Ionic conductivity enhancement studies of composite polymer electrolyte based on poly (vinyl alcohol)-lithium perchlorate-titanium oxide

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Abstract

In this study, poly (vinyl alcohol) (PVA), lithium perchlorate ($LiClO_4$) and nano-sized titanium oxide (TiO_2) were employed as host polymer, dopant salt and inorganic filler respectively. The influence of the inorganic filler on ionic conductivity, structural and morphological properties of the polymer matrix are investigated. Ionic conductivity of polymer electrolytes is measured by ac-impedance spectroscopy at ambient temperature. The polymer electrolyte exhibits the highest ionic conductivity of 1.26×10^{-4} S cm^{-1} upon addition of 8 wt. % TiO_2. Dielectric behavior proves that incorporation of nano-sized TiO_2 particles shows a significant effect on the dielectric constant of the polymer electrolyte system. XRD analyses disclose that the addition of TiO_2 reduces the crystallinity of the polymer electrolytes which enhances the flexibility of polymer chains. Copyright © 2017 VBRI Press.

Keywords: Dielectric constant, titanium oxide, ionic conductivity, loss tangent.

Introduction

An electrolyte is a material in which when dissolved in solvents, it could form a medium that is capable to conducts electricity. The dissolved electrolyte will split into cations and anions which could help in the electric conduction of the medium. Generally, in order to produce a highly efficient electrolyte, the medium needed to be able to able to allow fast ionic transport, inert to all the cell components such as electrodes, thermally stable and chemically stable [**1**]. Studies have been done throughout the decades and the researchers have found out composite polymer electrolytes (CPEs) could fulfil the discussed properties and could emerge as a highly efficient electrolyte.

CPE can act as ionic conductor that consists of polymer, organic or inorganic salt and inorganic filler. CPEs have attracted widespread interest in electrochemical devices such as fuel cells, sensors, electrochromic display devices and supercapacitors. CPEs-based electrochemical devices have shown several advantages over liquid electrolytes, such as elimination of solvent leakage, superior thermal stability and light in weight. CPE has been researched widely and undergoes a huge number of advancement. For instance, Puguan *et al.* has successfully produced a CPE by the addition of zirconium dioxide (ZrO_2) fillers into their (PVdF-HFP)-$LiCF_3SO_3$ solid polymer electrolytes. The addition of the ZrO_2 increases the ionic conductivity of their polymer electrolyte by two orders of magnitude [**2**].

Nevertheless, the study of CPE in the field of biodegradable polymers was still very much lacking. Non-biodegradable polymer such as PVdF-HFP does not undergo decomposition naturally. Energy is needed in order to decompose the polymers. However, this decomposition will produce carbon dioxide which contributes to global warming. Therefore, researchers implement green technology to minimize the environment impact. Poly (vinyl alcohol) (PVA) with 99%+ hydrolyzed is a synthetic biodegradable polymer. In addition, PVA was also known to have O-H groups attached to the CH_4 carbons. These O–H groups can be a source of hydrogen bonding for polymer complexes formation. The conductivity and crystallinity of the polymer electrolytes containing PVA and $LiClO_4$ were investigated in the initial study. It was noted that the mechanical properties of the PVA-$LiClO_4$ system is deteriorated sharply. The thin film formation becomes more difficult with increasing the content of lithium salts although the ionic conductivity of polymer electrolytes is enhanced [**3**].

