

Study of the Effect of Poly (Ethylene Carbonate) Concentration on the Ionic Transport of PLA- LiCF₃SO₃ Based Polymer Electrolyte

Fairuzdzah Ahmad Lothfy^{1,2}, Hartini Ahmad Rafeaie³, Siti Zafirah Zainal Abidin^{2,4*} and Ab Malik Marwan Ali^{2,4*}

¹Applied Sciences Centre, Universiti Teknologi MARA Pahang, 26400, Bandar Tun Abdul Razak Jengka Pahang, Malaysia

²Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

³Centre of Foundation Studies, Universiti Teknologi MARA Selangor, Kampus Dengkil, 43800 Dengkil, Selangor, Malaysia

⁴Ionic Materials and Devices (iMADE) Research Laboratory, Institute of Science, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

*Corresponding author (e-mail: ammali@uitm.edu.my, szafirah@uitm.edu.my)

Polymer electrolytes with high ionic conductivity are presently of considerable interest due to their potential use as electrolytes in electrochemical devices. However, the development and real-world applications of polymer electrolytes are restricted by their weak ionic conductivity at ambient temperature. The ionic conductivity of polymer electrolytes was enhanced by the addition of plasticizers at the appropriate concentrations. Therefore, the objective of this investigation is to optimize the ionic conductivity of the polymer-based electrolyte by incorporating varying weight percentages of polypropylene carbonate (PC) into the PLA-LiCF₃SO₃-based electrolyte. The PLA-LiCF₃SO₃ exhibits a maximal ionic conductivity of $9.05 \times 10^{-3} \text{ Scm}^{-1}$ at ambient temperature, which is approximately 25 wt. % PC (PC-25). PC-25 has a diffusion coefficient (D) of $6.06 \times 10^{-20} \text{ cm}^{-3}$, a number density of $2.44 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$, and an ionic mobility of $9.33 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \cdot \text{s}$. The ionic transport system is influenced by the structural features of the polymer host, as evidenced by the maximum amorphousness degree of the PC-25 found through X-ray diffraction (XRD) spectroscopy. The results suggest that the PC-25 system, which is comprised of PLA-LiCF₃SO₃ with a 25 wt.% PC, has the potential to be a viable option for use as an electrolyte in energy storage devices.

Keywords: Polylactic acids; polylactic acid; polypropylene carbonate; ionic conductivity; amorphousness

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Polymer electrolytes (PEs) have garnered significant interest from researchers over the past forty years due to their distinctive characteristics, such as electrode-electrolyte interaction, simplicity in salt doping, manufacturing, and favorable mechanical properties [1]. The potential utilization of PEs in diverse domains has generated sustained interest. PEs have been utilized in several applications including electrochromic devices, capacitors, batteries, photoelectrochemical cells, and sensors [2].

A few of polymer electrolyte currently has been studied is synthetic polymer such as polypropylene (PP), polyvinyl carbonate (PVC), polyvinylidene fluoride (PVDF), and others, are utilized as electrolyte hosts [3], [4]. Synthetic polymers are non-biodegradable and have an influence on petroleum resources, making them environmentally harmful. To reduce e-waste, synthetic polymers as polymer hosts are being replaced by biomaterials. Natural polymers and biopolymers are used interchangeably, and are often characterized by

cost-effectiveness, good solvent compatibility, high film-forming capability, and natural abundance. Consequently, polylactic acid (PLA), a naturally occurring polymer, has been selected as the polymer host for this investigation. In addition to possessing degradation capabilities, the PLA satisfied the minimum requirements of a polymer substrate that, according to its chemical structure, is enriched in numerous oxygen-containing functional groups. The insertion of salt ions enables the formation of dative bonds due to the near proximity of these ions to functional groups within the polymer structure. The selection of lithium salt for blending with PLA is attributed to the fact that lithium ion (Li⁺), characterized by its low mass, high energy, and power density, which is an ideal charge carrier source in PEs [2].

Nevertheless, the utilization of polymer electrolytes is impeded by their relatively low ionic conductivity at room temperature. This minimal conductivity is the result of a weak ion-conductive

mechanism. The dynamics of polymer chains are critical for transporting ions in polymer electrolytes. As a result, the movement of chains within PE's multiphase complex structures and the modification of these structures to improve ion conductivity are highly intriguing. It is common to incorporate plasticizers with a lower molecular weight into PE systems to improve ionic conductivity.

The plasticizers endow the polymer electrolytes with high ion mobility and salt-solvating power. Researchers have reported that plasticizers modify polymers' morphology to increase their flexibility by increasing the distance between molecules and decreasing the number of polar groups in the polymer chain. The conductivity of electrolytes at room temperature can be increased by employing the plasticizer such as propylene carbonate (PC), ethylene carbonate (EC), or low molecular weight polyethylene glycols [5]. Research has unequivocally demonstrated that ion conductivity can be significantly enhanced through the reduction of crystalline regions in the polymer matrix, which occurs upon the introduction of plasticizer molecules [6]. The ion transport in polymer electrolytes is thought to be mostly through the amorphous phase of the polymer rather than the crystalline phase [7]. Numerous studies have thus concentrated on augmenting the amorphous phase of the host polymer matrix to enhance the ionic conductivity of SPEs [7]. The molecules of the plasticizer intercalate between the polymer chains, obstructing their interaction and recrystallization. In addition, plasticizers promote the dissociation of ions. As a result, ion conductivity increases in plasticized polymeric electrolytes because of the increased fraction of liberated ions and the accelerated motion of polymer chains. Nevertheless, the impact of plasticizer on the properties of the SPE is contingent upon the plasticizer's viscosity and the interplay between the plasticizer of the polymer and the ion [8].

Therefore, different concentrations of polypropylene carbonate (PC) were introduced into the system as a plasticizer in this investigation. To achieve the greatest ionic conductivity of this PLA-LiCF₃SO₃ polymer electrolyte system, the optimal concentration must be obtained. The current study investigated the impact of PC concentration on the electrical and structural characteristics of electrolyte films composed of PLA-LiCF₃SO₃ solid polymer composite.

