

FORMATION, MORPHOLOGICAL, MOLECULAR INTERACTION AND IONIC CONDUCTIVITY OF SiO₂ FILLED PMMA/PEG ELECTROLYTES

(Pembentukan, Morfologikal, Interaksi Molekul dan Kekonduksian Ionik Elektrolit PMMA/PEG Terisi SiO₂)

Nurul Dhabitah Basri¹, Famiza Abdul Latif^{1,2}, Ruhani Ibrahim^{1,2}, Fazni Susila Abdul Ghani^{1,2},
Sharil Fadli Mohamad Zamri^{1,2*}

¹Faculty of Applied Sciences,

²Synthesis and Application of Conducting Polymer Research Group,
Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

*Corresponding author: sharil7240@uitm.edu.my

Received: 20 November 2020; Accepted: 16 February 2021; Published: xx April 2021

Abstract

In this study, silicon dioxide (SiO₂) was used as a filler in the preparation of polymer electrolytes containing poly(methyl methacrylate) (PMMA) and poly(ethylene glycol) (PEG). The role of SiO₂ as a filler in the formation, morphology molecular interaction, and ionic conductivity of PMMA/PEG electrolytes films was investigated. PMMA/PEG blends were doped with lithium tetrafluoroborate (LiBF₄) with incorporation of various weight percentages of SiO₂ as a filler. The samples were prepared via the solvent casting method with tetrahydrofuran (THF) as a solvent. PMMA/PEG electrolyte films were characterised using Fourier transform infrared (FTIR) spectroscopy, optical microscopy (OM), and electron impedance spectroscopy (EIS). It was observed that the opacity of the polymer electrolyte films increased as the weight percentage of SiO₂ increased. Meanwhile, it was noted that the intensity of FTIR peaks at 1723 cm⁻¹, 1386 cm⁻¹, and 1239 cm⁻¹ which corresponded to C=O and O-CH₃ of PMMA, and C-O-C of PEG, respectively, decreased with increased SiO₂ weight percentage. Furthermore, phase separation was observed in OM analysis between PMMA and PEG in the PMMA/PEG blends. Interestingly, the dispersion of PEG-rich phase in the polymer films increased with increased SiO₂ weight percentage. EIS analysis showed that the ionic conductivity of PMMA/PEG electrolyte films increased with increased SiO₂ weight percentage up to 3% with maximum ionic conductivity of 5.55×10^{-6} S cm⁻¹. However, the ionic conductivity of PMMA/PEG electrolyte films decreased when the weight percentage of SiO₂ increased beyond 3%.

Keywords: lithium tetrafluoroborate, poly(ethylene glycol), poly(methyl methacrylate), silicon dioxide, polymer electrolytes

Abstrak

Dalam kajian ini, silikon dioksida (SiO₂) telah digunakan sebagai pengisi dalam penyediaan elektrolit polimer yang mengandungi poli(metil metakrilat) (PMMA) dan poli(etilena glikol). Peranan SiO₂ sebagai pengisi dalam pembentukan, morfologikal, interaksi molekul, dan kekonduksian ionik elektrolit PMMA/PEG filem telah dikaji. Adunan PMMA/PEG telah dicampurkan dengan litium tetrafluoroborat (LiBF₄) dengan tambahan pelbagai peratusan berat SiO₂ sebagai pengisi. Sampel telah disediakan dengan kaedah larutan tuang dengan tetrahidrofuran (THF) sebagai pelarut. Filem elektrolit PMMA/PEG telah dicirikan menggunakan spektroskopi inframerah transformasi Fourier (FTIR), mikroskop optikal (OM) dan spektroskopi elektron impedan

(EIS). Pemerhatian menunjukkan bahawa kelegapan filem elektrolit polimer meningkat dengan peratusan berat SiO₂ meningkat. Sementara itu, diperhatikan bahawa keamatan puncak FTIR pada 1723 cm⁻¹, 1386 cm⁻¹ dan 1239 cm⁻¹ sepada C=O dan O-CH₃ bagi PMMA, dan C-O-C bagi PEG berkurang dengan peratusan berat SiO₂ meningkat. Selanjutnya, analisis OM menunjukkan bahawa terdapat fasa pemisahan antara PMMA dan PEG dalam adunan PMMA/PEG. Menariknya, serakan fasa PEG dalam filem polimer telah meningkat dengan peratusan berat SiO₂ meningkat. Analisis EIS menunjukkan bahawa kekonduksian ionik daripada filem telah meningkat dengan penambahan peratusan berat SiO₂ sehingga 3% dengan kekonduksian ionik tertinggi 5.55 X 10⁻⁶ S cm⁻¹. Walau bagaimanapun, kekonduksian ionik filem telah menurun apabila peratusan SiO₂ telah tambah melebihi 3%.

