Correlation Between Structural and Ionic Transport Properties of Lithium-ion Hybrid Gel Polymer Electrolytes Based PMMA-PLA

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Research Article

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Abstract

In this work, the investigation on hybrid gel polymer electrolytes (HGPEs) comprising polymethyl methacrylate (PMMA)-polylactic acid (PLA) incorporate with LiTFSI were carried out. The HGPEs samples were characterized for their structural, thermal and ionic conduction properties via FTIR, XRD, DSC, and EIS. FTIR analysis show the indication of the interaction between PMMA-PLA hybrid polymer and LiTFSI with the appearance of peak and changes in peak shifting at the coordinating site from polymer blend. The DSC analysis shows that the glass transition temperature (T_g) of HGPEs was decreased as the LiTFSI content increases, suggesting that the HGPEs system has good thermal stability. The ionic conductivity was calculated based on the Cole-Cole plot and the incorporation of LiTFSI with 20 wt. % into hybrid polymer matrixes revealed the maximum ionic conductivity of $1.02 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature as the amorphous phase increases. The dissociation of ions and transport properties of the PMMA-PLA-LiTFSI systems was determined via dielectric response approach and it was found that number density ($\bar{n}$), mobility (μ), and diffusion coefficient (D) of mobile ions follows ionic conductivity trend.

Introduction

Polymers are at the forefront of the materials revolution, where their uses grow faster than any other structural compound. Polymers may even be accentuated based on the appearance of functionalities according to their applications. The first report of an observation of ionic conductivity in polymer complexes with dopant salt-based electrolytes is the beginning of polymer electrolytes (PEs) [1]. Since then, PEs have attracted worldwide attention for application in various energy storage devices, particularly in lithium-ion batteries. PEs composed of dissolving salts in high molecular weight polymer hosts form salt-polymer complexes due to the interaction between oxygen atoms in the polymer matrix and cation in the salt [2]. This solvent-free and conductive ion system has been developed to replace the conventional liquid electrolytes with their ability over safety in terms of leakage problems, flammability, and corrosion [3].

PEs should possess properties approximating high ionic conductivity at ambient temperature, appreciable cation transference number, good mechanical strength, wide electrochemical stability window, and excellent chemical and thermal stability [4–6]. Therefore, the use of gel polymer electrolytes (GPEs) has been recognized as one of the promising routes addressing the above requirement for application in electrochemical devices. In GPEs, the liquid component is trapped in the polymer matrix, thus preventing the liquid leakage, improving device application safety [7]. The presence of liquid in GPEs has increased the cation mobility, thus leading to a boost of room temperature ionic conductivity [8]. The reported GPEs generally distribute high ionic conductivities at a range of $\sim 10^{-4}$ to $10^{-3} \text{ S cm}^{-1}$ [9–11]. The implementation of GPEs also offers additional benefits, including mechanically and thermally stable, have sufficient electrochemical stability, or even have advantages of shape controllability [12, 5]. The recent studies on the suitable polymer matrix as a host for GPE have been widely explored. Among these

polymers are poly(methyl methacrylate) (PMMA) [12, 13], poly(ethylene oxide) (PEO) [14], polyacrylonitrile (PAN) [15], poly(vinylidene fluoride) (PVDF) [16, 17] and PVC [18].

Nevertheless, those single polymer-based GPE could not completely meet the requirements for practical application on properties like long-term stability of cycle performance, superior mechanical and tensile strength, as well as good corrosion resistance [19, 8, 20]. To accomplish the required demand, blending two different polymer methods has been considered for enhancing the physicochemical properties of gel polymer electrolytes [17, 21]. This method, also referred to as hybrid polymer in some cases and can interact chemically or physically, depends on their structural and physical properties against their parent components [22]. When two or more polymers were blended and achieve a homogenous phase, it leads to the formation of a miscible blend where one polymer is assigned to absorb the active component of electrolytes. In contrast, the another polymer remain as an undissolved inert second phase [23]. Hence, providing toughness to the polymer electrolytes and also offered more vacant sites for charge carriers coordination. Shi et al. [8] reported that the polymer blending is a useful technique for designing conducting polymer materials with a variety of attractive properties such as high ionic conductivity. This is due to the provided more space volume for ion mobility, give a large amount of ions transport number, and enhance the mechanical and thermal properties. Moreover, the blending method can be more valuable because of ease of preparation and can control the properties of polymer electrolytes by changing the composition of the blended polymer [24]. It is also known as low-cost production yet could improve the limitation of polymer electrolytes [25].

