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EFFECT OF ELECTRON BEAM IRRADIATION ON GEL POLYMER ELECTROLYTES: CHANGE IN MORPHOLOGY, CHEMICAL STRUCTURE AND ELECTROCHEMICAL

JAMILAH KARIM[1], PUTERI INTAN ZULAIKHA SYED MAHADZIR[2], SITI AMINAH MOHD NOOR[3], MARIAH ZULIANA DZULKIPLI[1], RUZALINA BAHARIN[4], AZIZAN AHMAD[1], MOHD SUKOR SU'AIT[2], NUR HASYAREEDA HASSAN[1,*]

[1]*Faculty of Science and Technology, Universiti Kebangsaan Malaysia*
43600 UKM Bangi, Selangor, Malaysia
[2]*Solar Energy Research Institute, Universiti Kebangsaan Malaysia*
43600 UKM Bangi, Selangor, Malaysia
[3]*Chemistry Department, Centre for Defence Foundation Studies*
National Defense University of Malaysia,57000 Kuala Lumpur, Malaysia
[4]*Malaysia Nuclear Agency, 43000, Kajang, Selangor, Malaysia*
**Corresponding author*: syareeda@ukm.edu.my

ABSTRACT

GPEs (gel polymer electrolytes) are seen as a potential replacement for standard liquid electrolytes. It has been demonstrated that dispersion of nanofiller in GPEs improves electrolyte properties such as reduced reactivity, reduced leakage, enhanced safety, improved form flexibility, and manufacturing integrity. Meanwhile, the electrochemical process is accelerated by using electron beam (EB) radiation. The goal of this study was to investigate the properties of $BMIMBF_4$ (PVDF-HFP) GPEs (physicochemical, thermal, morphological, and electrochemical) after in-situ surface modification of zirconia with vinyltriethoxysilane (VTES) coupling agent, as well as the effect of 8 MeV energy EB irradiation the radiation effect on GPE conductivity was conducted by using impedance analyzer in the frequency range of 0.1-10 MHz. The change in chemical interaction, and morphology was analyzed by of Attenuated Total Reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), Field Emission Scanning Electron Microscopy (FESEM) and Transmission Electron Microscopy (TEM) respectively for before and after irradiation. The morphology analysis shows surface smooth until 4 wt. % loading of ZIP-VTES with the average particle size 20 nm. The chemical change was confirmed from the ATR-FTIR results which showed that peak intensities corresponding to hydrogen bonds increased and shifted with increase in electron doses, which clearly indicated a strong interaction between polymer gel and zirconia. The maximum conductivity was observed to be 5.63×10^{-1} S/cm for 10 kGy and 0.61 value of lithium-ion transference number obtained at 298 K for 10 kGy dose.

Keywords: electron beam; $BMIMBF_4$-(PVDF-HFP)-$LiCO_4$; zirconia; surface modification; gel polymer electrolyte

INTRODUCTION

Development of gel polymer electrolytes (GPEs) is essential to overcome the issues in liquid electrolytes applications mainly leakage of flammable liquid electrolytes. Generally, blending, copolymerization, and crosslinking are used to improve the properties of polymer matrices and produces GPEs that perform well in battery application. However, more importantly, the use of appropriate inorganic fillers in GPEs has recently emerged as one of the most promising methods to enhance the ionic conductivity and ion transfer, which results in the GPEs

performing well in battery application [1]. In the 2000s, the effect of particle size of inorganic fillers in GPEs was extensively studied [2-41]. In the 2010s, another effective method, surface modification, was proposed to enhance the dispersion and affinity of inorganic fillers within organic compounds. To facilitate interactions at the nanofiller surface and possibly improve the electrochemical properties of GPEs, researchers have explored fillers that are surface-modified to polymer electrolytes with several interesting conclusions [42-46]. Walkowial et al. [47] and Kurc et al. [48-49] modified the surface of a new hybrid TiO_2/SiO_2 filler for GPEs. The original hybrid fillers were modified by grafting functional groups, such as methacryloxy or vinyl groups, on the surface of the fillers. The surface modification chemistry of the filler not only improve the electrochemical properties but also the mechanical property of the GPE. Besides that, electron beam (EB) irradiation technique is also becoming an advanced approach to optimize the physical properties of polymer materials such as dielectric, electrical, structural, and thermal properties [50-52].

However, the modification depends upon the irradiation dose rate and material characteristics. Modified polymer electrolytes are prominent materials for a wide range of potential applications like polymer light-emitting diode [53-54], solid state battery, optical display [55], and electronic device [56-57]. Whenever EB energy interacts with polymer material it induces change in the molecular structural arrangement such as ionization, displacing atoms, carbonization, and production of free radicals; as a result, chain scission and cross linking leading to degradation occur. The radiation not only alters the chemical structure of the polymer, but it can also enhance the presence of trapped charges or creates defects in the polymer matrix. In other words, irradiated polymers can convert them from insulators to good electrical conductivity materials which is a good sign and these materials can be used in various electronic applications [54-68]. EB irradiation is a rapidly developing technique owing to its simple and pollution-free use to improve the physiochemical properties of the polymers [69-70]. It can change the structure and thermal properties of copolymers and break the crystal into micro–Polar Regions that interact only through electrostatic coupling [71]. The degree of crystallinity of the polymer electrolytes have been reported to decrease in most of the semi crystalline polymers at high dose irradiation [67]. The copolymers after exposure to high energies can exhibit high electromechanical performance, and such materials are used in sensor and transducer applications [72].

