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Inorganic Filler Sizes Effect on Ionic Conductivity in Polyethylene Oxide (PEO) Composite Polymer Electrolyte

Y.L. Yap[1,*], *A.H. You*[1], *L.L. Teo*[1], *H. Hanapei*[2]

[1] Centre for Advanced Devices and Systems, Faculty of Engineering and Technology, Multimedia University, Jalan Ayer Keroh Lama, 75450 Melaka, Malaysia
[2] Telekom Research and Development, Telekom Malaysia Innovation Centre, Lingkaran Teknokrat Timur, 63000 Cyberjaya Selangor, Malaysia
[*]E-mail: ylyap@mmu.edu.my

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In the present work, the effect of inorganic fillers with different particle sizes on the composite polymer electrolytes consist of Polyethylene Oxide (PEO), Lithium Trifluoromethanesulfonate ($LiCF_3SO_3$) and Ethylene Carbonate (EC) has been explored. Composite polymer electrolytes have been prepared via solution-casting technique. Impedance spectroscopy was conducted at room temperature on the resulted electrolytes. FTIR and SEM/EDX analysis were carried out to further investigate the effect of fillers. Addition of the micron-range inorganic fillers into the polymer electrolyte film leads to an improvement in the ionic conductivity, i.e. from 1.701×10^{-5} S/cm to 2.970×10^{-5} S/cm (with addition of Al_2O_3) and 3.570×10^{-5} (with addition of SiO_2). However, the conductivity was reduced when inorganic fillers with smaller particle size (i.e. nano-range) are employed. The SEM results showed that the filler was well distributed in the polymer matrix; the surface of electrolyte film became rougher after the addition of nano-range fillers. The interaction between PEO and additives was characterized by FTIR analysis to confirm the forming of the complexation.

Keywords: Composite Polymer Electrolytes; PEO; Inorganic Filler; Impedance Spectroscopy

1. INTRODUCTION

Ongoing studies and efforts to further develop solid polymer electrolyte (SPE) are widely reported in the literature [1–4] due to their wide potential in application as solid electrolyte and separator in solid state devices such as lithium rechargeable polymer batteries. The weakness of electrochemical instability in the conventional liquid electrolyte system is caused by repeated oxidation and restoration reaction at the interface between the electrode and electrolyte. Generally, SPE is a film that possesses transport properties comparable with that of common liquid ionic solutions and it is popular due to its good mechanical strength, high ionic conductivity at ambient and sub-ambient temperature, appreciable transference number and better compability with electrodes. SPE plays two major roles in lithium ion battery: (i) as a separator in the battery system because of its rigid structure, at the same time to avoid the electrical contact between the anode and the cathode; (ii) the medium in which the ions are transported between the anode and cathode during the cell operations. Thus, the polymer electrolyte should act as good electrical insulator but at the same time it should has high ionic conductivity [5]. These materials have a wide range of usage not only in lithium batteries but also, in other electrochemical devices such as fuel cell, super capacitors and electrochronic devices, etc. [1,6–9].

Fast ionic conduction in high molecular mass PEO-based SPE doped with sodium salts was suggested earlier by Wright and coworkers [10]. The main focus of various researchers on the PEO-based SPE is to attain the films containing large and stable amorphous phases, possibly with a low glass transition temperature, T_g, in order to obtain a good flexibility of the polymer chains which are responsible for the ion transport. Several efforts have been taken to modify and enhance PEO-based SPE, including: (i) preparation of cross-linked polymer networks, random, block or comb-like copolymers, with short chains of ethylene oxide, in order to minimize crystallization, (ii) utilization of doping salts which form low-temperature eutectics with pristine PEO phase (plasticizing salts), (iii) utilization of organic plasticizers to increase the flexibility of the host polymer chains, and (iv) addition of inorganic or organic additives, with the aim of reducing the crystallizing ability of the polymer without reducing the mechanical properties of the electrolytes [10].

