

Nanocomposite solid polymeric electrolyte of 49% poly(methyl methacrylate)-grafted natural rubber–titanium dioxide–lithium tetrafluoroborate (MG49-TiO₂-LiBF₄)

S. P. Low · A. Ahmad · H. Hamzah · M. Y. A. Rahman

Received: 30 July 2010 / Revised: 14 November 2010 / Accepted: 15 November 2010 / Published online: 1 December 2010
© Springer-Verlag 2010

Abstract A nanocomposite polymer electrolyte consisting of 49% poly(methyl methacrylate)-grafted natural rubber (MG49) as a polymer matrix, lithium tetrafluoroborate (LiBF₄) as a dopant salt, and titanium dioxide (TiO₂) as an inert ceramic filler was prepared by solution casting technique. The ceramic filler, TiO₂, was synthesized in situ by a sol–gel process. The ionic conductivity was investigated by alternating current impedance spectroscopy. X-ray diffraction (XRD) was used to determine the structure of the electrolyte, and its morphology was examined by scanning electron microscopy (SEM). The highest conductivity, $1.4 \times 10^{-5} \text{ S cm}^{-1}$ was obtained at 30 wt.% of LiBF₄ salt addition with 6 wt.% of TiO₂ filler content. Ionic conductivity was found to increase with the increase of salt concentration. The optimum value of conductivity was found at 6 wt.% of TiO₂. The XRD analysis revealed that the crystalline phase of the polymer host slightly decreased with the addition of salt and filler. The SEM analysis showed that the smoother the surface of the electrolyte, the higher its conductivity.

Keywords 49% poly(methyl methacrylate)-grafted natural rubber (MG49) · Nanocomposite polymer electrolyte (NCPE) · Ionic conductivity · XRD · Morphology

Introduction

During the twentieth century, most synthetic polymers have been used as structural materials or as electric insulators. However, in the past 20 years, synthetic polymers have been tailored as electrolytes or ion conductors when combined with appropriate salts [1]. Conductive polymer–salt complexes were firstly described in the early 1970s and were rapidly adopted by the electrochemical community who recognized the potential of a flexible, plastic, ion transporting medium for vital applications such as energy storage and electrochemical displays [2]. Therefore, modification of liquid electrolytes to gel polymer electrolytes and later replaced by solid polymer electrolyte have drastically been developed to widen the use of polymer electrolytes [3]. Nanocomposite polymer electrolytes are referred to the dispersion of small fractions of low-dimension particles in the conventional solid polymer complexes. This did not only result in an increase in room temperature conductivity by several orders of magnitude but also enhanced the mechanical property of the electrolytes as well as the interfacial activity of electrode/electrolyte during charge–discharge process during battery operation [4–6].

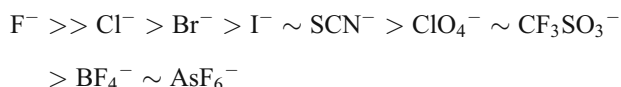
Heveaplus MG with 49% (MG49) of PMMA produced by the grafting the PMMA chains to the rubber molecules. This graft copolymer of natural rubber latex and methyl methacrylate has gained attention due to its polar characteristics which can serve as a conducting medium as it has

S. P. Low · A. Ahmad (✉) · H. Hamzah
School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600, Bangi, Selangor, Malaysia
e-mail: azizan@ukm.my
e-mail: azizanukm@yahoo.com

A. Ahmad · H. Hamzah
Polymer Research Center, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600, Bangi, Selangor, Malaysia

M. Y. A. Rahman
College of Engineering, Universiti Tenaga Nasional, 43009, Kajang, Selangor, Malaysia
e-mail: yusri@uniten.edu.my

polar substitutes to transport lithium ions and also low T_g to enhance chain mobility [7]. There are two ways of increasing the ionic conductivity of polymer electrolyte: by suppression of crystallization of polymer chains to improve polymer chain mobility and by increasing the ion carrier concentration. The suppression of crystallization of the polymer chain can be realized by inorganic filler blend [8]. The inorganic TiO_2 particles have been identified as the ceramic filler that improved the ionic conductivity and cation transference number because of the weakening of the polyether oxygen– Li^+ interactions as reported by Chung et al. [9] on the effect of nanosize ceramic fillers TiO_2 , Al_2O_3 , and SiO_2 in poly(ethylene)oxide (PEO)- LiClO_4 ; however, the high surface energy of TiO_2 resulted in the aggregation of the particles during the preparation of the polymer–ceramic nanocomposites through mechanical blending of nanosize TiO_2 particles, polymer, and salt in a compatible solvent. Hence, sol–gel process was employed to overcome this problem wherein the nano-sized ceramic fillers are precipitated in situ in the polymer matrix through a series of hydrolysis and condensation reactions of suitable precursor [6, 10, 11]. The increase of the ion carrier concentration can be realized by using highly dissociable salts and increase in salt concentration [1, 8]. According to Gray [1], the most suitable choices of anions for low-dielectric constant dipolar polymer-based polymer electrolytes are those to the right of the preceding series:



These are large anions with delocalized charge and low lattice energies as they have little tendency to form ion pairs. Since all the anions in lithium salts are counter ions of strong acids, the difference in conductivity is presumably due to the difference in lattice energies of the salts. LiBF_4 is among one of the lithium salts which has low lattice energy (699 kJ mol^{-1}) and therefore allows easier solvation of Li^+ ions by the polymer matrix, which facilitates a higher ionic conductivity [12]. In this present study, MG49- LiBF_4 - TiO_2 nanocomposite polymer electrolyte was prepared, in which nano-sized TiO_2 particles were precipitated by in situ synthesis after the lithium ions had been initially installed in the solid polymer network. This in situ approach had been successfully used in the synthesis of TiO_2 -derived, PEO-based [10, 11], and PVdF-based [13] composite polymer electrolyte which exhibited excellent ionic conductivity and uniform distribution of TiO_2 in the polymer. The room temperature conductivity, structure, and morphology of the electrolyte samples were examined by impedance spectroscopy technique, X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively.

Experimental

Materials

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

Sample preparation

The nanocomposite polymer electrolyte samples were prepared by solution casting technique. Three grams of MG49 rubber was sliced into smaller sizes and dissolved in stopped flasks containing 75 ml of tetrahydrofuran (THF) for 24 h. The solution was then stirred with efficient magnetic stirring for the next 24 h. The LiBF_4 salt was prepared separately in THF solution and stirred until complete dissolution. These two solutions were mixed and further stirred for 24 h to obtain a homogenous solution. A calculated amount of ethyl alcohol, titanium ethoxide, and potassium chloride solution (58:1:0.025) were added into the solution under continuous stirring. The TiO_2 content of the nanocomposite polymer electrolyte was 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 particle size [14, 15]. The hydrolysis and condensation reactions of titanium ethoxide could be represented by the following equations [10, 11, 13]:

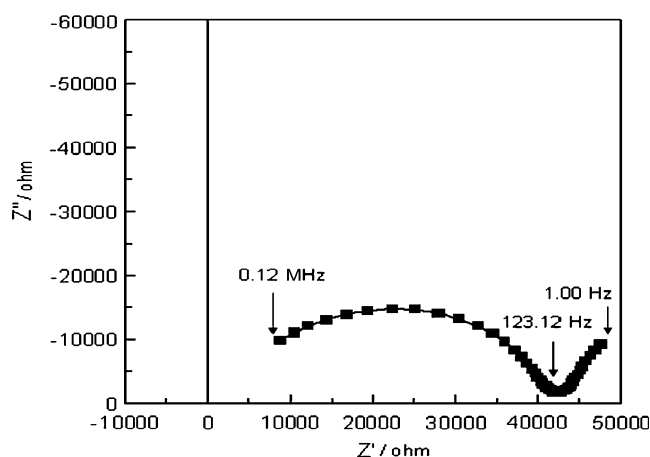
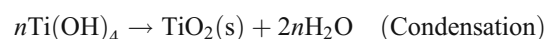
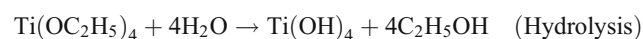


Fig. 1 Typical impedance plot for MG49- LiBF_4 - TiO_2

Table 1 Ionic conductivities of MG49-TiO₂-LiBF₄ at room temperature

Ionic conductivity (S cm ⁻¹)					
Wt.% LiBF ₄	Wt.% TiO ₂				
	2	4	6	8	10
10	1.1E-09	2.3E-10	1.2E-09	6.01E-09	1.5E-09
15	3.5E-09	3.6E-09	1.7E-07	8.3E-08	1.1E-08
20	1.5E-06	4.3E-09	3.9E-06	9.8E-07	6.8E-07
25	6.1E-07	3.8E-07	9.7E-06	1.8E-06	1.7E-06
30	1.2E-07	1.1E-06	1.4E-05	1.6E-06	6.4E-07

The solution was stirred for another 3 h before it was transferred to a teflon petri dish to allow the solvent to evaporate. 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 under vacuum for 48 h to completely remove any trace amount of the residual solvent.

Characterization

The ionic conductivity measurements were carried out by alternating current (AC) impedance spectroscopy using a high frequency resonance analyzer 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 $\sigma = l / (AR_b)$. XRD model D5000 Siemens was used to observe the appearance and disappearance of the crystalline or the amorphous phase of the electrolyte samples. The data were collected from the range of diffraction angles 2θ from 5° to 35° at the scanning rate of 0.025°s⁻¹. The morphology of the electrolyte was examined by SEM Philip XL 30 model with magnification of $\times 5,000$.