It is also important to understand the charge transport mechanism in the polymers by studying the electrical conductivity and dielectric relaxation upon EB irradiation [69, 73] Few studies have reported changes in thermal property, structural arrangement, surface morphology, and electrical conductivity upon EB irradiation. Joykumar Singh et al. (2004) reported the enhanced ionic conductivity of electron beam irradiated PEG: LiClO4 polymer electrolyte films, i.e. 7.27×10^{-7} S/cm for an unirradiated sample and 1.31×10^{-5} S/cm for 15 kGy irradiated sample [61]. These values are well comparable and consistent with the observed result. The literature review revealed that very little work has been reported on electron beam induced effect on conductivity of gel polymer. Thus, in the present investigation $BMIMBF_4$-PVDF(HFP)-$LiCO_4$ gel polymer electrolytes filled *in-situ* surface modification zirconia using silane coupling agent (VTES) were prepared and were exposed to 8 MeV electron beam with different doses to study the effect of electron beam irradiation on ionic conductivity, lithium transference number, chemical structure and morphology of the gel electrolytes.

EXPERIMENTAL

Materials and sample preparation

Poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP average M_n = 4,000,000), 1-butyl-3- methylimidazolium tetrafluoroborate ($BMIMBF_4$ 98%), lithium perchlorate ($LiClO_4$ 99.99%), zirconium (IV) isopropoxide (ZIP, 70%), vinyltriethoxysilane (VTES, 99 %), acid hydrochloric (HCl 37 %), potassium chloride (KCl 99%) and acetone were procured from Sigma Aldrich. In this study 90 wt. % ($BMIMBF_4$), 10 wt. % of (PVDF-HFP) and 10 wt. % $LiClO_4$ were used without any further purification. $BMIMBF_4$-(PVDF-HFP)- $LiClO_4$ was dissolved in acetone under stirring until a clear homogeneous solution was obtained. ZIP, VTES, HCl and H_2O were then added in the above solution with the mole ratio 1:0.25:2:0.05. It was synthesized based on Noor et. al [74]. The mixture again stirred for 2h until a viscous solution of was obtained. The mixture was aging for 3 days at room temperature and drying at 80 ^{0}C in the oven.

Characterizations

FESEM analysis was carried out to provide topographical and elemental information of the GPEs using Carl Zeiss Evo MA10-FESEM. The gel polymer electrolytes were sputter coated with gold to avoid sample charging. The accelerating voltage used was 15kV and magnification of 100kx. TEM was performed to produce morphological information, particles size and distribution in the GPEs. GPEs were prepared using a microtome in liquid nitrogen of LEICA ULTRACUT UCT & LEICA EMFCS. The specimen was placed on a copper grid. Then, TEM microscopic observation was carried out with a JEOL TEM-2100. The accelerating voltage used was 200kV and magnification of 30000x. ATR-FTIR was carried out to investigate the functional groups and chemical bonds in molecules based on standard transmission, reflection and ATR imaging that occur in the gel polymer electrolytes. ATR-FTIR was conducted using Perkin-Elmer model Spectrum 400 FT-IR/NIR with Imaging System. Measurements were made in the range 4000–600 cm^{-1} with a resolution of 4 cm^{-1}. Conductance was measured using a locally designed dip cell probe consisting of two platinum wires sheathed in glass. The cell constant was determined with a solution of 0.01 M KCl at 25 ℃. To determine the ionic conductivity of the prepared GPEs, impedance spectra were measured using VersaSTAT 3 Princeton Applied Research over a frequency range of 0.1 Hz–10 MHz with a 30 mV amplitude. The obtained data was analyzed using Versastudio Software. The lithium transference number (t_{Li+}) was determined by DC polarization technique using VersaSTAT3 analyzer. The DC current was monitored as a function of time on the applicant at a fixed 30 mV DC bias voltage across the sample using lithium as both working and counter electrodes (Li/sample/Li). Based on the Bruce and Vincent calculation method, the actual type of charge carrier was determined based on following equation:

$$T_{Li+} = \frac{I_{ss}\,(\Delta V - I_o R_o)}{I_o\,(\Delta V - I_{ss} R_{ss})}$$

where I_{ss} is the steady state current, I_o the initial current (t = 0), R_o and R_{ss} are the interfacial resistance before and after polarization, that determined from AC impedance measurements

RESULTS AND DISCUSSION

Electron Microscopies (FESEM and TEM)

Surface morphology of the prepared $BMIMBF_4$-(PVDF-HFP)-$LiClO_4$ with different wt. % of ZIP and ZIP-VTES were show in Fig. 1. From the FESEM micrograph, the surface of the gel polymer is smooth until 4 wt. % and stared to show agglomeration as increase the ZIP loading. The same trend was shown for the ZIP-VTES loading. However, it is clearly shown that ZIP-VTES were less agglomerate compared to ZIP. Since 4 wt.% ZIP-VTES shown the best morphology, as it is smooth and well distribution of ZIP-VTES, it has been chosen to be different weight percent : A) 2 wt. % ZIP; B) 4 wt. % ZIP; C) 6 wt. % ZIP; D) 8 wt. % ZIP; E) 2 wt. % ZIP-VTES; F) 4 wt. % ZIP-VTES; G) 6 wt. % ZIP-VTES; H) 8 wt. % ZIP-VTES exposed with electron beam.

