

Research Article

Effect of LiBF₄ Salt Concentration on the Properties of Plasticized MG49-TiO₂ Based Nanocomposite Polymer Electrolyte

A. Ahmad,^{1,2} M. Y. A. Rahman,³ S. P. Low,¹ and H. Hamzah^{1,2}

¹ School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

² Polymer Research Center, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

³ College of Engineering, Universiti Tenaga Nasional, 43009 Kajang, Selangor, Malaysia

Correspondence should be addressed to A. Ahmad, azizan@ukm.my and M. Y. A. Rahman, yusri@uniten.edu.my

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A nanocomposite polymer electrolyte (NCPE) comprising of 49% poly(methyl methacrylate) grafted natural rubber (MG49) as polymer host, titanium dioxide (TiO₂) as a ceramic filler, lithium tetrafluoroborate (LiBF₄) as dopant salt, and ethylene carbonate (EC) as plasticizer was prepared by solution casting technique. The ceramic filler, TiO₂, was synthesized *in situ* by a sol-gel process. The ionic conductivity, chemical interaction, structure, and surface morphology of nanocomposite polymer electrolyte have been investigated as a function of wt% LiBF₄. The interaction between lithium ions and oxygen atoms occurred at carbonyl and ether groups. The crystalline phase of polymer host slightly decreases with the addition of salt. TGA and DTG analysis suggested that the thermal stability of the electrolyte decreases with the salt content. The ionic conductivity of the electrolyte was found to increase with the increase of salt concentration and then decreased after an optimum value. The highest conductivity achieved was $5.2 \times 10^{-4} \text{ S cm}^{-1}$ at 25 wt% of LiBF₄.

1. Introduction

Lithium polymer batteries, utilizing polymer electrolyte as separator as well as carrier of ions, have been used as power sources for portable electronic equipment due to their high energy density [1]. Polymer electrolyte refers to the complexation of polymeric material with alkali metal salt [2]. Compared with liquid electrolyte used in most present commercial rechargeable Li⁺ batteries, polymer electrolyte offers shape versatility, flexibility, and lightness and have many potential advantages in the continuing trend towards electronic miniaturization [3]. The majority of commercial lithium polymer batteries were mostly fabricated with Li⁺-salt solution as electrolytes immobilized in a variety of polymer matrices. The motivation behind using lithium salt as ion source is based on the fact that lithium, being the lightest of all metals, when used as an anode in contact with Li⁺-salt electrolytes, provides a wider electropositive

potential window. Hence, the batteries based on Li/Li⁺-salt facilitate a very high energy density [2, 4]. Modified natural rubber- (NR-) based solid polymer electrolyte has been reported to have an ability to enhance the contact between an electrolytic layer and an electrode in batteries' system due to its elasticity that can result in flat, thin, and flexible film. Furthermore, modified natural rubber has low glass transition temperature, T_g , soft elastomer characterization at room temperature and also can act as a polymeric solvent [5]. Research on modified natural rubber like poly(methyl methacrylate)-grafted natural rubber (MG) has been carried out and exhibits ionic conductivity. This is because of the fact that MG has oxygen atoms, which can act as electron donor atoms in the structure of the polymer host. The oxygen atoms with the lone pair of electron form a coordinate bond with Li⁺ ion from salt and, hence, form a polymer complex [5–7].

However, the ionic conductivity of such polymer electrolyte at ambient temperature is rather low. Thus, in order

to enhance the room temperature ionic conductivity of the polymer electrolytes, several strategies have been developed that include incorporating organic solvents (plasticizer) to form plasticized or gel polymer electrolyte [8], doped with inorganic fillers to make composite polymer electrolyte [1, 3, 9] and synthesizing new polymer [5–7]. Plasticization is an effective way to improve the ionic conductivity of polymer electrolyte, and among a number of plasticizers, the most used plasticizers are low molecular weight organic solvents such as propylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) [8]. Plasticizers reduce the glass transition temperature, T_g , of the polymer electrolyte which helps to increase the segmental motion of the polymer backbone and generate free volume. Therefore, the ions can migrate easily through the void resulting in ionic conductivity enhancement. Besides that, the high dielectric constant and low viscosity of plasticizers also enable them to incorporate with the polymer host to facilitate the formation of dissociated ions [2, 6, 10]. This approach leads to a high ambient conductivity but promotes deterioration of the electrolyte's mechanical properties and increases its reactivity toward the lithium metal anode [3].