Table 2 Comparison of room temperature ionic conductivity of various electrolytes with TiO₂ filler

Electrolyte system	σ (S cm ⁻¹)	Reference
MG49-TiO ₂ -LiBF ₄	1.4×10^{-5}	–
PMMA-TiO ₂ -LiIm/LiBeTi	1.7×10^{-3}	[6]
PEO-TiO ₂ -LiBF ₄	7.0×10^{-7}	[10]
PEO-TiO ₂ -LiClO ₄	5.5×10^{-5}	[11]

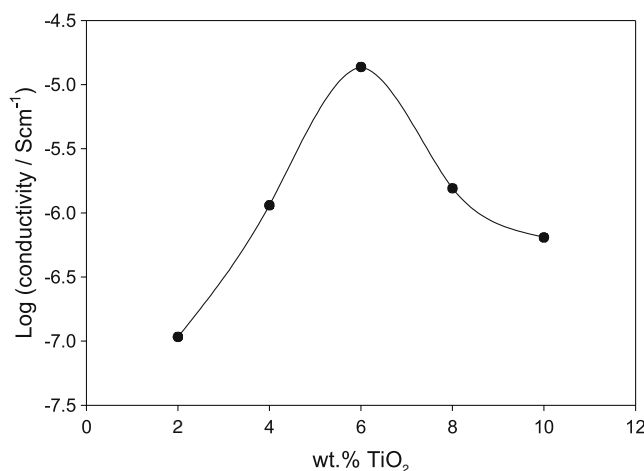


Fig. 2 Variation of room temperature ionic conductivity of MG49—(30 wt.% LiBF₄ with TiO₂ content

Results and discussion

Ionic conductivity

A high room temperature ionic conductivity is a very important aspect for the practical application of lithium batteries [13]. The resulting conductivity is represented by the overall mobility 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 compensate for the retarding effect of the ion clouds [16]. The point of intersection between the arc in the high frequency range and the straight line in the low frequency range coincides with the bulk resistance of the electrolyte film shown in Fig. 1. The room temperature ionic conductivities of the electrolyte (MG49-LiBF₄-TiO₂) were expressed in Table 1. The highest ionic conductivity of 1.4×10^{-5} S cm⁻¹ was obtained at 30 wt.% of LiBF₄ and

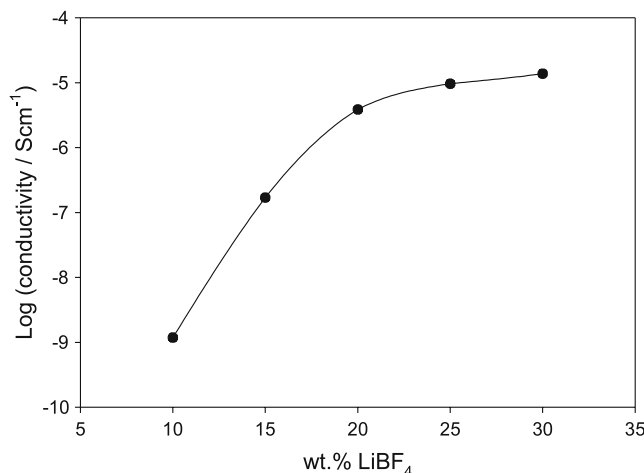


Fig. 3 Variation of room temperature ionic conductivity of MG49-(6 wt.% TiO₂ with LiBF₄ content

