



The effect of [EMIm]BF₄/Li⁺ Ionic liquid on PEO-based solid polymer electrolyte membranes characteristics as lithium-ion batteries separator

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Lithium-ion batteries have liquid electrolytes, which are corrosive and volatile, that would cause leakage and explosion during the rechargeable process at high temperatures. To overcome these problems, it is necessary to change the liquid electrolyte into a solid one, namely a solid polymer electrolyte. This work has prepared the solid polymer electrolyte membranes by casting various 1-ethyl-3-tetrafluoroborate, [EMIm]BF₄/Li⁺ ionic liquid, and PEO. In this study, [EMIm]BF₄/Li⁺, a Li⁺ ion-attached ionic liquid, has been synthesized using a simple metathesis reaction between 1-ethyl-3-methylimidazolium-bromide, [EMIm]Br, and lithium tetrafluoroborate, LiBF₄ salt. [EMIm]Br has been synthesized from 1-methylimidazole and bromoethane precursors using Microwave Assisted Organic Synthesis (MAOS) method. The functional groups and structures of [EMIm]Br and [EMIm]BF₄/Li⁺ have been confirmed by Fourier Transform Infrared (FTIR) and Nuclear Magnetic Resonance (NMR) spectra analysis. The analysis of ionic conductivities, crystallinities, mechanical properties, surface morphologies, and thermal stabilities have been confirmed by using Electrochemical Impedance Spectroscopy (EIS), X-ray Diffraction (XRD), and tensile tester, Scanning Electron Microscopy (SEM), and Thermogravimetry Analysis (TGA), respectively. The highest ionic conductivity is 1.83 x 10⁻³ S.cm⁻¹ at room temperature for polymer electrolyte membrane with 16% weight of the [EMIm]BF₄/Li⁺ ionic liquid and also exhibits good mechanical flexibility and thermal stability.

Keywords: Electrochemical Impedance Spectroscopy (EIS), Ionic liquid, Lithium-Ion batteries (LIB), MAOS method, Solid polymer electrolytes

1 Introduction

Production of environmentally friendly and efficient energy sources has become crucial in recent decades, primarily if related to global warming and the limitation of fossil fuels¹. Focus on this problem, so the need for batteries technology has developed through various studies, either the continuous improvement of the electrochemical system or the finding of new types of chemical batteries². Since first commercially introduced in 1991 by Sony Corporation, lithium-ion batteries (LIBs) are rapidly becoming the primary energy storage for many electronic applications¹⁻³. LIBs are widely implemented as a source of energy because of their favorable properties such as high energy densities, long life cycles, and higher operating voltages compared to

previous systems, such as NiCd (Nickel-Cadmium) and NiMH (Nickel-Metal Hydride)¹⁻³.

However, the use of LIBs is still having problems. The use of liquid electrolytes causes leakage due to the corrosive properties of the material used. Also, it has a low boiling point, which releases an explosion when charging at high temperatures⁴. Many modifications have been done to solve the problems to produce both good performances and safety of LIB. One of the modifications is focused on separators and electrolytes⁵.

Solid polymer electrolyte membranes replacing the liquid electrolytes to improve the performance of LIB has been widely reported and has recently become to be more attention due to their advantages. They are easy to process ability, flexible, electrochemical stable, safe, and long life time⁶. Research of solid polymer electrolyte membranes as a separator in LIB is special attention to

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modifying various polymers to increase ionic conductivities with good mechanical strength and thermal properties⁷. The modifications include copolymerization, cross-linking, composite polymers (blends), polymers doped with ionic liquids, biodegradable polymer, etc⁸⁻⁹. Polymer electrolytes for lithium-ion batteries applications have been developed from polymeric materials, such as polyethylene (PE), polypropylene (PP)³, polyvinyl chloride (PVC), polyvinylidene fluoride (PVDF)², polyethylene oxide (PEO), polyvinyl alcohol (PVA)⁵, etc.

In this work, poly(ethylene oxide) (PEO) was selected as a matrix of the polymer electrolyte membranes. This polymer has been widely used because it is non-toxic and has a high melting point, good structural integrity, and low glass transition temperature, which contributes to ion transport at room temperature¹⁰. This polymer is also compatible when mixing with the lithium salts and has high segmental flexibility for Li⁺ ion transport in the amorphous phase¹¹⁻¹⁵. However, the high degree of crystallinity of PEO hinders the ion conduction leading to low conductivity ($10^{-7} - 10^{-8} \text{ S.cm}^{-1}$)¹⁶⁻¹⁸. The efforts have been done to overcome the problem such as blending the polymer, using ceramic filler and plasticizers¹⁹. The utilization of plasticizers such as ethylene carbonate (EC), propylene carbonate (PC), Dimethyl Formamide (DMF), etc., can improve the ionic conductivities but still lack mechanical strength to decrease the performance. In recent years, incorporating ionic liquids into PEO as a dopant has been preferable. Incorporating ionic liquids with bulky cations (e.g., EMIm⁺) will increase the free volume of Li⁺ ion conduction²⁰.

Ionic liquids are molten salts at low temperatures (<100 °C). These compounds are generally composed of an organic cation and an organic or inorganic anion²¹. Ionic liquids incorporation has been a promising approach to enhance LIB performances because of their attractive properties, such as wide electrochemical windows, high conductivity, high thermal stability, non-combustion, non-volatile and non-toxic²²⁻²⁴. Some ionic liquids can improve polymer electrolytes performances in previous research are 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm]PF₆)¹⁹, 1-ethyl-3-methylimidazolium ethylsulfate ([EMIm][EtSO₄])²⁵, 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIm]BF₄)²⁶, 1-ethyl-3-methylimidazolium acetate ([EMIm]Ac)²⁷⁻²⁸, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIm]TFSI)²⁹ and 1-butyl-3-methylimidazolium chloride ([BMIm]Cl)²⁴. Those are the imidazolium-derived ionic liquids that are

favorable compared with pyrrolidinium-based ionic liquids. Imidazolium-based ionic liquids have lower viscosities and higher ionic conductivities; therefore are useful for higher power applications²⁹.

This study aimed to study the effect of 1-ethyl-3-methylimidazolium tetrafluoroborate containing Li⁺-ion, [EMIm]BF₄/Li⁺ on PEO-based solid polymer electrolyte membranes and to find optimum condition as a potential separator for LIBs. The ionic liquid of 1-ethyl-3-methylimidazolium tetrafluoroborate containing Li⁺-ion, [EMIm]BF₄/Li⁺, has been selected and successfully synthesized through a metathesis reaction between 1-ethyl-3-methylimidazolium bromide, [EMIm]Br as precursor and lithium tetrafluoroborate (LiBF₄) directly. In this research, the characterizations were conducted to analyze functional groups, ionic conductivities, crystallinities, mechanical properties, and thermal stabilities through Fourier transform infra-red (FTIR), electrochemical impedance spectroscopy (EIS), X-ray Diffraction (XRD), tensile tester and thermogravimetry analysis (TGA), respectively. In addition, to analyze of the molecular structure of [EMIm]Br was carried out through nuclear magnetic resonance (NMR).