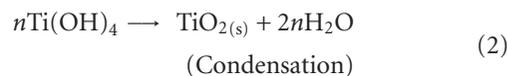
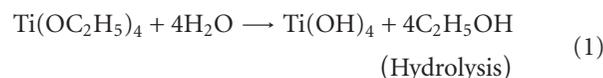
Alternatively, the addition of inorganic filler, namely, ceramic filler to the polymer electrolytes has recently become an attractive approach due to the mechanical stability and enhanced ionic conductivity and to electrolyte-electrode interface stability [3, 9]. It has been well established that the addition of ceramic fillers improved the conductivity of polymer host and their interfacial properties in contact with the lithium electrode [1, 3, 9]. The concentration and the particles size of the inert solid particles play a significant role in improving these physical properties as the smaller the particles size is, the larger the conductivity enhancement will be [4]. In part, because of this idea, nanocomposite polymer electrolyte (NCPE) in which dispersion of small fraction of low dimension particles in the conventional solid polymer complexes is presently the focus of many studies [1, 3, 10–12]. According to [13], the filler particles inhibit the crystallization of polymer chains and, hence, decrease the degree of crystallinity (or increase the proportion of amorphous phase) in polymer. This, in turn, lowers the temperature of stabilization of the amorphous phase in the polymer electrolyte and, hence, increases the practical applicable range of conductivity of the electrolyte [4, 11–13]. The inorganic TiO_2 particle has been identified as the ceramic filler that improved the ionic conductivity and cation transference number mostly because of the weakening of polyether oxygen- Li^+ interactions as reported from the work by Chung et al. [14] who studied the effect of ceramic nanoparticles fillers such as TiO_2 , Al_2O_3 , and SiO_2 in PEO- LiClO_4 electrolyte system. However, the presence of surface hydroxyl groups in TiO_2 resulted in aggregation of particles during the preparation of polymer-ceramic nanocomposites through mechanical blending of TiO_2 nanoparticles, polymer, and salt in a compatible solvent. Hence, sol-gel process was employed to overcome this problem wherein the ceramic nanoparticle fillers are precipitated *in-situ* in the polymer matrix through a series of hydrolysis and

condensation reactions of suitable precursor [12, 15, 16]. In this work, MG49- TiO_2 - LiBF_4 -EC nanocomposite polymer electrolytes were prepared, in which TiO_2 nanoparticles were precipitated by *in situ* sol-gel synthesis after the lithium salt was added in the solid polymer network. This *in situ* approach had been successfully used in the synthesis of TiO_2 -derived, PEO-based [15, 16], and PVdF-based [1] composite polymer electrolyte which exhibited excellent ionic conductivity property and uniform distribution of TiO_2 in the polymer. The objective of this work is to study the effect of LiBF_4 salt concentration on the chemical interaction, morphology, structure, thermal stability, and ionic conductivity of MG49-6 wt% TiO_2 -50 wt% EC- LiBF_4 polymer electrolyte system.

2. Experimental and Characterization

2.1. Materials. MG49 was commercially obtained from Green HPSP (M) Sdn. Bhd. Lithium tetrafluoroborate salt (LiBF_4), ethylene carbonate (EC), titanium (IV) ethoxide ($\text{Ti}(\text{OC}_2\text{H}_5)_4$), potassium chloride (KCl), and ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) were supplied by Aldrich. All the materials were used without further purification.

2.2. Sample Preparation. The polymer electrolyte samples were prepared by solution casting technique. 3 grams of MG49 rubber was sliced into grain size and dissolved in stopped flasks containing 75 mL of tetrahydrofuran (THF) for 24 hours. The solution was then stirred with efficient magnetic stirring for the next 24 hours. The LiBF_4 and EC solution were prepared separately in THF solution and stirred until completely dissolved. These two solutions were mixed and further stirred for 24 hours to obtain a homogenous solution. A calculated amount of ethyl alcohol, titanium ethoxide, and potassium chloride solution (58 : 1 : 0.025) was added into the solution under continuous stirring. The TiO_2 contents of the polymer electrolytes were calculated by assuming complete conversion of titanium ethoxide into TiO_2 . The residual water in ethyl alcohol was adequate for hydrolysis, and the addition of KCl solution was to control the formation of particles size [17, 18]. The hydrolysis and condensation reaction of titanium ethoxide are represented by the following equations, respectively [1, 15, 16].