Kata kunci: litium tetrafluoroborat, poli(etilena glikol), poli(metil metakrilat), silikon dioksida, elektrolit polimer

Introduction

Polymer electrolytes (PEs) have attracted the attention of many researchers in recent years due to their applicability in electrochemical devices, such as supercapacitors [1], lithium batteries [2], and solar cells [3]. This is due to the superior features of PEs over liquid electrolytes, such as easy processability [4], safe, non-flammable, and non-leakage property [5]. PEs can be divided into three major categories, namely solid polymer electrolytes (SPEs), gel polymer electrolytes (GPEs), and nanocomposite polymer electrolytes (NCPEs) [6]. The advantages of SPEs are that they give no issue of corrosive solvent leakage and are long lasting, [7] while GPEs have high flexibility and are leakage free [8]. However, both systems are unable to give adequate ionic conductivity at ambient temperature, which limits their application in various electric and electronic devices [8, 9].

Recently, several studies have been carried out by many researchers to subdue this limitation. Many improvements have been embraced, such as adding plasticiser [10], polymer blends [11], and nano-filler [12]. Vignarooban et al. [13] declared that the addition plasticiser in PE systems has the ability to increase the amorphous region, which decreased crystallinity of PE. In addition, the incorporation of plasticiser gives better physical and mechanical properties of electrolytes in the form of flexibility and elasticity [14]. It also encourages the augmentation of the segmental movement of the polymer backbone, which subsequently helps ionic transport along the polymer chains [14]. Examples of plasticisers that have been used in previous studies are ethylene carbonate (EC) [15], dimethylformamide (DMF) [16], and propylene carbonate (PC) [17].

From all the proposed strategies, polymer blend system is very interesting to be explored since it is wisely adjustable. In a polymer blending system, a mixture of two or more different polymers is mixed homogeneously in a suitable solvent. The technique will not produce new covalent bonds between the polymers [18]. It is the most decent technique to be used [19] because polymer blend systems offer superior characteristics, such as good conductivity [11], and better thermal and mechanical properties compared to single polymer systems. Examples of polymer electrolytes prepared via polymer blend technique are polyethylene oxide(PEO)/PMMA/poly(vinylidene fluoride hexafluoropropylene)(P(VDF-HFP)) [20], P(VDF-HFP)/poly(vinyl alcohol)(PVA) [21], and PMMA/poly(methyl methacrylate grafted natural rubber)(PMMA-g-NR) [18] electrolytes.

Dispersions of nano-particle filler with a high dielectric constant being in polymeric system [22] help to enhance the conductivity of the polymer blend. Stephan and Nahm [23] studied the presence of filler in PE, usually also known as nanocomposite polymer electrolytes (NCPEs), and found that it could enhance ionic conductivity and provide a better interfacial property in lithium batteries. In addition, one of the significant discoveries of Gozdz and Tarascon was that the expansion of highly dispersed silica to P(VDF-HFP) matrix significantly improved solvent absorption ability, thus led to the improvement of measured conductivities [24]. Since then, a number of nanoparticle fillers have been investigated including aluminium oxide (Al₂O₃) [11], silicon dioxide (SiO₂) [25], and titanium dioxide (TiO₂) [26].

The polymer host is a major component in the PE because it acts as a polymer matrix that prompts a net dipole moment [27]. Some of the polymer hosts that have been explored for preparation of PE are poly(vinyl chloride) (PVC) [28], PMMA [29], PEO [30], and poly(vinylidene fluoride) (PVDF)[11]. PMMA has been receiving the most attention from researchers due to its high ionic conductivity [31], reasonable wettability, and chemical and thermal stability [32]. PMMA is considered as an ideal polymer host for PEs owing to its transparent polymer that has a high degree of amorphous [19] and non-tacking characteristics [29].

This study investigated the effects of various weight percentage of SiO₂ filler on NCPE films of PMMA/PEG electrolytes. The effects of the filler on the formation, morphology, molecular interaction, and ionic conductivity of the films are reported.

Materials and Methods

Materials

Preparation of polymer electrolytes film were PMMA (M_w = 350 000 g mol⁻¹) (Aldrich), PEG (M_w = 5800 g mol⁻¹) (Aldrich), SiO₂ (15 nm) (Aldrich), LiBF₄ (Sigma Aldrich), and THF (Sigma Aldrich) as a solvent.

Preparation of polymer stock solutions

PMMA (5.0 g) and PEG (2.5 g) were dissolved separately in 250 mL of tetrahydrofuran (THF) under stirring condition at ambient temperature for 24 hours.