The structure of polymer membrane as the matrixes plays a critical role in the performances of GPEs. The amorphous and crystalline phase of GPE may be attributed to the higher ionic conduction in the system and solid mechanical support to the polymer electrolytes backbone. PMMA, presents good electrode-electrolyte interfacial with Li metal anode, lightweight, amorphous in nature, and more excellent dimensional stability [20, 26]. It is also well known that PMMA provide excellent mechanical properties when blending with another polymer [23, 2]. On the other hand, PLA is biodegradable polymer with outstanding properties like renewable in nature, environmental friendly, good mechanical properties, and, affordable in price [27, 28]. Despite these excellent properties, PLA suffers from high crystalline structures, which need to take into consideration. Many efforts have been established to improve PLA toughness, including polymer blending, copolymerization, adding plasticizers and, adding ionic dopant salt [29, 30].

For the practical design of GPEs for advanced rechargeable Li^+ batteries, the transport properties mechanism must be thoroughly understood. Ionic conductivity is crucial parameter need to consider when it comes to the choice of GPE materials [31]. Therefore, dissolving inorganic salts is well-known the most efficient way to increase the ionic conductivity of the electrolytes. Ionic dopant salt played a critical part in preparing PE as it could provide conducting species to the GPEs by diffusion of ion transport into the polymer complex. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt is chosen due to its excellent properties in terms of enhancing the electrochemical properties of the GPEs [32]. Several successful models of calculating the transport properties have been introduced based on the analysis

and modification of the characterization, including impedance spectroscopy, fourier transform infrared spectroscopy (FTIR) [33], and nuclear magnetic resonance spectroscopy (NMR) measurement [34]. Theoretically, electrical impedance spectroscopy (EIS) has proven to be a powerful tool in investigating the charge transport of electronic and ionic charge carriers as well as mass transport through diffusion and convection processes [35]. Earlier studies reported transport parameters could be determined from several approaches using data from impedance analyzer, namely Arof-Noor (A-N) method, Rice and Roth model method, and Broadband Dielectric Response (BDR) method [36–38]. However, among these methods, the A-N method (Nyquist/Cole-Cole plot fitting method) is most applicable to be used since they can calculate the transport properties for both conditions of the Cole-Cole plot consists of semicircle-spike and spike only [39]. In addition, this method also can be applied in various conditions without having specific requirements such as Rice and Roth method are capable of being used only for Arrhenius behavior systems. Meanwhile, BDR method is limited for the Cole-Cole plot with semicircle-spike [40].

Therefore, in this present work, the hybrid gel polymer electrolytes (HGPEs) systems compose of PMMA-PLA hybrid polymer incorporated with various content of LiTFSI are prepared. The influences on LiTFSI content into hybrid polymer systems based HGPEs were investigated along with the transport properties mechanism as the main objective. The physicochemical properties of HGPEs was determined to find out the possibility of present HGPEs systems as in the application of the lithium-ion battery.

Methodology

Preparation of hybrid gel polymer electrolyte

The PMMA (M.W. 996,000), PLA (M.W. 120,000) and LiTFSI materials used in this work were obtained from Aldrich Co., Shandong Zhi Shang Chemical Co. LTD and Aldrich Chemistry, respectively. The materials were dried in the vacuum oven with 50 °C for 3 to 4 hours to remove moisture. Based on our previous work [41], the percentage ratio of 80:20 of PMMA-PLA was employed in the present system as a host polymer. The tetraethylene glycol dimethyl ether (TEGDME) obtained from Acros Organics was immersed with a molecular sieve (4Å, Sigma Aldrich) prior to preparing hybrid gel polymer electrolytes. PLA was first dissolved in 0.8 mL TEGDME until the powder is completely dissolved. Then, the different weight percentages of LiTFSI (5 to 35 wt.%) were incorporated into the solution. After achieving a homogenous solution, PMMA was added and continued stirred until gel properties were formed. The gelled samples were stored with argon and vacuum conditions before further analysis. Table 1 shows the designation and variation of the HGPEs content.

Characterization of PMMA-PLA-LiTFSI systems

Fourier Transform Infrared Spectroscopy (FTIR)

The molecular interaction between hybrid polymer host and lithium ion was investigated using FTIR analysis. The measurement was carried out by FT-IR Nicolet 6700 Thermo-Fisher Scientific consists of an

Attenuated Total Reflection (ATR) accessory with a zinc selenide (ZnSe) crystal in the wavenumber range of 700 to 4000 cm^{-1} . The FTIR spectra was recorded using a resolution of 2 cm^{-1} at room temperature.