The solution was vigorously stirred for another 3 hours before it was transferred to a teflon petri-dish to allow the solvent to evaporate completely. This process resulted in homogenous, flat, freestanding, and flexible films with thickness in the range of 0.3-0.4 mm. These films were further dried at 50°C in a vacuum oven for 48 hours to completely remove any trace amount of the residual solvent.

2.3. Characterization. The reflection fourier transform infrared (ATR-FTIR) spectra were recorded using Perkin-Elmer model Paragon 500 spectrometer in the frequency range of 500–4000 cm^{-1} with scan resolution of 5 cm^{-1} . XRD model D-5000 Siemen was used to observe the appearance and disappearance of the crystalline or the amorphous phase. The data was collected from the range of diffraction angle 2θ from 5° to 35° at the rate of $0.025^\circ \text{ s}^{-1}$. The morphology of the nanocomposite polymer electrolyte was examined by a scanning electron microscopy (SEM) Philip XL 30 model with magnifications of 5,000x. The thermal stability analysis was performed on the samples by TGA and DTG in the temperature range from 50°C to 550°C . The ionic conductivity measurements were carried out by AC impedance spectroscopy using high frequency resonance analyzer (HFRA) model 1255 with applied frequency from 155 kHz to 1 Hz. The 16 mm diameter of disc shape sample was sandwiched between two stainless steel block electrodes. The measurements were conducted at room temperature. The ionic conductivity (σ) was calculated from the bulk resistance (R_b) obtained from the intercept of real impedance axis, film thickness (l), and the product of effective contact area (A) according to the equation $\sigma = [l/(AR_b)]$.

3. Result and Discussion

3.1. FTIR Analysis. The FTIR spectra were recorded to identify the interaction between MG49-TiO₂ with the EC plasticizer and the LiBF₄ salt. The interest has been on oxygen atom, which acted as electron donor atom in the structure of the polymer host and formed a polymer-salt complex with lithium salt [6, 7, 19]. According to previous report, the fundamental frequencies observed in MG49 can be assigned to the functional groups found in natural rubber and PMMA [6, 7, 20, 21]. Figures 1 and 2 represent the FTIR spectra of MG49-TiO₂-LiBF₄-EC in the region of 1950–1550 cm^{-1} and 1500–900 cm^{-1} , respectively. The ester functional group in PMMA appears in a strong and sharp peak of C=O symmetric stretching at 1726 cm^{-1} as seen in Figure 1. Upon the addition of LiBF₄ and EC in the MG49-TiO₂ system, the intensity of C=O symmetric stretching peak was reduced and shifted to lower a wave number which is at 1722 cm^{-1} . This observation is in a good agreement with the results reported previously [6, 7, 19–21], where the shift of the intensity peaks confirmed the interaction between lithium ion and oxygen atom in the structure of the polymer host to form a coordinate bond and polymer salt complex. A new band evolved at the lower frequency side (1626–1639 cm^{-1}) which corresponds to C=C stretching of natural rubber and its intensity increases with an increase of lithium salt concentration. The C=O bands due to Fermi resonance of skeletal breathing in EC can be found at 1773 cm^{-1} and 1804 cm^{-1} which is similar to the finding reported in [19]. This C=O band seems to be broadened in the plasticized polymer-salt complex indicating that the plasticizer just interacts physically with the polymer and salt. No chemical interaction occurred between the plasticizer and the polymer or between the plasticizer and the salt as reported earlier in [7, 19, 21]. The broadening of C=O band may be also