Preparation of PMMA/PEG electrolyte films containing SiO₂ filler

PMMA (25 mL) and PEG (5 mL) solutions were mixed in 250 mL screw cap bottles. Then, specific amounts of SiO₂ (0-7%) were added into the solutions under continuous stirring for another 24 hours. Next, 0.2 g of LiBF₄ salt was added into each of the solutions as shown in Table 1. The solutions containing SiO₂ and LiBF₄ were stirred again for 24 hours. The resultant polymer blend solutions were then casted into petri dishes and left overnight under nitrogen gas flow. Finally, the obtained films were peeled off using forceps and dried in an oven at 50 °C for 24 hours.

Characterisation

Fourier transform infrared spectroscopy

FTIR was used to investigate the presence of PMMA and PEG functional groups. The samples were analysed using ATR Nicolet 6100 with frequency range of 4000 to 400 cm⁻¹ at 16 times scanning rate.

Optical microscopy

The phase separation between PMMA and PEG in PMMA/PEG electrolytes was examined by Nikon ECLIPSE ME 600 at 20× magnification.

Electronic impedance spectroscopy

The ionic conductivity of PMMA/PEG electrolyte films was analysed using a Hioki 3532-01 LCR High Tester. The frequency range from 100Hz to 1MHz was used to measure the conductivity at room temperature. The ionic conductivity equation is shown below [1, 7]:

$$\sigma \text{ (ionic conductivity)} = \frac{t(\text{thickness of samples})}{R_b(\text{bulk resistance}) \times A(\text{surface area samples})} \quad (1)$$

Table 1. Materials composition of P

Film Samples (%)	PMMA (g)	PEG (g)	Mass of Filler (g)	Weight of LiBF ₄ (g)
0	0.5	0.05	0.000	0.2
1	0.5	0.05	0.005	0.2
3	0.5	0.05	0.015	0.2
5	0.5	0.05	0.025	0.2
7	0.5	0.05	0.035	0.2

Results and Discussion

The formation of PMMA/PEG electrolyte films containing various weight percentages of SiO₂ filler is shown in Figure 1. It was observed that the opacity of films increased as the weight percentage of SiO₂ increased. Furthermore, the films visually changed to yellowish-brown after being dried overnight in an oven. This phenomenon was due to interaction between the salt, filler, and polymers in the system. Singh et al. [34] reported that the same observation was observed when potassium iodide was doped into starch.

FTIR spectra of the polymer electrolyte films (Figure 2) show the peaks at 1723 cm⁻¹ [35] and 1386 cm⁻¹ [36] corresponded to C=O and O-CH₃ of PMMA, respectively. Meanwhile, the peaks recorded at 1239 [4, 37] and 728 cm⁻¹ [38] corresponded to C-O-C of PEG and BF₄⁻ of LiBF₄, respectively. It was observed that the intensity of FTIR peaks, which corresponded to C=O and O-CH₃ of PMMA, C-O-C of PEG, and BF₄⁻ of LiBF₄ decreased as the weight percentage of SiO₂ increased. This is possibly due to the complexation between polymers and salt with filler. A similar observation was reported by Farheen et al. [39] in PEO/PMMA/LiClO₄ electrolyte containing TiO₂. Besides that, Sharma et al. (2012) also reported the same observation when Al₂O₃ was added in PEO/PMA/EC electrolyte [35].

The suggested interactions between O atoms in C=O and O-CH₃ of PMMA, C-O-C of PEG with Li⁺ ion of LiBF₄ are depicted in Figure 3. The lower intensity of FTIR peaks was observed for sample with 0% of SiO₂ filler probably due to the strong interactions of Li⁺ ions in LiBF₄ with O atoms in the functional groups, which restricted their vibration bonds [40].

The intensity of C=O, O-CH₃, C-O-C, and BF₄⁻ increased when the weight percentage of SiO₂ filler was increased up to 3%, probably due to the interaction between O atoms in the functional groups and H atoms of silanol group (Si-OH) of SiO₂ with Li⁺ ion of LiBF₄ (Figure 4). Interestingly, the intensity of FTIR peaks, which corresponded to C=O, O-CH₃, C-O-C, and BF₄⁻ decreased when the weight percentage of SiO₂ was beyond 3%.

Figure 5 shows OM micrographs of PMMA/PEG electrolyte films at various weight percentages of SiO₂. Figure 5(a) shows that phase separation was observed between PMMA rich-phase and PEG rich-phase, indicated by brownish-orange colour background and numerous dark brown patches, respectively. The phase separation indicated that PMMA and PEG were incompatible. PEG was recognised as dark brown patch colour because 10% of PMMA/PEG electrolytes was made up of PEG.