X-ray Diffraction (XRD)

XRD analysis was performed on a Rigaku MiniFlex II Diffractometer outfitted with nickel-filtered $\text{Cu K}\alpha$ ($\lambda = 0.154 \text{ nm}$) energized at 30 kV, and 15 mA. The gelled samples were spread onto a glass slide before placed onto the sample holder. The PMMA-PLA-LiTFSI based HGPEs were scanned at room temperature ranging from $2\theta = 5^\circ$ to 80° .

Differential scanning calorimetry (DSC)

DSC analysis was measured under nitrogen flow rate 20 ml min^{-1} using a computerized differential scanning calorimetry (DSC) (Netzsch Polyma 240). Sample weighing $\sim 5\text{--}6 \text{ mg}$ is hermetically sealed in an aluminum crucible. The gelled samples underwent a heating and cooling process from 30°C to 300°C at a heating rate of $10^\circ\text{C min}^{-1}$. The final heating scan was used to determine the glass transition (T_g) from the endothermic reaction's mid-point.

Electrical impedance spectroscopy (EIS)

The prepared samples were subjected to alternating current (ac)-impedance spectroscopy. The prepared samples were placed into the stainless-steel coin cell blocking electrodes and then positioned into a battery jig cell. The real impedance, Z' and imaginary impedance, Z'' were measured using HIOKI 3532-50 LCR Hi-TESTER in a frequency of 50 Hz to 1 MHz. In each measurement, the bulk resistance, R_b was obtained from the Cole-Cole plot. The ionic conductivity was calculated using following relation:

$$\sigma = \frac{d}{R_b A} \quad (1)$$

where d is sample thickness, while A is area of the coin cell.

Results And Discussion

FTIR Studies

The information pertaining to ion-polymer interaction and molecular structure in PMMA-PLA-LiTFSI systems were determined from FTIR analysis. According to Dhatarwal [20] the interaction that occurred in the polymer electrolytes matrixes can be confirmed by the appearance of new peaks or disappearance, shifted, and changes in intensities or shape of existing peaks.

To better understand the interaction between PMMA-PLA hybrid polymer and LiTFSI, Figure 1 depicts FTIR spectra for PMMA-PLA, raw LiTFSI and PMMA-PLA-LiTFSI hybrid gel polymer electrolytes. It reveals that the IR spectrum of PMMA-PLA hybrid polymer shows a peak at 2872 cm^{-1} which is assigned to C-H

stretching, COOC stretching at 1728 cm^{-1} , O-CH₃ stretching at 1451 cm^{-1} , CH₃ stretching at 1350 cm^{-1} , and C-O-C stretching at 1100 cm^{-1} [41]. Meanwhile, the IR spectra for LiTFSI showing the functional group of the S-N stretching at 740 cm^{-1} , symmetric bending mode of CF₃ at 788 cm^{-1} , asymmetric S-N-S stretching mode at 1050 cm^{-1} , bonding mode vibration of C-SO₂-N at 1130 cm^{-1} , CF₃ asymmetric stretching mode at 1193 cm^{-1} and C-SO₂-N bonding mode vibration at 1346 cm^{-1} . In the present work, the IR spectra for PMMA-PLA hybrid polymer system are highlighted into 3 selected regions, as shown in Figure 2 which is believed to have occurred when LiTFSI was introduced into the system.

Figure 2 (region 1) shows that at 1731 cm^{-1} , the peak intensity was slightly decreased as increasing the LiTFSI content. The intensity of COOC stretching decreased from 20% to 12% as demonstrated in Figure 3. This could be explained due to the interaction between Li⁺ ions and the hybrid polymer matrix at the oxygen atom of the ester group (C=O), where the oxygen atom has two lone pairs of electrons, resulting in a coordination bond [42]. As increased with LiTFSI content, it can be noted that it would supply more Li⁺ ions, which triggered many ions to migrate to the hybrid polymer backbone. Moreover, it is well known that carbonyl (C=O) stretching is intense band which easier to detect the peak changes when charge carriers were added. The changes of intensity at C=O band also is believed were caused from the change in dipole moment that occurs during the vibration. The coordination of Li⁺ ion in this system was occurred via ion hopping mechanism where the ions migrated by hop from one site to the neighbouring vacant site in the polymer backbone. In addition, the O-CH₃ stretching mode of PMMA at 1451 cm^{-1} in region two was noticed with the decreasing of peak intensity to broader peak as LiTFSI was added into the system. This might be attributed to the oxygen atom of O-CH₃ group that triggered Li⁺ ions to attach to it, caused a coordinative bond to form [43].