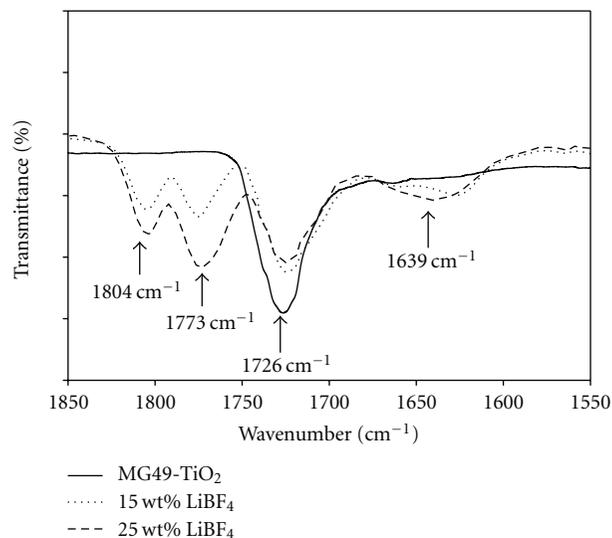


FIGURE 1: FTIR spectra of MG49-TiO₂, MG49-TiO₂-EC with 15 wt% LiBF₄ and 25 wt% LiBF₄ in the region of 1850–1550 cm^{-1} .

due to the association between the redistribution of charge accompanying the formation of ionic pairs and aggregation which attributed to the carbonyl group (C=O) and oxygen atom in the EC ring [22]. According to Figure 2, the vibrational peaks found in MG49-TiO₂ at 1434, 1269, and 1146 cm^{-1} are assigned to O–CH₃ asymmetric bending, C–O symmetric, and C–O–C asymmetric stretching of PMMA [6, 19, 21]. These peaks have been shifted to 1447, 1277, and 1150 cm^{-1} with the addition of LiBF₄ and EC, and the intensities of these peaks were reduced with further addition of salt concentration into the polymer electrolyte system which confirmed that the complexation has occurred. According to Noor et al. [23], the complexation that occurs in C–O–C group was through the bond formation between the Li⁺ and the lone pair of the oxygen atom from the polymer host. The peak at 1073 cm^{-1} of BF₄[−] anion observed in the plasticized polymer complexes has been used as an indicator for the dissociation of LiBF₄ [24]. However, the intensity of this peak increases as the LiBF₄ concentration was increased. These behaviors indicate that there was a certain amount of lithium salt that was able to be dissolved in the polymer matrix. Hence, it limits the number of lithium ion generated in the electrolyte [23]. Therefore, the ionic conductivity value falls after reaching an optimum value as can be seen in the ionic conductivity result.

3.2. XRD Analysis. X-ray diffraction (XRD) analysis provides a wide range of information on crystal structure, crystal orientation, crystallinity, crystallite size, and phase changes of materials which are characterized by the presence of sharp diffraction rings or peaks. In amorphous material, there is no long order present; however, the noncrystalline samples are characterized by one or two broad humps [25]. The X-ray diffraction patterns of LiBF₄ salt, MG49-TiO₂, and MG49-TiO₂-LiBF₄-EC complexes are presented in Figure 3. LiBF₄ salt peaks are observed at the diffraction

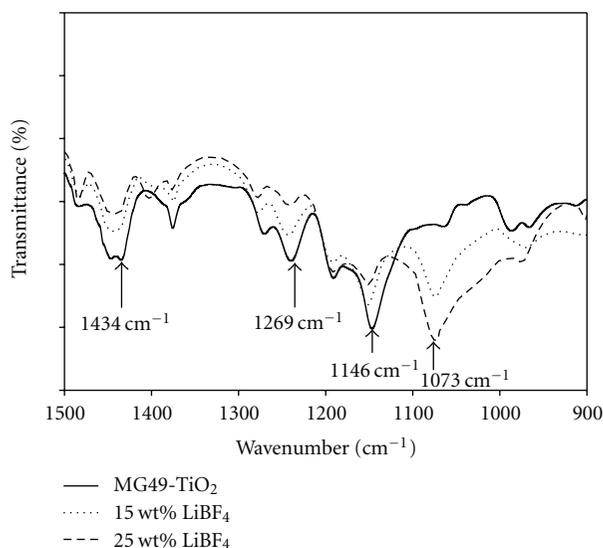


FIGURE 2: FTIR spectra of MG49-TiO₂, MG49-TiO₂-EC with 15 wt% LiBF₄ and 25 wt% LiBF₄ in the region of 1500–900 cm⁻¹.