EXPERIMENTAL

Methodology

The synthesis of polylactic acid (PLA; Good Fellow: Mw. 116k g/mol) at a 10% (w/v) concentration was accomplished by dissolving PLA in 10 mL of 1-4 dioxane at 50 °C for 6 hours. The second solution was prepared by diluting 50 wt% of lithium trifluoromethane sulfonate (LiCF₃SO₃; purity: 97.0%, Thermo Fisher Scientific, United States) in 10 mL of methanol at

room temperature. Both solutions were blend and continuously stirred until a homogeneous solution was achieved. Therefore, to produce plasticized polymer blend electrolytes, different quantities of propylene carbonate (PC; R/M Chemical Malaysia; molecular mass: 102.09 g/mol) were incorporated into the mixture as a plasticizer (PC). The PC was varied with a variation of (5, 10, 15, 20, 25) wt.%. Each sample was stirred at 50 °C for 24 hours. The homogenous solution wee dried with slowly evaporated at room temperature. The electrolyte samples were labeled as PC-5, PC-10, PC-15, PC-20, and PC-25, representing PLA: LiCF₃SO₃ with 5 wt.%, 10 wt.%, 15 wt.%, 20 wt.%, and 25 wt.% of PC, respectively. The conductivity and structural characteristics of these samples have been determined.

Characterization

The conductivity properties of the samples were determined using EIS, while the structural properties were investigated using XRD, and ATR-FTIR spectroscopy. Electrochemical impedance spectroscopy (EIS) was employed to determine the ionic conductivity of the polymer electrolyte film, which involved the placement of a solid electrolyte between two stainless steels. The ZiveSP2 Impedance Potentiostat was employed to conduct EIS analysis at frequencies ranging from 10 μHz to 2 MHz. ATR-FTIR analysis was carried out using a PerkinElmer Spectrum spectrometer. with wavenumbers ranging from 400 to 4000 cm⁻¹ at room temperature. X-ray Diffraction was analyzed in the range of 2θ = 5°–60° with a scan rate of 5 °/min at room temperature.

RESULTS AND DISCUSSION

Impedance and conductivity analysis

Electrochemical impedance spectroscopy (EIS) is a relatively new and widely used technique for extracting useful information from complex electrochemical systems in order to investigate the electrical electrochemical properties of polymer electrolytes such as bulk resistance (R_b), ionic conductivity, electrode-electrolyte contact behavior, and charge carrier type (ions or electrons) and the interfacial region of electronically conducting electrodes [9], [10]. Figure 1 illustrates that the R_b value for PLA-LiCF₃SO₃ BPEs decreases from 232Ω to 24.89Ω as the PC concentration increases to 25 wt.%. In Figure 1 (a-e), the semicircle in the high-frequency region was not present due to the fact that the preponderance of the anions and cations in the electrolyte were transported in the opposite direction, towards the stainless-steel electrodes, to produce the double layer capacitor at the electrode-electrolyte interfaces [7]. The employment of the electrical equivalent circuit (EEC) model indicates to be a method for analyzing the electrochemical impedance spectroscopy (EIS) of each electrolyte system [11]. The cation migration in a PLA-BPEs can be represented by a series-connected

capacitor and resistor equivalent circuit element. The EEC fitting parameters are shown in Table 1. The Z_{CPE} is given in Equation (1).

$$Z_{CPE} = \frac{\cos(\frac{\pi n}{2})}{C\omega^n} - \frac{\sin(\frac{\pi n}{2})}{C\omega^n} \quad (1)$$

where the angular frequency is denoted by the symbol of ω , the CPE capacitance is denoted by the letter C , and the imaginary axis deviation of the Nyquist plot is denoted by the letter n . The Nyquist plot demonstrates that only the resistive component of the electrolyte dominates. As illustrated in the inset of Figure 1 (a-e), the CPE and R_b are connected in series in the high

frequency region. It demonstrates that most of the anions and cations in the BPEs undergo a transfer to the electrodes' surface, resulting in the formation of a double layer. This process causes the semicircle to vanish in electrolyte systems [11]. In this case, the values of Z' and Z'' of the EEC can be demonstrated mathematically Equation (2) and Equation (3), respectively.