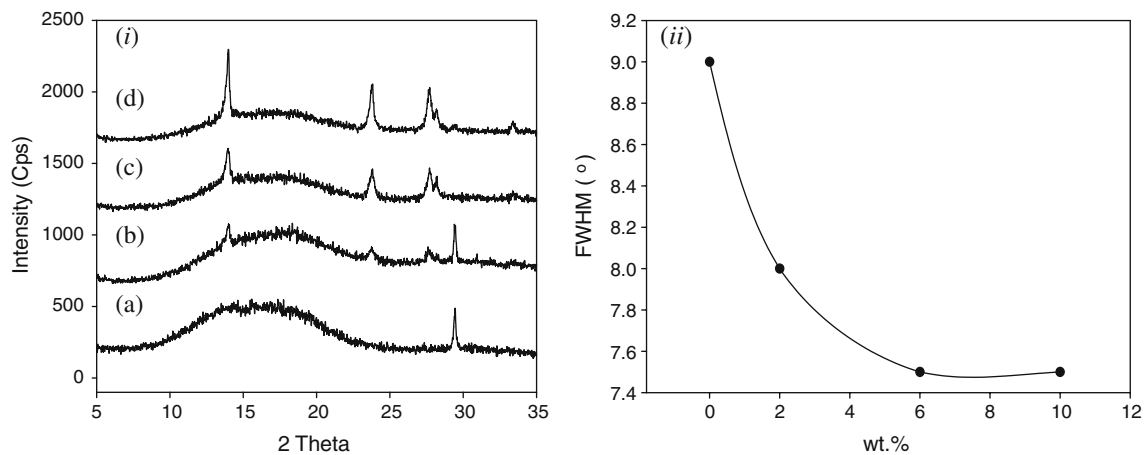


Fig. 4 *i* XRD pattern for MG49-(6 wt.% TiO₂) (a) and (b) to (d) MG49-(30 wt.% LiBF₄-TiO₂) with TiO₂ content of 2, 6, and 10 wt.%. *ii* FWHM value plot of MG49-TiO₂-(30 wt.% LiBF₄) with TiO₂ content of 2, 6, and 10 wt.%

at 6 wt.% of TiO₂. This finding proves that the presence of TiO₂ increased the conductivity by a few orders as Su'ait et al. [17] obtained the highest conductivity of 2.3×10^{-7} S cm⁻¹ for the polymer electrolyte system of MG49-LiBF₄. Table 2 illustrates the room temperature ionic conductivity of various electrolytes with TiO₂ filler. It was found that from the table, the conductivity of the electrolyte developed in this work is higher than that with PEO as a polymer host. This indicates that MG49 is more conductive than PEO. The results shown in the table also proved that the presence of nanoparticles TiO₂ enhanced the conductivity significantly.

Figure 2 shows the room temperature ionic conductivity of MG49-(30 wt.% LiBF₄) with the variation of the weight percent of TiO₂ filler. The introduction of the filler into the electrolyte system will reduce the degree of crystallinity of the electrolyte as illustrated in the XRD

patterns shown in Fig. 3. The TiO₂ fillers will promote more free lithium ions from the inorganic salt of LiBF₄ to transfer in the electrolyte [18]. The addition of the optimum amount which is 6 wt.% of TiO₂ had induced the most favorable environment for Li⁺ ions to attain higher conductivity. This is because the high dielectric constant of TiO₂ assists the lithium salt to dissociate more easily in the polymer matrix [5]. The mechanism proposed for the enhancement of conductivity was the presence of disorder due to the interactions between the 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 the stiffening of the polymer but allows higher mobility of the Li⁺ ions through an interfacial region [5, 9–11, 13]. Therefore, addition of filler particles created a new pathway for the lithium ions. Besides that, the interaction of TiO₂ nano-

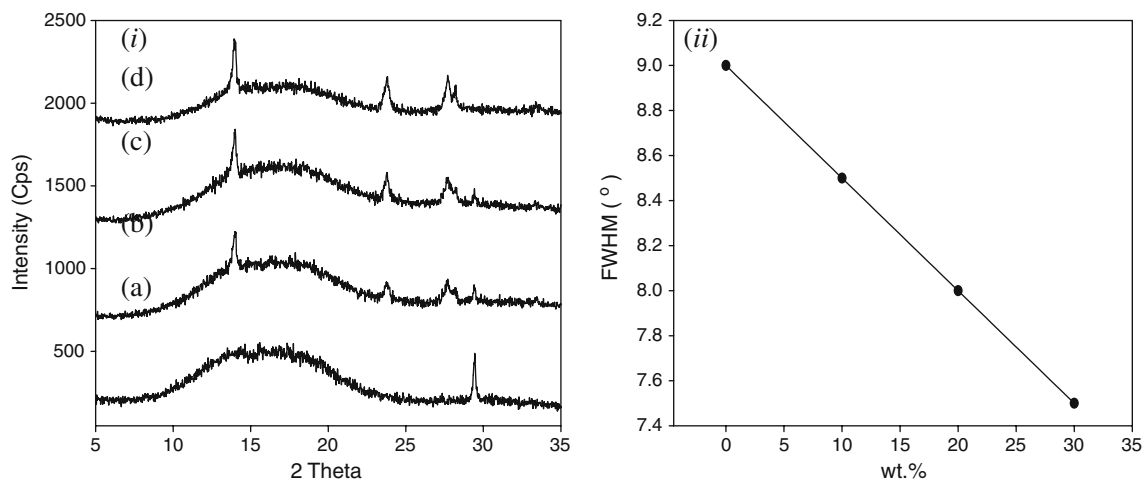


Fig. 5 *i* XRD pattern for MG49-(6 wt.% TiO₂) (a) and (b) to (d) MG49-(6 wt.% TiO₂-LiBF₄) with LiBF₄ content of 10, 20, and 30 wt.%. *ii* FWHM value plot of MG49-(6 wt.% TiO₂-LiBF₄) with LiBF₄ content of 10, 20, and 30 wt.%