2 Materials and Methods

2.1 Apparatus and chemicals

The apparatus used in this work were Microwave Oven (Sharp R-2487J), hotplates (Thermo Scientific Super-Nuova Multiplace), magnetic stirrers, vacuum evaporator (BOECO GERMANY, RVO 400 SD), vacuum filtration (Lab Companion VE-11), pycnometer, desiccator, vacuum oven, screw micrometers. The chemicals used were PEO (MW = 6×10^5 Da, Sigma Aldrich), bromoethane (Fluka, freshly distilled, 99%), 1-methylimidazole (Sigma Aldrich, 99%), and LiBF₄ (Sigma-Aldrich, 99%). The solvents used were chloroform (CHCl₃), *n*-hexane, acetonitrile, methanol, and dichloromethane purchased from Merck. The chemicals were used directly without further purifications.

2.2 Green synthesis of [EMIm]Br and [EMIm]BF₄/Li⁺ ionic liquid

[EMIm]Br ionic liquid precursor was synthesized using the microwave-assisted organic synthesis (MAOS) method. We didn't use a standard microwave Discover SP reactor²⁷; instead, we used a domestic microwave oven. Each 4.11 g (0.05mol) 1-methylimidazole and 5.45 g (0.05mol) bromoethane were mixed and then entered to microwave reactor with 100 watts for 15 minutes and 50 °C. A 1-methylimidazole and bromoethane were dissolved

into chloroform, stirred for 24 hours, and heated in a domestic microwave oven. [EMIm]Br ionic liquid was obtained using extraction (water : chloroform = 1:1). Water fraction, then, distilled vacuum to purely produce [EMIm]Br ionic liquid. The functional groups and molecular structure of ionic liquids were confirmed with FTIR and NMR, respectively.

In addition, the metathesis reaction of [EMIm]Br ionic liquid and LiBF₄ salt (6 hours, in a methanol solvent) and removal of Br⁻ using Tollens reagent, obtained the [EMIm]BF₄ contains Li⁺-ion, [EMIm]BF₄/Li⁺ ionic liquid, was then analyzed by FTIR. The difference between [EMIm]Br and [EMIm]BF₄/Li⁺ ionic liquid product physically is shown in Fig. 1(a and b). [EMIm]Br is a brown solid while [EMIm]BF₄/Li⁺ is a clear liquid.

2.3 Preparation PEO + [EMIm]BF₄/Li⁺ ionic liquid-based solid polymer electrolyte membranes

The PEO-based polymer electrolyte membranes doped with [EMIm]BF₄/Li⁺ ionic liquid were prepared using a casting solution technique. PEO and [EMIm]BF₄/Li⁺ ionic liquid was dissolved in

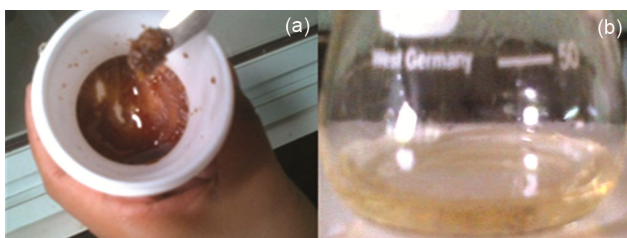


Fig. 1 — (a) [EMIm]Br, and (b) [EMIm]BF₄/Li⁺ ionic liquid (source: synthesis products).

acetonitrile. The mixture was stirred for 24 h to obtain a homogeneous viscous solution. The solutions were poured onto the glass plate and vaped at room temperature, then dried in the vacuum oven and desiccator for a week. The polymer electrolyte membranes were prepared with comparing between PEO and [EMIm]BF₄/Li⁺ as follows i.e. (91: 9), (88:12), (84:16) and (77:23) % w/w. All of them were characterized using Fourier Transform Infrared (FTIR), Electrochemical Impedance Spectroscopy (EIS), Instron tensile tester, X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Thermogravimetry Analysis (TGA) to confirm the functional groups, ionic conductivities, mechanical properties, crystallinities, surface morphology, and thermal stabilities. The summary of PEO + [EMIm]BF₄/Li⁺ solid polymer electrolytes preparation is modelled in Fig. 2.

2.4 Characterizations

2.4.1 FTIR analysis

Functional group studies of ionic liquids and polymer electrolytes membranes were carried out with Fourier transform infra-red, FTIR (type: FTIR Bruker, Alpha FT-IR Spectrometer) in the range of 400 – 4000 cm⁻¹.

2.4.2 NMR analysis

Structural studies of [EMIm]Br ionic liquid were carried out with nuclear magnetic resonance, NMR, (spectrometer NMR 500 Hz, JEOL, JNM ECA 500), while [EMIm]BF₄/Li⁺ was analyzed by FTIR only. The [EMIm]Br ionic liquid samples were prepared by dissolving them in the appropriate solvent, methanol (CD₃OD), in the NMR tube and then measured.

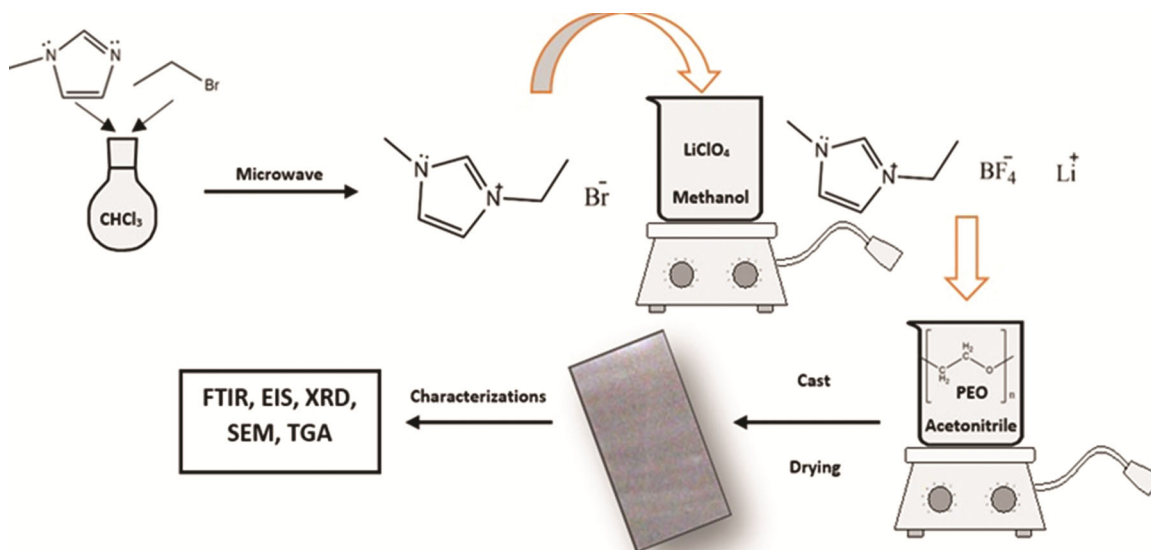


Fig. 2 — Model of PEO + [EMIm]BF₄/Li⁺ solid polymer electrolyte preparation.

2.4.3 EIS analysis

Conductivities studies of polymer electrolytes membranes were carried out with electrochemical impedance spectroscopy (EIS, merk Agilent, type E490A, precision LCR) in the range 20 Hz – 2 MHz. The solid polymer electrolytes membranes were prepared in 2.2 cm x 4.4 cm with minimal humidity at ambient temperature. The moisture was removed by drying the samples inside of oven vacuum. The EIS results were displayed in the Nyquist plot.