Fig. 2 shows a series of SEM micrograph of ZIP-VTES systems with different doses of electron beam. As electron beam expose to the 4 wt. % loading of ZIP-VTES, waxy type particles appear on the surface, but it seems that the size of the waxy particles observed is very small in the case of 10 kGy dose. As increase the dose to 15 kGy, agglomeration started to occur and further to agglomerate at 20 kGy. These changes in the morphology confirm the irradiation effects the polymer backbone chain in the gel polymer electrolyte. To further study the distribution and sizes of the ZIP-VTES particle with and without electron beam exposure, micrograph of TEM in Fig. 3 was referred. The particle at 4 wt. % loading of ZIP-VTES shows homogeneity distribution with the size averagely 50 nm. After being exposed to electron beam at 10 kGy, the particle size become smaller in average 20 nm and still in good homogeneity distribution. This indicates the electron beam exposure not only improve the morphology of the GPE, but also enhance the homogeneity distribution of the ZIP-VTES particle as well as reduced the sizes of nanoparticle.

Attenuated Total Reflectance-Fourier Transform Infra-red (ATR-FTIR)

Fig. 4 represents the FTIR spectra of $BMIMBF_4$-(PVDF-HFP)-$LiClO_4$ and of $BMIMBF_4$-(PVDF-HFP)-$LiClO_4$ with different weight percentage of ZIP:VTES. For the $BMIMBF_4$-(PVDF-HFP)-$LiClO_4$, the C-H stretching modes can be observed at 2877, 2964, 3121 and 3161 cm^{-1}, the C-N stretching mode of the imidazole ring at 1573, 1466 and 1169 cm^{-1}, while the asymmetric bending of C-N at 622 cm^{-1}. Four identical vibration modes of BF_4^- can be seen in two regions, being one triple antisymmetric (1045, 1033, 1015 cm^{-1}) and one single symmetric B-F stretching (752 cm^{-1}). The mixed mode of CH_2 rocking and CF_2 asymmetric stretching of PVDF-HFP and the $BMIMBF_4$ shows at 844 cm^{-1}. As reported by Shalu et.al this peak is prominent because is indicates the amorphous phase for gel polymer electrolytes [76].