$$Z' = R + \frac{\cos(\frac{\pi n}{2})}{C\omega^n} \quad (2)$$

$$Z'' = \frac{\sin(\frac{\pi n}{2})}{C\omega^n} \quad (3)$$

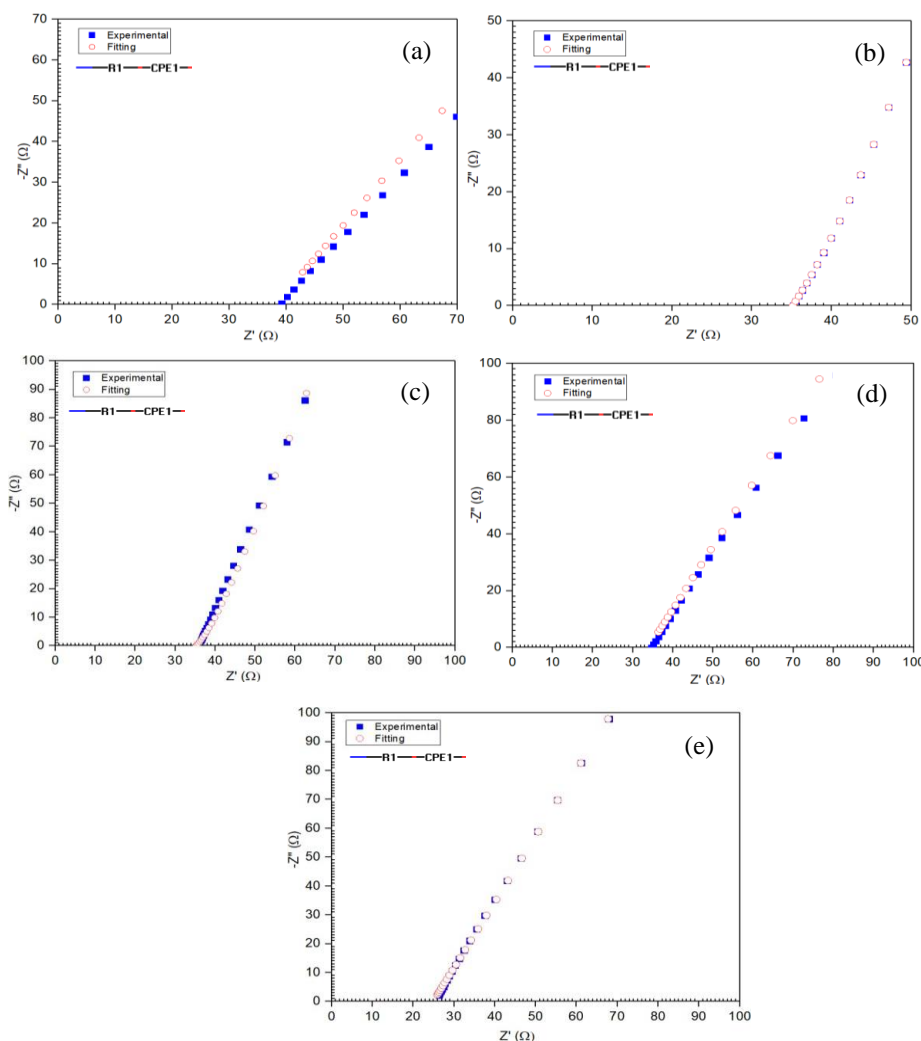


Figure 1. Experimental and EEC fitting plots for samples with various concentrations of PC in PLA-LiCF₃SO₃ BPEs (a) PC-5 (b) PC-10 (c) PC-15 (d) PC-20 and (e) PC-25.

In Table 1, K represents the reciprocal of the capacitance at low frequencies. Since there is just one spike in the Nyquist plot, the ion mobility (μ), diffusion coefficient (D), and number density (n_i) of ions are calculated by using the Equation 4.

$$D = D_o \exp\{-0.0297[\ln D_o]^2 - 1.4348 \ln D_o - 14.504\} \quad (4)$$

D_o is referring to the Equation 5.

$$D_o = \left(\frac{4k^2 l^2}{R_b^4 \omega_{min}^3} \right) \quad (5)$$

where l is the film thickness and ω_{min} is the angular frequency corresponding minimum to Z' value. The mobility (μ) of the ions is determined using Equation 6.

$$\mu = \left(\frac{eD}{k_b T} \right) \quad (6)$$

where K_b represents the Boltzmann constant and T represent the absolute temperature, density of ions, n_i is determined using Equation 7.

$$n_i = \frac{\sigma_{dc}}{e\mu} \quad (7)$$

In accordance with Table 2, the D and μ values increased as the PC increased from 5 to 25 wt. %. D is improved as a result of the increase in chain flexibility in PLA-LiCF₃SO₃ BPEs, which indirectly increased the μ and n_i values, leading to a rise in conductivity. The increment of these values can also result in a decrease in the force of attraction between the anions and cations of salt by PC [11].

Figure 2 illustrates the conductivity that varies with the concentration of PC in PLA-LiCF₃SO₃ BPEs

at ambient temperature. The specific interaction between PC, LiCF₃SO₃, and PLA is revealed by the conductivity's interdependence with PC concentration. DC conductivity increases as PC concentration increases, as indicated by observations. In BPEs, the ether and ester group of PC functions as an alternative mechanism for the movement of free ions from salt. Consequently, PC boasts a high concentration of ether and ester groups, which enables it to dissociate a greater quantity of salt and weaken the intra and inter-hydrogen bonding in the polymer matrix. This leads to an increase in amorphous structures, which are crucial for the ion transport process. The presence of a concentration exceeding 25 wt.% in the sample renders it is impossible to prepare as a result of its inadequate mechanical properties. It is due to plasticizers decreased the mechanical strength of PEs [12]. The results indicate that the maximal conductivity of PLA-LiCF₃SO₃ BPEs was achieved at $9.053 \times 10^{-3} \text{ Scm}^{-1}$. DC conductivity was exhibited by orderly PLA-LiCF₃SO₃ BPEs at a maximum of $7.03 \times 10^{-4} \text{ Scm}^{-1}$. The conductivity increases as the concentration of PC increases due to the increase in the D , μ , and n_i [12]. The conductivity values are in alignment with the calculated values in Table 2, and these results are in line with the Rice and Roth model as indicated in Equation 8.

$$\sigma = \frac{2}{3} \left[\frac{(Ze)^2}{k_B T m} \right] \eta E_A \tau \exp\left(\frac{E_A}{k_B T}\right) \quad (8)$$

where, σ , Z , e , E_A , and m represent conductivity, density, valency, and mass, respectively, of the conducting ions. T , k_B , e , and represent the absolute temperature, Boltzmann constant, electronic charge, and time required for ions to travel between sites, respectively.

Table 1. The EEC fitting parameters for plasticized electrolyte systems at room temperature.

Sample	n(rad)	K(F ⁻¹)	R _b (Ω)	CPE (F)
PC-5	0.65	5.32 x 10 ⁴	38.26	1.08 x 10 ⁻⁵
PC-10	0.78	1.44 x 10 ⁵	34.97	1.10 x 10 ⁻⁵
PC-15	0.81	8.93 x10 ⁴	35.91	1.12 x 10 ⁻⁵
PC-20	0.72	9.26 x 10 ⁴	32.97	1.16 x 10 ⁻⁵
PC-25	0.74	4.81 x 10 ⁴	24.89	2.08 x 10 ⁻⁵

Table 2. The μ , D and n values at room temperature.