There are many ways can be employed to work out the complications as mentioned above. Based on the findings, the addition of inert fillers has shown enormous improvement on the electrochemical performance on polymer salt system [**4-8**]. Incorporation of inorganic filler such as ZrO_2, Al_2O_3, Sm_2O_3, SnO_2 and V_2O_5 into solid polymer electrolyte can enhance conductivity, mechanical stability, electrochemical stability, cation transference number and thermal stability towards electrode materials. High dielectric constant of fillers can also reduce interfacial resistance [**9-12**]. The improvements are attributed to the presence of disordered chains coming from the interactions between the polymer and ceramic filler. The Lewis acid nature of the filler could weaken the interaction between the polymer and the lithium ions. This interaction has thus accelerated the dissociation of lithium salt. Hence it eases the mobility of Li^+ and increases the number of ion species. The inert filler in the solid polymer electrolyte system also plays other useful roles in forming particle networks into polymer bulk (particle dispersion) which inhibits the crystallization and reorganization of polymer chains (solid plasticizer). Nevertheless, the addition of inert filler has capability to enhance the electrochemical properties without contributing in ionic conduction process. The main aim of this work is to study the effect of TiO_2 on the PVA-$LiClO_4$ system is investigated by electrical impedance spectroscopy (EIS) and X-ray diffraction (XRD).

Experimental

Materials

PVA (Aldrich, 99%+ hydrolysed), $LiClO_4$ (Merck) and TiO_2 (Aldrich <100 nm) were used as-received without further treatment or purification.

Preparation of composite polymer electrolyte

Thin films consisting of PVA, $LiClO_4$ and TiO_2 are prepared by solution casting technique with distilled water as solvent. The mixtures are stirred overnight, cast in a Petri dish and then allowed to evaporate slowly in the oven at 70 °C. This procedure yields mechanically stable and free-standing films. The films are placed in desiccator to remove remaining moisture. The designations of polymer electrolytes with various percentage of TiO_2 are presented in **Table 1**.

Table 1. Ionic conductivity, relaxation time and crystallite size of polymer electrolytes and their designation.

Designation	Polymer complex ($PVA:LiClO_4:TiO_2$)	Relaxation time ($\times 10^{-7}$ s)	Crystallite Size (Å)
PLT-0	60:40:0	19.89	46.9
PLT-4	57.6:38.4:4	6.12	38.1
PLT-8	55.2:36.8:8	2.09	29.5
PLT-10	54:36:10	795.67	65.2

Electrochemical Impedance Spectroscopy (EIS) studies

The thickness of the films is measured by means of a micrometer screw gauge. The composite polymer electrolytes are sandwiched between two stainless-steel blocking electrodes. Ionic conductivity measurements are carried out using HIOKI 3532-50 LCR Hi-Tester interfaced to a computer. The AC frequency is ranged from 50 Hz to 5 MHz. The measurement is taken from room temperature to 80 °C.

X-ray diffraction (XRD) studies

XRD analysis is carried out to investigate the crystalline nature of composite polymer electrolytes. The XRD patterns were recorded on a Siemens D 5000 diffractor meter with Cu-Kα radiation (λ = 1.54060 Å), over the range of 2θ=5-80° at ambient temperature.

Results and discussion

Temperature dependence ionic conductivity studies

Fig. 1 depicts the Arrhenius plots of the ionic conductivity of PVA-$LiClO_4$-TiO_2 polymer complexes in the temperature range of ambient temperature to 353 K.

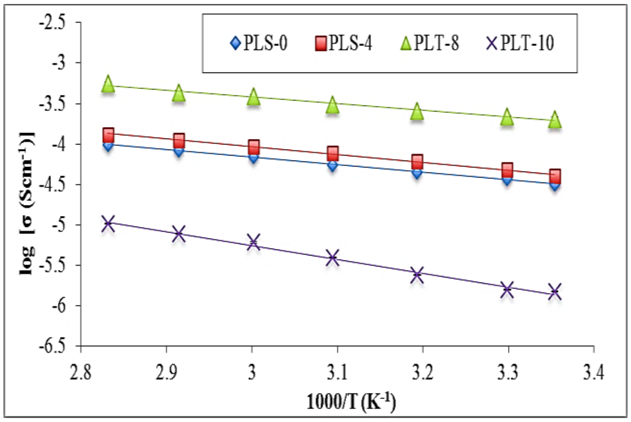

Fig. 1. Arrhenius plot of ionic conductivity of PLT-0, PLT-4, PLT-8 and PLT-10.