The conductivities data was obtained from Eq. (1):

$$\sigma = \frac{l}{RxA} \quad \dots(1)$$

where, σ is the conductivity ($S\text{ cm}^{-1}$), l is the distance of the electrode (cm), R = impedance, and A is area (cm^2), a wide electrode x thick membrane in cm. The instrument used has a value of $l = 1.5$ cm and the electrode width = 0.4 cm.

2.4.4 XRD analysis

Crystallinities studies of polymer electrolytes membranes were carried out with a diffractometer (type PW1710) in the range $2\theta \sim 5 - 45^\circ$. The XRD analysis were displayed by diffractogram.

2.4.5 SEM Analysis

Morphological studies of polymer electrolytes membranes were carried out with scanning electron microscopy (SEM, Type JEOL-JSM-6510LV). SEM analysis was performed on surface morphology and cross-section at a voltage of 10 kV and magnification of 5000.

2.4.6 Mechanical properties measurement

Mechanical studies of polymer electrolytes membranes were carried out with Instron tensile tester, while Young's modulus was determined using Eq. (2)³⁰.

$$\text{Young's Modulus} = \frac{\text{stress}}{\text{strain}} \quad \dots(2)$$

2.4.7 Thermogravimetry analysis

Thermal analysis of solid polymer electrolytes membranes was carried out with thermal gravimetric analysis (TGA, merk Linseis, type STA PT 1600).

3 Results and Discussion

3.1 Synthesis of [EMIm]Br and [EMIm]BF₄/Li⁺

The synthesis of [EMIm]Br occurred involves the S_N2 substitution mechanism. The lone pair of 1-methylimidazole acts as a nucleophile attacking the bromoethane, which acts as an electrophile while releasing the bromide ion as an excellent leaving group. The product obtained was [EMIm]Br ionic liquid. The product was then washed by extracting n-hexane five times. The lower phase, [EMIm]Br, was separated, then evaporated at a temperature of up to 100 °C. The evaporation results were then analyzed with FTIR. The density of [EMIm]SBr ionic liquid was 1.3125 g/mL, and the yield was 82%.

Figure 3(a) illustrates the synthesis reaction scheme of 1-ethyl-3-methylimidazolium-bromide, which was occurred through nucleophilic substitution reaction (S_N2). The figure shows the nitrogen atom of 1-methylimidazole acts as a nucleophile attacking bromide-bonded carbon atom to produce 1-ethyl-3-methylimidazolium cation and release bromide anion, as a good leaving group effect. The product, [EMIm]Br, appeared as a hygroscopic brown solid (Fig. 1(a)).

The synthesis of [EMIm]BF₄/Li⁺ was conducted through a metathesis reaction (anion exchange) by mixing the liquid precursor [EMIm]Br ion with the LiBF₄ salt (containing the BF₄ anion). The by-products obtained, namely Li⁺ ions and Br⁻ ions, were separated using Tollens reagent ([Ag(NH₃)₂]⁺ solution). AgBr precipitates were formed in this process, and ammonia gas (NH₃) was evaporated at a

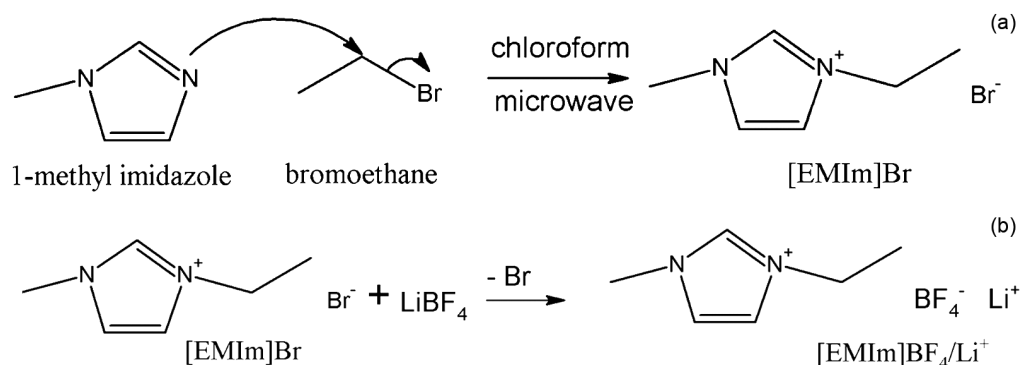


Fig. 3 — Proposed mechanism of synthesis for (a) [EMIm]Br, and (b) [EMIm]BF₄/Li⁺ ionic liquids.

temperature of about 50 °C. Metathesis reaction did not require large amounts of energy, so it does not require the use of heat in synthesis. The formation of [EMIm]BF₄/Li⁺ ionic liquid shows physical changes such as color if compared to [EMIm]Br ionic liquid.

Meanwhile, the Li⁺ ion did not need to be separated so that the [EMIm]BF₄ ionic liquid contains Li-ions, [EMIm]BF₄/Li⁺. The ionic conductivity of [EMIm]BF₄/Li⁺ was 4.82 x 10⁻³ S cm⁻¹, with a yield of 44.51%. The low yield of this product was due to the difficulty of separating the bromide ion using the Tollens reagent. The proposed mechanism of the simple metathesis reaction between [EMIm]Br ionic liquid and LiBF₄ salt is depicted in Fig. 3(b). The figure depicted that the Li⁺ ion-attached [EMIm]BF₄ ionic liquid was designed to form dual functions of ionic liquid; both are dopant and lithium-ion sources.

3.2 IR analysis

IR studies were carried out to investigate the main functional groups of [EMIm]Br, [EMIm]BF₄/Li⁺ ionic liquid, pure PEO, and PEO + [EMIm]BF₄/Li⁺ ionic liquid-based solid polymer electrolytes. The IR spectra of [EMIm]Br and [EMIm]BF₄/Li⁺ ionic liquids are depicted in Fig. 4(a and b). The peaks relate to O-H vibrations of [EMIm]Br at 3447 cm⁻¹, with a broad

peak showing evidence due to quaternary amine salt [EMIm⁺] formation with Br⁻ anion. In [EMIm]BF₄/Li⁺, there is a shift to a lower wavenumber at 3445 cm⁻¹ with a broad peak, indicating the [EMIm⁺] cations have interacted with BF₄⁻ anion. The peaks at 3162 cm⁻¹ and 3093 cm⁻¹ are stretching vibrations of =C-H in the imidazole ring of [EMIm]Br ionic liquid, while in [EMIm]BF₄/Li⁺ ionic liquid shown at 3153 cm⁻¹ and 3098 cm⁻¹, which confirms no significant changes relate to these vibrations. The C-H aliphatic vibrations of [EMIm]Br and [EMIm]BF₄/Li⁺ ionic liquid have the same wavenumber at 2995 cm⁻¹.

The C=C stretching vibrations are also no different wavenumbers, at 1634 cm⁻¹ and 1635 cm⁻¹, to [EMIm]Br and [EMIm]BF₄/Li⁺ ionic liquid, respectively. The C=N stretching vibrations are at 1573 cm⁻¹ and 1572 cm⁻¹ to [EMIm]Br and [EMIm]BF₄/Li⁺ ionic liquid, respectively. The -CH₂ and -CH₃ bending vibrations of [EMIm]Br and [EMIm]BF₄/Li⁺ ionic liquid are significantly different. The -CH₂ and -CH₃ bending vibrations of [EMIm]Br ionic liquid is clearly shown at 1459 cm⁻¹, 1393 cm⁻¹, and 1337 cm⁻¹, while those are not clearly shown to the [EMIm]BF₄/Li⁺. These characteristic peaks have appeared due to the interaction between F atoms (from BF₄⁻ anions) and carbon atoms of the imidazole ring.