Sample	D (cm ² s ⁻¹)	μ (cm ² V ⁻¹ s)	n_i (cm ⁻³)
PC-5	1.41 x 10 ⁻⁶	5.40 x 10 ⁻⁵	8.52 x 10 ¹⁹
PC-10	1.59 x 10 ⁻⁶	6.09 x 10 ⁻⁵	1.00 x 10 ²⁰
PC-15	1.60 x 10 ⁻⁶	6.13 x 10 ⁻⁵	1.01 x 10 ²⁰
PC-20	2.40 x 10 ⁻⁶	9.17 x 10 ⁻⁵	1.76 x 10 ²⁰
PC-25	2.44 x 10 ⁻⁶	9.33 x 10 ⁻⁵	6.06 x 10 ²⁰

This conductivity value also suggests that the physicochemical properties of the individual plasticizers, such as the high dielectric constant of PC ($\epsilon' = 64$), significantly contribute to the improvement of conductivity performance [13]. The impact of the plasticizer on mobility and conductivity was attributed to changes in properties, including the dielectric constant, polymer-plasticizer interaction, and ion plasticizer coordination [1]. The inclusion of PC is designed to increase the free volume of PLA-LiCF₃SO₃ BPEs, which will result in a greater ionic conductivity due to the increased free volume within the polymer, the more readily occurring polymer chain rotation, and the easier ion transport in PLA-LiCF₃SO₃ BPEs [12]. This result is comparable to that of Gupta et al. (2017) regarding the effect of glycerol on the ionic conductivity of lithium tetraborate-hydroxyethyl cellulose (Li₂B₄O₇-HEC) BPEs, which increased from $3.8 \times 10^5 \text{ Scm}^{-1}$ to $4.4 \times 10^3 \text{ Scm}^{-1}$ [14]. PC, which has a very low molecular weight of 102.89 gmol^{-1} , also makes salts dissolve better and adds more charge carriers, which helps the ionic hopping mechanism [15].

Furthermore, the incorporation of PC into the PLA polymer matrix alters the physical characteristics and enhances the segmental mobility and amorphous nature of the film, thereby increasing the conductivity of PLA-LiCF₃SO₃ BPEs [14]. This interaction enhances the ionic conductivity of polymer electrolytes. PC

molecules are relatively small in size, which enables them to easily penetrate the polymer matrix and interact with polymer chain molecules. This results in a reduction in the cohesive force between polymer chains and an increase in chain flexibility [14]. The dissociation of the ionic dopant facilitated the migration of the cation through the plasticizer-rich phase, resulting in the formation of liberated Li⁺ ions. This will result in a reduction in fragmentation (or an increase in linkage) of the plasticizer-rich phase, which will facilitate the transport of ions. The increase in conductivity was also believed to be caused by the dissociation of the ionic dopant, which leads to the production of free Li⁺ ions and their effortless migration through the plasticizer-rich phase [1]. This research is comparable to that of Ulaganathan et al. (2010), who reported that Li⁺ ion conduction in the polyvinyl acetate (PVAc)-based hybrid polymer electrolyte system PVAc/polyvinylidene fluoride-hexafluoropropylene/lithium perchlorate/ethylene carbonate (PVAc/PVDF-HFP/LiClO₄/EC) achieves the maximal conductivity of $3.98 \times 10^{-4} \text{ S cm}^{-1}$ at 303 K. The report stated that the plasticizer would dissolve sufficient charge carriers and provide a more mobile medium for the ions to improve the sample's conductivity [16]. As a result, the incorporation of PC into the PLA-LiCF₃SO₃ BPEs facilitated the dissociation of ion pairs into free ions and increased the segmental mobility of the polymer chain, thereby facilitating the movement of ions in the host matrix.

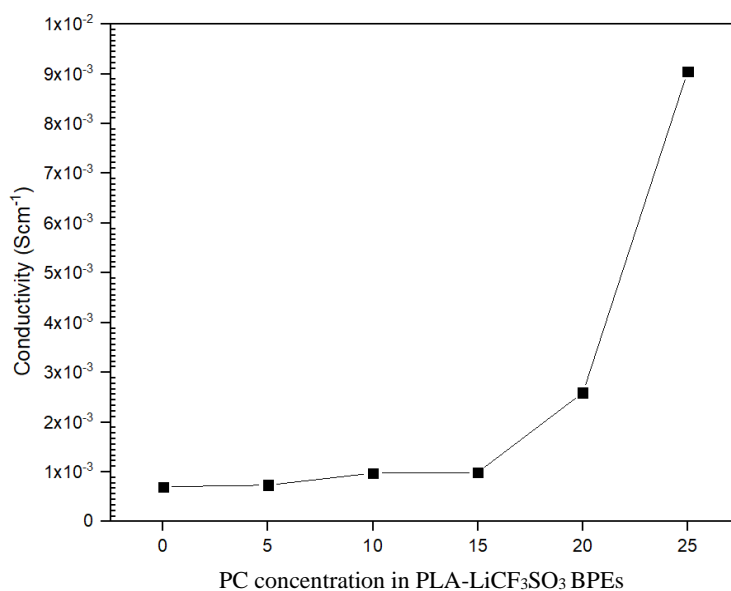


Figure 2. Conductivity of different concentration of PC (wt.%) in the PLA-LiCF₃SO₃ BPEs.

ATR-FTIR Analysis

Figure 3 (a) illustrates the alteration in peak intensity as the concentration of PC increases from 0 to 25 wt.%, while Figure 3 (b) illustrates the enlargement of PC-0 in Figure 3 (a). The interactions between the salt atoms, plasticizer molecules, and PLA polymer chains may be responsible for the observed changes. First, the Li⁺ ions function as Lewis' acids and interact with the Lewis base ether groups on the PLA polymer molecules. Second, the carbonyl oxygen in PC plasticizer molecules is an electron donor [8]. Therefore, it interacts with Li⁺ ions with great affinity. As a result, it competes with CF₃SO₃⁻ anions and ether groups of the PLA polymer chains to absorb Li⁺ ions. This results in the formation of Li⁺-CF₃SO₃⁻ ion-ion, Li⁺-PLA ion-dipole, and Li⁺-PC ion-molecule interaction [8]. This results in improved chain mobility of Li⁺ in the system, which indirectly contributes to the greater conductivity value. These interactions are depicted in Figure 3. After introducing the PC in PLA- LiCF₃SO₃, the finding revealed a new peak at 1558 cm⁻¹. This peak corresponds to the PC peak at 1556 cm⁻¹ (Figure 4), which shifted to 1558cm⁻¹ after being mixed with PLA- LiCF₃SO₃ BPEs. A few PC-0 peaks are shifted by interaction from 1741, 1637, 1462, 1382, 1363, and 1267 cm⁻¹ to 1756, 1643, 1465, 1386, 1358, and 1273 cm⁻¹ for PC-25. After incorporating the PC into the BPEs, the new peak at 1032 cm⁻¹, which corresponds to the free ion of SO₃⁻, is clearly visible. Aside from that, the region of C-O and C=O band assignment increased as PC concentration in PLA-LiCF₃SO₃ BPEs