Interestingly, Figures 5(b) - (e) show that the dark brown spots were accumulated and became darker compared to Figure 5(a). This indicated that the dispersion of PEG-rich phase improved when the weight percentage of SiO₂ increased by up to 7%. This observation proved that SiO₂ filler could interact with PEG-rich phase via hydrogen bond as claimed by Yuan et al. [41]. However, Figure 5 shows that the phase separation between the polymers still existed although higher weight percentage of SiO₂ in the system indicated that PMMA/PEG blend was an immiscible system. A similar observation was reported by Elmér and Jannasch [43].

Ionic conductivity of PMMA/PEG electrolyte films at ambient temperature is depicted in Table 2. The result indicated that the ionic conductivity increased with the increased weight percentage of the SiO₂ filler up to 3% with the maximum ionic conductivity value of $55.5 \times 10^{-7} \text{ Scm}^{-1}$. The ionic conductivity then decreased when the weight percentage of the SiO₂ filler was added beyond 3%. The same observation was reported by Latif et al. [44]. They found that the highest ionic conductivity of PMMA/50% epoxidized natural rubber (ENR 50) electrolytes was at 3% of SiO₂ filler.

The ionic conductivity is associated with the interaction between Li⁺ ion from LiBF₄ and O atoms from PMMA and PEG as shown in Figure 3 and Figure 4. At 0% of SiO₂, Li⁺ ion tends to attach strongly to the O atoms in C=O and O-CH₃ of PMMA and C-O-C of PEG. Therefore, the strong interaction resulted in low free ion and restrict ionic movement in the PMMA/PEG electrolyte. Interestingly, the dissociation of LiBF₄ was higher in the polymer system when the weight

percentage of SiO_2 was increased up to 3%. This phenomenon resulted in increased ionic conductivity due to the formation of hydrogen bonding between H atom in Si-OH of SiO_2 and O atom of PMMA (Figure 4) that weakened the Li^+ - O interaction. As a consequence, the Li^+ ions detached easily from the O atom [45] and the number of free ion increased. Unfortunately, further increase in the weight percentage of SiO_2 filler beyond 3% led to the gradual decrement of ionic conductivity of

the system. This was probably because the system was congested with a high amount of SiO_2 [46]. In other words, SiO_2 particles dispersed in polymer films and got close to each other, causing agglomeration. Previous studies stated that congestion of filler led to the obstacle effect and restricted the movement of the polymer chains, hence reduced ionic conductivity [14, 39].

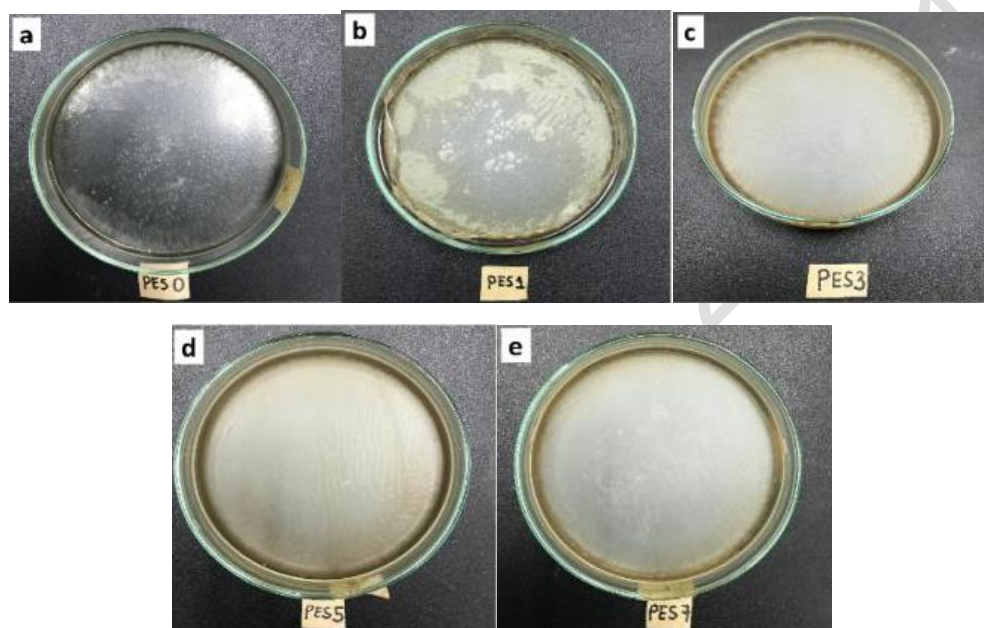


Figure 1. Formation of PMMA/PEG electrolytes films containing different weight percentages of SiO_2 of (a) 0%, (b) 1%, (c) 3%, (d) 5%, and (e) 7%