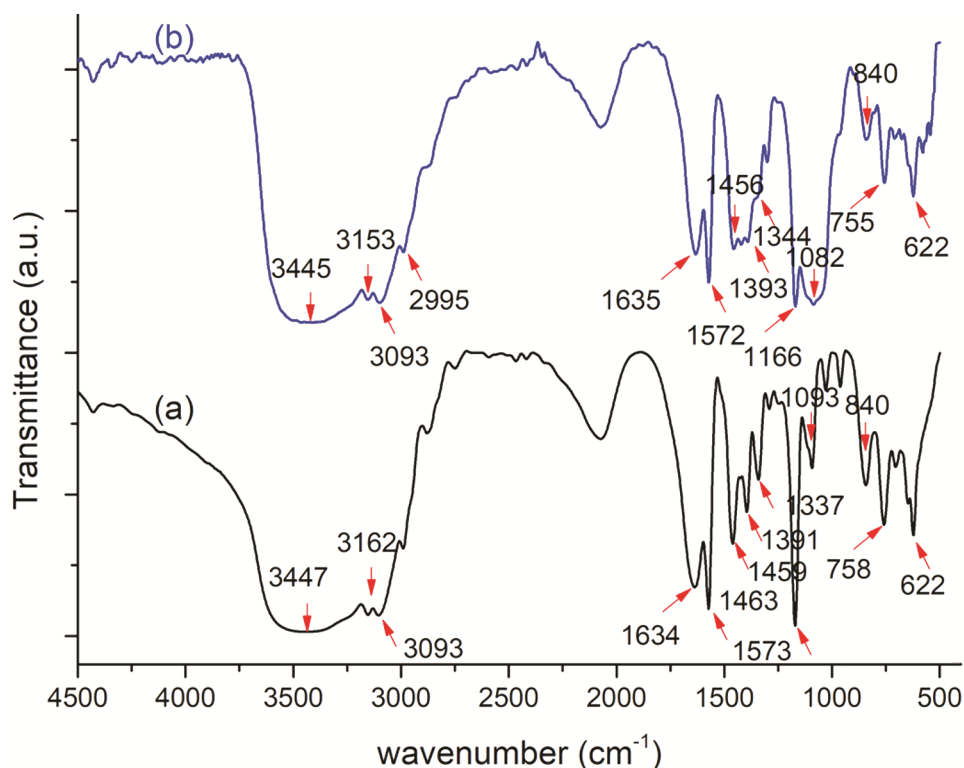


Fig. 4 — IR spectra of (a) [EMIm]Br, and (b) [EMIm]BF₄/Li⁺ ionic liquid.

The C-N stretching vibrations of [EMIm]Br and [EMIm]BF₄/Li⁺ ionic liquid were at 1172 cm⁻¹ and 1166 cm⁻¹, respectively. The C-N stretching vibrations (from methyl group and imidazole ring) differently appear to [EMIm]Br and [EMIm]BF₄/Li⁺. The C-N stretching vibrations peaks of [EMIm]Br and [EMIm]BF₄/Li⁺ are at 1172 cm⁻¹ and 1082 cm⁻¹, respectively. The broader peak of [EMIm]BF₄/Li⁺ indicates F atoms' interaction (from BF₄⁻ anions) with carbon atoms from alkyl groups of the imidazole ring.

Based on IR analysis, it was confirmed that synthesized ionic liquids were [EMIm]Br and [EMIm]BF₄/Li⁺. A peak at 840 cm⁻¹ is due to C-H bending out of the plane imidazole ring. A peak at 758 (756) cm⁻¹ and 622 cm⁻¹ is due to the C-N stretching vibration of both [EMIm]Br and [EMIm]BF₄/Li⁺. A significantly different vibrations mode is at wavenumber 1000-1400 cm⁻¹ region due to interaction F atom of BF₄⁻ anion to the alkyl group of [EMIm]⁺ cation.

The IR spectra of pure PEO and PEO + [EMIm]BF₄/Li⁺ ionic liquid-based solid polymer electrolytes were depicted in Fig. 5. The most significant vibrational modes and wavenumbers exhibited by pure PEO are -CH₂- wagging 842 cm⁻¹; -CH₂- twisting mode at 962 cm⁻¹; -CH₂- bending

vibrations, divided into two peaks at 1342 cm⁻¹ and 1360 cm⁻¹; -CH₂- stretching broad peak at 2877 cm⁻¹; O-H stretching vibration observed at 3528 cm⁻¹; and, C-O-C stretching mode, divided into three peaks at 1160 cm⁻¹; 1104 cm⁻¹, 1060 cm⁻¹, respectively. The doublet CH₂ and C-O-C stretching triplet modes confirmed the existence of PEO crystallinity.

[EMIm]BF₄/Li⁺ ionic liquid incorporation to PEO formed PEO + [EMIm]BF₄/Li⁺ ionic liquid-based solid polymer electrolytes cause some significant peaks of pure PEO to shift and disappear. These are due to complexation or interaction between the ether oxygen of PEO and cations (EMIm⁺ and Li⁺). The geometry complexation of PEO ether oxygen with [EMIm]BF₄/Li⁺ is shown in Fig. 6 as adapted from the previously proposed mechanism²⁴. The proposed possible interaction is also similar to the previous possible interaction between the PVP backbone with the cation of ionic liquid [EMIm⁺] or Li⁺²⁵. Two peaks of CH₂ bending mode at 1360 cm⁻¹ and 1342 cm⁻¹ for pure PEO shift to a single peak centered at 1347 cm⁻¹. The incorporation of [EMIm]BF₄/Li⁺ causes the C-O-C stretching triplet modes to change to a single peak at 1104 cm⁻¹ as a consequence of the interaction of [EMIm⁺] and Li⁺ cation to the PEO backbone¹⁸.