angle of 14°, 21°, 23°, 26°, 28°, 32°, 39°, 44°, and 55°. Moreover, MG49-TiO₂ shows a sharp diffraction peak at 29°, which has been identified earlier [26] and is assigned to the polyisoprene/methyl methacrylate monomer. Therefore, the sharp single peak and the hump in the region from 8° to 23° illustrate the partial crystallization behavior of MG49. However, the diffraction peaks of rutile or anatase of TiO₂ were not observed in MG49-TiO₂, indicating that the formed TiO₂ is noncrystalline as a result of *in-situ* sol gel synthesis [1]. Upon the addition of LiBF₄ and EC into the MG49-TiO₂, the peaks correspond to LiBF₄ could be seen at 14°, 23°, and 28°. The hump of the polymer host seems to be broadened and the MMA monomer peak almost disappears with the increase in the salt concentration. This indicates that the crystallinity degree in polymer host was reduced and could be considered as a possible reason for higher mobility of charge carrier, thus leading to higher conductivity value obtained [6]. According to Gray [2], the salt concentration affects the overall conductivity through crystalline complex.

3.3. Morphological Studies. SEM micrographs of pure MG49, MG49-TiO₂, and MG49-TiO₂-EC with various wt% of LiBF₄ are shown in Figure 4. It can be seen from Figure 4(a) that pure MG49 shows a rough and uneven surface morphology which represents the partial crystalline phase in MG49. The formation of TiO₂ nanoparticles was confirmed and homogeneously dispersed on the MG49 surface with the particle diameter from 60 nm to 100 nm which was a consequence of the uniform precipitation of TiO₂ in the polymer matrix by sol-gel reaction [14, 15] as seen in Figure 4(b) with magnification of 15,000x. Therefore, the uneven surface morphology of MG49 become more even with the formation of TiO₂ nanoparticles on the matrix as seen in Figures 4(b) and 4(c) which shows the plasticized nanocomposite polymer electrolyte with 25 wt% of LiBF₄,

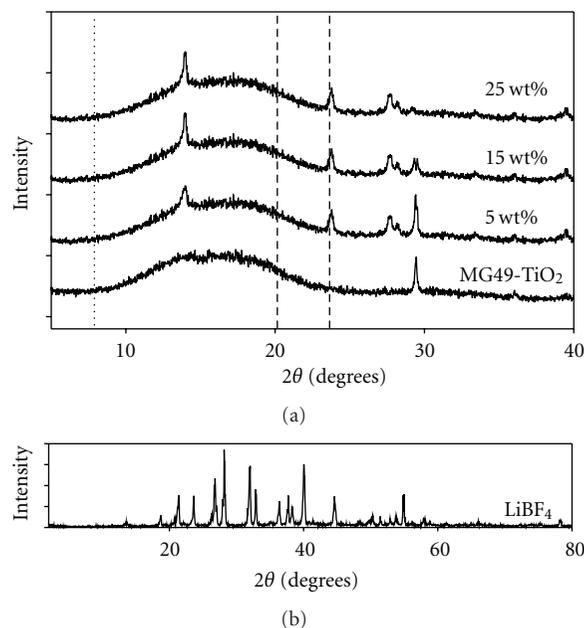


FIGURE 3: XRD pattern of LiBF₄, MG49-TiO₂, and MG49-TiO₂-LiBF₄-EC with various LiBF₄ content.

respectively. In this system, the surface morphology of the electrolyte becomes smoother with the addition of salt. Moreover, this surface morphology has darker tone color if compared with the SEM micrograph shown in Figures 4(a) and 4(b) which represents a more amorphous phase as suggested by Monikowska et al. [27]. Thereby, the smooth surface morphology is closely related to the reduction of crystallinity phase with the addition of salt and indicates that salt was completely dissolved in the matrix. It suggests the existence of interaction between the salt and the polymer host as discussed in FTIR analysis section. According to the previous reports [23, 26, 27], the conducting ions move more freely in the electrolyte with smoother surface morphology and therefore cause the enhancement in the conductivity. This is because smoother surface with more amorphous phase makes the electrolyte more flexible.