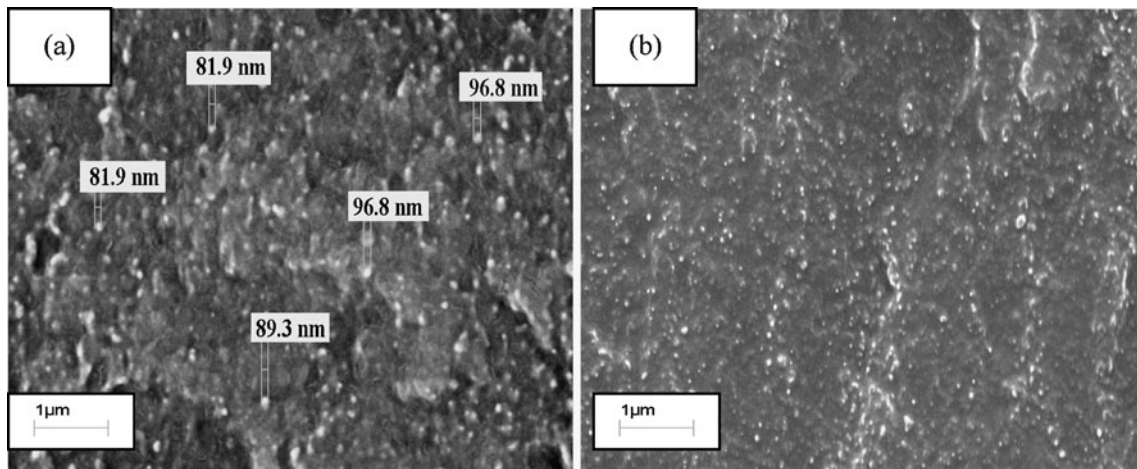


Fig. 6 SEM micrograph for MG49-(6 wt.%)TiO₂ nanocomposite with **a** $\times 15,000$ and **b** $\times 5,000$

particles with lithium salt and polymer chain promotes a network with improved mechanical stability of the electrolyte film [19]. The decrease in conductivity at higher TiO₂ addition may represent agglomeration of primary particles

to bigger particles which then leads to a lower surface area of the filler and immobilizes the polymer chains [5, 10, 20].

Figure 3 shows the conductivity of MG49-(6 wt.%) TiO₂-LiBF₄ polymer electrolyte with the variation of