rose. The area of these ranges illustrates the way Li⁺ ions interact in PLA BPEs. This is in accordance with a study conducted by Gupta et al. (2019), which observed that the presence of glycerol also resulted in changes in the band region between 800 and 1200 cm⁻¹. This information was provided on both the alcoholic (C-O) stretching bands and the uneven and isobilateral (C-O-C) stretching vibration bands [1]. Figure 5 displayed the percentage of C-O and C=O interactions at samples with various PC concentrations in PLA- LiCF₃SO₃. The increase in the percentage of interacting bands may be attributable to the increase in amorphous properties of PLA-LiCF₃SO₃ BPEs aligned with the addition of PC concentration. The plasticizer has an effect on the segmental motion of the polymer, which contributes to the increase in the polymer's amorphous degree [17]. Figure 6 depicts the schematic effect of PC plasticizer on the ion dissociation and increase in amorphous phase. Earlier studies found that the addition of PC increases the amorphous humps, which they attributed to the disruption of the hydrogen bonds that formed the crystalline phase in the polymer substrate [18]. This Li⁺ ion transport mechanism can be characterized as the movement of Li⁺ ions between complex sites, aided by the segmental motion of the PLA matrix [19]. Consequently, the migration of Li⁺ ions became easier and the interaction between Li⁺ ions and PLA increased. The interaction may be a result of the rising proportion of C-O and C=O interactions. Figure 6 depicts this phenomenon as it occurred.

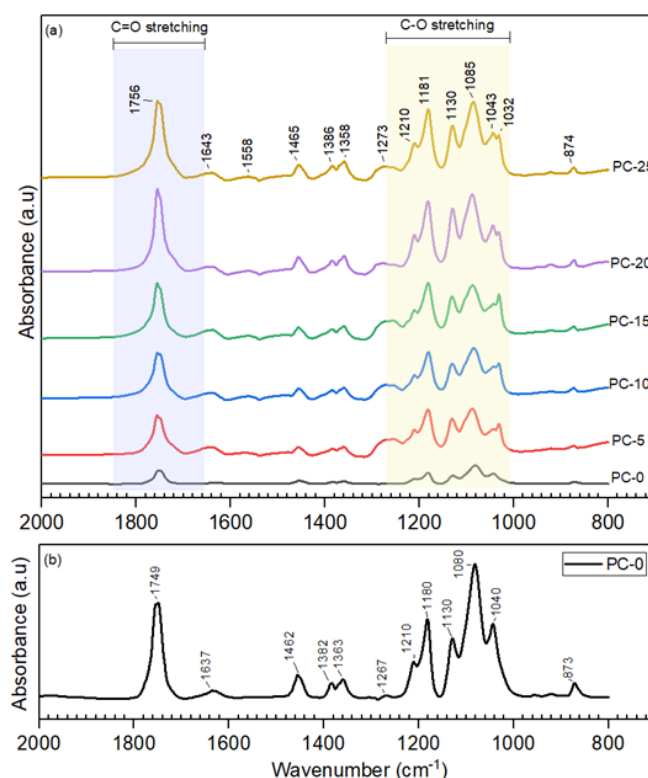


Figure 3. ATR-FTIR spectra of (a) different concentration of PC in PLA- LiCF₃SO₃ (b) Enlargement spectra for PC-0.

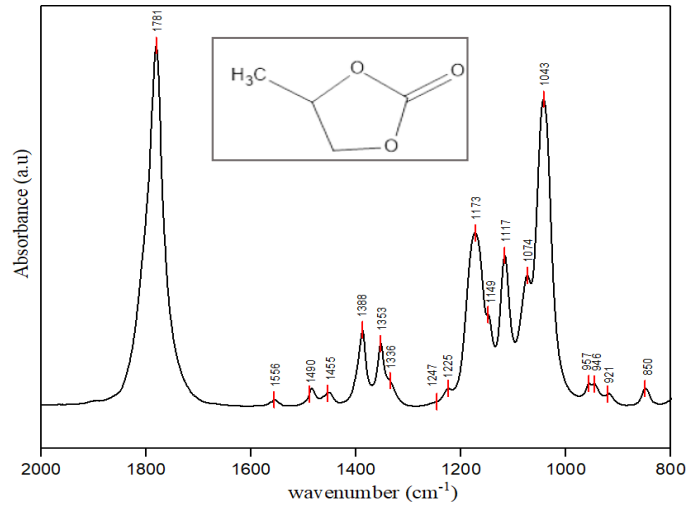


Figure 4. ATR-FTIR spectra of propylene carbonate plasticizer (PC).

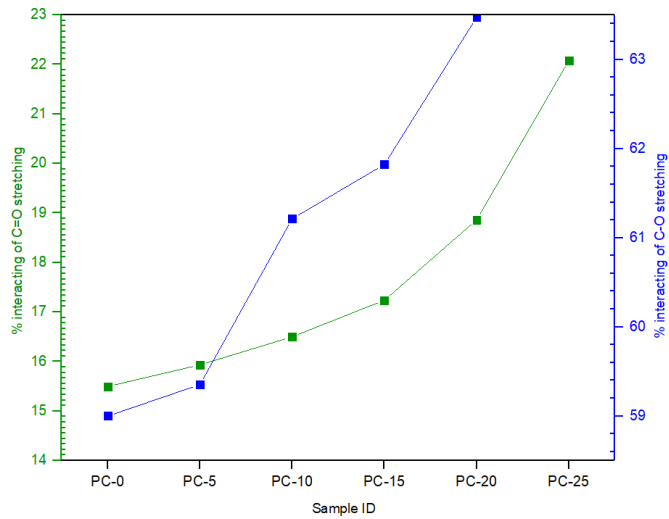


Figure 5. Interacting percentage (%) of C=O and C-O stretching ions in PC-0, PC-5, PC-10, PC-15, PC-20, and PC-25.