3.4. Thermal Analysis. Thermal analysis has been performed on the electrolytes to confirm that the solvent was completely removed from the preparation step. The TGA curves of the electrolytes were presented in Figure 5. According to the results reported in [23, 25], the initial weight loss of 3 to 10% mainly results from the moisture absorption upon the process of sample loading, the loss of solvent from the electrolyte, or the presence of any other volatile impurities in the polymer complexes. The initial weight loss of the electrolyte increases accordingly with the increase of wt% of salt in the electrolyte system. This is due to the hygroscopic nature of the salt as reported in [23]. As can be seen from the DTG curves shown in Figure 6, MG49-TiO₂ nanocomposite was found to be stable up to a final one-step degradation which is around 382°C. The thermal degradation of the NCPE involves three steps with the presence of salt. The

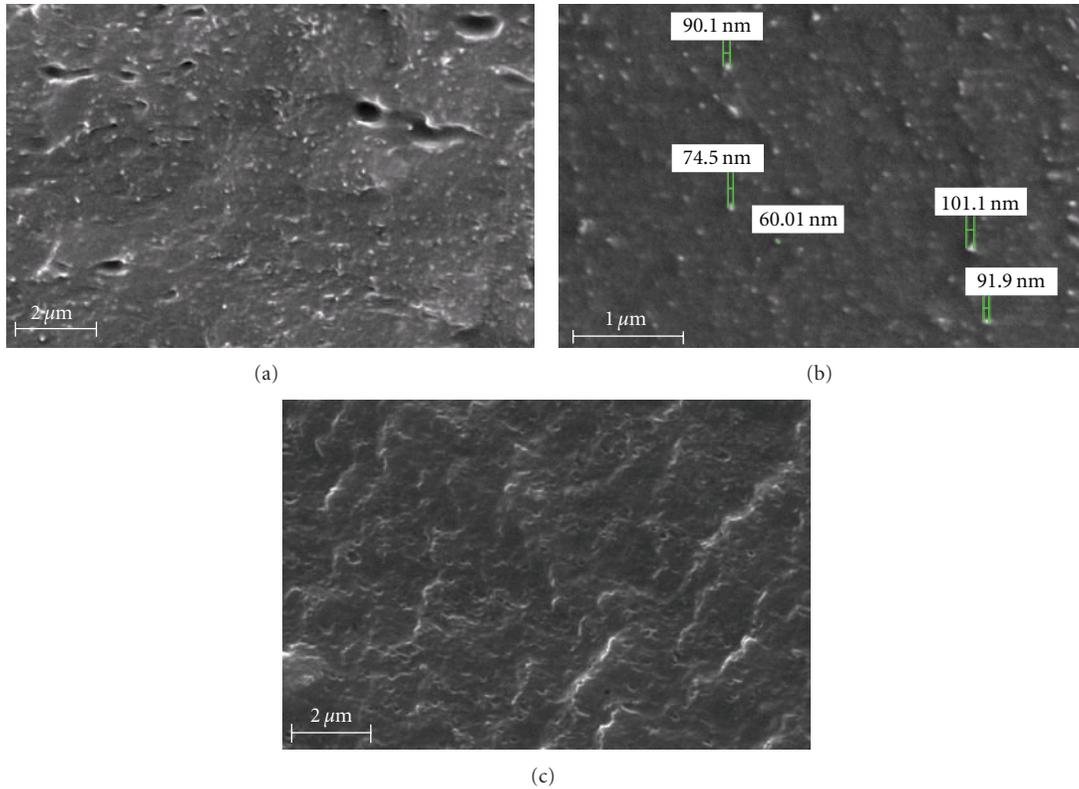


FIGURE 4: SEM micrographs of (a) MG49, (b) MG49-TiO₂ with 15,000x, and (c) 25 wt% LiBF₄.