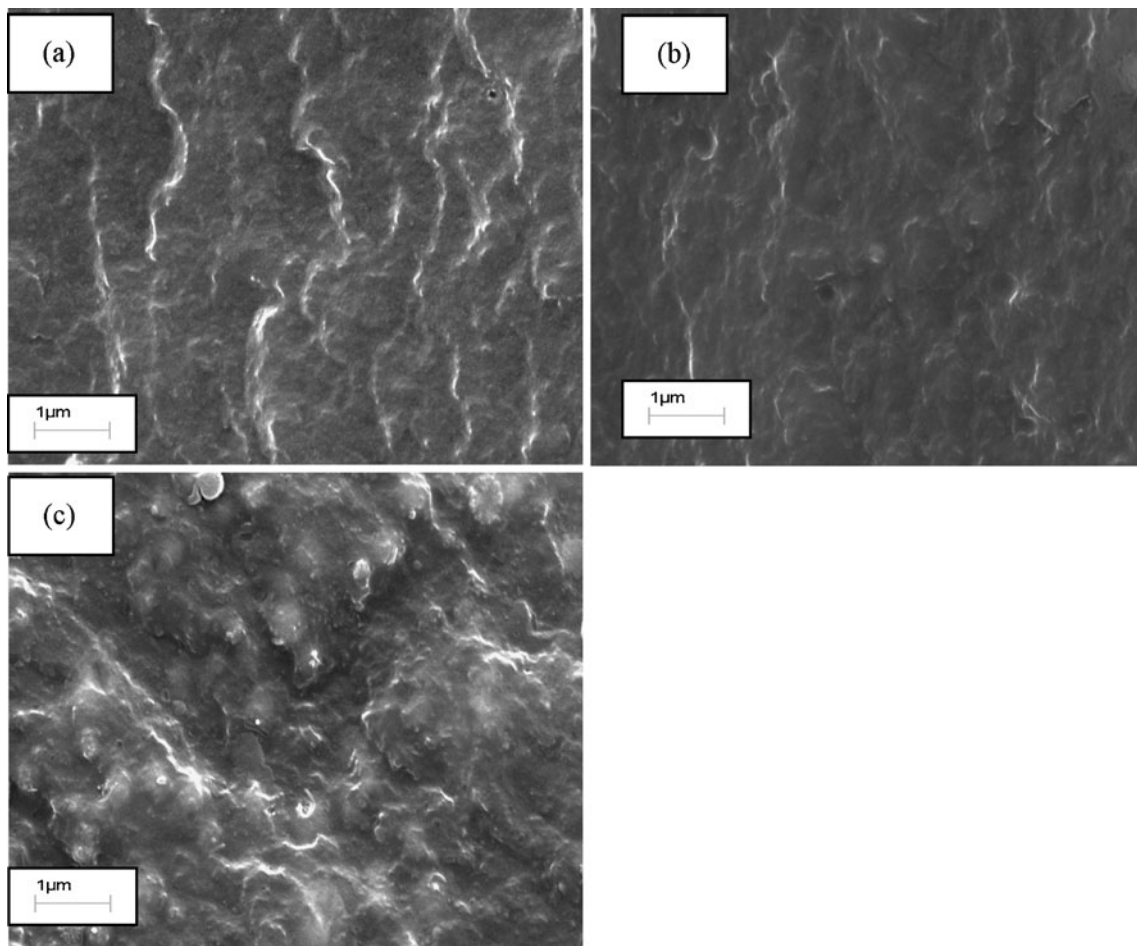


Fig. 7 SEM micrograph for MG49-(30 wt.%) LiBF₄ with various TiO₂ content **a** 2 wt.%, **b** 6 wt.%, and **c** 10 wt.% with a magnification of $\times 5,000$

weight percent LiBF_4 salt. The conductivity increases with the addition of LiBF_4 and achieved highest conductivity at 30 wt.% LiBF_4 . When the salt concentration increases, the number of conducting species as well as mobility also increase [17, 18]. The conducting species, which are the free mobile ions, will also decrease the degree of crystallinity of the polymer host through favorable free volume, and therefore, the ion migration takes place easily [16, 18]. Thus, the effect of lithium salt content on crystallization of the electrolyte is indicated by the XRD patterns shown in Fig. 3. The highest conductivity yielded also indicates the effective interaction between oxygen atoms and Li^+ ion in the electrolyte where a coordinate bond was formed in the polymer–salt complexes between Li^+ and oxygen atoms. The interaction that occurs was explained by the FTIR investigation reported elsewhere [6, 7, 16, 17]; however, further salt addition above 30 wt.% LiBF_4 will make the electrolyte tend to crystallize as the free ions become saturated and causes the ions to be so close to one another, thus the conductivity decreases.

XRD analysis

The behavior of the dominant crystalline phase in the $\text{MG49-LiBF}_4\text{-TiO}_2$ polymer electrolyte system can be predicted from the XRD patterns in order to indicate the change in dominant crystalline phase with LiBF_4 or TiO_2 content [13]. Figures 4 and 5 show the XRD patterns for the polymer electrolyte of $\text{MG49-TiO}_2\text{-(30 wt.\% LiBF}_4\text{)}$ and $\text{MG49-(6 wt.\% TiO}_2\text{)-LiBF}_4$, respectively within the diffraction angle from 5° to 35° . In Figs. 4a and 5a, the clear and sharp diffraction peaks and the hump in the region from 6° to 26° illustrates the partial crystallization of MG49. The full width at half maximum (FWHM) value of the hump at the region 6° to 26° was calculated in order to determine the degree of crystallinity of the polymer host. The characteristic diffraction peaks of rutile or anatase of TiO_2 were not observed, indicating that the TiO_2 is non-crystalline [21].

According to Fig. 4b–d, the intense peak corresponds to the polymer host and the hump becomes broader with increasing TiO_2 content in $\text{MG49-(30 wt.\% LiBF}_4\text{)}$ polymer

