A novel approach on ionic liquid-based poly(vinyl alcohol) proton conductive polymer electrolytes for fuel cell applications

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Abstract

The preparation of proton conducting-polymer electrolytes based on poly(vinyl alcohol) (PVA)/ammonium acetate (CH₃COONH₄)/1-butyl-3-methylimidazolium chloride (BmImCl) was done by solution casting technique. The ionic conductivity increased with ionic liquid mass loadings. The highest ionic conductivity of \((5.74 \pm 0.01) \text{ mS cm}^{-1}\) was achieved upon addition of 50 wt% of BmImCl. The thermal characteristic of proton conducting-polymer electrolytes is enhanced with doping of ionic liquid by showing higher initial decomposition temperature. The most conducting polymer electrolyte is stable up to 250 °C. Attenuated total reflectance-Fourier Transform Infrared (ATR-FTIR) confirmed the complexation between PVA, CH₃COONH₄ and BmImCl. Polymer electrolyte membrane fuel cell (PEMFC) was fabricated. This electrochemical cell achieved the maximum power density of 18 mW cm\(^{-2}\) at room temperature.

1. Introduction

Depletion of non-renewable fossil fuel catalyzes the development of environmentally friendly alternative energy sources. Fuel cells are promising candidates as power sources for a wide range of applications, ranging from portable devices to electric vehicles [1,2]. Fuel cells are of great interest in the recent research due to their attractive properties. They offer many advantages, such as environmentally benign, high energy efficiency and lower emission of pollutants [3,4]. Fuel cells also do not require the need for rapid recharging process in the presence of electricity compared to the lithium rechargeable batteries [5]. Apart from that, fuel cells exhibit higher energy density than the batteries [6]. The main component in PEMFCs is the proton exchange membrane (PEM) which is used as proton (or charge carriers) provider from anode to cathode. The basic requirement of PEM is the membrane must be proton conductive with some satisfactory properties like excellent mechanical strength and chemically stable. Perfluorosulfonated membrane, Nafion produced by DuPont has widely been used as host polymer in PEMFCs. However, high methanol transfer is the main shortcoming of using Nafion as primary polymer membrane in fuel cells [6,7]. High methanol crossover may cause the loss of fuel, slow methanol oxidation kinetics and formation of carbon monoxide (CO) intermediate on the platinum catalyst layer at the cathode as well as cell polarization. As a consequence, the performance of this electrochemical cell could be decreased...
It also possesses some drawbacks such as expensive, high water swelling characteristic which reduces the lifespan of the membrane and decrease in conductivity at elevated temperature [9]. So, the utilization of Nafion membrane in fuel cell is limited. Therefore, many attempts have been done to overcome the weakness of Nafion.

Non-perfluorosulfonated polymer membrane was employed to replace Nafion in DMFC. Poly(vinyl alcohol) (PVA) is a potential material because of its cheaper price [2]. PVA is a biodegradable semi-crystalline synthetic polymer bearing with hydroxyl functional group [7,10,11]. Superior chemical stability, non-toxic, high hydrophilicity, ease of preparation and biocompatibility are advantages of PVA [10–13]. Furthermore, PVA exhibits excellent thermal and chemical stabilities and high abrasion resistance as well as high flexibility [13,14]. PVA also possesses high dielectric permittivity and excellent capacity for charge storage which is an important feature for a supercapacitor, as reported by Hirankumar et al. [15]. In order to prepare proton-conducting polymer electrolytes, ammonium salt must be embedded to provide the charge carriers as it is well-known as proton donor. Ammonium acetate (CH$_3$COONH$_4$) was chosen in this project due to its plasticizing effect. However, the ionic conductivity is relatively low. Therefore, much effort has been devoted to enhance the ionic conductivity, for instance polymer blending, addition of plasticizer, incorporation of filler, mixed salt system and doping of ionic liquid. Among all these approaches, impregnation of ionic liquid can be considered as the most feasible method because it is well known as environmentally friendly compound. Ionic liquid brings multiple advantages such as wider electrochemical stability, relatively high conductivity, negligible vapor pressure, high resistance to chemical substances and excellent thermo-stability, as reported in our previous works [16–18].

Several PVA-based fuel cells had been fabricated and analyzed by researchers. Higa and his co-workers fabricated a direct methanol fuel cell (DMFC) with a polymer electrolyte membrane where PVA is cross-linked 2 mol% of 2-methyl-1-propanesulfonic acid (AMPS). The maximum power density of 2.4 mW cm$^{-2}$ was delivered by this DMFC [7]. In addition, PVA-based nanocomposite polymer electrolytes were frequently used as separator in direct methanol alkaline fuel cell (DM AFC) and studied by Yang CC research group. The maximum power density of 15.3 mW cm$^{-2}$ was achieved using PVA/potassium hydroxide (KOH) with doping of 20% of fumed silica [6]. However, lower maximum power density of 7.54 mW cm$^{-2}$ was obtained in PVA/titania (TiO$_2$)-based DMFC [4]. Sekhon et al. synthesized polymer electrolyte containing poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-co-HFP), triflic acid (HCF$_3$SO$_3$) and 2,3-dimethyl-1-octylimidazolium triflate (DM0ImTf) for a PEMFC. Power density of 2.4 mW cm$^{-2}$ was obtained in PVA/titania (TiO$_2$)-based DMFC [7].