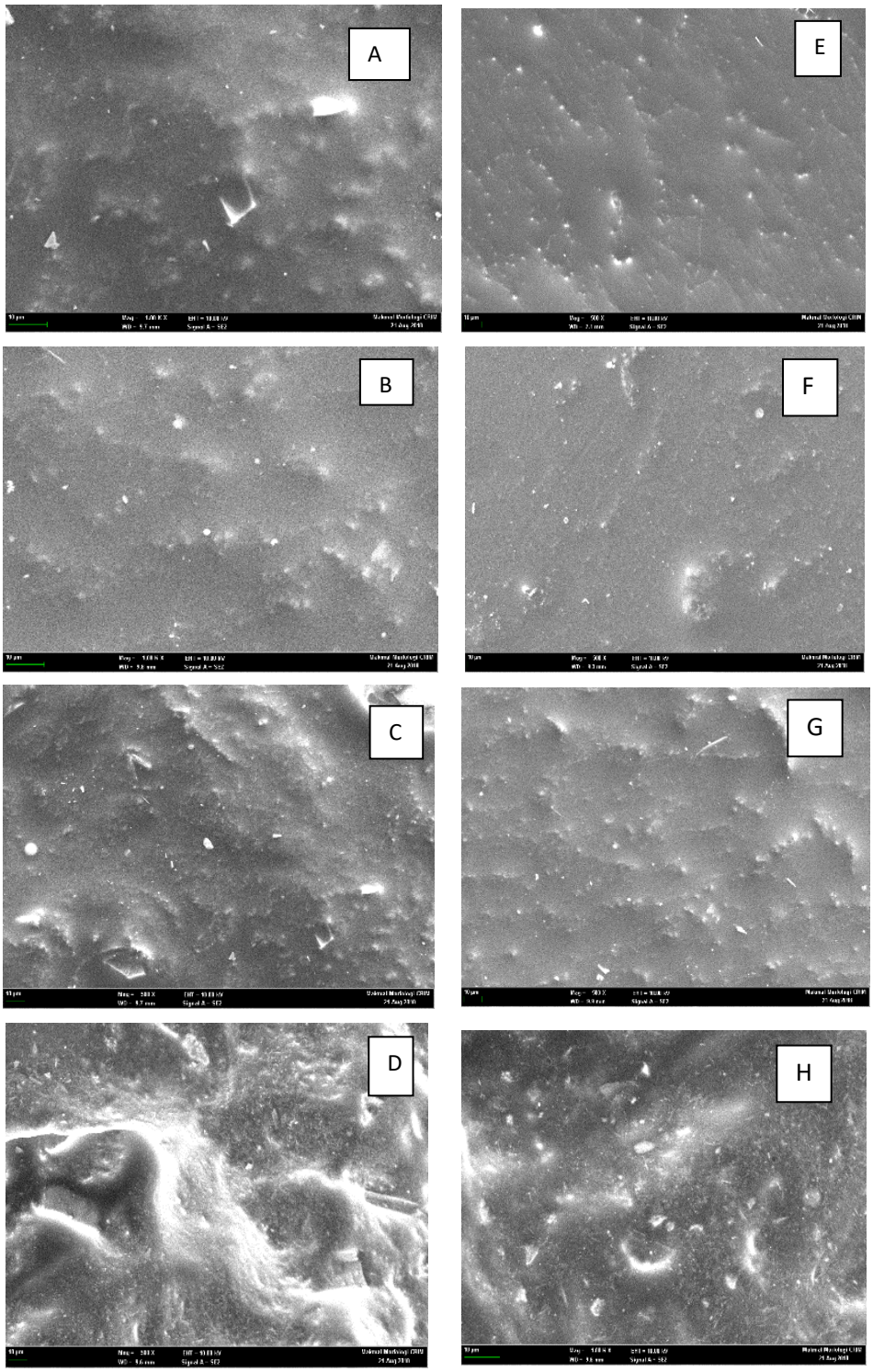

Fig. 1 FESEM micrographs of $BMIMBF_4$-(PVDF-HFP)-$LiCO_4$ gel polymer electrolytes with different weight percent: A) 2 wt. % ZIP; B) 4 wt. % ZIP; C) 6 wt. % ZIP; D) 8 wt. % ZIP; E) 2 wt. % ZIP-VTES; F) 4 wt. % ZIP-VTES; G) 6 wt. % ZIP-VTES; H) 8 wt. % ZIP-VTES

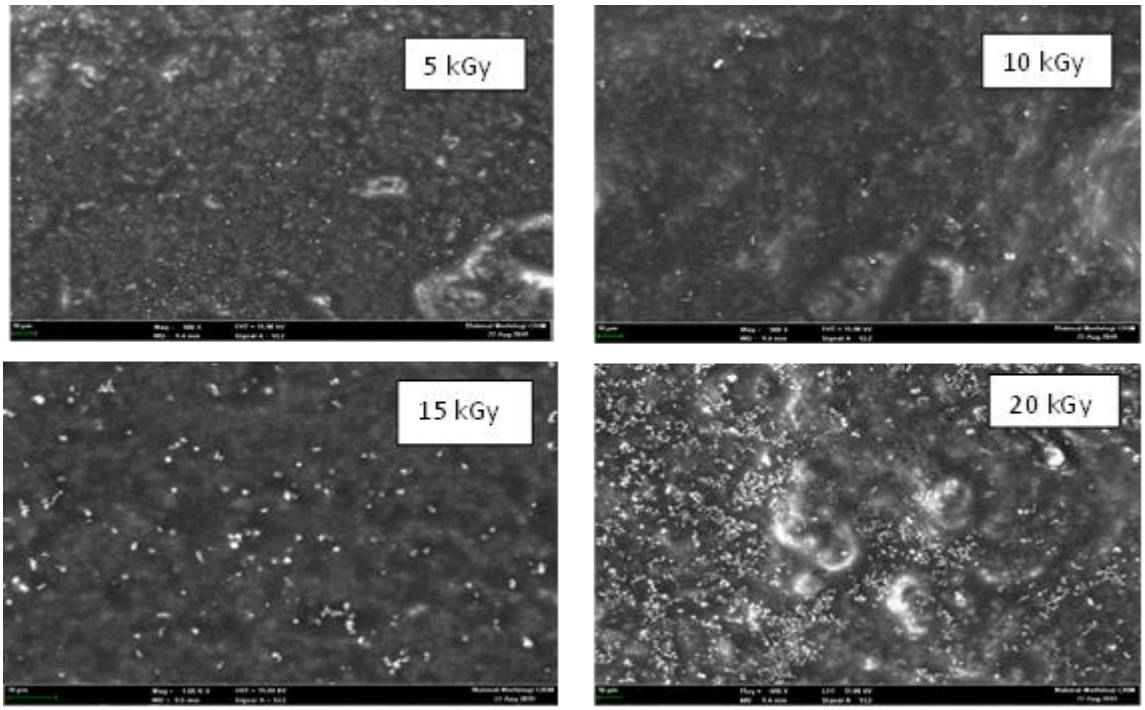

Fig. 2 FESEM micrographs of $BMIMBF_4$-(PVDF-HFP)-$LiCO_4$-4 wt. % ZIP-VTES gel polymer electrolytes with different doses (kGy) of electron beam