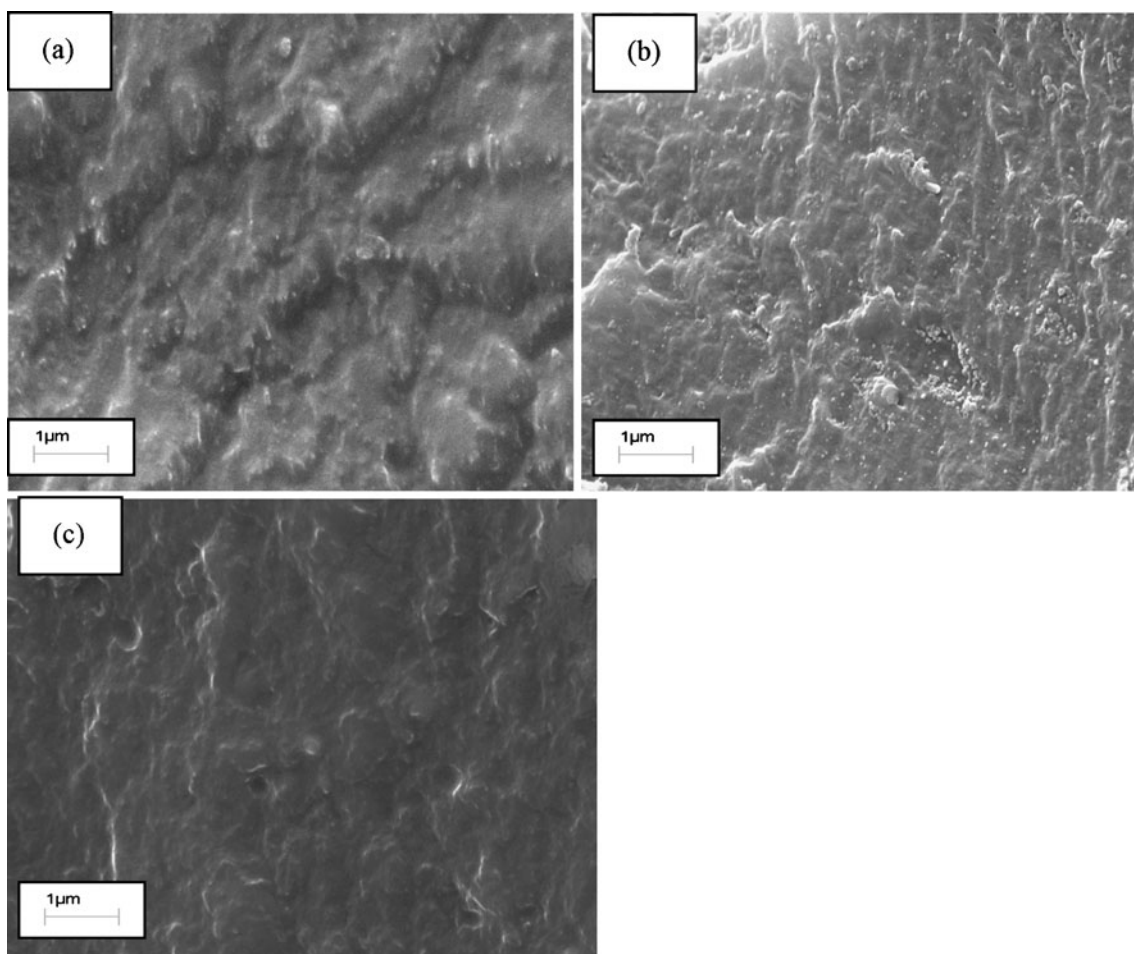


Fig. 8 SEM micrograph for $\text{MG49-(6 wt.\%TiO}_2\text{)}$ with various LiBF_4 content **a** 10 wt.%, **b** 20 wt.%, and **c** 30 wt.% with a magnification of $\times 5,000$

electrolyte. This result in the peak of LiBF_4 salt at 14° becomes sharper. The FWHM plot also shows a decreasing value with the increasing TiO_2 content. Therefore, this result suggested that the crystalline phase decreases with increasing TiO_2 content because the fine particles of TiO_2 in polymer host has lead to the broadening of hump and suppressed the crystallinity of the polymer host [13, 22]. The restriction of crystallization and increase of the amorphous phase could be considered as a possible reason for higher mobility of charge carrier, thus lead to higher conductivity of the electrolyte [19].

The intense peak and the hump of the polymer host become broader as the LiBF_4 content increases in the MG49-(6 wt.%) TiO_2 polymer electrolyte system, as shown in Fig. 5i. The FWHM value decrease gradually with the increase in the LiBF_4 content from 10 to 30 wt.%. This shows that complexation occurs between the polymer hosts, MG49 and LiBF_4 [13]. As mentioned earlier, the highest ionic conductivity was obtained with the addition of 6 wt.% of TiO_2 and 30 wt.% of LiBF_4 in MG49. This finding confirmed the results reported elsewhere [13, 17–22] that amorphous regions provide high ionic conductivity compared to the crystalline or semi-crystalline region. The salt affects the overall conductivity through crystalline complex formation, intramolecular cross-linking of the polymer chains and degree of salts dissociation number of charge carriers [1].

Morphological studies

The morphology of MG49-(6 wt.%) TiO_2 electrolytes are shown in Fig. 6. As observed from Fig. 6a with magnification of $\times 15,000$, nanoparticles TiO_2 are homogeneously dispersed on MG49 surface with the diameter of particle from 60 to 100 nm which was a consequence of the uniform precipitation of TiO_2 in the polymer matrix by sol–gel reaction [9, 10]. In Fig. 6b with the magnification of $\times 5,000$, the surface morphology of the nanocomposite is rough. Figure 7 shows the morphologies of MG49-(30 wt. % LiBF_4) electrolytes with the variation of TiO_2 content. In this system, a 6-wt.% addition of TiO_2 (Fig. 7b) seems to be the optimum as it possesses the smoothest surface compared with a 2-wt.% (Fig. 7a) and a 10-wt.% (Fig. 7c) addition of TiO_2 . The effect of LiBF_4 on the morphology of the MG49-(6 wt.%) TiO_2 electrolytes are described by SEM micrographs shown in Fig. 8. After a 10-wt.% salt addition into MG49-(6 wt.%) TiO_2 electrolyte, the improvement of surface morphology can be observed and it is shown in Fig. 8a. The rough surface changed to a smooth surface due to the addition of salt. In this electrolyte system, the rough surface of the electrolyte becomes smoother with further addition of salt (20 and 30 wt.%) as shown in Fig. 8b and c. The smooth morphology is closely related to the reduction