Despite the numerous research works are going on at present, practical lithium batteries based on SPE have remained impalpable. Some of the problems that hindered the development of SPE include low conductivity at ambient temperature and their reactivity with the lithium metal electrode in solvent plasticized polymer systems [5,9]. The main difficulty to solve these problems is due to the ionic conductivity and mechanical strength of a polymer electrolyte being disparate to each other, i.e. mechanical strength of the electrolyte decreases as conductivity increases. In order to overcome this obstacle, high surface area inorganic fillers such as Al_2O_3, ZrO_2, TiO_2, TiO_2 and hydrophobic fumed silica are added into the polymers matrices and are called composite polymer electrolyte (CPE). The primary reasons to incorporate these fillers are twofold: (i) enhancement in ionic conductivity at low temperature and (ii) improvement of the stability at the interface with the electrode. Incorporation of the fillers will help to inhibit the recrystallization of the polymer and decrease the glass transition temperature of the CPE and hence enhance the conductivity [9]. Besides, it can be explained that the enhancement of ionic conductivity is due to the Lewis acid-base type interactions of mobile ionic species with the O^{2-} or OH^{-} groups on the surface of the filler grains. According to this interactions model, inorganic filler surface groups containing cross-linking centers for the PEO segments and for the anions, hence decrease the tendency of polymer reorganization and establish the structural modifications of the polymer chains. In addition, Lewis acid–base interactions between the polar surface groups of the inorganic oxide filler and the electrolyte ionic species yield a better extent of salt dissociation through formation of ion–inorganic oxide complex. Due to the heavy mass of the ion–inorganic oxide complex, the conductivity in this composite is not likely to be contributed directly from the movement of these complexes. Instead, the major conducting path is still originated from the local diffusion within the amorphous polymer matrix and the ion transport is achieved through sequential replacement of ion to adjacent vacancy [11].

Several studies demonstrated an increase in conductivity after the addition of the different inorganic fillers [11–13]. Besides, it was reported that the conductivity in composite polymer electrolyte is not a linear function of the filler concentration [14]. Hence, the focus of this study is to investigate the effect of different types and especially the effect of fillers particle sizes on the composite polymer electrolyte. In order to achieve the target, the wt% compositions of several complexes of PEO-based polymer electrolyte have been fixed in this study, while different filler types (SiO_2, Al_2O_3, TiO_2) and various particle sizes (<10 μm, <50 nm, <25 nm) were employed. In particular, the particle size difference is almost three orders of magnitude for the selected fillers in this study.

2. EXPERIMENTAL

2.1 Samples preparation

The performance of a solid state lithium battery is dependent upon the successful identification of a suitable SPE. In this paper, the PEO-based electrolyte films were prepared using the solution cast method. Polymers (PEO), plasticizers (EC), lithium salt ($LiCF_3SO_3$) and inorganic fillers were added accordingly with appropriate solvent. Several inorganic fillers were being selected in this study, i.e. Silicon Dioxide (SiO_2), Aluminum Oxide (Al_2O_3) and Titanium (IV) Oxide (TiO_2). Through solution casting method, the host polymer, PEO (Aldrich), with average molecular weight of 1,000,000 g/mol and EC (Merck) were dissolved in Tetrahydrofuran (Merck), the mixture was stirred with magnetic stirrer at room temperature. $LiCF_3SO_3$ and inorganic fillers with different particle sizes were added according to appropriate ratio into the mixture. $LiCF_3SO_3$, SiO_2 (<10 μm), Al_2O_3 (<10 μm, <50 nm) and TiO_2 (<25 nm) were obtained from Aldrich. The stirring of the mixtures were continued several hours. The resulted homogenous solutions were then cast in the petri dishes and allowed to be evaporated slowly at room temperature until the electrolyte films were formed. The films were then kept in the desiccators for further drying before the measurement and characterization to be carried out.