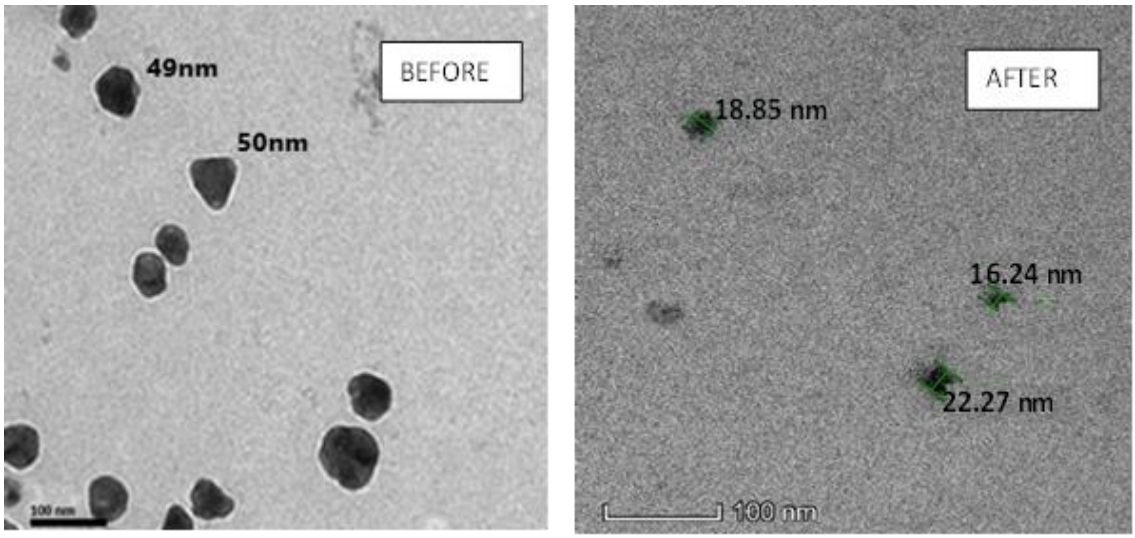

Fig. 3 TEM micrographs of $BMIMBF_4$-(PVDF-HFP)-$LiCO_4$-4 wt. % ZIP-VTES gel polymer electrolytes before radiated and after radiated (10 kGy)

The characteristic peaks of pure $LiClO_4$ are found absent in the polymer electrolytes complexes which confirm good complexation of the salt with host polymers. The disappearance or shifting of frequency rom pure polymers shows an interaction of the polymers with salt in gel polymer electrolytes samples [77-78]. As introduce ZIP:VTES to the gel polymer electrolytes, new peak occur for the hydrogen-bonded chains in zirconia particles can be observed at the band around 3620 cm^{-1}. In these gel polymer electrolytes system, the hydrogen-bonded chains were detected at 3621 and 3634 cm^{-1}. This observation shows that a broad band of hydrogen-bonded chains was split into two bands and shifted to higher wavenumbers, indicating a strong interaction between the BF_4^- anion and the hydroxyl group of the zirconia. This interaction is

due to the strong electronegativity of the F atom. Besides, as the loading percentage of ZIP;VTES increases, more particles provides, gives strong interaction and shift the peak to a higher wavenumber [76]. The CH_2 rocking and CF_2 asymmetric peaks spilt into two bands and shifted to 838 and 877 cm^{-1} indicating strong amorphous phase was form as the zirconia and VTES was introduce. The respective peak positions in these gel polymer electrolytes are summarized in Table 1.