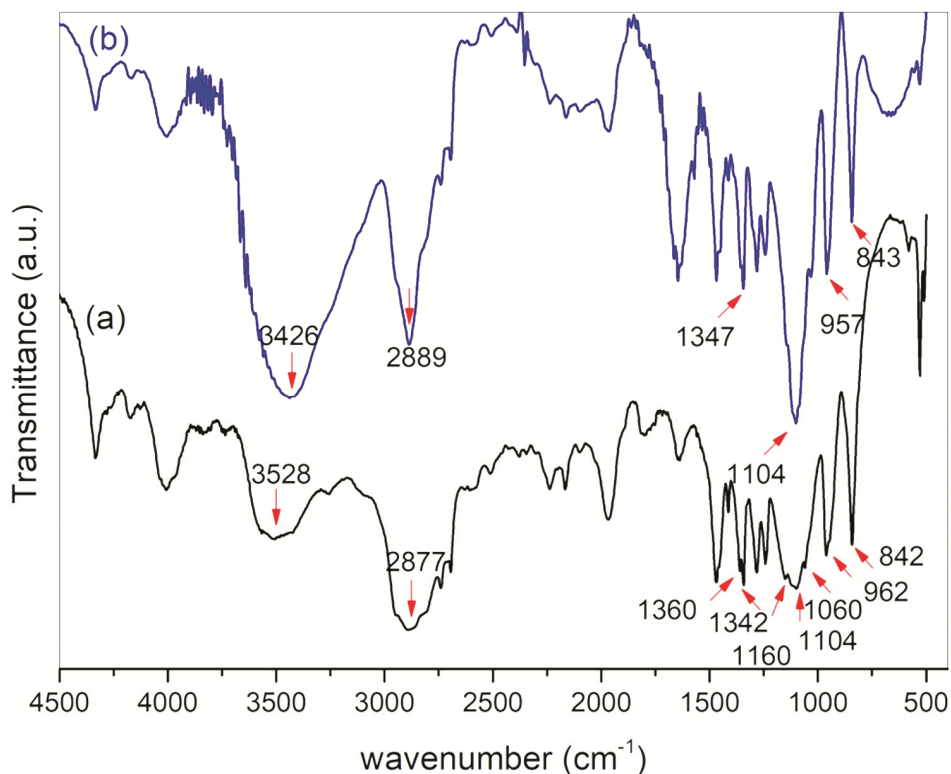


Fig. 5 — IR spectra of (a) Pristine PEO, and (b) PEO + *x* w% [EMIm]BF₄/Li⁺.

3.3 Molecular structure of [EMIm]Br ionic liquid

The molecular structure analysis of [EMIm]Br ionic liquid precursor was conducted using ¹H-NMR and ¹³C-NMR, which indicate the number of hydrogen atoms in the compound. The ¹H-NMR spectrum of [EMIm]Br can be seen in Fig. 7(a). Based on Table 1, the structure of [EMIm]Br can be described as follows. The proton signal *a* (δ: 1.54 ppm; 3H, *t*) has three protons which are bonded to carbon atom *A* and coupled proton-bonded carbon atom. This signal is the most shielded due to –the CH₃ group's location is far and not bonded directly to the electron-withdrawing group (N-atom of imidazole ring). The singlet proton signal *b* (δ: 3.98 ppm; 3H, *s*) is bonded to carbon atom *B*, a Nitrogen atom of the sp³-bonded methyl group of the imidazole ring. The quartet proton signal *c* (δ: 4.32 ppm; 2H, *q*) is bonded to carbon atom *C* in an imidazole ring with three protons.

The doublet proton signal *d* (δ: 7.74 ppm; 1H, *d*) is bonded to the carbon atom in the imidazole ring, and also the doublet proton signal *e* (δ: 7.74 ppm; 1H, *d*) is bonded to the carbon atom *E*. The singlet proton signal *f* (δ: 9.10 ppm; 1H, *s*) is the least protected signal. This signal is attached to carbon *F* without coupling to the protons-bonded carbon atom.

To identify carbon signals, ¹³C-NMR analysis was also carried out. Figure 7(b) and Table 2 present the ¹³C-NMR spectrum of [EMIm]Br ionic liquid. The number of carbon atoms from the spectroscopic analysis of ¹³C-NMR is 6, which corresponds to the number of carbon atoms in the molecular structure [EMIm]Br. Based on the chemical shift in Table 2,

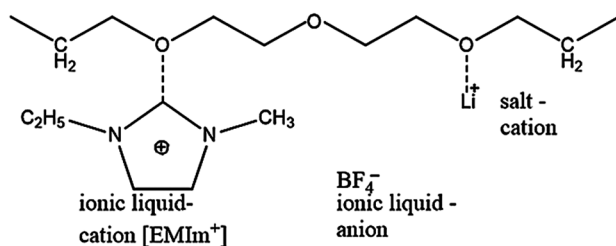


Fig. 6 — Possible geometry of complexation of PEO ether oxygen with [EMIm]BF₄/Li⁺ (adapted from the previously proposed mechanism²⁴).

Table 1 — ¹H-NMR analysis of [EMIm]Br

Proton (Figure 8)	δ, ppm (H, multiplicity)
<i>a</i>	1.54 (3H, <i>t</i>)
<i>b</i>	3.98 (3H, <i>s</i>)
<i>c</i>	4.32 (2H, <i>q</i>)
<i>d</i>	7.73 (1H, <i>d</i>)
<i>e</i>	7.74 (1H, <i>d</i>)
<i>f</i>	9.0 (1H, <i>s</i>)

which confirmed the successfully synthesized [EMIm]Br.

The results of ¹H-NMR and ¹³C-NMR analysis of [EMIm]Br are summarized as follows:

¹H NMR (500 MHz, CD₃OD): δ (ppm) 1.54 (3H, *t*); 3.94 (3H, *s*); 4.32 (2H, *q*); 7.73 (1H, *d*), 7.74 (1H, *d*); 9.10 (1H, *s*). ¹³C NMR (500 MHz, CD₃OD): δ (ppm) 15.88; 36.81; 46.14; 123.39; 124.99; 137.63.

The analysis concluded that [EMIm]Br ionic liquid has been successfully synthesized by 1-methylimidazole and bromoethane precursors. This result is similar to [EMIm]Br ionic liquid in the previous research²⁷.

3.4 Ionic conductivity studies

The ionic conductivities for the membrane samples are shown in Table 3. Table 3 shows that the pure PEO membrane has the lowest ionic conductivity. The results indicated that the ionic conductivity of pure PEO is low compared to the PEO membrane mixed with ionic liquids. The ionic liquid contributed to the mobilization of ions (Li⁺) increases.

The ionic conductivity generally depends on several factors, such as ionic conducting species concentration, cationic or anionic types of charge carriers, mobility and

Table 2 — ¹³C-NMR analysis of [EMIm]Br ionic liquid

Carbon atom (Fig. 9)	Chemical shift, (δ), ppm
<i>A</i> (C-C)	15.88
<i>B</i> (C-N)	36.81
<i>C</i> (C-N)	46.14
<i>D</i> (C=C aromatic)	123.39
<i>E</i> (C=C aromatic)	124.99

Table 3 — Ionic Conductivities data of PEO-[EMIm]BF₄/Li⁺ polymer electrolyte membranes and some previous research results

Sample	% w/w of Plasticizers	Ionic conductivities (S cm ⁻¹)	Ref.
PEO (pure)	0	6.34 x 10 ⁻⁷	
PEO + 9% [EMIm]BF ₄ /Li ⁺	9	1.78 x 10 ⁻⁴	
PEO + 12% [EMIm]BF ₄ /Li ⁺	12	2.67 x 10 ⁻⁴	In this work
PEO + 16% [EMIm]BF ₄ /Li ⁺	16	1.83 x 10 ⁻³	
PEO + 23% [EMIm]BF ₄ /Li ⁺	23	3.55 x 10 ⁻⁴	
PEO + 10% LiPF ₆ + 20% [BMIm]PF ₆	20	1.5 x 10 ⁻⁸	[19]
[(PEO) _{0.9} +(C ₆ H ₁₆ N ₂ O ₄) _{0.1}] _{0.99} + [EC+PEG] _{0.01}	10	4.37 x 10 ⁻⁷	[35]
PEO + 8% HCF ₃ SO ₃ + 50 w/w% DMA	50	4.26 x 10 ⁻³	[14]
PEO + 20% LiTFSI + 30% [BMPyr]TFSI	30	2.54 x 10 ⁻⁵	[37]