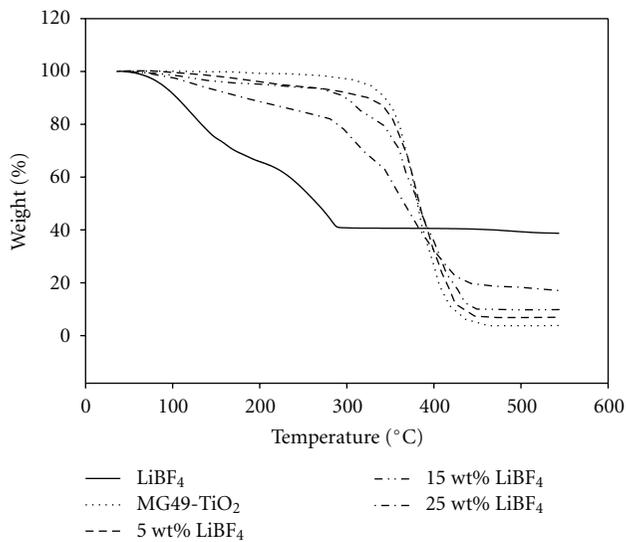


FIGURE 5: TGA curves of MG49-TiO₂ and MG49-TiO₂-EC with the variation of wt% LiBF₄.

first degradation step is due to the degradation of salt which is in the range of 272°C–290°C. The second step is due to the degradation of nanocomposite MG49-TiO₂ which is in the range of 363°C–372°C. Lastly, the final degradation which is around 428°C–438°C is the consequences of the complex formation happened as been described in FTIR analysis. Therefore, this finding supports the complexation that occurred between polymer host and salt. It can be seen

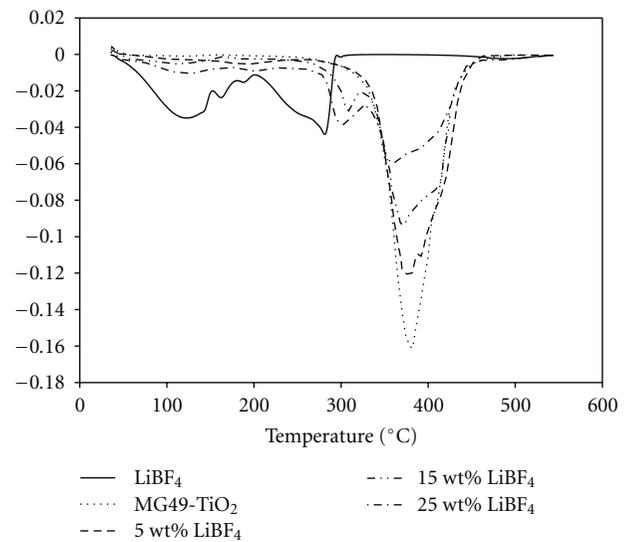


FIGURE 6: DTG curves of MG49-TiO₂-EC with the variation of wt% LiBF₄.

that the residual increases accordingly to the increase of LiBF₄ and this suggested that the salt decreases the thermal stability of the nanocomposite polymer electrolyte.

3.5. Ionic Conductivity. Conductivity is a crucial property to be considered to produce a better polymer electrolyte. The resulting conductivity is represented by overall mobility

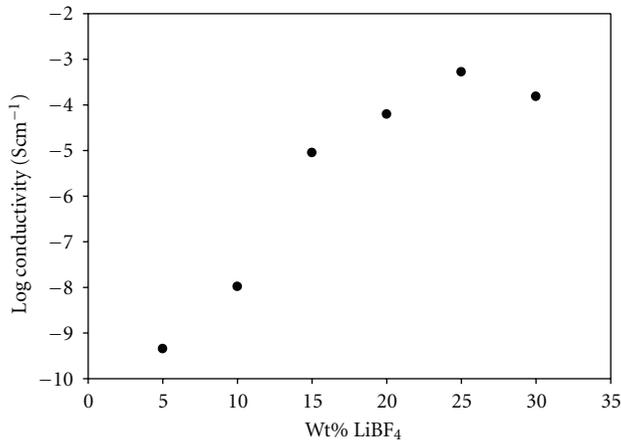
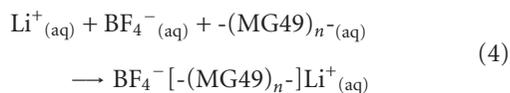


FIGURE 7: Variation of ionic conductivity of MG49-TiO₂-LiBF₄-EC electrolyte with the LiBF₄ content.