Furthermore, the peak at 1100 cm^{-1} assigned to the C-O-C stretching vibration of PMMA-PLA was observed to slightly shift to the lower wavenumber (1093 cm^{-1}) and become broader, then slowly start to disappear with the increasing LiTFSI content. The shifting and decreasing intensity of the peak is suggested due to the existence of the highly electronegative oxygen atom originating from C-O-C group that caused interaction between PMMA-PLA and Li⁺ moieties from lithium salt. As a result, this ion-dipole interaction hindered the rotation of the polymer chain and affected the ionic mobility by reducing energy barrier, thus allowing an increment of Li⁺ ions in the hybrid polymer backbone [44,45]. Sim et al. also reported the complexation between ether groups with Li⁺ ion could influence the surrounding of the electron of the fundamental characteristic peaks [46]. In addition, the peak at 1146 cm^{-1} corresponding to skeletal C-O-C stretching of pure PLA. The incorporation of lithium salt into hybrid polymer complex have shifted the wavenumber to the lower value and increased peak intensity (1133 cm^{-1}). The cation of Li⁺-TFSI is expected to coordinate with the polar groups in the PLA resulting in the complexation. Moreover, new peaks were noticed at wavenumber 1059 cm^{-1} which are believed to belong to S-N-S stretching of LiTFSI.

Nevertheless, it is highly recommended to study the interaction mechanism between hybrid polymer and lithium salt for a clearer view of how they interact with each other, which caused the peak changes, thus leading to the improvement of HGPEs performance. Figure 4 illustrated the proposed mechanism diagram to explain the interaction that occurred in the hybrid polymer complexes. Prior to Lithium salt, PMMA interacts with PLA through dipole-dipole forces between oxygen atoms from PMMA and carbon atoms from PLA [41]. When LiTFSI was incorporated into the system, they will be separated into Li^+ cations and TFSI⁻ anions. As discussed above, Li^+ tends to coordinate with the oxygen of ester groups from both PMMA and PLA (Figure 4(b)). The coordination of cation at ester groups had taken place during the complexation, where Li^+ migration happened by hopping from one site to another in the polymer backbone, as shown in Figure 4(c). Therefore, the migration of Li^+ ions is considered to have a crucial role in the transportation of ions, leading to the enhancement of ionic conductivity.

XRD characterization

Figure 5 demonstrates the XRD pattern of hybrid gel polymer electrolytes with various content of LiTFSI. It is clear from the figure that the PMMA-PLA hybrid polymer reveals a broad peak centered at $2\theta = 21^\circ$, exhibiting the amorphous nature of the host polymer. The modification in amorphousness of hybrid polymer can be observed as the diffraction peak became less intense upon the addition of LiTFSI 10. It can be explained due the interaction between hybrid polymer and lithium salt has occurred. In addition, the peak intensity is gradually decreased and shifted to lower 2θ with the addition of LiTFSI content to a sample containing 20 wt.%, denoted as LiTFSI 20. This phenomenon could indicate the increase in the amorphous nature of the polymer electrolyte systems due to the interaction between the lithium salt and host hybrid polymer [9]. Hodge et al. [47] reported that additional molecules like solvent and salt could reduce the crystallinity degree of peak intensity, thus performing an amorphous phase.

The incorporation of lithium salt into the present polymer electrolyte systems has broadened the hump and decreased the peak intensity, indicating that the hybrid polymer backbone became soft and improved the segmental motion of the electrolyte system [48]. Moreover, when the electric field was applied to the systems, it caused lithium-ion to form a new dative bond with the other group from the hybrid polymer complex, as mention in the proposed interaction mechanism. This phenomenon surprisingly helps ions move freely and improve the polymer chain's flexibility, resulting in the rise of the amorphous nature of HGPE. Besides, the decrement in peak intensity suggests an increase in amorphousness that helps in the migration of ions in the electrolyte system, which is responsible for enhancing ionic conductivity. However, the amorphous phase above LiTFSI 20 seems started to decrease. This can be explained due to the aggregation of lithium salt in the polymer blend backbone, which leads to the reappearance of the crystallinity peak [49]. A similar study reported by Ramesh et al. [50] found to be in good agreement with the present finding where at high LiTFSI content, the peaks intensity is slightly increased and sharper, indicating higher degree of crystallinity. Although hybrid polymer host provided more vacant site for ion coordination, the rise concentration of Li^+ ions as increase the LiTFSI content caused limited space and ions start to form a neutral ion pairs, hence contribute to the crystalline nature of the electrolyte systems.