Table 1. Complexes compositions of PEO-based polymer electrolytes

Sample ID	wt%				Filler Type
	PEO	EC	$LiCF_3SO_3$	Filler	
PE1	65	18	17	13	–
PE2	52	18	17	13	SiO_2 (<10 μm)
PE3	52	18	17	13	Al_2O_3 (<10 μm)
PE4	52	18	17	13	Al_2O_3 (<50 nm)
PE5	52	18	17	13	TiO_2 (<25 nm)

In order to study the influence of different types and particle sizes of the fillers on the ionic conductivity of the polymer electrolytes, several complexes of PEO-based polymer electrolytes have been examined in this work, namely, the samples with the following wt% compositions [15]. Table 1 shows the complexes compositions of PEO-based polymer electrolytes

2.2 Characterizations

The influences and effects of different inorganic fillers (SiO_2, Al_2O_3 and TiO_2) on the conductivity behavior of the resulted samples have been investigated using Electrochemical Impedance Spectroscopy (EIS). The EIS measurement of the films was conducted using Solartron SI1260 Impedance/Gain-Phase Analyzer in the frequency ranging from 1 Hz to 1 MHz. The thickness of the resulted electrolyte film was measured using micrometer screw gauge and the film was sandwiched between two stainless steel electrodes with diameter of 1.0 cm under spring pressure. The average thickness for the resulted electrolyte films was 0.61 mm. The ionic conductivity of the samples was determined using the equation, $\sigma = t / R_b A$, where t is the thickness of the film and A is the effective film-electrode contact area. The bulk resistance, R_b is obtained from the complex impedance plot.

Furthermore, Fourier Transform Infrared (FTIR) characterization was performed on the polymer electrolyte films using the Nicolet iS10 FTIR spectrometer and the surface morphology of the films was observed and studied by using Scanning Electron Microscopy (SEM), as to explain the reported conductivity result. FTIR spectroscopy is an analysis technique that provides information regarding the molecular structure and chemical bonding of materials while the SEM provides high-resolution images of the samples which help in the surface morphology study of the resulted films. Lastly, Energy-dispersive X-ray (EDX) spectroscopy was performed on the electrolyte films as the elemental analysis.

3. RESULTS AND DISCUSSIONS

3.1 Ionic conductivity

Generally, the ionic conductivity of the films depends on the overall mobility of ion and polymer, which is determined by the free volume around the polymer chain [16]. Table 2 shows the conductivity results of PEO−EC−$LiCF_3SO_3$−filler polymer electrolyte complexes as discussed previously [15]. Ionic conductivity of the electrolyte films was found to be improved with the addition of SiO_2 (<10 μm) and Al_2O_3 (<10 μm). The percentages of improvement are 109.9 % and 74.6 % for SiO_2 and Al_2O_3, respectively. Both the particle sizes for these SiO_2 and Al_2O_3 are in the micron-range. Similar observations have been reported [14,17] for the PEO-based composite polymer electrolytes incorporation with different types of inorganic fillers. The presence of filler particles enhances the ionic conductivity substantially, and the degree of enhancement depends on the surface area of the filler. Dissanayake et al. have reported the maximum conductivity result for PEO−$LiCF_3SO_3$−Al_2O_3 (17.5 wt% of Al_2O_3) polymer electrolyte at 3.96×10^{-6} Scm^{-1} while compare with the filler-free electrolyte at 5.55×10^{-7} Scm^{-1} [17]. The steric hindrance effect of the inorganic filler contributed to the retention of the amorphous phase of polymer electrolyte and the ion transport mainly takes place by intra-chain and inter-chain hopping of ionic species in the amorphous regions. Due to its large surface area, inorganic fillers prevent local PEO chain reorganization with the result of locking in at ambient temperature a higher degree of disorder which in turn favours fast ionic transport [14,18]. This mechanism is likely to be the dominant conductivity enhancement mechanism operating in the resulted polymer electrolyte with micron-range inorganic fillers at ambient temperature, which is below the PEO crystallization temperature (i.e. 70°C) [14].