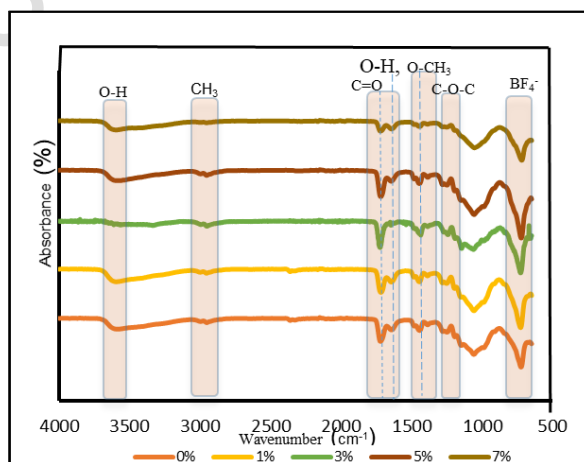


Figure 2. FTIR spectra of PMMA/PEG at different weight percentages of SiO_2

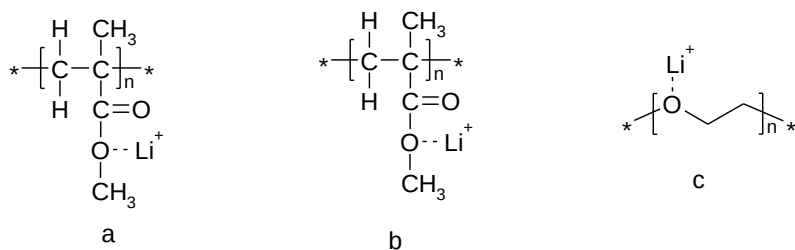


Figure 3. Suggested interaction between PMMA/PEG with Li⁺ ion

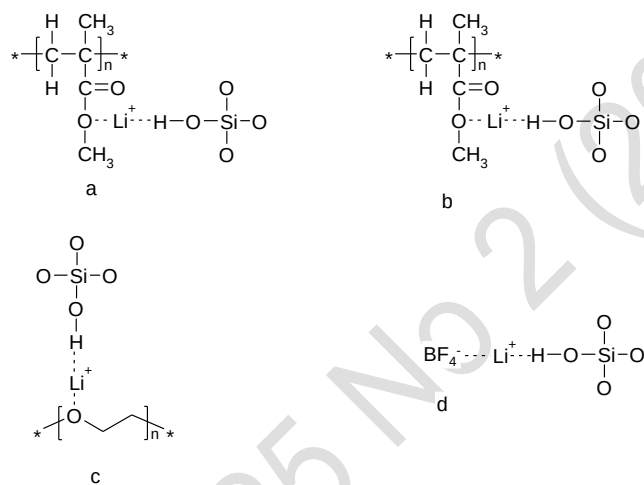


Figure 4. Suggested interaction between PMMA/PEG with Li⁺ ion and SiO₂

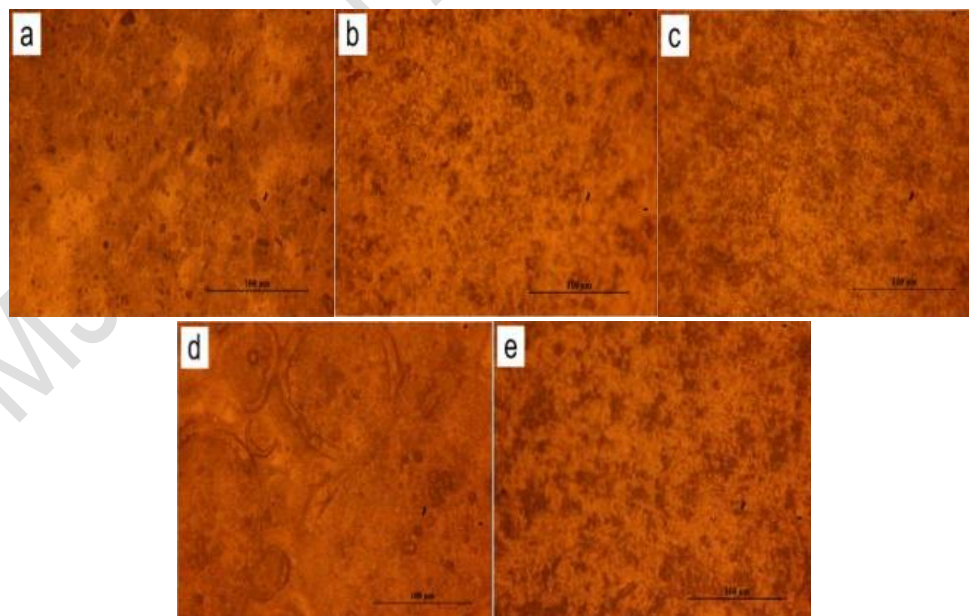


Figure 5. OM micrographs of PMMA/PEG electrolytes films at different weight percentages of SiO₂ filler: (a) 0%, (b) 1%, (c) 3%, (d) 5%, and (e) 7% at 20× magnification