DSC characterization

DSC analysis has been used widely to investigate the thermal degradation, phase transition, and crystallization of the polymers [50]. The selected contents of LiTFSI into the hybrid polymer PMMA-PLA based HGPEs were presented in Figure 6. The glass transition, T_g can be observed from a slight drop in heat flow from exothermic reaction to endothermic reaction [51]. A single T_g peak was noticed for each sample, implying the homogenous and compatibility of the PMMA-PLA polymer blend [52]. The T_g peak was varied based on different content of lithium salt, and sample LiTFSI 20 shows the lowest T_g value. The decreasing of T_g value could be interpreted by inter- and intra-molecular interaction of ester group from PMMA-PLA during the Li^+ coordination that triggered the polymer chain segmental motion increased with the enhancement of coordinating site flexibility, thus reduce T_g temperature. As tabulated in Table 2, T_g value decreases and further shifts to the lower temperature with an increasing weight percentage of LiTFSI. This can be interpreted based on the chain flexibility of the hybrid polymer backbone reflected by T_g value. In addition, it is believed the presence of TEGDME as a solvent in present systems also could likely affects the behavior of the DSC results. According to Li et al., TEGDME has lower volatility as well as shows high Li salt solubility [53]. Hence, is expected will improve the thermal stability of HGPEs [54]. Furthermore, TEGDME has plasticizer effects where they able to weakened the dipole-dipole interaction between the PMMA-PLA chain, which will allow the lithium ions to move freely through the network of hybrid polymer host chains [55]. In other words, the solvation of lithium cations with the oxygen of the ester functional group from the polymer host is enormously decreased.

Nevertheless, the polymer chain became tougher as more LiTFSI content was added that contributed to the increment of energy barrier, resulting in T_g peak shifted to the higher temperature. This finding was found to be in good agreement with an earlier study reported by He and Kyu [56] who discovered that lithium salt incorporation at high content had increased the T_g temperature. They also claimed that lithium salt has broadened the T_g peak related to the polymer network heterogeneity. In addition, Yazdani et al. [57] also reported similar pattern of T_g peak as present work, indicating amorphous nature of the samples.

Ionic conduction analysis

Figure 7 exhibited the complex impedance plot for PMMA-PLA-LiTFSI hybrid gel polymer electrolytes system at room temperature. The R_b value can be determined from the Cole-Cole plot obtained via impedance measurement in the intercept of the higher frequency region on the real impedance axis.

From Figure 7, it can observe that there are two types of Cole-Cole plot: (a) incomplete semicircle with spike, and (b) only spike. The presence of semicircle at high frequency could be due to a combination in parallel between R_b and constant phase element (CPE). CPE also can be denoted as “leaky capacitor” or bulk capacitance, indicating the migration of lithium-ions in the hybrid gel polymer electrolytes. The interface of electrode/electrolytes can regard as a capacitor since the present work used stainless steel

coin cell as a blocking electrode. Meanwhile, spike at low frequency is attributed to the connection in series of R_b and CPE which cause by the polarization effect at the electrode/electrolyte interface [58]. Therefore, the Cole-Cole plot consist of both semicircle and spike as demonstrated in Figure 7 for sample LiTFSI 5 can be represented by R_b connected in parallel with CPE_1 and fitted in series by another CPE_2 . Thus, the real and imaginary impedance of the bulk capacitance can be appointed as following equation [59]:

$$Z_r = \frac{\cos(\frac{\pi p}{2})}{k^{-1} \omega^p} \quad (1)$$

and

$$Z_i = \frac{\sin(\frac{\pi p}{2})}{k^{-1} \omega^p} \quad (2)$$

Hence, the relations of real and imaginary parts of a Cole-Cole plot composing a semicircle and spike are given by the equations [60]:

$$Z_r = \frac{R + R^2 k_1^{-1} \omega^{p_1} \cos(\frac{\pi p_1}{2})}{1 + 2R k_1^{-1} \omega^{p_1} \cos(\frac{\pi p_1}{2}) + R^2 k_1^{-2} \omega^{2p_1}} + \frac{\cos(\frac{\pi p_2}{2})}{k_2^{-1} \omega^{p_2}} \quad (3)$$