of the crystallinity of the polymer host due to the presence of salt and indicates that salt was completely dissolved in the matrix [23]. The reduction of MG49 crystallinity arises from a random distribution of TiO_2 and dissociation of salt which may introduce the topological disorder in the electrolyte. Hence, this resulted in more amorphous phase and makes the electrolyte more flexible, resulting in an increase in the segmental motion of the polymer [18, 23]. This statement supports the highest yielded conductivity.

Conclusions

The nanocomposite polymer electrolyte of MG49- TiO_2 - LiBF_4 system was prepared by solution casting technique. Ceramic filler, TiO_2 formed by in situ within the polymer matrix via sol–gel process. The effect of LiBF_4 and TiO_2 on the ionic conductivity, crystallinity, and morphology of MG49-based nanocomposite polymer electrolyte was investigated by AC impedance spectroscopy, XRD, and SEM, respectively. Room temperature ionic conductivity was found to increase with the weight percentage of LiBF_4 and weight percentage of TiO_2 . The conductivity reached the maximum value of $1.4 \times 10^{-5} \text{ S cm}^{-1}$ at 30 wt.% LiBF_4 , and 6 wt.% TiO_2 . The X-ray diffraction showed the reduction of the crystalline phase with the addition of salt and filler. TiO_2 particles were found to be well distributed in the polymer matrix at the nanometer size and the rough surface of the electrolyte becomes smooth due to the addition of salt and filler based on the SEM observation.

Acknowledgements The authors would like to extend their gratitude towards Universiti Kebangsaan Malaysia (UKM) for allowing this research to be carried out. This work was supported by the UKM grant of UKM-GUP-NBT-082-27-108 and UKM-OUP-NBT-28-142-209.

References

1. Gray FM (1991) Solid polymer electrolyte—fundamentals and technological applications. RSC Material Monographs, London
2. Brandell D (2005) Understanding ionic conductivity in crystalline polymer electrolytes. Digital comprehensive summaries of Uppsala dissertations from the Faculty of Science and Technology 34, Uppsala Universitet
3. Rajendran S, Sivakumar M, Subadevi R (2004) Mater Lett 58:641
4. Agrawal RC (2007) Nanocomposite polymer electrolytes: materials and application aspects. Solid State Ion Proceeding, India
5. Johansson P, Jacobsson P (2004) Solid State Ion 170:73
6. Ahmad S, Agnihotry SA, Ahmad S (2008) J Appl Poly Sci 107:3042
7. Alias Y, Ling I, Kumutha K (2005) Ionics 11:414
8. Murata K, Izuchi S, Yoshihisa Y (2000) Electrochim Acta 45:1501
9. Chung SH, Wang Y, Persi L, Croce F, Greenbaum SG, Scrosati B, Plichta (2001) J Power Sources 644:97

10. Liu Y, Lee JY, Hong L (2003) *J Appl Poly Sci* 89:2815
11. Pan CY, Feng Q, Wang LJ, Zhang Q, Chao M (2007) *J Cent South Univ Techno* 03-0348-05
12. Rajendren R, Ramesh M, Usha M (2008) *J Power Sources* 180:880
13. Wang YJ, Kim D (2007) *Electrochim Acta* 52:3181
14. Assamann SE, Widoniak J, Maret G (2004) *Chem Matter* 16:6
15. Taslim R, Rahman MYA, Salleh MM, Umar AA, Ahmad A (2009) *Phys B* 404:1420
16. Ramesh S, Ang GP (2010) *Ionics* 16:465
17. Su'ait MS, Ahmad A, Rahman MYA (2008) *Ionics* 15:497
18. Ahmad A, Rahman MYA, Ali MLM, Hashim H, Kalam FA (2007) *Ionics* 13:67
19. Lin CW, Hung CL, Venkateswarlu M, Hwang BJ (2005) *J Power Sources* 146:397–401
20. Aravindan V, Vickaraman P (2009) *Poly Eng Sci* 49:2109
21. Li ZH, Zhang HP, Zhang P, Wu YP, Zhou XD (2008) *J Power Sources* 184:562
22. Shanmukaraj D, Wang GX, Murugan R, Liu HK (2008) *J Phys Chem Solids* 69:243
23. Noor SAM, Ahmad A, Talib IA, Rahman MYA (2010) *Ionics* 16:161