PLT-8 was found to exhibit the highest ionic conductivity of 1.26×10^{-4} S cm^{-1} with addition of 8wt. % of TiO_2 at room temperature. Our results are comparable to the already reported results which are summarized in **Table 2**.

Table 2: Summary of reported results similar to this work.

Electrolyte Material	Highest ionic conductivity ($S\ cm^{-1}$)	Reference
PVdF-PVA-NH_4SCN	1.09×10^{-3}	[13]
PVA-PMA-SiO_2-BMITFSI	8.30×10^{-4}	[14]
PVA–PVdF–$LiClO_4$	3.04×10^{-5}	[15]
PVA-$LiClO_4$-TiO_2	1.26×10^{-4}	Present work

Temperature dependence of ionic conductivity has been employed to study the conduction mechanism in the polymer electrolytes. The temperature dependent plot is fitted with the Arrhenius relationship using the equation below.

$$\sigma = A\exp\left(\frac{-E_a}{kT}\right) \qquad (1)$$

where A is a constant, E_a is activation energy in eV, k is Boltzmann constant and T is the absolute temperature in K. The linear relationship of ionic conductivity with temperature indicates that the polymer electrolytes follow

Arrhenius theory where the regression value is approximate to unity. **Fig. 1** indicates that the ionic conductivity of polymer electrolytes increases with temperature and suggests that the process is thermally activated. Migration of the charge carriers (Li^+) in nanocomposite polymer electrolytes probably occurs quite similar to that in ionic crystals, where ions jump into neighboring vacant sites; a phenomenon known as ion hopping mechanism [**16**]. The vibration mode in the polymer segment is promoted at higher temperature which leads to rapid ionic hopping mechanism. The bonding between the oxygen atoms of PVA and Li^+ becomes weaker at elevated temperature. The interaction between oxygen atom and charge carrier is gradually reduced as temperature is increased. Therefore, the weak interaction could promote the decoupling process of charge carriers from segmental motion of polymer matrix and lead to formation of vacant sites. Consequently, the Li^+ ion at adjacent sites will hop and try to occupy the vacant site and then allowing itself to be coordinate with the chain in the polymer matrix once again. Hence, the increment of temperature promotes the fast ion conduction which leads to increment of ionic conductivity. Furthermore, as seen in the figure, there was no huge changes in the ionic conductivity after the increase in temperature. Similar results were found in other articles as well and this actually shows that there is no phase transition occurring in the temperature dependence studies [**17**, **18**].

The activation energy, E_a of the nanocomposite polymer electrolytes is calculated by fitting the temperature plots with of Arrhenius theory and was generally defined as the energy required to overcome the reorganization and reformation of the polymer chain with Li^+. The E_a value for PLT-0, PLT-4, PLT-8 and PLT-10 is 0.186 eV, 0.185 eV, 0.171 eV and 0.340 eV, respectively. The E_a value for composite polymer electrolyte is in the order of 0.171-0.340 eV. This implies that the discrepancy in E_a value is highly dependent on the content of TiO_2. Upon doping of TiO_2 into the polymer system, E_a value decreases slightly with increase the concentration of TiO_2. The PLT-8 has lower E_a value compared to PLT-0 and PLT-4. Therefore, this result infers that PLT-8 requires lesser energy to break the physical and chemicals bonds in the polymer network. As a result, the ionic conduction is more favorable on PLT-8 sample. Apart from that, E_a value for PLT-10 is found to be increased. This can be ascribed to the formation of ion aggregates and neutral ion pairs which requires more energy to weaken the coordinative bonds in the polymer matrix. The E_a value of the polymer electrolyte samples was in agreement with the ionic conductivity studies of our previous work [**19**] where the E_a is inversely proportional to the ionic conductivity.