Table 2. Ionic conductivity of PMMA/PEG electrolytes with different weight percentages SiO₂ filler at room temperature

SiO ₂ (%)	0	1	3	5	7
Ionic Conductivity (S cm ⁻¹) (x10 ⁻⁷)	11.4	13.8	55.5	22.2	2.65

Conclusion

SiO₂ filled PEG/PMMA electrolytes were successfully prepared via the solvent casting method. The addition of SiO₂ in PEG/PMMA electrolyte improved the formation and morphology of the film. Molecular interactions between polymers, salt, and filler were successfully proven. The phase separation of polymer films improved but conducted the opacity of the polymer films. Interestingly, the incorporation of SiO₂ filler fluctuated the ionic conductivity of the PMMA/PEG electrolyte films. The highest ionic conductivity was recorded at $55.5 \times 10^{-7} \text{ S cm}^{-1}$ at 3% SiO₂. This finding is important to conduct further research on the physical and thermal properties of SiO₂ filled PMMA/PEG electrolytes.

Acknowledgement

The authors would like to acknowledge Universiti Teknologi MARA for the technical support for this study.

References

1. Aziz, S. B., Woo, T. J., Kadir, M. F. Z. and Ahmed, H. M. (2018). A conceptual review on polymer electrolytes and ion transport models. *Journal of Science: Advanced Materials and Devices*, 3: 1-17.
2. Marcinek, M., Syzdek, J., Marczewski, M., Piszcz, M., Niedzicki, L., Kalita, M. and Wiczorek, W. (2015). Electrolytes for Li-ion transport – Review. *Solid State Ionics*, 276: 107-126
3. Mohd, S., Zulazlan, A., Zulkifli, S., Akmal, M., Mainal, A., Subramanian, B. and Sabirin, N. (2015). Polymer electrolyte liquid crystal system for improved optical and electrical properties. *European Polymer Journal*, 66: 266-272.
4. Xiao-Yuan, Y., Xiao, M., Shuang-Jin, W., Qi-Qiang, Z. and Yue-Zhong, M. (2010). Fabrication and characterization of PEO/PPC polymer electrolyte for lithium-ion battery. *Journal of Applied Polymer Science*, 115(5): 2718-2722
5. Wang, A., Xu, H., Liu, X., Wang, S., Zhou, Q., Chen, J. and Zhang, L. (2017). High electrochemical performances of solid nano-composite star polymer electrolytes enhanced by different carbon nanomaterials. *Composites Science and Technology*, 152: 68-75.
6. Stephan, A. M. (2006). Review on gel polymer electrolytes for lithium batteries. *European Polymer Journal*, 42: 21-42.
7. Ngai, K. S., Ramesh, S., Ramesh, K. and Juan, J. C. (2018). Electrical, dielectric and electrochemical characterization of novel poly(acrylic acid)-based polymer electrolytes complexed with lithium tetrafluoroborate. *Chemical Physics Letters*, 692: 19-27.
8. Xiao, W., Wang, Z., Zhang, Y., Fang, R., Yuan, Z., Miao, C. and Jiang, Y. (2018). Enhanced performance of P(VDF-HFP)-based composite polymer electrolytes doped with organic-inorganic hybrid particles PMMA-ZrO₂ for lithium ion batteries. *Journal of Power Sources*, 382: 128-134.
9. Kumar, S., Prajapati, G. K., Saroj, A. L. and Gupta, P. N. (2019). Structural, electrical and dielectric studies of nano-composite polymer blend electrolyte films based on (70-x) PVA-x PVP-NaI-SiO₂. *Physica B: Condensed Matter*, 554: 158-164.
10. Ganesan, S. V., Mothilal, K. K., Selvasekarapandian, S. and Ganesan, T. K. (2017). Studies on conductivity, morphology and thermal stability of PMMA-PSAN based Solid Polymer Electrolytes using SiO₂ as nanofiller. *International Journal of ChemTech Research*, 10(7): 55-65.