and

$$Z_i = \frac{R^2 k_1^{-1} \omega^{p_1} \sin(\frac{\pi p_1}{2})}{1 + 2R k_1^{-1} \omega^{p_1} \cos(\frac{\pi p_1}{2}) + R^2 k_1^{-2} \omega^{2p_1}} + \frac{\sin(\frac{\pi p_2}{2})}{k_2^{-1} \omega^{p_2}} \quad (4)$$

where k^{-1} corresponds to the bulk capacitance of the HGPEs, meanwhile, k_2^{-1} is denoted as capacitance which occurred due to the formation of electrical double layer at the interface of electrode/electrolyte during the impedance measurement. ω is angular frequency ($2\pi f$), R is equivalent to the bulk resistance, p_1 is assigned as the ratio of the angle between the diameter of the semicircle and the imaginary axis to the right angle subtended by the real and imaginary impedance axis and p_2 is the skew parameter that controls the degree of the tendency of the spike from the Z_r axis.

It is noticeable the incomplete semicircle has completely disappeared and was replaced with only spike in the impedance plot when 10 wt.% to 35 wt.% of LiTFSI was incorporated into the system. This phenomenon is suggested because only the resistive component of the electrolyte was remained [61]. The impedance plot consist of only spike in present work shows the spike did not begin at origin, thus the

equivalent circuit is containing the R_b and CPE connected in series. The relations between the Z_r and Z_i based on the equivalent circuit can be expressed as:

$$Z_r = R + \frac{\cos(\frac{\pi p_2}{2})}{k_2^{-1} \omega^{p_2}} \quad (5)$$

and

$$Z_i = \frac{\sin(\frac{\pi p_2}{2})}{k_2^{-1} \omega^{p_2}} \quad (6)$$

The R_b value decreased with the increment of LiTFSI content where sample LiTFSI 20 reveals the lowest R_b value, indicating will give highest ionic conductivity due to mobile charge carrier increased. Table 3 listed the parameter for the circuit element of all the HGPEs systems studied at room temperature. The value of parameters obtained from the fitting method was determined by trial and error until the fitted points as determined by trial and error until the fitted points accurately approximate the Cole-Cole plot.

The variation of ionic conductivity for PMMA-PLA hybrid polymer incorporated with different contents of LiTFSI based HGPEs is plotted in Figure 8. The addition of lithium salt into the hybrid polymer systems is a vital method as it could provide charge carriers (Li^+) from Li^+ -TFSI dissociation, which then contribute to the ionic conductivity enhancement. It can observe that there is an increment of ionic conductivity value from $10^{-6} \text{ S cm}^{-1}$ to $10^{-3} \text{ S cm}^{-1}$ when LiTFSI was introduced into the system. The increases in ionic conductivity with the increasing content of lithium salt are mainly caused by the dissociation of lithium ions, leading to the rise in mobile ions and ionic mobility [62]. In other words, this increment pattern could be divided into two factors: (1) segmental mobility, which influences the charge carrier mobility in the polymer matrix, and (2) concentration of mobile charge carrier, which depends on the interaction between the Li^+ and hybrid polymer host chain [31,63]. By blending PMMA with PLA also could be one of the reasons that help ionic conductivity to increase at a higher value. PMMA-PLA hybrid polymer is suggested can offer more vacant sites for ions conduction via ion-dipole interaction of Li^+ and oxygen of ester group from both PMMA and PLA as demonstrated in Figure 4. This finding further was supported by XRD analysis where the amorphous phase of PMMA-PLA increased with the presence of LiTFSI into the systems. The amorphous nature of the hybrid polymer systems provided a huge free volume space and facilitate fast Li^+ ion migration in the polymer network. Moreover, the addition of LiTFSI substantially reduces the T_g value of the hybrid polymer, indicating ease of the formation of the ion pairs as proven from DSC analysis and increases the segmental mobility, thus enhancing the ionic conductivity. Thus, the optimized contents of LiTFSI salt in the PMMA-PLA hybrid polymer system will result in higher ionic conductivity.

The optimum ionic conductivity of the complexes' electrolytes was observed at the PMMA-PLA-LiTFSI system with 20 wt.% LiTFSI is $1.02 \times 10^{-3} \text{ S cm}^{-1}$. It can be noticeable in Table 4 that the ionic conductivity of present work is compatible with previous work. The optimum ionic conductivity is achieved due to the balance between the increasing lithium-ion and decreasing ionic mobility. Also, the increase in free mobile ions number is one of the contributors to achieving the maximum ionic conductivity. This is because the presence of mobile ions could provide the higher amorphous structure of the polymer through favorable free volume, and therefore the ion migration will take place easily [63]. On the other hand, blending PMMA-PLA as host polymer in the present system can improve conduction properties as it offers more space volume for ionic mobility when incorporated with a lithium salt.