Dielectric relaxation studies

The frequency dependence of the real dielectric relaxation curves for PLT-0, PLT-4, PLT-8 and PLT-10 are shown in **Fig. 2**. The dielectric behavior of the polymer electrolyte can be defined by the dielectric function ε as defined below:

$$\varepsilon = \varepsilon' + j\varepsilon'' = \varepsilon' - j\left(\frac{\sigma}{\omega\varepsilon_o}\right) \tag{2}$$

where, the real part is the ε' (dielectric constant) and the imaginary part is the ε'' (dielectric loss), σ is ionic conductivity, ω is angular frequency and ε_o is permittivity of free space. The ε' and ε'' are evaluated using the impedance data by the following equation:

$$\varepsilon' = \frac{C_p \times L}{\varepsilon_0 \times A} \tag{3}$$

where, C_p is the parallel equivalent static capacitance, L is the thickness of the polymer film in cm and A is the surface area of the film in cm^2. The ε' rises sharply towards low frequencies which is resulting from electrode polarization effect. Charge accumulation can be observed occurring at the electrode/electrolyte interface due to the dispersion at the low frequency region as well [**20**, **21**]. The periodic reversal of the electric field occurs very fast when there is no excess ion diffusion in the direction of the field at high frequency. Hence, there is no polarization occurred. Since the mobile ions are unable to accumulate at the interface, therefore it leads to decrease of ε' at high frequency.

Incorporation of TiO_2 into polymer system shows a higher ε' value as shown in **Fig. 2**. TiO_2 particles in polymer electrolytes will promote the Lewis acid-base interaction and lead to the dissociation of lithium salt into free ion species. Dissociation of $LiClO_4$ aggregates would favor the interaction between the free ion species and oxygen atom from PVA when there is more number of free charge carriers that exist in the polymer matrix. Hence, the number of free charge carriers is increased as well as the ionic conductivity. Besides, the dissociation of $LiClO_4$ increases the number of anion (ClO_4^-), which leads to increment of the equivalent capacitance.

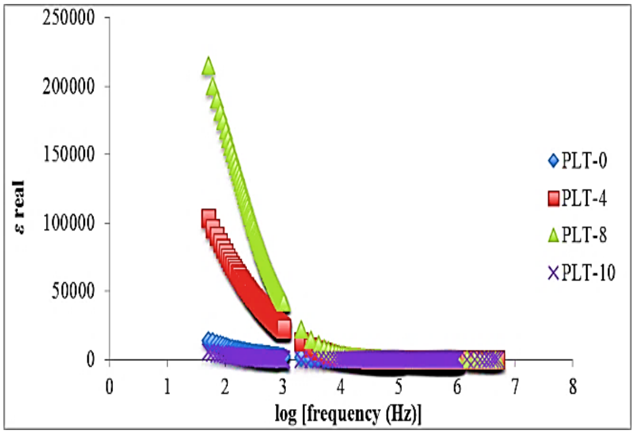

Fig. 2. Variation of real part of dielectric constant (ε') with frequency at ambient temperature for PLT-0, PLT-4, PLT-8 and PLT-10.

From **Fig. 2**, it can be observed that the dielectric constant increases with increasing the weight percentage of TiO_2. PLT-8 achieves the highest ε' value and this indicates that PLT-8 has more number of charge carriers compared to other samples. However, as the weight percentage of TiO_2 further increases up to 10 wt. %, the dielectric constant shows a sudden decline, which is ascribed to the formation of TiO_2 aggregates. Hence the dissociation of lithium salt has become tougher and this impedes the ionic conductivity of the sample.

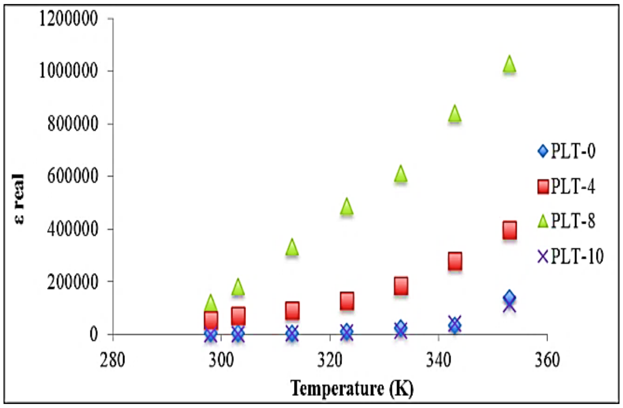

Fig. 3. Variation of real part of dielectric constant (ε') as a function of temperature for PLT-0, PLT-4, PLT-8 and PLT-10 at 200Hz.