11. Kuppu, S. V., Jeyaraman, A. R., Guruviah, P. K. and Thambusamy, S. (2018). Preparation and characterizations of PMMA-PVDF based polymer composite electrolyte materials for dye sensitized solar cell. *Current Applied Physics*, 18(6): 619-625.
12. Salman, A. L. I. D., Jani, G. H. and Fatalla, A. A. (2017). Comparative study of the effect of incorporating SiO₂ nano-particles on properties of polymethyl methacrylate denture bases. 10(3): 1525-1535.
13. Vignarooban, K., Dissanayake, M. A. K. L., Albinsson, I. and Mellander, B. (2014). Effect of TiO₂ nano-filler and EC plasticizer on electrical and thermal properties of poly(ethylene oxide) (PEO) based solid polymer electrolytes. *Solid State Ionics*, 266: 25-28.
14. Ataollahi, N., Ahmad, A., Hamzah, H., Rahman, M. Y. A. and Mohamed, N. S. (2015). Comparative study of the properties of plasticized (PVDF-HFP)-MG49-LiBF₄ blend polymer electrolytes. *Russian Journal of Electrochemistry*, 51(3): 227-235.
15. Johan, M. R., Shy, O. H., Ibrahim, S., Mohd Yassin, S. M. and Hui, T. Y. (2011). Effects of Al₂O₃ nanofiller and EC plasticizer on the ionic conductivity enhancement of solid PEO-LiCF₃SO₃ solid polymer electrolyte. *Solid State Ionics*, 196(1): 41-47.
16. Sekhar, P. C., Kumar, P. N. and Sharma, A. K. (2012). Effect of plasticizer on conductivity and cell parameters of (PMMA+NaClO₄) polymer electrolyte system. *Journal of Applied Physics*, 2(4): 01-06.
17. Das, S. and Ghosh, A. (2015). Ionic conductivity and dielectric permittivity of PEO-LiClO₄ solid polymer electrolyte plasticized with propylene carbonate. *AIP Advances*, 5(2): 1-9.
18. Shukur, M. F., Kadir, M. F. Z., Ahmad, Z. and Ithnin, R. (2012). Transport properties of chitosan/PEO blend based proton conducting polymer electrolyte. *Advanced Materials Research*, 488-489: 114-117.
19. Ngai, K. S., Ramesh, S., Ramesh, K., and Juan, J. C. (2016). A review of polymer electrolytes: Fundamental, approaches and applications. *Ionics*, 22(8): 1259-1279.
20. Shi, J., Yang, Y. and Shao, H. (2017). Co-polymerization and Blending based PEO/PMMA/P(VDF-HFP) gel polymer electrolyte for rechargeable lithium metal batteries. *Journal of Membrane Science*, 547: 1-10.
21. Tiautit, N., Puratane, C., Panpinit, S. and Saengsuwan, S. (2014). Effect of SiO₂ and TiO₂ nanoparticles on the performance of dye-sensitized solar cells using PVDF-HFP/PVA gel electrolytes. 56: 378-385.
22. Srivastava, N. and Tiwari, T. (2009). New trends in polymer electrolytes a reviews. *E-Polymers*, 146: 1-17.
23. Stephan, A. M. and Nahm, K. S. (2006). Review on composite polymer electrolytes for lithium batteries. *Polymer*, 47: 5952-5964.
24. Kurc, B. (2014). Precipitated silica as filler for polymer electrolyte based on poly(acrylonitrile)/sulfolane. *Journal of Solid State Electrochemistry*, 18(7): 2035-2046.
25. Zhu, A., Shi, Z., Cai, A., Zhao, F. and Liao, T. (2008). Synthesis of core-shell PMMA-SiO₂ nanoparticles with suspension-dispersion-polymerization in an aqueous system and its effect on mechanical properties of PVC composites. *Polymer Testing*, 27(5): 540-547.
26. Cao, J., Wang, L., Shang, Y., Fang, M., Deng, L., Gao, J. and He, X. (2013). Dispersibility of nano-TiO₂ on performance of composite polymer electrolytes for Li-ion batteries. *Electrochimica Acta*, 111: 674-679.
27. Zhang, R., Chen, Y. and Montazami, R. (2015). Ionic liquid-doped gel polymer electrolyte for flexible lithium-ion polymer batteries. *Materials*, 2015: 2735-2748.
28. Ramesh, C. H., Reddy, M. J., Kumar, J. S. and Reddy, K. N. (2014). Structural and transport properties of PVC blend PEG doped with Mg(ClO₄)₂ solid polymer electrolyte. *AIP Conference Proceedings*, 1391: 1389-1391.
29. Mohamad Zamri, S. F. and Abdul Latif, F. (2015). Effects of acid modified SiO₂ on ionic conductivity and blend properties of LiBF₄ doped PMMA/ENR 50 electrolytes. *Advanced Materials Research*, 1107: 187-193.