However, beyond 20 wt.% of LiTFSI, it shows the decreasing of ionic conductivity. The high lithium-ion content can explain this trend contributed from LiTFSI, which will give a greater tendency towards the ion aggregation and formation of neutral ion pairs. In addition, the high content of lithium salt could lead to overcrowded lithium ions and form a linkage between the salt itself, causing it to crystallize, which restricts the movement of free ions to move freely in the host polymer complex. As the free mobile ions decreased, hence triggered the reduction of ionic conductivity.

The dielectric studies are considered very useful in understanding the behavior of the hybrid polymer and its complexes with a lithium salt. From the dielectric properties studies, we can obtain the critical information into the charge distribution, ionic transport phenomenon, and the effects on the interface of electrode/electrolyte by polarization [68,40]. Figure 9 depicts the variation of the dielectric constant, ϵ_r , as a function of frequency at room temperature for all PMMA-PLA-LiTFSI HGPEs samples. The observed highest ϵ_r value at low frequency can be ascribed due to the presence of a space charge effect and triggered the charge carriers to accumulate at the interface of electrode/electrolyte, which is known as non-Debye behavior with no single relaxation time [69]. The space charge effect concerning the frequency is denoted as ion diffusion [70].

It can be noted from Figure 9, the ϵ_r value decreases with increasing frequency. The contribution of charge carriers can explain the decreasing pattern at high frequency decreases with increasing frequency due to high periodic reversal of the field at the electrode/electrolyte interface [71]. However, sample LiTFSI 20 and LiTFSI 25 show sudden drop and then rise again of ϵ_r value at high frequency. This situation might be due to the presence of trapped liquid in the hybrid gel polymer electrolyte, which causes higher ionic conductivity [8]. It can be observed at a higher frequency, only sample LiTFSI 5 reveals the constant value, indicating the creation of semicircle occurred in the Cole-Cole plot [36]. The ϵ_r of LiTFSI 10 to LiTFSI 35 is observed to decrease as frequency increased with no constant value, resulting in that the Cole-Cole plot only consists of the spike as shown in Figure 7.

Transport properties studies

There are various approaches have been developed to investigate the transport properties in terms of the number density of charge carrier ($\bar{n}$), mobility of charge carriers (μ) and diffusion coefficient of charge

carriers (D). They have included the fitting method [72], Rice and Roth model method [37], Broadband Dielectric Response (BDR) method [38] and FTIR deconvolution [73]. In this present work, the transport properties are evaluated using the fitting method since it was the most suitable method. It can extract the transport parameters from both semicircle-spike and only spike provided by the Cole-Cole plot without any special characteristic.

The transport parameters can be calculated from the following relations [39]:

$$D = \frac{(k_2 \varepsilon_r \varepsilon_o A)^2}{\tau_2} \quad (8)$$

$$\mu = \frac{eD}{k_b T} \quad (9)$$

$$\eta = \frac{\sigma}{\mu e} \quad (10)$$

where k_b is assigned as Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), T is temperature measured in kelvin, $\tau_2 = 1/\omega_2$ is a time constant corresponding to the maximum dissipative loss curve, where ω_2 is the angular frequency corresponding to the minimum imaginary impedance. e is electric charge constant ($1.602 \times 10^{-19} \text{ C}$), k_2 is $1/C$ where C can be obtained from the fitting Cole-Cole plot as listed in Table 3, ε_o is permittivity constant ($8.85 \times 10^{-14} \text{ F cm}^{-1}$), A is area of the blocking electrode interface, σ is ionic conductivity, and lastly ε_r can be obtained from the dielectric constant data at high-frequency range which ε_r start to display a constant value. Nevertheless, equation (8) only can be applied for sample LiTFSI 5 since only that system exhibits a constant value. Therefore, the value of D for sample LiTFSI 10 to LiTFSI 35 which containing only spike in impedance plot can be expressed as [40]:

$$D = D_o \exp^{[-0.0297 (\ln(D_o))^2 - 1.4348 (\ln(D_o)) - 14.504]} \quad (11)$$

where D_o is

$$D_o = \frac{4k_2^4 d^2}{R_b^4 \omega_2^3} \quad (12)$$

where d is thickness of the HGPEs sample.