Fig. 3 shows that the ε' of polymer electrolyte typically increases with increasing the temperature. This is mainly owing to the decrease in viscosity of the materials [**22**]. In addition, PVA exhibits a semi-crystalline nature, which consists of crystalline phase and amorphous phase; therefore, the crystalline phase dissolves progressively into amorphous phase with increase in temperature. This in turn influences the polymer dynamics and thus the dielectric behaviour. In other words, the rise of dielectric constant can correlate with molecular mobility. As the temperature increases, it leads to greater molecular mobility which facilitates the diffusion of ions in the space charge polarization. Apart from that, high temperature will favor the salt dissociation in the polymer matrix. This is due to the thermal energy which can break the chemical bonds in $LiClO_4$ easily to form free ion species. So, the ε' increases with temperature.

Frequency dependence of loss tangent

The loss tangent (*tan δ*) is the ratio of loss factor to the dielectric constant, also a measurement of the ratio of the electrical energy lost to the energy store in a periodic electrical field. The *tan δ* is determined by following expression:

$$\tan\delta = \frac{\varepsilon'}{\varepsilon''} \tag{4}$$

The relaxation time, τ of each sample was calculated by equation:

$$\tau = \frac{1}{2\pi f_m} \tag{5}$$

where, f_m represent the frequency corresponding to the peak. **Fig. 4 (a)** and **(b)** depict the variation of loss tangent as a function of frequency for polymer electrolytes incorporated with different weight percent of TiO_2 at room temperature. The relaxation time value for each sample is presented in Table 1.

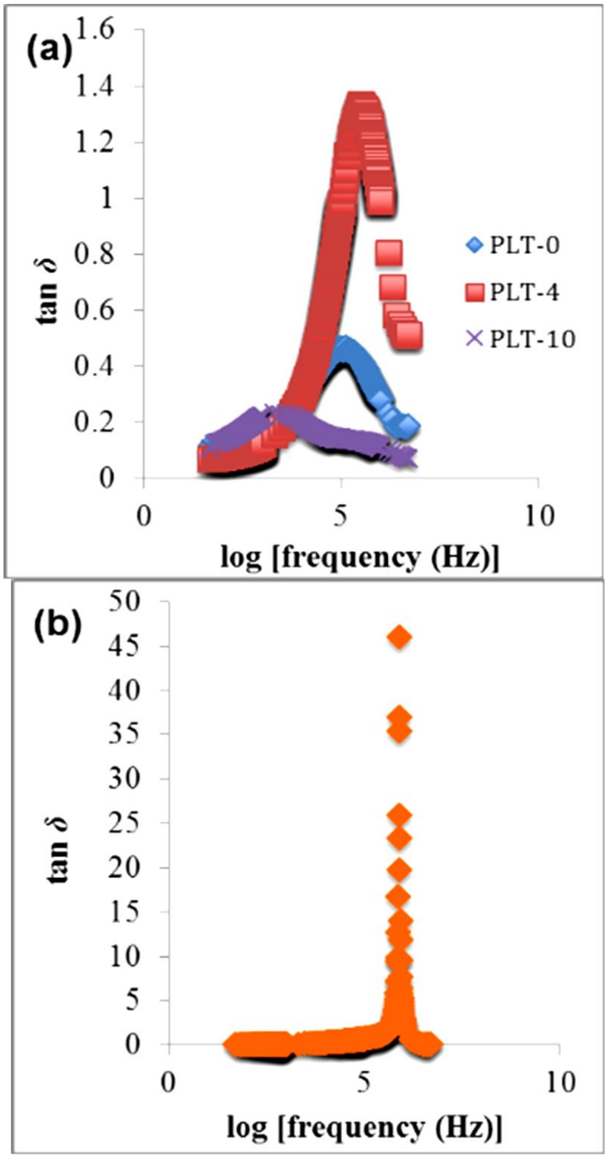

Fig. 4. Variation of tanδ with frequency for PLT-0, PLT-4 and PLT-10 (a) and PLT-8 (b) at room temperature.