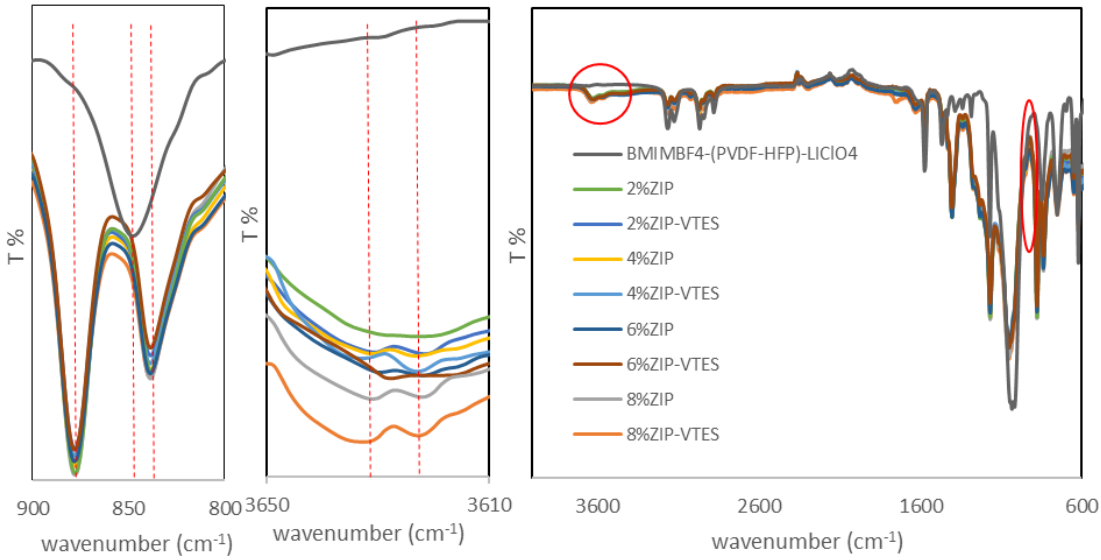

Fig. 4 FTIR spectra of $BMIMBF_4$-(PVDF-HFP)-$LiClO_4$ and of $BMIMBF_4$-(PVDF-HFP)-$LiClO_4$ with different weight percentage of ZIP:VTES.

Fig. 5 illustrates the FTIR spectra of unirradiated and irradiated of the $BMIMBF_4$-(PVDF-HFP)-$LiClO_4$- 4 wt. % ZIP-VTES. The chemical changes due to electron beam irradiation are identified from the variation in FTIR peaks intensity and frequency shifts compared with that of the unirradiated. The lists of peak assignments are also listed in Table 1. The electron beam radiation at different doses is responsible for imidazolium ring scission, especially at C(2)–H and C(5)– H in the imidazolium ring. This scission could account for the formation of free radicals and imidazolium oligomers, but more important for this study is the hydroxylation of the imidazolium cation in the presence of trace amounts of absorbed water [65], which could explain the band 3600cm^{-1} shifted as electron beam introduce to gel polymer electrolytes. It is show in Fig. 5 the peak slightly shifted to low wavenumber indicating strong interaction occur on the hydrogen bond silanol. Also carbonyl groups are formed possibly through terminal chain oxidation and/or imidazolium ring scission at 1630cm^{-1} [79]. These changes corroborate the morphological changes observed in FESEM and TEM analysis.

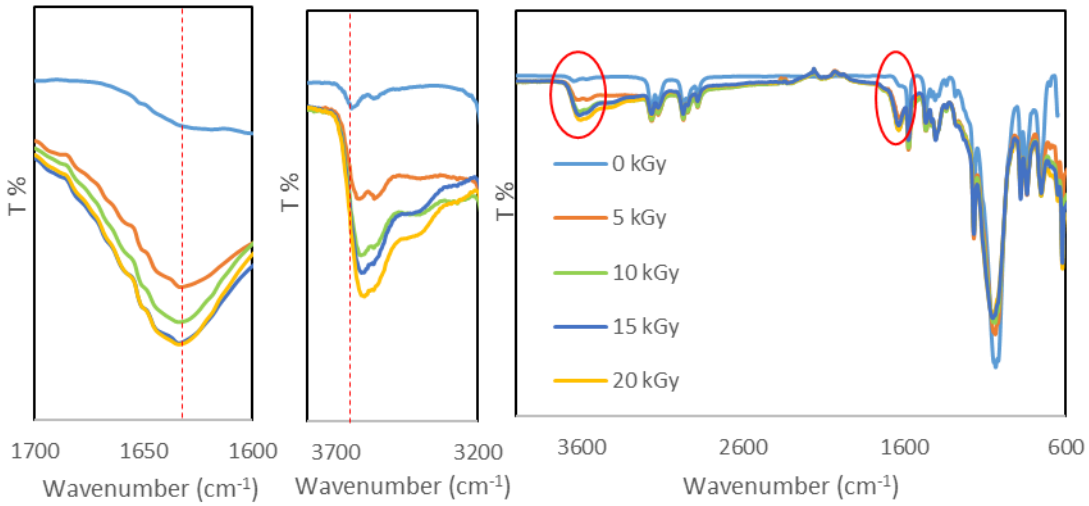

Fig. 5 FTIR spectra of $BMIMBF_4$-(PVDF-HFP)-$LiClO_4$- 4 wt. % ZIP-VTES expose at different dose

Table 1 Chemical vibration modes for $BMIMBF_4$-(PVDF-HFP)-$LiClO_4$, $BMIMBF_4$-(PVDF-HFP)-$LiClO_4$-ZIP:VTES (unirradiated) and irradiated $BMIMBF_4$-(PVDF-HFP)-$LiClO_4$- 4 wt. % ZIP-VTES

Chemical Vibration modes	Wavenumber (cm^{-1})		
	$BMIMBF_4$-(PVDF-HFP)-$LiClO_4$	Unirradiated $BMIMBF_4$-(PVDF-HFP)-$LiClO_4$-ZIP:VTES	Irradiated $BMIMBF_4$-(PVDF-HFP)-$LiClO_4$-ZIP:VTES
hydrogen-bonded group	-	3621, 3624	3600
C-H stretching	2877, 2964, 3121, 3161	3156, 2967, 870	3149,2999,2881
C-N stretching mode of the imidazole ring	1573, 1466, 1169	1560	1545
asymmetric bending of C-N	622	1068	-
vibration modes of BF_4^-	1045, 1033, 1015	1045, 1034, 1016	-
CH_2 rocking and CF_2 asymmetric	844	877, 838	-
OH− stretching bands	-	-	1630