Figure 10 showing the plot of transport properties for PMMA-PLA-LiTFSI based HGPEs system. It can be observed from the plot that the number density of the charge carrier inclined with the LiTFSI content. More lithium ions dissociated as increased the content of LiTFSI has contributed to improving the transportation of the Li^+ ions and responsible for enhancing the ionic conductivity. This finding was

supported by the rise of μ and D , which play critical parameters in the conduction trend until the optimum content was obtained. The increasing σ value up to 20 wt.% LiTFSI may be attributed to the improvement of Li^+ dissociation to be coordinated with the COOC ester group from PMMA-PLA hybrid polymer and was found in agreement with the interaction that occurred in the FTIR analysis [74]. In addition, the enhancement of μ , and D values up to LiTFSI 20 could be explained due to the availability of vacancy in the hybrid polymer matrix, thus created more pathways and smoothest the facilities of ion transport for ionic conduction. It is also believed that the addition of LiTFSI promotes more dissociation of Li^+ and thus, increased the diffusion rate, resulting in the rise amounts of D , which enhanced the ionic conductivity[59].

However, at the high content of LiTFSI, overcrowding of Li^+ occurred, and many quantities of trapped ions required more energy (due to limitation of space) to move in the polymer matrix, resulting in the decrement of ionic mobility and ion diffusion. It is believed that the space volume offered by PMMA-PLA hybrid polymer did not provide enough to support the number of Li^+ supplied by LiTFSI above 20 wt.%. In addition, the number of charge carriers decreased at high content due to the large amount of Li^+ leads to the tendency to form an ion aggregate and neural ion pairs, which in turn, reduces the ionic conductivity. Based on the findings, it can be suggested that the transport parameters are predominantly align with the ionic conductivity trend where they responsible to boost Li^+ coordination to the optimum value.

Conclusion

New hybrid gel polymer electrolytes comprising PMMA-PLA hybrid polymer complexed with LiTFSI system were successfully prepared. FTIR studies revealed the interaction of PMMA-PLA with LiTFSI through intra- and inter-molecular interaction between lithium ion and oxygen atoms of ester group from hybrid polymer backbone. The complexation in the HGPEs system with different LiTFSI salt contents has been confirmed to be at COOC, O-CH₃, and C-O-C groups. The free volume space provided by PMMA-PLA has facilitated the coordination and transportation of Li^+ ions in the hybrid polymer matrix. This led to the improvement of amorphous phase and decrement of glass transition of the polymer electrolytes which has been ascertained by XRD and DSC analysis, respectively. The incorporation of LiTFSI to the PMMA-PLA hybrid polymer complexes has resulted in the decrement of R_b value, leading to an increase to the optimum ionic conductivity with $1.02 \times 10^{-3} \text{ S cm}^{-1}$ for sample containing 20 wt.% LiTFSI. The dielectric behaviour helps understand the behaviour of HGPEs samples and was found to be follow non-Debye trend. Transport properties were investigated using a fitting method and found σ , μ , and D play a critical role in ionic conduction behaviour. As conclusion, we expect the outstanding result shown in this present work can be of importance for the advancement of practical application in lithium-ion battery.

Declarations

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Tables

Due to technical limitations, tables are only available as a download in the Supplemental Files section.

Figures

Figure 1

IR spectra for PMMA-PLA, raw LiTFSI and different content of LiTFSI based HGPEs.

Figure 2

Selected regions of IR spectra for HGPEs systems.

Figure 3

Changes of peak intensity at COOC group for varied LiTFSI content.

Fig. 4 Schematic diagram of proposed molecular interaction mechanism of (a) hybrid polymer PMMA-PLA, (b) LiTFSI with PMMA-PLA, and (c) ion hopping in the HGPEs system.

Figure 4

Schematic diagram of proposed molecular interaction mechanism of (a) hybrid polymer PMMA-PLA, (b) LiTFSI with PMMA-PLA, and (c) ion hopping in the HGPEs system.

Figure 5

XRD pattern of hybrid gel polymer electrolyte at selected content of LiTFSI.

Figure 6

DSC thermograms at selected contents of LiTFSI.

Figure 7

Cole-Cole plot for all HGPEs system.

Figure 8

Ionic conductivity versus weight percentage of LiTFSI salt in HGPEs samples.

Figure 9

Frequency dependence of dielectric constant for the HGPEs system at room temperature.

Figure 10

(a) number of ions and (b) mobility of charge carrier and diffusion coefficient versus content of LiTFSI.

Supplementary Files

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