From **Fig. 4(a)** and (b), tan δ increases with frequency until a maximum, and then decreases with further increase in frequency. The occurrence of peak for each sample can be seen in these figures. The presence of these peaks imply the presence of relaxation dipoles in Li^+ ions in all the samples. Presence of loss tangent peak has separated the bulk material and the electrode surface polarization phenomena in the low frequency dielectric dispersion. Electrode polarization phenomena occur due to the formation of double layer at the electrode-electrolyte boundary.

The tangent loss peaks are shifted to higher frequency as the mass fraction of TiO_2 increases gradually. Meanwhile, the relaxation time is reduced when the peak is shifted towards higher frequency [**23**]. The shifting of peak to higher frequency illustrates the increase in the cations mobility upon reduction in the relaxation time.

Based on reported relaxation time value, the relaxation time is inversely proportional to ionic conductivity of polymer electrolytes. The crystalline region will become lesser as more TiO_2 particles are added. Therefore, polymer segment is now more flexible to orient. Eventually, the relaxation time becomes shorter [**24**].

The intensity of the loss tangent peak is also correlated to the number of free charge carriers for the sample. The increase of peak intensity in TiO_2-based nanocomposite polymer electrolytes also implies the increased area under the loss tangent peak. There is more number of free Li^+ ions participate in the relaxation processes to enhance the ionic conductivity of the polymer electrolytes when the intensity of loss tangent peak becomes higher with increasing the TiO_2 concentration [**25**]. The loss tangent peak for PLT-8 shows higher peak intensity and bigger area than other samples as shown in **Fig. 4(b)**. This entails that PLT-8 has more number of free charge carriers that contribute in relaxation processes as well as ionic conductivity value.

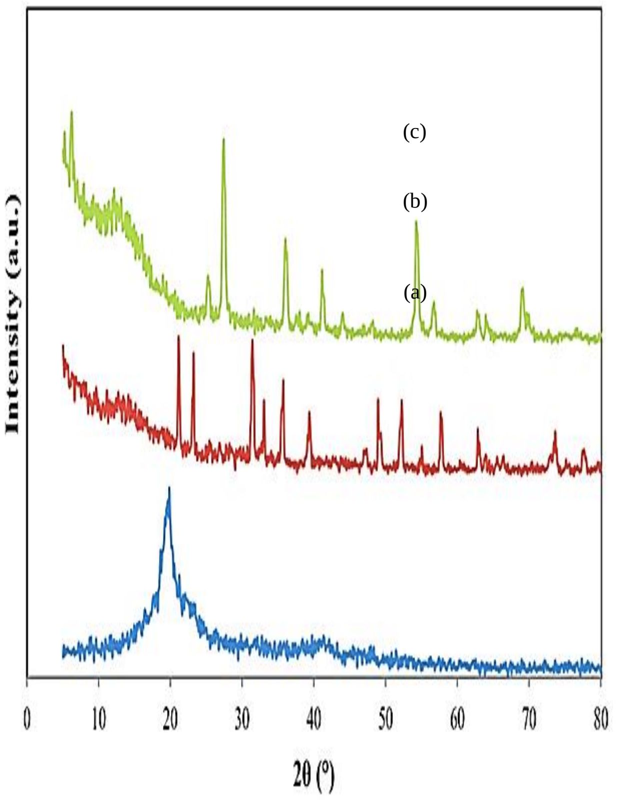

Fig. 5. XRD patterns for (a) PVA (b) $LiClO_4$ and (c) TiO_2 powder.