Ionic conductivity

Ionic conductivity was measured at four different loadings of ZIP and ZIP-VTES from 2 to 8 wt.% as shown in Fig. 6a. Overall, the ionic conductivity increases steadily with increasing zirconia content up to 4 wt.% before the ionic conductivity dropped at 6 and 8 wt.% of ZIP and ZIP-VTES. The ionic conductivity of $BMIMBF_4$-(PVDF-HFP)-$LiClO_4$ added ZIP at 4 wt. % loading gives the highest conductivity value 1.03×10^{-2} S cm^{-1}. Apart from that, the presence of the inorganic ceramic filler give rise to steric effect in which it contributes to the retention of the amorphous phase of polymer electrolytes. According to Croce et al., addition of nano-filler influences the recrystallization kinetics of the polymer and increases local amorphicity [81]. Eventually, this improved ion transport which primarily take place through intra-chain and inter-chain hopping of ionic species in the amorphous regions [82]. Further increase in the filler content beyond 4 wt% resulted in the reduction of ionic conductivity. The aggregation of the nano-particles which is strongly interacting with the polymer chains takes place and causes ionic immobility as proven previously in FESEM section. It is also suggested that the addition of filler content increases the stiffness of polymer segment, thereby suppressing the polymer chain motion [83-84]. This phenomenon can be attributed to the close proximity of filler grains leading to a “blocking” effect imposed by the more abundant filler grains and further immobilizes the long polymer chains [82].

As introduce VTES to the gel polymer electrolytes, the same trend of conductivity are shown. The ionic conductivity increases up to 4 wt. % of ZIP-VTES before it dropped with the highest value 1.43×10^{-2} S cm^{-1}. VTES act as surface modification to the zirconia produce in the gel polymer. In this case the zirconia can act both as the 'filler' and the source of charge carriers. Functionalized zirconia nano-particles, where the surface of the ZrO_2 was decorated with VTES groups and the charge was neutralized with Li^+[81-82]. The conductivity of $BMIMBF_4$-(PVDF-HFP)-$LiClO_4$ added ZIP-VTES at 4 wt. % expose to different electron beam dose were shown in Fig. 6b. The conductivity increases up to 10 kGy of irradiation before the conductivity dropped as per in Table 2. The highest conductivity achieved was 5.63×10^{-1} S cm^{-1}. It is also observed that with increase in electron beam dose, the conductivity was found to increase which could be attributed to the inter-chain polymer interaction, formation of single or multiple ionic radical to the large electronic energy loss along their trajectories thereby increasing the free charge carriers in the gel polymer electrolyte [85]. The charge carriers are easily transported by the hopping mechanism through the defects created by radiation energy and freeing the dipoles present in the polymer chain [86-87]. This can be seen in the increment of ionic conductivity for about 1.5 magnitude order when the 4 wt.% ZIP VTES systems introduced to 10 kGy electron beam (from 1.03×10^{-2} S/cm to 5.63×10^{-1} S/cm). Besides, irradiation dose is attributed to the degradation of the polymer chains due to the chain scissoring resulting in reduced molecular weight at higher dosage. The low-molecular-weight polymers with salts exhibit high conductivity as compared to high-molecular-weight polymers because of reduction in the crystallinity with increased amorphous content, as reported by Abdel Hamid [87]. However, as the power of irradiation increases to 15 kGy, the ionic conductivity reduced dramatically to 1 magnitude order of 5.55×10^{-2} S/cm and further reduced to 1.12×10^{-2} S/cm at 20 kGy of electron beam. This might be due to the cross-linking of ionic radicals may stop the orientation of ions with the applied field, which leads to reduction in the population of induced free radicals, hence the polarization of trapped and bound charges failed. This process manifests that the irradiation-induced charge gradually failed to follow the applied field causing a reduction in the electronic oscillations at higher energy dosage [75].