As comparing the conductivity between different filler types (SiO_2 and Al_2O_3) with same particle size (<10 μm), both compositions encountered an increase in the conductivity after the addition of the fillers. Nevertheless, the differences of the improvement between these two types of fillers are insignificant. Hence, these results demonstrated that filler types (SiO_2 and Al_2O_3) showing minor influence on the conductivity of the electrolyte films if compare with the particle sizes.

Table 2. Ionic conductivity of PEO−EC−$LiCF_3SO_3$−filler composite polymer electrolyte

Sample ID	Filler Type	Conductivity (Scm^{-1})
PE1	–	1.701×10^{-5}
PE2	SiO_2 (<10 μm)	3.570×10^{-5}
PE3	Al_2O_3 (<10 μm)	2.970×10^{-5}
PE4	Al_2O_3 (<50 nm)	4.843×10^{-6}
PE5	TiO_2 (<25 nm)	1.683×10^{-5}

Closer inspections of the obtained results clearly revealed that the conductivity enhancement in the resulted polymer electrolytes is not directly proportional to the reduction of the fillers particle sizes. When the particle sizes of Al_2O_3 reduced from micron-range (<10 μm) to nano-range (<50 nm), the ionic conductivity of the electrolyte films were observed to be decreased from 2.970×10^{-5} Scm^{-1} to 4.843×10^{-6} Scm^{-1}, even lower than the result obtained for filler-free films, where this decrement was in one order of magnitude lower. As for comparison, the filler-free film in this study is reported to have the conductivity of 1.701×10^{-5} Scm^{-1}. These results demonstrated that smaller filler particles show insignificant influence in the improvement of the conductivity. This phenomenon is probably due to the immobilization of the long polymer chains. Addition of fine (nano-sized) fillers into the electrolyte film may cause the filler grains getting closer to each other that the blocking effect imposed by the more abundant filler grains could make the long polymer chains more immobilized, leading to the decrease in conductivity. Reduction of the conduction pathways will thus lead to the decrement of the conductivity. Fig. 1 shows the complex ac impedance spectra of PEO-EC-$LiCF_3SO_3$-SiO_2 (<10 μm) electrolyte at room temperature. The impedance spectra shows only a nearly linear curve which corresponds to the lower frequency region. Hence, it confirmed that the current carriers in the electrolyte are ions and the majority of the conduction only by the ions not by the electrons in this composition (with Li salts, plasticizer and inorganic fillers) [5].

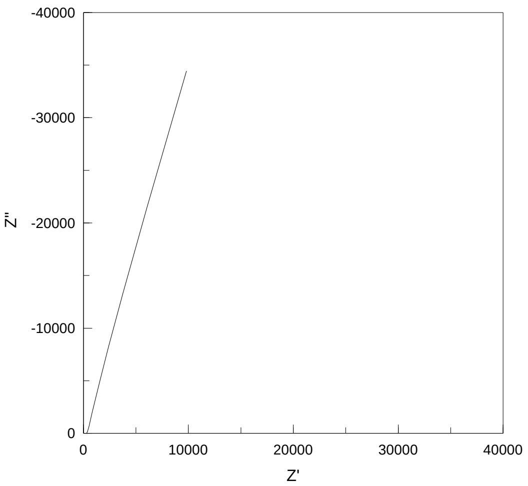

Figure 1. Room Temperature complex ac impedance spectra of PEO-EC-$LiCF_3SO_3$-SiO_2 (<10 μm)

3.2 Morphology and elemental analysis

Figures 2(a) and 2(b) show the SEM micrographs for polymer electrolyte films with/without the addition of the fillers (SiO_2 <10 μm), while figs. 3(a) and 3(b) show the micrographs for the films with the addition of Al_2O_3 with different particle sizes (<10 μm and <50 nm.). Generally, the resulted SEM photographs show that the fillers were homogeneous distributed and dispersed in the polymer matrix as a consequence of the uniform precipitation of fillers in the polymer matrix through the solution cast method. The addition of fillers has modified the PEO-based electrolyte surface morphology. Through the comparison between Figs. 2(a) and 2(b) at ×5000 magnification, a smoother surface morphology was shown after the addition of the SiO_2 (<10 μm) filler.