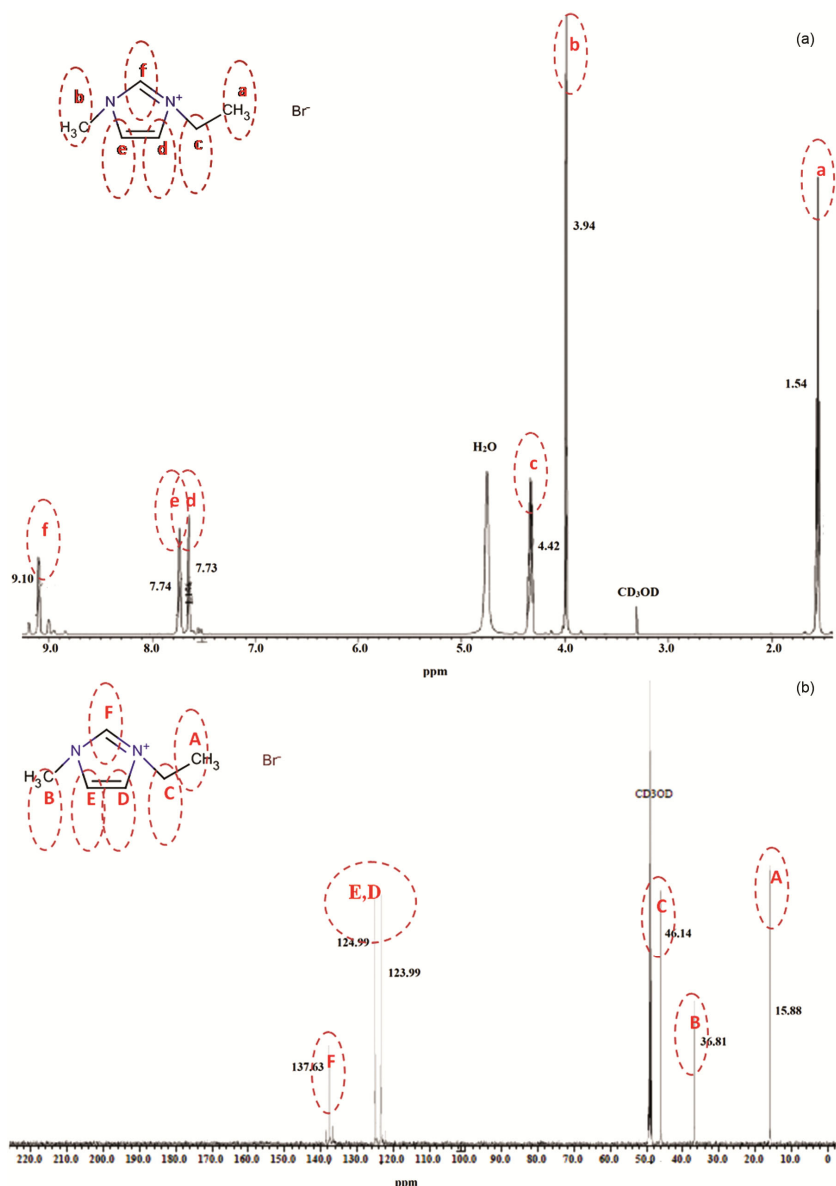


Fig. 7 — NMR spectra (a) ¹H-NMR spectrum and (b) ¹³C-NMR spectrum of [EMIm]Br ionic liquid

temperature³¹⁻³³. Besides several factors, the ionic conductivity of polymer electrolytes is also strongly influenced by three major elements, and those are (1) concentration of amorphous fraction, (2) concentration of mobile cations and (3) concentration of additional transit sites³⁴.

The ionic conductivity increases with increasing doping of [EMIm]BF₄/Li⁺ ionic liquids content until the incorporation of 16% weight (optimum ionic conductivity, $1.83 \times 10^{-3} \text{ S cm}^{-1}$). The presence of an amorphous fraction in the polymer electrolytes matrix permits the transportation of mobile cations along the polymer backbone. The [EMIm]BF₄/Li⁺ incorporation weakens the inter-ion Coulomb force between the Li⁺

ions and BF₄⁻ ions, ultimately breaking the connecting bonds. In this case, the ionic liquid acts as a spacer inter-chain of the polymer backbone, as explained by the previous report³⁵; it also enhances the amorphous content¹³.

The bond breakage will allow the number of mobile Li⁺ ions available in the amorphous phase to coordinate with the vacant sites. Therefore, more frequent Li⁺ ions hopping occur, resulting in high ionic conductivity. On the other hand, additional transit sites are available upon [EMIm]BF₄/Li⁺ miscibility. These transit sites provide an alternative pathway for the hopping of Li⁺ ions when there is no neighboring vacant site is available in the polymer backbone.

Therefore, continuous hopping of Li⁺ ions is ensured with the presence of additional transit sites that supports the increase in ionic conductivity. Further increase in the [EMIm]BF₄/Li⁺ content leads to a constant increase in the ionic conductivity³⁴. Generally, ionic conductivity in polymer electrolyte systems is caused by salt dissociation that makes free charge carrier/ions migrate³⁵. However, Gupta *et al.*³⁶ established that total ionic conductivity is due to the flow of ions (anion, Li⁺, ionic liquid cation) in polymer electrolytes. Nevertheless, anion and cation aggregated at the electrolyte-electrode interface and decomposed on the electrode surface to form a passive layer³⁵.

After the optimum condition (16% weight of [EMIm]BF₄/Li⁺), the [EMIm]BF₄/Li⁺ ionic liquid incorporation of 23 w/w% to polymer electrolytes decreases ionic conductivity to be $3.55 \times 10^{-4} \text{ S cm}^{-1}$. The decreasing ionic conductivity is due to [EMIm]⁺ cation providing steric hindrances for Li⁺ ions mobiles³⁴. Table 3 also compares the optimum conditions for adding some plasticizers to the PEO matrix. It is observed that the optimum conductivity value in this research is better than the results of other studies^{18-19,35,37-38}, except for the DMA plasticizer solvent addition¹³. DMA solvent, however, is not advantageous in terms of mechanical and thermal stability for energy storage devices application due to the tendency of high solvent evaporation to operate at high temperatures.

Figure 8(a and b) show the Nyquist plot representatives of pure PEO and (PEO + [EMIm]BF₄/Li⁺ ionic liquid) solid polymer electrolyte membranes, respectively. The impedance measurement was conducted at the range of 20 Hz – 2 MHz. Pure PEO membrane showed a higher impedance ($R_b = 2.17 \times 10^8$ ohm) than PEO + ionic liquid membrane ($R_b = 2.45 \times 10^5$ ohm). Hence, the (PEO + [EMIm]BF₄/Li⁺ ionic liquid) membrane ionic conductivity was higher than pure PEO. Both pure PEO and (PEO + ionic liquid) membranes showed ions migration mechanisms through charge transfer and diffusion. A semicircle curve indicates the charge transfer mechanism, while spikes indicate diffusion. The Nyquist plots as studied in this research were similar to the previous research plot pattern³⁹.