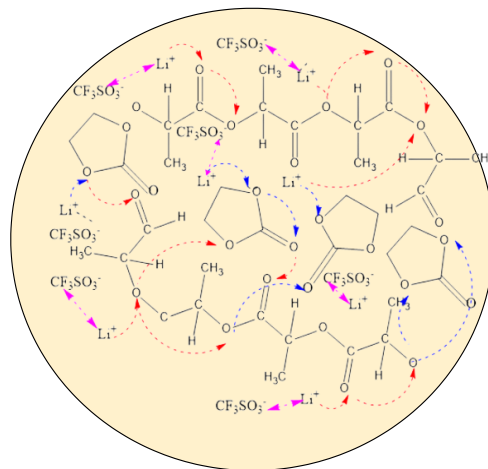


Figure 6. Proposed mechanism of hopping Li⁺ ion interactions: Li⁺-CF₃SO₃⁻ ion-ion interaction (◀---▶), Li⁺-PLA ion-dipole interaction(-->), and Li⁺-PC ion-molecule interaction (--▶).

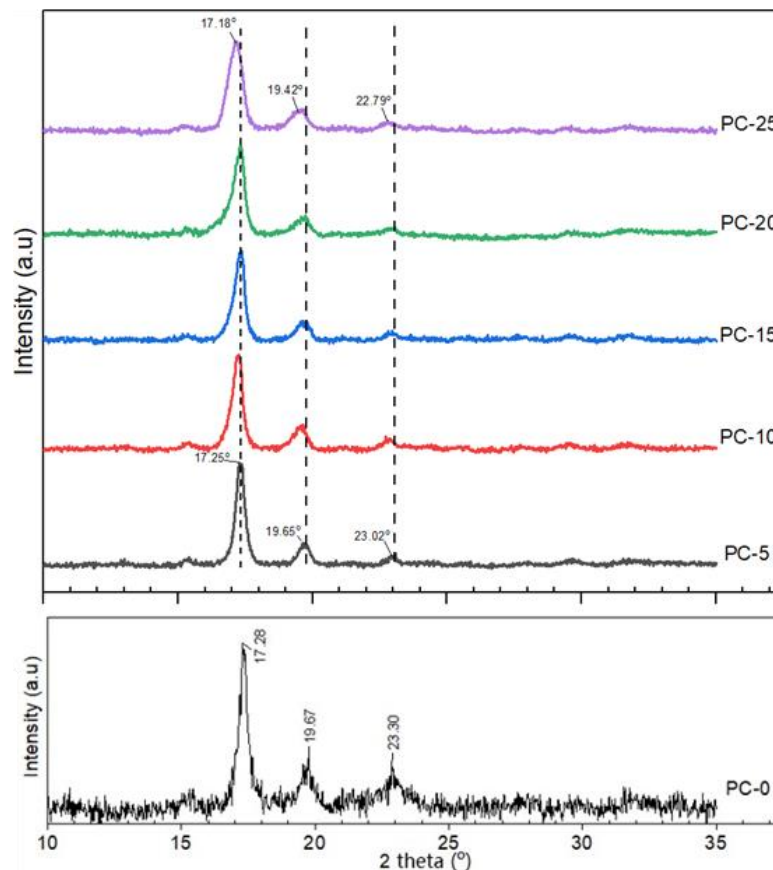


Figure 7: XRD spectra of various concentration of polypropylene carbonate (PC) in [PLA-LiCF₃SO₃] BPEs.

XRD Analysis

Figure 7 depicts the X-ray diffractograms for various PC concentrations in PLA- LiCF₃SO₃ BPEs. As shown in the figure, the addition of PC modifies the crystal structure of PLA- LiCF₃SO₃ BPEs. The PC-0 has Bragg angles located at $2\theta = 17.28^\circ$, 19.67° , and 23.30° . By adding up to 25 wt.% PC, these peaks were shifted to $2\theta = 23.30^\circ$, 19.42° , and 22.79° , respectively. The changes in shape of these three peaks increased with increasing PC concentration. The changed shapes are in accordance with the Full Width at Half Maximum (FWHM) data. Figure 7 depicts the X-ray diffractograms for various PC concentrations in PLA- LiCF₃SO₃ BPEs. As shown in the figure, the addition of PC modifies the crystal structure of PLA- LiCF₃SO₃ BPEs. The PC-0 has Bragg angles located at $2\theta = 17.28^\circ$, 19.67° , and 23.30° . By adding up to 25 wt.% PC, these peaks were shifted to $2\theta = 23.30^\circ$, 19.42° , and 22.79° , respectively. The changes in shape of these three peaks increased with increasing PC concentration. The changed shapes are in accordance with the Full Width at Half Maximum (FWHM) data [1]. Figure 8 shows that the FWHM for these three peaks grew as the system's PC concentration rose. In comparison to the bare PLA- LiCF₃SO₃ BPEs sample, the FWHM of higher PC concentrations is broader, indicating that the crystal structures of the plasticized

electrolyte are more amorphous after the addition of PC to the systems. Figure 8 shows that the FWHM for these three peaks grew as the system's PC concentration rose. In comparison to the bare PLA- LiCF₃SO₃ BPEs sample, the FWHM of higher PC concentrations is broader, indicating that the crystal structures of the plasticized electrolyte are more amorphous after the addition of PC to the system [14]. The broader peak at the highlighted peaks suggest a higher degree of amorphous structure [20]. This finding aligns with Kesavan et al., (2014) discovery that the effect of ethylene carbonate (EC) on the polyethylene oxide: polyvinylpyrrolidone: lithium perchlorate (PEO: PVP: LiClO₄) system caused the hump to become relatively larger, suggesting that this is due to a decrease in crystallinity. This finding aligns with Kesavan et al., (2014) discovery that the effect of ethylene carbonate (EC) on the polyethylene oxide: polyvinylpyrrolidone: lithium perchlorate (PEO: PVP: LiClO₄) system caused the hump to become relatively larger, suggesting that this is due to a decrease in crystallinity [21]. Arunkumar et al. (2017) also reported that by increasing the concentration of EC in polyvinyl chloride- polybutylmethacrylate-lithium perchlorate (PVC-PBMA-LiClO₄) electrolyte, the amorphous nature increased, as evidenced by the broad halo broadness [6]. PC can dissociate more LiCF₃SO₃ and disrupt the hydrogen bonds between