However, the loss tangent peak in PLT-10 is shifted to low frequency as illustrated in **Fig. 4(a)**. This phenomenon implies the increase in relaxation time. Longer relaxation time might reduce the Li^+ mobility and inhibit the ion conduction owing to the formation of neutral ion pair or aggregates, resulting to the formation of thick interfacial layer within the grain boundary. Consequently, the intensity of loss tangent peak is decreased as shown in the **Fig. 4(a)**. We suggest that the number of free charge carrier has been decreased when the mass fraction of TiO_2 is more than 8 wt. %. As a result, ionic conductivity of PLT-10 is decreased beyond the optimum level.

X-ray diffraction (XRD) studies

XRD diffractogram for pure PVA, $LiClO_4$ and TiO_2 is indicated in **Fig. 5**. The diffraction peak of PVA is at angle of 2θ=19.8° which reveals the semi-crystalline nature of PVA. The characteristic peak of TiO_2 was obtained at angles of 2θ=25.2°, 27.4°, 36°, 41.1°, and 54.2° whereas characteristic peak of $LiClO_4$ was obtained at angles of 2θ= 21.1°, 23.2°, 31.3°, 35.7° and 39.3°. **Fig. 6 (a), (b), (c) and (d)** indicate the XRD diffractogram for PLT-0, PLT-4, PLT-8 and PLT-10, respectively. The sharp peak at 2θ=31.3° for PLT-0 in **Fig. 6** is assigned to the crystalline peak of $LiClO_4$. The crystalline peak is mainly due to the crystalline structure of $LiClO_4$. This infers that $LiClO_4$ does not fully dissociated and be recrystallized in the polymer matrix. The shifting of relative diffraction peak observed in PLT-0, PLT-4, PLT-8 and PLT-10 is mainly due to the incorporation of $LiClO_4$ and TiO_2. This result discloses that complexation has occurred between PVA, $LiClO_4$ and TiO_2.

Variation of peak intensity of relative diffraction peak is an indicator to evaluate the amorphous characteristic of polymer electrolyte. The relative peak intensity at angle of 2θ=19.8° is decreased with broadening feature as depicted in **Fig. 6**. This implies that $LiClO_4$ disrupted the arrangement in the polymer segment of PVA. Incorporation of 2 wt. % of TiO_2 into polymer matrix indicates no discernible effect on the reduction of peak intensity. This is because of the inadequate amount to dislocate the polymer network which causes an insignificant increase in amorphous degree along the polymer backbone [**26**]. Upon addition of 8 wt. % and 10 wt. % of TiO_2, the relative peak intensity is reduced greatly. Therefore, we conclude that the crystalline region in PVA decreases with increasing the weight percentage of TiO_2.

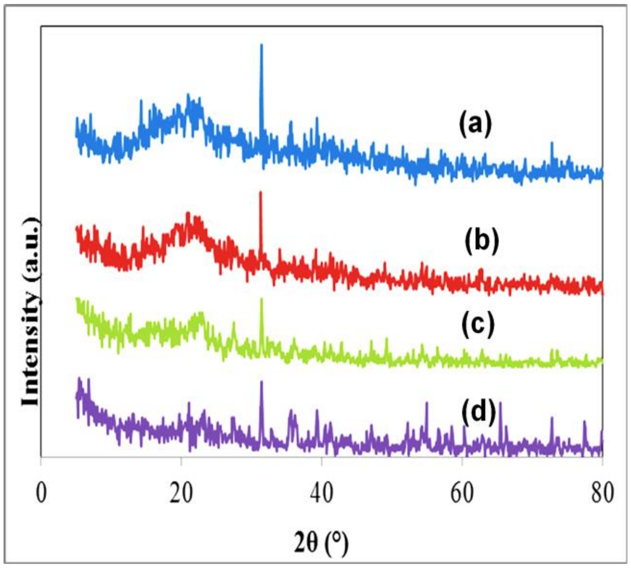

Fig. 6. XRD patterns for (a) PLT-0, (b) PLT-4, (c) PLT-8, and (d) PLT-10.