3.5 Crystallinities studies

The crystallinities studies were conducted by using X-ray diffraction (XRD). The XRD pattern of pure PEO has many typical dominant peaks in the range

$2\theta \sim 19^\circ$ and 23° ; even according to Kumar *et al.*¹⁴ (2017), these peaks correlate to the partial crystalline nature while some weak peaks at 2θ : 15.21° ; 16.79° ; 26.35° ; 27.13° ; 36.4° ; and 39.79° (Fig. 9). Table 4 shows the differences of 2θ -shifted as influenced by the incorporation of 16% and 23% weight of [EMIm]BF₄/Li⁺ ionic liquid to the PEO-based matrix. The decreasing of peaks intensities was the effect of [EMIm]BF₄/Li⁺ ionic liquid incorporation to the PEO-based matrix that indicating the crystallinity reduced as depicted in Fig. 9.

The slightly 2θ -shifted was appropriate to the previous result, explaining that the complexation between polymer and plasticizer makes the 2θ -shifted lower. In Table 4 and Fig. 9, we can see the prominent two peaks shift to lower 2θ at 18.79° and 19.18° (16% weight of ionic liquid incorporation) and also at 19.18° and 23.41° (23% weight of ionic liquid incorporation). This decreasing crystallinity indicates

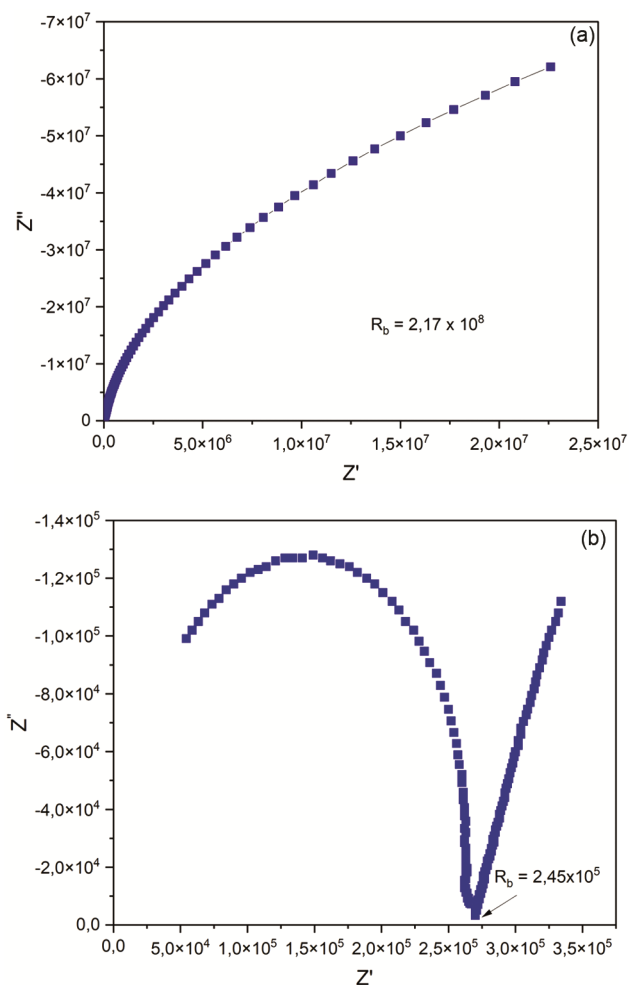


Fig. 8 — Nyquist plot representative of (a) pure PEO, and (b) pure PEO + [EMIm]BF₄/Li⁺ ionic liquid.

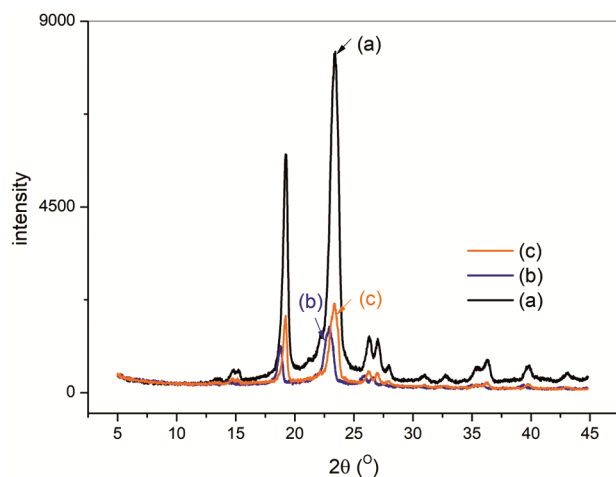


Fig. 9 — Diffractogram of (a) Pure PEO, (b) PEO + 16% weight of [EMIm]BF₄/Li⁺, and (c) PEO + 23% weight of [EMIm]BF₄/Li⁺.

Table 4 — XRD analysis of polymer electrolytes membranes

Material	2θ – main peaks	2θ – weak peaks
Pure PEO	19.31; 23.41	15.21; 26.35; 27.13; 36.4; 39.79
PEO + 16% [EMIm]BF ₄ /Li ⁺	18.79; 22.89	14.56; 25.97; 26.61; 35.84; 39.43
PEO + 23% [EMIm]BF ₄ /Li ⁺	19.18; 23.41	15.21; 26.11; 26.33; 36.35; 39.69

that the polyelectrolyte membrane's amorphous nature increases, leading to an increase in the conductivity of the polyelectrolyte membrane. The ionic liquid cation of the [EMIm]BF₄/Li⁺ ionic liquid contributes to increase the ionic liquid-doped PEO's pore sizes. Therefore, the Li⁺ ions can move more freely and efficiently than the pure PEO matrix. Besides that, the weakening of the hydrogen bond between PEO chains may occur because of the possible interaction of imidazolium cations and BF₄⁻ of the ionic liquid with oxygen and hydrogen atoms attached to the carbon backbone PEO²¹.

Incorporating 23% weight of [EMIm]BF₄/Li⁺ ionic liquid in the polymer electrolytes membrane causes increasing crystallinity. This phenomenon is confirmed by shifting to higher 2θ angle and increasing the peaks' intensities relatively compared to 16% (w/w) of [EMIm]BF₄/Li⁺ ionic liquid incorporation to the PEO-based matrix still lower intensity than the pure PEO-based membrane. The crystallinity increase was caused by forming ionic liquid aggregation that probably occurred. A substantial portion of the ionic liquid was not entrapped in the polymer host and deposited on the surface when the film formed. Changes in amorphousness of PEO-[EMIm]BF₄/Li⁺ polymer

electrolytes membranes will affect the conductivity and flexibility of the samples^{31,36}.

3.6 Morphological studies

Figure 10 shows the morphology of pure PEO and PEO + 16 w/w% [EMIm]BF₄/Li⁺, which indicates the difference of pore sizes. Pure PEO shows smaller pore sizes and was denser than ionic liquid-doped PEO. Increasing pore sizes indicates an increase in amorphous content and hence the reduced crystallinity in the material^{19,29}. As a plasticizer, the ionic liquid acts as a spacer inter-chain giving visible pore-like. Here is preferred to ionic conduction increasing caused this condition facilitates the free charge carrier/ions³⁵. PEO + 16% weight of [EMIm]BF₄/Li⁺ polymer electrolytes membrane has more porous surface leads to facilitate ionic motion (Li⁺-ion)^{29,40}. It has been ensured that ionic liquid significantly gives free-volume and large spaces into polymer electrolyte membranes.