PLA polymer chains. Schematically the role of PC on ion dissociation and increase of amorphous phase is shown in Figure 9. The small molecular size of the PC plasticizer causes the crystalline form of the PLA-LiCF₃SO₃ BPEs to be disrupted [12]. This is owing to the fact that adding low molecular weight PC to a complex system encourage inter-intrachain separation as a result of PC being trapped in the polymer matrix [12]. Upon addition of PC, amorphous humps are enhanced, and they attributed to the disruption of

hydrogen bonds that built up crystalline phase through the polymer host. A conclusion can be drawn that the PC has decreased the number of active centers, reducing the intramolecular and intermolecular interactions between the polymer chains. Consequently, this enhances the overall amorphous phase of the prepared samples, which serves as a pathway for ion conduction and enhances charge carrier transport [22]. This phenomenon was the result of increased ionic conductivity.

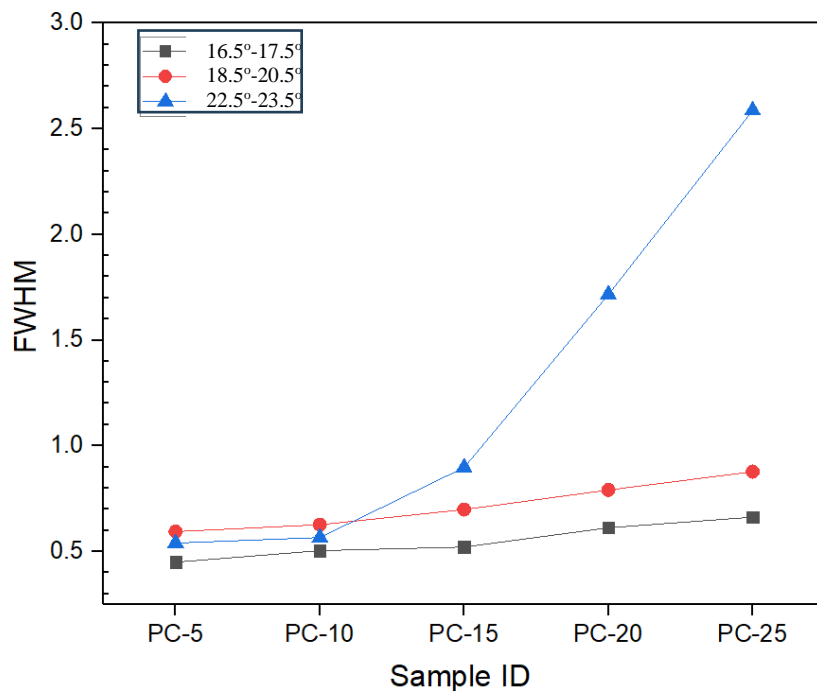


Figure 8. Full Width Half Value Maximum (FWHM) of different peak range (Θ°) for various samples ID (different concentration wt.% of PC).

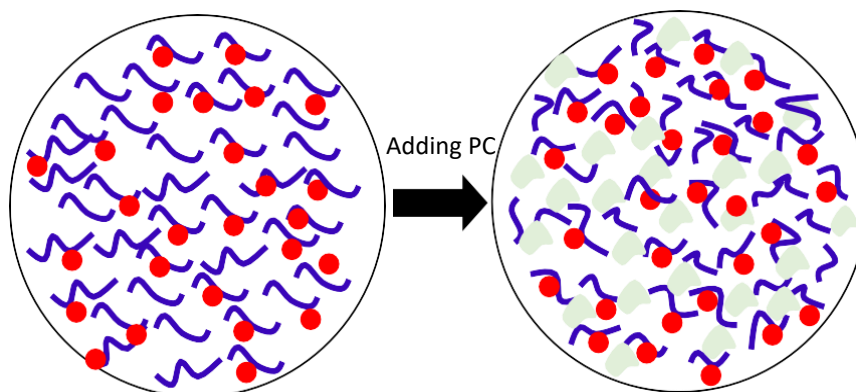


Figure 9. Schematically the role of PC on ions dissociation and increase of amorphous phase

CONCLUSION

In conclusion, the optimal conductivity of PLA-LiCF₃SO₃ achieved at room temperature is $9.05 \times 10^{-3} \text{ Scm}^{-1}$ with the addition of 25 wt.% PC. The diffusion coefficient (D), ionic mobility, and number density were measured to be $2.44 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$, $9.33 \times 10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}$, and $6.06 \times 10^{20} \text{ cm}^{-3}$. The complexation of PC and PLA-LiCF₃SO₃ in all samples was observed through changes in the ATR-FTIR spectra. The growing fraction of C-O and C=O interactions can be used to justify the increased interaction of Li⁺ ions with PLA and PC. The inclusion of PC increased the amorphousness of the samples, as seen by a broadening of their FWHM. Samples containing 25 wt.% PC in PLA-LiCF₃SO₃ had the largest percentage interaction between PC and PLA-LiCF₃SO₃ BPEs at C=O and C-O-C, as well as the highest amorphousness.