High degree of crystallinity of pure PVA is due to its hydroxyl groups on its side-chain [**27**]. The crystallinity of PVA can be decreased when the hydroxyl group on its side chain has reacted with the Li^+ conducting species and TiO_2. Hence the number of hydroxyl group remaining in the PVA could be decreased. Thus, the crystallinity of PVA is also decreased [**26**]. Consequently, a decrease in relative peak intensity at angles of $2\theta=19.8°$ can be seen in each sample. The reduced peak intensity results an increase of the amorphous characteristic of polymer electrolytes. High amorphous degree of polymer electrolytes causes high flexibility of polymer backbone which results in greater ionic diffusivity and ion mobility [**28**]. Therefore, polymer electrolyte with flexible backbone and good ion mobility will favor the ionic conduction. PLT-8 displays the lowest peak intensity in comparison to the other samples. This finding implies that PLT-8 exhibits the highest ionic conductivity with the highest amorphous degree of the polymer chains.

However, some crystalline peaks are observed in PLT-10. This is attributed to excessive amount of TiO_2 nano-scaled particles which causes the formation of ion aggregates. The formation of aggregates debilitates dissociation of salt into mobile ions. As a consequence, the recrystallization of $LiClO_4$ in polymer matrix leads to the reduction in ionic conductivity. This result was in good agreement with ionic conductivity studies. Results also show that dispersion of TiO_2 decreases the peak intensity of crystalline peak at $2\theta= 31.3°$ corresponding to $LiClO_4$. This behaviour also shows that lithium salt can dissociated into free charge carriers easily upon the addition of TiO_2.

Crystallite size at the relative diffraction peak at angle of $2\theta=19.8°$ has been calculated using the Scherrer equation:

$$L = \frac{0.9\lambda}{\beta \cos\theta} \tag{6}$$

where, λ is the wavelength of the impinging X-ray beam, β is the full width at half maximum intensity of the XRD peak and θ is the glancing angle. The calculated crystallite size of polymer electrolyte at relative diffraction peak for each sample is presented in **Table 1**. These results signify that the incorporation of TiO_2 reduces the crystallite size and crystallinity of polymer electrolytes. Smaller crystallite size can produce a more flexible polymer segment which favours the ionic transportation. It also deduces that PLT-8 produces the smallest crystallite size and thereby achieves the highest ionic conductivity of PLT-8 compared to other samples. However, PLT-10 has bigger crystallite size compared to PLT-8, which is attributed to the excessive amount of TiO_2 added into the polymer matrix. Consequently, the ionic conductivity of nanocomposite polymer electrolyte containing 10 wt.% of TiO_2 is decreased.

Conclusion

A series of nano-composite polymer electrolytes was successfully prepared by solution casting technique. PLT-8 exhibits the highest ionic conductivity of 1.26×10^{-4} S cm^{-1} with addition of 8wt.% of TiO_2. The polymer electrolytes system obeys the Arrhenius rule which infers the ionic hopping mechanism as shown in temperature dependence-ionic conductivity studies. Incorporation of TiO_2 had increased the number of ion species based on dielectric permittivity study. However, frequency dependence of loss tangent result reveals that the relaxation time was reduced. Shorter relaxation time can enhance the ion mobility when TiO_2 particles were incorporated into polymer electrolytes. Furthermore, XRD data discloses that the addition of TiO_2 increases the degree of amorphous nature of polymer electrolytes.

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Author's contributions

Conceived and supervised the plan: S. Ramesh; Performed the expeirments: Chin-Shen. Lim; Data analysis: Chin-Shen. Lim, K. H. Teoh; Wrote the paper: Chin-Shen. Lim, H. M. Ng, Chiam-Wen Liew. Authors have no competing financial interests.

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