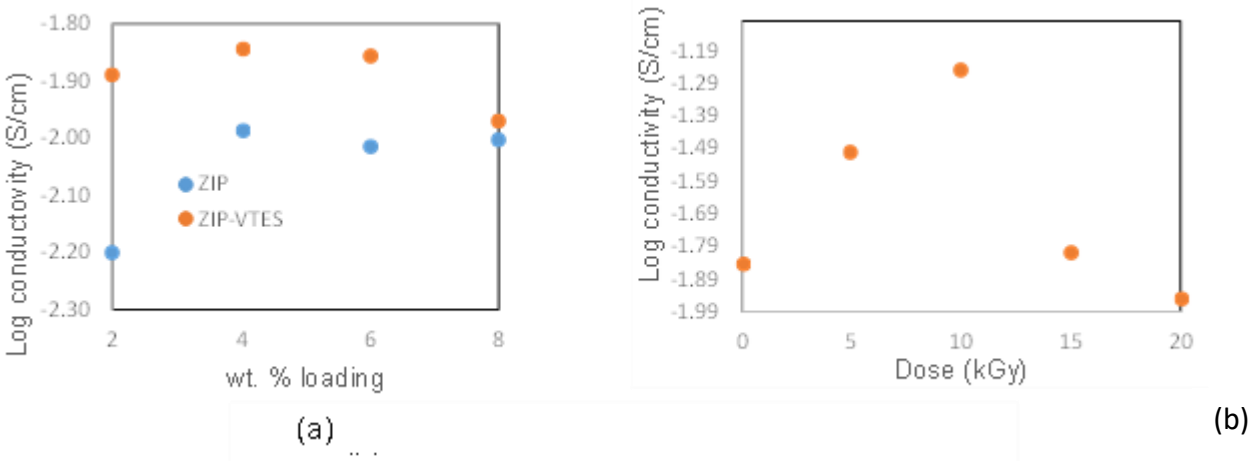

Fig. 6 Graph of ionic conductivity of the $BMIMBF_4$-PVDF(HFP)-$LiCO_4$ gel polymer electrolytes: a) different weight percent of ZIP and ZIP-VTES ; b) different dose radiation

Table 2 Conductivity value of the $BMIMBF_4$-(PVDF-HFP)-$LiCO_4$- 4 wt. % ZIP-VTES expose at different dose

Dose (kGy)	Log Conductivity (S/cm)
5	8.99×10^{-2}
10	5.63×10^{-1}
15	5.55×10^{-2}
20	1.12×10^{-2}

Lithium transference number

Fig. 7 depicts the DC polarization and impedance results during the determination of lithium transference number (T_{Li+}) for $BMIMBF_4$-(PVDF-HFP)-$LiCO_4$- 4 wt. % ZIP-VTES at 10 kGy. From the graph, the initial decrement of DC current was observed and this is due to the formation of electrochemical layer and have reached a steady state after ca. 200 s. T_{Li+} was calculated using Bruce and Vincent formula as stated n methodology section. The T_{Li+} obtained is 0.61 at room temperature. These values indicate the percentage contributions of lithium ions in the ionic conduction. In previous study, T_{Li+} for ceramic filler in gel polymer electrolyte without radiation is 0.46 at room temperature [88]. The increased T_{Li+} value is due to the electrolyte's structural modifications induced via Lewis acid interactions between the ceramic surface states and both the anions and the polymers segments which were explained earlier [83]. Zirconia surface groups provide cross-linking centers for the GPE, thus lowering the GPE reorganization tendency and there by promoting structural modifications of the polymer chains. This, in turn, establishes Li+ conducting pathways at the zirconia surface. The ceramic is that of promoting surface conducting pathways. Lithium ions are expected to move freely along these ceramic surface pathways and thus, under these conditions, a consistent enhancement of the cation transference number is logically expected [3].

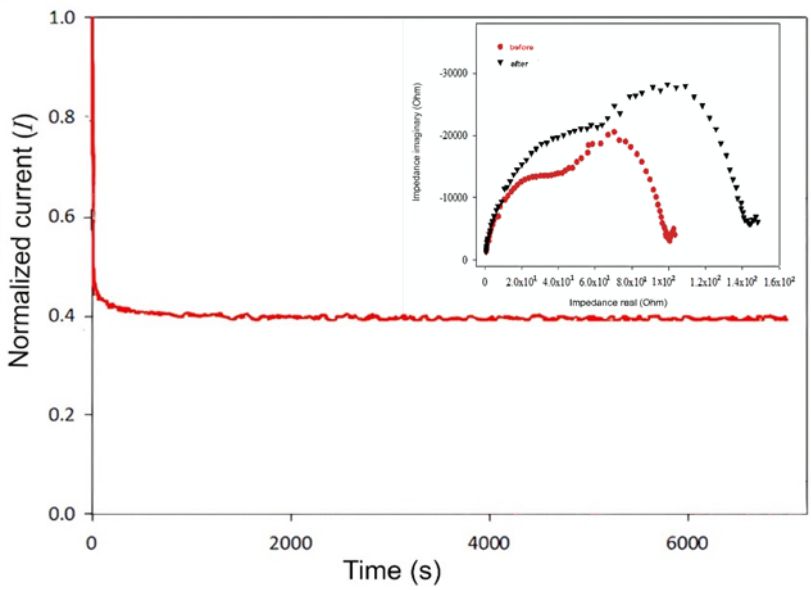

Fig. 7 Lithium transference number of Li/sample/Li cell for BMIMBF4-(PVDF-HFP)-LiCO4- 4 wt. % ZIP-VTES at 10 kGy

CONCLUSION

The surface morphology of the irradiated gel polymer changes as compared to unirradiated. FT-IR result showed the band 3600 cm^{-1} shifted to low wavenumber indicating strong interaction occur on the hydrogen bond and the gel polymer. The dose of electron beam irradiation has significantly enhanced ionic conductivity of the gel polymer electrolyte because of chain scissoring and additional pathway for ion transportation by hopping mechanism. The introduction of electron beam to the GPE, has improved the lithium transference number. In conclusion it can be stated that these gel polymer electrolytes can be gives better electrochemical properties in order to be a new class of materials for device applications.

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