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REFERENCES

1. Gupta, S. & Varshney, P. K. (2019) Effect of plasticizer on the conductivity of carboxymethyl cellulose based solid polymer electrolyte. *Polymer Bulletin*, **76**(12), 6169–6178.
2. Tan, W. L., Abu Bakar, M. & Abu Bakar, N. H. H. (2013) Effect of anion of lithium salt on the property of lithium salt-epoxidized natural rubber polymer electrolytes. *Ionics*, **19**(4), 601–613.
3. Nofal, M. M., Shujahadeen B. Aziz, Hewa O. Ghareeb, Jihad M., Hadi Elham M. A. & Dannoun, S. I. A. S. (2022) Impedance and Dielectric Properties of PVC:NH₄I Solid polymer electrolytes (SPEs): Steps toward the fabrication of SPEs with high resistivity. *Materials*, **15**(2143), 1–15.
4. Wu, Y., Li, Y., Wang, Y., Liu, Q., Chen, Q. & Chen, M. (2022) Advances and prospects of PVDF based polymer electrolytes. *Journal of Energy Chemistry*, **64**, 62–84.
5. Frech, R. & Chintapalli, S. (1996) Effect of propylene carbonate as a plasticizer in high molecular weight PEO-LiCF₃SO₃ electrolytes. *Solid State Ionics*, **85**(1–4), 61–66.
6. Asnawi, Ahmed S. F. M., Aziz, S. B., Nofal, M. M., Hamsan, M. H., Brza, M. A., Yusof, Y. M., Abdilwahid, R. T., Muzakir, S. K. & Kadir, M. F. Z. (2020) Glycerolized Li⁺ ion conducting chitosan-based polymer electrolyte for energy storage EDLC device applications with relatively high energy density. *Polymers*, **12**(6), 1–19.
7. Ahmed, H. T., Jalal, V. J., Tahir, D. A., Mohamad, A. H. & Abdullah, O. G. (2019) Effect of PEG as a plasticizer on the electrical and optical properties of polymer blend electrolyte MC-CH-LiBF₄ based films. *Results in Physics*, **15**, 1–7.
8. Banitaba, S. N., Semnani, D., Heydari-Soureshjani, E., Rezaei, B. & Ensafi, A. A. (2020) The effect of concentration and ratio of ethylene carbonate and propylene carbonate plasticizers on characteristics of the electrospun PEO-based electrolytes applicable in lithium-ion batteries. *Solid State Ionics*, **347**, 1–10.
9. Aziz, S. B., Brza, M. A., Brevik, I., Hafiz, M. H., Asnawi, A. S. F. M., Yusof, Y. M., Abdulwahid, R. T. & Kadir, M. F. Z. (2020) Blending and characteristics of electrochemical double-layer capacitor device assembled from plasticized proton ion conducting chitosan:Dextran: NH₄PF₆ polymer electrolytes. *Polymers*, **12**(2103), 1–18.
10. Gurusiddappa, J., Madhuri, W., Suvarna, R. P. & Dasan, K. P. (2016) Conductivity and dielectric behavior of polyethylene oxide-lithium perchlorate solid polymer electrolyte films. *Indian Journal of Advances in Chemical Science*, **4**(1), 14–19.
11. Aziz, S. B., Nofal, M. M., Abdulwahid, R. T., Ghareeb, H. O., Dannoun, E. M., Abdullah, R. M., Hamsan, M. H. & Kadir, M. F. (2021) Plasticized sodium-ion conducting PVA based polymer electrolyte for electrochemical energy storage—EEC modeling, transport properties, and charge-discharge characteristics. *Polymers*, **13**(5), 1–19.
12. Gohel, K. & Kanchan, D. K. (2019) Effect of PC:DEC plasticizers on structural and electrical properties of PVDF–HFP:PMMA based gel polymer electrolyte system. *Journal of Materials Science: Materials in Electronics*, **30**(13), 12260–12268.
13. Wohlfarth, C. (2008) Data extract from Landolt-Börnstein IV/17: Static dielectric constants of pure liquids and binary liquid mixtures. In *Dielectric Constant of Propylene Carbonate*, Springer, 225–228.
14. Gupta, S. & Varshney, P. K. (2017) Effect of plasticizer concentration on structural and electrical properties of hydroxyethyl cellulose (HEC)-based polymer electrolyte. *Ionics*, **23**(6), 1613–1617.
15. National Center for Biotechnology Information (2023) PubChem Compound Summary for CID 7924, Propylene Carbonate. In *National Library*

- of Medicine*. <https://pubchem.ncbi.nlm.nih.gov/compound/Propylene-Carbonate>.
16. Ulaganathan, M. & Rajendran, S. (2010) Li ion conduction on plasticizer-added PVAc-based hybrid polymer electrolytes. *Ionics*, **16**(7), 667–672.
 17. Kobayashi, K., Pagot, G., Vezzù, K., Bertasi, F., Di Noto, V. & Tominaga, Y. (2021) Effect of plasticizer on the ion-conductive and dielectric behavior of poly(ethylene carbonate)-based Li electrolytes. *Polymer Journal*, **53**(1), 149–155.
 18. Aziz, S. B., Hadi, J. M., Dannoun, E. M. A., Abdulwahid, R. T., Saeed, S. R., Marf, A. S., Karim, W. O. & Kadir, M. F. Z. (2020) The study of plasticized amorphous biopolymer blend electrolytes based on polyvinyl alcohol (PVA): Chitosan with High Ion Conductivity for Energy. *Polymers*, **12**(1938), 1–21.
 19. Yang, M. & Hou, J. (2012) Membranes in lithium ion batterie. *Membranes*, **2**(3), 367–383.
 20. Marf, A. S., Abdullah, R. M. & Aziz, S. B. (2020) Structural, morphological, electrical and electrochemical properties of PVA: CS-based proton-conducting polymer blend electrolytes. *Membranes*, **10**(4), 1–25.
 21. Kesavan, K., Mathew, C. M. & Rajendran, S. (2014) Lithium ion conduction and ion-polymer interaction in poly(vinyl pyrrolidone) based electrolytes blended with different plasticizers. *Chinese Chemical Letters*, **25**(11), 1428–1434.
 22. Asnawi, A. S. F. M., Aziz, S. B., Nofal, M. M., Yusof, Y. M., Brevik, I., Hamsan, M. H., Brza, M. A., Abdulwahid, R. T. & Kadir, M. F. Z. (2020) Metal complex as a novel approach to enhance the amorphous phase and improve the EDLC performance of plasticized proton conducting chitosan-based polymer electrolyte. *Membranes*, **10**(6), 1–20.