30. Choudhary, S. (2017). Dielectric dispersion and relaxations in (PVA-PEO)-ZnO polymer nanocomposites. *Physica B: Condensed Matter*, 522: 48-56.
31. Muchakayala, R., Song, S., Wang, J., Fan, Y., Benggeppagari, M., Chen, J. and Tan, M. (2017). Development and supercapacitor application of ionic liquid-incorporated gel polymer electrolyte films. *Journal of Industrial and Engineering Chemistry*, 59: 79-89
32. Cheng, X., Pan, J., Zhao, Y., Liao, M. and Peng, H. (2018). Gel polymer electrolytes for electrochemical energy storage. *Advanced Energy Materials*, 8(7): 1-16.
33. Zamri, S. F. M., and Latiff, F. A. (2013). SiO₂ filler as interface modifier in PMMA/ENR 50 electrolytes. *Advanced Materials Research*, 812: 120-124.
34. Singh, R., Bhattacharya, B., Rhee, H. and Singh, P. K. (2014). New biodegradable polymer electrolyte for dye sensitized solar cell. *International Journal of Electrochemical Sciences*, 9: 2620-2630.
35. Sharma, P., Kanchan, D. K., and Gondaliya, N. (2012). Effect of nano-filler on structural and ionic transport properties of plasticized polymer electrolyte. *Open Journal of Organic Polymer Materials*, 2(2): 38-44.
36. Alias, Y., Ling, I., and Kumutha, K. (2005). Structural and electrochemical characteristics of 49% PMMA grafted polyisoprene-LiCF₃SO₃-PC based polymer electrolytes. *Ionics*, 11(5-6): 414-417.
37. Soydan, A. M. and Akdeniz, R. (2017). Polymer electrolytes based on borane/poly(ethylene glycol) methyl ether for lithium batteries. *Journal of Chemistry*, 2017: 1-7.
38. Sharil Fadli, M. Z., Famiza, A. L., and Siti Izzati Husna, M. A. (2019). Morphology, ionic-molecular interaction and ionic conductivity behavior of PMMA/ENR 50 electrolytes containing carboxylic acids modified SiO₂ fillers. *Key Engineering Materials*, 821: 419-425.
39. Farheen, S., and Mathad, R. D. (2015). Effect of nano filler on conductivity in PEO-PMMA-LiClO₄ polymer electrolyte. *International Journal of Advanced Science and Technology*, 81: 49-52.
40. Wang, H., Li, H., Xue, B., Wang, Z., Meng, Q. and Chen, L. (2005). Solid-state composite electrolyte Lil/3-hydroxypropionitrile/SiO₂ for dye-sensitized solar cells. *Journal of the American Chemical Society*, 127(17): 6394-6401.
41. Yuan C. Y., Chen S. Y., Tang J. C., Yang H. C. and Chen-Yang Y. W. (2006). Physical and electrochemical properties of low molecular weight poly(ethylene glycol)-bridged polysilsesquioxane organic-inorganic composite electrolytes via sol-gel process. *Journal of Applied Polymer Science*, 116(5): 2658-2667.
42. Sun, Z., Li, Y., Zhang, S., Shi, L., Wu, H., Bu, H. and Ding, S. (2019). G-C₃N₄ nanosheets enhanced solid polymer electrolytes with excellent electrochemical performance, mechanical properties, and thermal stability. *Journal of Materials Chemistry A*, 7(18): 11069-11076.
43. Elmér, A. M. and Jannasch, P. (2006). Solid electrolyte membranes from semi-interpenetrating polymer networks of PEG-grafted polymethacrylates and poly(methyl methacrylate). *Solid State Ionics*, 177(5-6): 573-579.
44. Latif, F., Mohamad Zamri, S. F., and Aziz, M. (2015). Anions effect on the electrical properties of PMMA/ENR 50 blend electrolytes. *Advanced Materials Research*, 1107: 145-150.
45. Silakul, P. and Magaraphan, R. (2019). Polymer electrolyte developed from natural rubber-polyacrylic acid cotrimethoxysilyl propyl methacrylate grafted fumed silica and its application to dye sensitized solar cell. *Polymer Composites*, 40(1): 304-314.
46. Ahmad, A., Rahman, M. Y. A., Low, S. P. and Hamzah, H. (2011). Effect of LiBF₄ salt concentration on the properties of plasticized MG49-TiO₂ based nanocomposite polymer electrolyte. *ISRN Materials Science*, 2011: 1-7.
47. Zamri, S. F. M., Latif, F. A., Ali, A. M. M., Ibrahim, R., Azuan, S. I. H. M., Kamaluddin, N., and Hadip, F. (2017). Exploration on effects of 15 nm SiO₂ filler on miscibility, thermal stability and ionic conductivity of PMMA/ENR 50 electrolytes. *AIP Conference Proceedings*, 1809: 020049.