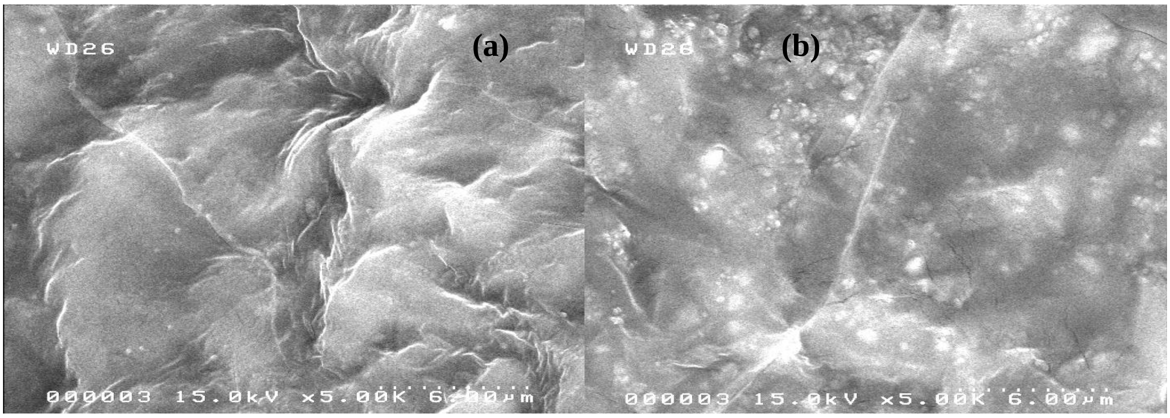

Figure 2. SEM micrographs of PE-based electrolyte films: (a) without inorganic filler and (b) with SiO_2 <10 μm

The smooth surface morphology is closely related to the reduction of PEO crystallinity phase of a polymer electrolyte film [5,11]. The surface roughness is associated with high surface free energy, and a possible explanation for its presence is that it facilitates the attachment of particles to the nucleus and in this way contributes to faster kinetics of nucleation. It can be seen from Fig. 2(b) that the added fillers were homogeneous distributed in the polymer matrix, the surface morphology becomes smoother with the addition of micron-sized fillers, which represents a more amorphous phase. The conductivity will increase as a consequence of the increase of amorphous phases in a polymer electrolyte. These results have been proved with the better ionic conductivity of the PE2 and PE3 films as discussed in the previous section. A smoother surface with more amorphous phase will cause the electrolyte becomes more flexible, the conducting ions will move more freely in the electrolyte with smoother surface morphology and thus the conductivity enhancement is detected.