3.7 Mechanical properties studies

Excellent mechanical properties are essential for the safe handling and mechanical stability of LIBs^{29,40}. In this research, mechanical studies were conducted by the tensile tester. The addition of [EMIm]BF₄/Li⁺ ionic liquid introduces the migration of component ions in the polymer electrolyte and enhances the flexibility of PEO chains. The mechanical properties of Young's modulus of PEO + x% weight of [EMIm]BF₄/Li⁺ ionic liquid are shown in Fig. 11. The Young's modulus significantly decreases by introducing a plasticizer of [EMIm]BF₄/Li⁺⁴¹, which means Young's modulus decreases and the elasticity increases (elongation at break increase). The mechanical properties of PEO + x% weight of [EMIm]BF₄/Li⁺ used for LIB are critical due to the improvement in flexibility, leading to the increase in segmental motion of PEO-chains and hence overall ionic conductivity¹⁹.

The highest flexible polymer electrolyte membrane was a 16% weight [EMIm]BF₄/Li⁺-doped PEO matrix. This result confirmed that incorporating [EMIm]BF₄/Li⁺ enhances segmental motion and flexibility (the lowest Young's modulus), increasing Li⁺ ion mobile. Analog to the crystallinity case, incorporating 23% weight of [EMIm]BF₄/Li⁺ ionic liquid into polymer electrolyte membrane causes an increasing Young's modulus. This result explains that the high crystallinity make the mobility lower leading to increased rigidity²⁹. Based on the results, the effect

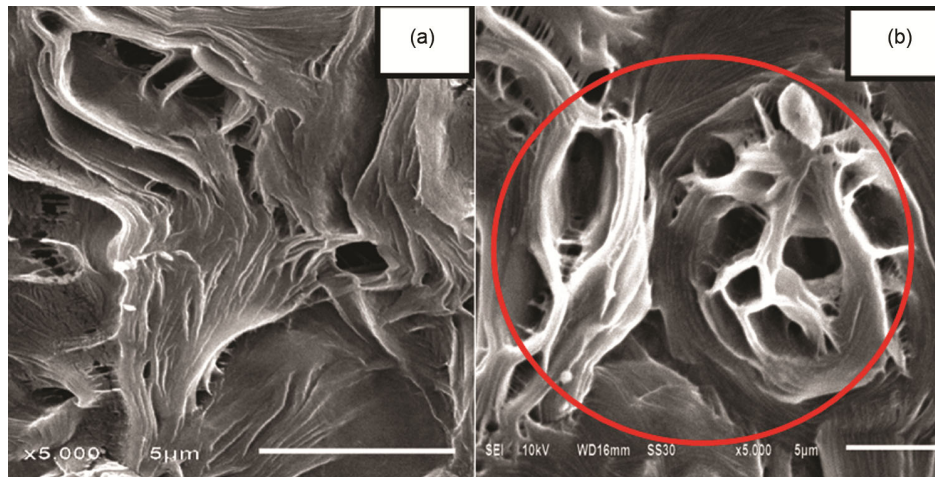


Fig. 10 — Morphological of (a) Pure PEO, and (b) PEO+16% (w/w) of [EMIm]BF₄/Li⁺.

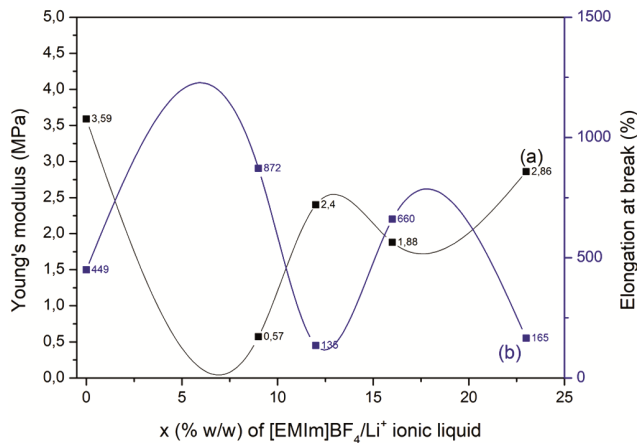


Fig. 11 — Mechanical analysis of (a) Young's modulus, and (b) Elongation at break for PEO-*x* w% [EMIm]BF₄/Li⁺.

of ionic liquid ultimately decreases Young's modulus. Still, it could increase the flexibility on the other side, so this condition is favorable, especially for LIB separator application. The influences of ionic liquid incorporation on mechanical properties were also studied in previous research. Ionic liquid enhances the tensile strength significantly without decreasing the ionic conductivities⁴².

3.8 Thermogravimetry analysis

The thermal stability of the separator plays a vital role in the safety of LIB because it could prevent short-circuiting contact between anode and cathode. The polymer electrolyte membrane of PEO doped with [EMIm]BF₄/Li⁺ ionic liquids are thermally stable up to more than pure PEO. Table 5 shows the decomposition temperature of polymer electrolyte membranes. In Table 5, we can depict both T_{onset} and T_{offset} .

Table 5 — Decomposition temperature of Polymer electrolyte membranes

Material	T_{onset} (°C)	T_{offset} (°C)
Pure PEO	180	245
PEO + 9% [EMIm]BF ₄ /Li ⁺	210	310
PEO + 12% [EMIm]BF ₄ /Li ⁺	225	335
PEO + 16% [EMIm]BF ₄ /Li ⁺	225	340
PEO + 23% [EMIm]BF ₄ /Li ⁺	230	348

The polymer electrolyte membranes' decomposition temperature increased as long as [EMIm]BF₄/Li⁺ ionic liquid incorporation increased. This result shows that PEO doped with [EMIm]BF₄/Li⁺ ionic liquid can withstand much higher temperature and enough for use in LIB. The highest decomposition temperature is at 230-348 °C in 23 w/w% [EMIm]BF₄/Li⁺ ionic liquid incorporation.

From the data, it can be concluded that the [EMIm]BF₄/Li⁺ ionic liquid-doped PEO matrix has better thermal properties than pure PEO even at high [EMIm]BF₄/Li⁺ ionic liquid incorporation²⁷. The effect of ionic liquid on increasing thermal stability was also proved with the previous result, where [EMIm]Ac ionic liquid can increase the maximum degradation of LiClO₄-complexed MC³¹. Many results also stated that ionic liquid incorporation improves thermal and mechanical properties to flexible properties²⁴. Based on the result of thermal decomposition onset, (PEO + [EMIm]BF₄/Li⁺) membranes fulfill the standard requirement as Li-ion batteries separator.

4 Conclusion

Polymer electrolyte membranes of PEO doped with various weight percentages (0%, 9%, 12%, 16%, and 23% w/w) of [EMIm]BF₄/Li⁺ were successfully prepared by solution casting technique. [EMIm]Br

ionic liquid has been successfully synthesized using the MAOS method with relatively good yield. The new [EMIm]BF₄/Li⁺ ionic liquid, Li⁺ ion-attached ionic liquid formulation, was synthesized by a simple metathesis reaction between [EMIm]Br ionic liquid and LiBF₄ salt. Incorporating [EMIm]BF₄/Li⁺ ionic liquid into the PEO matrix enhances ionic conductivity, decreases crystallinity, and increases flexibility and stability up to high temperatures. The highest ionic conductivity was 1.83 x 10⁻³ S.cm⁻¹ at room temperature for polymer electrolyte membrane with 16% (w/w) of [EMIm]BF₄/Li⁺ ionic liquid. Polymer electrolyte membrane with 16% weight of [EMIm]BF₄/Li⁺ ionic liquid was an excellent condition for LIBs application which offers the highest conductivity, highest flexibility, and good thermal stability (with decomposition temperature at 225-340 °C).

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