of ion and polymer determined by the free volume which leads to the increase in ionic and segmental mobility that will assist ion transport and practically compensates the retarding effect of the ion clouds [28]. The conduction process in this electrolyte system is due to the hopping of positive or negative charges from lithium salt doped in the polymer host. Ionic conductivity of MG49-TiO₂-LiBF₄-EC electrolytes with variation of wt% LiBF₄ was presented in Figure 7. It shows that the ionic conductivity increases as the salt content increases up to its optimum level in the polymer host. The increase in conductivity was due to the increase in the number of conducting species in electrolyte contributed by lithium salt that undergoes ion dissociation because of the presence of C=O in the side chain of MG49 [20]. These conducting species are also known as free mobile ions which may increase the amorphous structure of the polymer through favorable free volume, and therefore the ion migration takes place easily [22]. The mechanism of LiBF₄ dissociation and the complexation with polymer host is shown in the following equation as suggested by Ahmad et al. [29]:



The optimum conductivity was obtained at 25 wt% of LiBF₄ with the ionic conductivity of $5.2 \times 10^{-4} \text{ S cm}^{-1}$ and could be attributed to the increase in the rate of ion dissociation. The optimum conductivity is probably due to the effective interaction between the charge carriers and the polymer, which influences the segmental mobility of the polymer chains [7, 20]. Nevertheless, the ionic conductivity decreases after optimum salt addition due to ion association or ion aggregation [6, 7]. At higher salt concentration, the mean distance between ions becomes more significant because the ions become closer to one another and tend to associate. The dissolved Li⁺ ions coordinate to the oxygen in the carbonyl group in MG49 which may form

a transient crosslink between chain segments which reduce the mobility of the charge carriers and lead to a decrease in conductivity [10, 20]. However, this work obtained a higher conductivity than the finding by Su'ait et al. [6] as filler and plasticizer are added into this system. Studies of Pitawala and coworkers [30] also reported that the combined effect of plasticizer and filler increased the ionic conductivity by the structural modification associated with the polymer host and decreased the degree of crystallinity of the electrolyte. The high dielectric constant of TiO₂ assists the lithium salt to dissociate more easily in matrix [12]. The mechanism proposed for the enhancement of conductivity was the presence of disorder due to the interactions between polymer and ceramic, enhanced by the lewis acid nature of the filler, which leads to the weaker interactions between the polymer and the lithium ions. Hence, the interaction resulted in stiffening of the polymer but allows higher mobility of Li⁺ ions through an interfacial region. Therefore, the addition of filler particles created a new pathway for the lithium ions [31]. According to the results reported in the previous studies [19, 24, 30], the addition of plasticizer increased the ionic conductivity of polymer electrolyte system. This is because the high dielectric constant of the plasticizer increases the number of mobile ions by weakening the coulombic force between the anions and cations of the salt. Therefore, the dissociation of salt in the system has increased, and more free Li⁺ ions are produced. After all, the combined effect by the plasticizer and filler appears to contribute to the overall conductivity enhancement in the solid polymeric electrolyte.

4. Conclusions

Nanocomposite polymer electrolytes based on MG49-TiO₂-LiBF₄-EC system had been prepared via solution casting technique. The effect of LiBF₄ salt concentration on the ionic conductivity, chemical interaction, crystallinity, and morphology of plasticized MG49 based nanocomposite polymer electrolyte was investigated by AC impedance spectroscopy, XRD, and SEM. FTIR spectroscopy measurement showed the changes in the environment of functional groups, which leads to complexation as lithium salt concentration increases. The X-ray diffraction showed the reduction of crystalline phase with the addition of salt. TiO₂ particles were found to well distribute in polymer matrix at the nanometer level, and the rough surface of MG49 becomes smooth due to the addition of salt and plasticizer based on the observation from SEM. TGA and DTG analysis confirmed that the thermal stability of the electrolyte decreases with the salt content. From the impedance analysis, ionic conductivity was found to increase with wt% salt up to an optimum value. The conductivity reached the maximum value of $5.2 \times 10^{-4} \text{ S cm}^{-1}$ at 25 wt% LiBF₄.

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