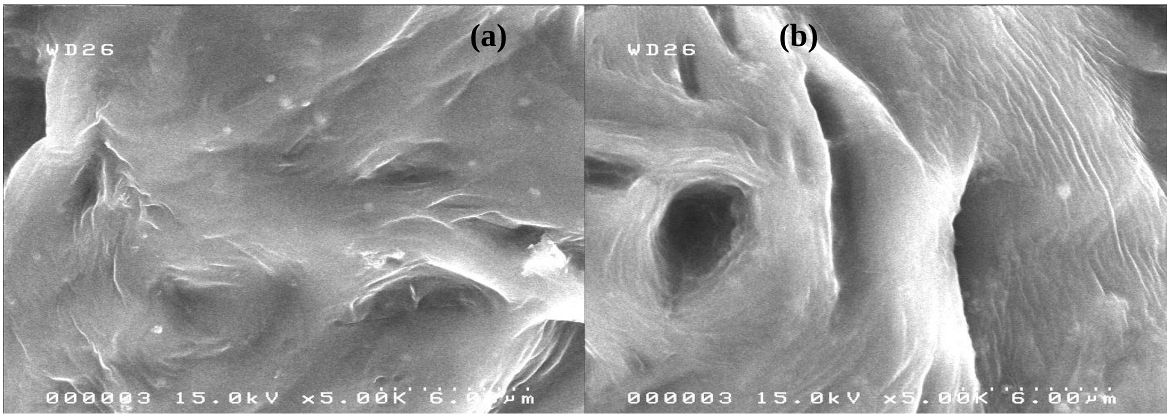

Figure 3. SEM micrographs of PE-based electrolyte films: (a) with Al_2O_3 <10 μm and (b) with Al_2O_3 <50 nm

However, the addition of nano-sized filler (Al_2O_3, <50 nm) has caused a dramatic change on the surface morphology of the film. As observed from Figs. 3(a) and 3(b) with the same filler type (Al_2O_3), the reduction of particle sizes for Al_2O_3 from micron-range to nano-range leads to a huge enhancement on the surface roughness of electrolyte film. A rough and uneven surface morphology represents the partial crystalline phase in the electrolyte film and it will decrease the ionic conductivity of this film, as encountered in the earlier conductivity study. Fig. 4 shows the EDX elemental analysis of PE2 sample with the addition of SiO_2. This result can be used as an evidence to confirm the existence of SiO_2 in the electrolyte film after the stirring, mixing and drying processes.

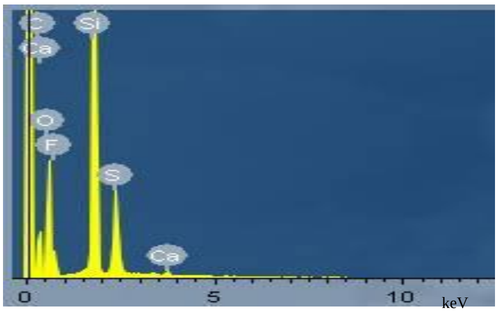

Figure 4. EDX elemental analysis of PE2 electrolyte film with SiO_2 (<10 μm)

3.3 FTIR analysis

Figure 5 shows the FTIR spectra of various compositions of PEO-based polymer electrolytes. Variation in intensity of the bands, shifting of the bands and appearance of new bands are the most frequently occurred observations in order to confirm the complexation of the polymer host with its additives [19].

Table 3. Vibrational modes and wavenumbers exhibited by PEO-based electrolytes

Sample ID	Wavenumbers (cm^{-1})			
	CH stretching	CH_2 scissoring	C−O−C stretching	CH_2 wagging
Reference [20]	2800-2935	1465-1485	950-1250	842
PE1	2881.74	1476.47	952.25	842.90
PE2	2879.72	1475.35	957.24	842.95
PE3	2882.39	1480.66	958.94	842.60
PE4	2879.08	1467.00	959.37	842.07
PE5	2877.59	1467.35	957.84	842.00

