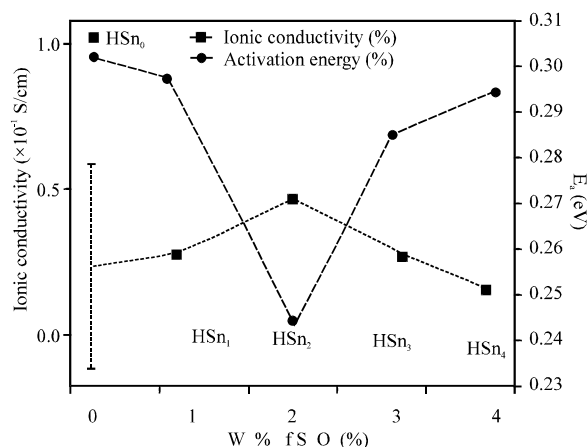


Fig. 5: The change in activation energy and ambient conductivities at different wt.% of nanoparticles

Ionic conductivity of HEC-MgTf₂-EMIMTf-SnO₂ SPE:

Figure 5 shows the change in activation energy and ambient conductivities at different wt.% of nanoparticles. HSn₂ 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 has 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 Sn⁴⁺ and O²⁻ ions on the nanoparticles will attract the Tf and Mg²⁺ ions, respectively through permanent dipole force which facilitate good transportation of ions

(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^{-4} and 5.78×10^{-5} 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.%), it's 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, HSn₁ 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 (Karuppasamy *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 ionic liquid and SnO₂ nanoparticles. The ionic conductivity at room temperature improved to 9.28×10^{-5} and 2.86×10^{-4} S/cm upon incorporation of ionic liquid and nanoparticles, respectively as compared to H20 (6.71×10^{-7} 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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