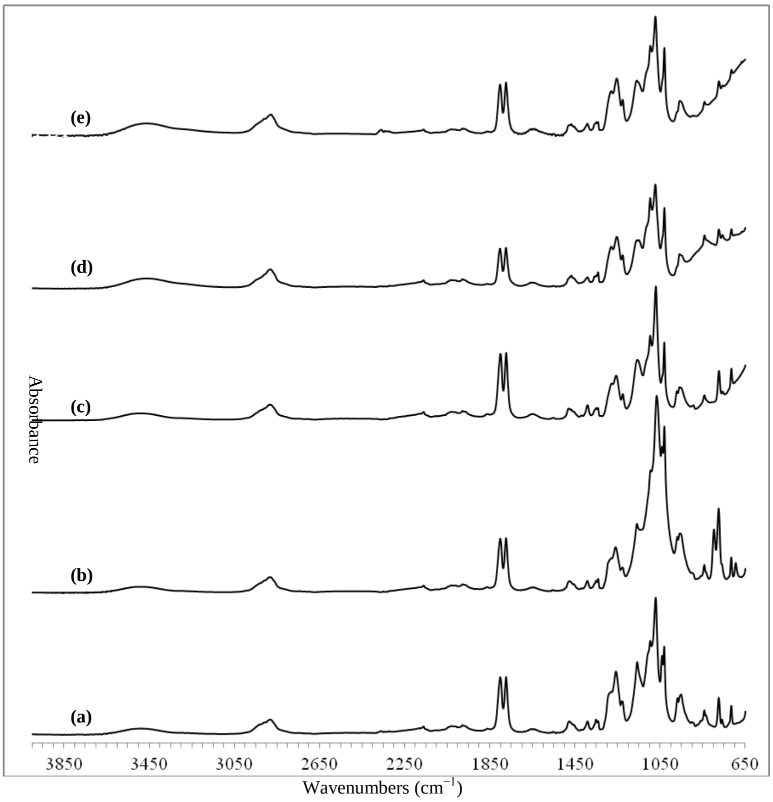

Figure 5. FTIR spectra of PEO-based electrolyte films: (a) without inorganic filler, (b) with SiO_2 (<10 μm), (c) with Al_2O_3 (<10 μm), (d) with Al_2O_3 (<50 nm) and (e) with TiO_2 (<25 nm)

The resulted peaks and wavenumbers of PEO in CH stretching, CH_2 scissoring, C−O−C stretching and CH_2 wagging are summarized in Table 3. As comparing between the same filler type (Al_2O_3), the peak of CH_2 scissoring are shifted from 1480.66 cm^{-1} to 1467.00 cm^{-1} while the filler size is decreased from micron-range (<10 μm) to nano-range (<50 nm). Similar wavenumber (1467.35 cm^{-1}) has been observed for another nano-range filler, i.e. TiO_2 with <25 nm. A large broad band at 3490.72 cm^{-1} for filler-free electrolyte, which is the characteristic frequency for $LiCF_3SO_3$ is found to be shifted to 3483.92 cm^{-1} (PE3), 2457.85 cm^{-1} (PE4) and 3464.20 cm^{-1} (PE5). Furthermore, the intensities of the resulted peaks at 2457.85 cm^{-1} (PE4) and 3464.20 cm^{-1} (PE5) are found to be increased. This can attributed to the change in environment and co-ordination state for $CF_3SO_3^{-1}$ ions in the complex, and hence confirmed the forming of different complexations with different filler types and sizes. Different complexations show different conductivity due to the binding structure of $CF_3SO_3^{-1}$ and its interaction with PEO [20].

4. CONCLUSION

PEO−EC−$LiCF_3SO_3$−filler system with different types and particle sizes of inorganic fillers have been developed and characterized. Conductivity as high as 2.970×10^{-5} Scm^{-1} was reported by polymer electrolyte film with Al_2O_3 (<10 μm) while film with Al_2O_3 (<50 nm) obtained lower conductivity as 4.843×10^{-6} Scm^{-1}. Results demonstrated that CPEs with micron-sized inorganic fillers obtained a smoother surface morphology and better ionic conductivity; hence, it revealed that conductivity of polymer electrolyte is not a linear function with the filler particle size. Besides, it is believed that the morphological property of a polymer electrolyte film is suitable to be used as one of the indicators of the amorphous or crystalline phase of the film, and the amorphous phase of the film is playing an important role on the increment of ionic conductivity of the film. Further investigations are currently in progress in order to further evaluate the impact of filler particle sizes on the properties of CPEs.

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