The current project is to explore the effect of ionic liquid onto the electrochemical properties of polymer electrolytes and fuel cells.

2. Experimental

2.1. Materials

Proton conducting polymer electrolytes comprising of PVA, CH$_3$COONH$_4$ and BmImCl were prepared in this present work. PVA (Sigma-Aldrich, USA, 99% hydrolyzed with molecular weight of 130000 g mol$^{-1}$), CH$_3$COONH$_4$ (Sigma, Japan) and BmImCl (Acros organic, USA) were used as polymer, salt and ionic liquid, respectively. All the materials were used as received.

2.2. Preparation of ionic liquid based-poly(vinyl alcohol) proton conducting polymer electrolytes

Ionic liquid based-poly(vinyl alcohol) proton conducting polymer electrolytes were prepared by solution casting technique. PVA was initially dissolved in distilled water. Appropriate amount of CH$_3$COONH$_4$ was subsequently mixed in PVA solution. The weight ratio of PVA:CH$_3$COONH$_4$ was kept at 70:30. Different mass fraction of BmImCl was thus embedded into the PVA-CH$_3$COONH$_4$ mixture to prepare ionic liquid-based proton conducting polymer electrolyte. CL 2, CL 5 and CL 6 were the designations of polymer electrolytes with respect to addition of 20 wt%, 50 wt% and 60 wt% of BmImCl, whereas CL 0 was for the polymer electrolyte without incorporation of BmImCl. The resulting solution was stirred thoroughly and heated at 70 °C for few hours until a homogenous colorless solution is obtained. The solution was eventually casted on glass Petri dish and dried in an oven at 60 °C to obtain a free-standing proton conducting polymer electrolyte film.

2.3. Characterization of ionic liquid based-PVA proton conducting polymer electrolytes

2.3.1. Ambient temperature-ionic conductivity studies

Freshly prepared samples were subjected to ac-impedance spectroscopy for ionic conductivity determination. The thickness of the film was measured by digital micrometer screw gauge. The ionic conductivity of the polymer electrolyte was measured by HIOKI 3532-50 LCR HiTESTER impedance analyzer over a frequency regime between 50 Hz and 5 MHz at ambient temperature. The data acquisition was recorded at a signal level of 10 mV. Proton conducting polymer electrolytes were sandwiched on the sample holder under spring pressure in the configuration of stainless steel (SS) blocking electrode/polymer electrolyte/SS electrode.

2.3.2. Thermogravimetric analysis (TGA)

TGA was accomplished by thermogravimetric analyzer, TA Instrument Universal Analyzer 2000 with Universal V4.7A software. Sample weighing 2–3 mg placed into 150 μl of silica crucible. The samples were then heated from 25 °C to 600 °C at a heating rate of 50 °C min$^{-1}$ in a nitrogen atmosphere with a flow rate of 60 ml min$^{-1}$.
2.3.3. Attenuated total reflectance-Fourier Transform Infrared (ATR-FTIR)

Themoscientific Nicolet iS10 FTIR Spectrometer (from USA) was employed to perform ATR-FTIR study. This spectrometer is equipped with an ATR internal reflection system. The FTIR spectra were recorded with a resolution of 4 cm\(^{-1}\) in transmittance mode over the wavenumber range from 4000 to 650 cm\(^{-1}\). The FTIR spectra and peak deconvolution were scrutinized by OMNIC 8 software which is provided by Thermo Fischer Scientific Inc. The transmittance mode of FTIR spectra was initially converted into absorbance mode for peak deconvolution process. In order to deconvolute the FTIR was initially converted into absorbance mode for peak deconvolution process. In order to deconvolute the FTIR spectra, baseline correction and curve fitting must be implemented. The FTIR curve was fitted with gaussian-lorentzian mixed mode.

2.4. Fuel cell fabrication

The most conducting polymer electrolyte was used for PEMFC fabrication. The polymer membrane was soaked in distilled water for 5 min prior the fabrication. The surface area of electrodes is 16 cm\(^2\). The polymer electrolyte was then placed in the PEMFC kit which is purchased from H-tec, Germany. The assembled kit was eventually subjected to the Electrolyzer 10 (from H-tec, Germany) for electrochemical analysis with hydrogen flow rate of 10 cm\(^3\) min\(^{-1}\) and oxygen flow rate of 5 cm\(^3\) min\(^{-1}\).

2.4.1. Cell performances

The performance of PEMFC was done by fuel cell measurement setup which is comprised of Programmable DC power supply (Model no: 3644A, Array Electronics Co. Ltd. from Taiwan), rheostat (Model no: ZX97E, Tinsley from United Kingdom) and Digital Bench Type True RMS multimeter (UT803, Uni-Trend from Guangdong, Zhina). DC power supply is employed to provide the current flow through the cell, whereas the rheostat is used to adjust the current flow. The measurements of voltage and current flow were probed using multimeter. The cell potential in every 10 mA of current was noted down, starting from 10 mA. The current density was determined by dividing the operational current into surface area of electrodes (16 cm\(^2\)). On the other hand, the power density was calculated using the fundamental equation below:

\[
P = IV
\]

where \(P\) is power (W), \(I\) is operational current (A) and \(V\) is cell potential (V). Again, the power density was eventually computed by dividing the power into surface area of electrodes.

3. Results and discussion

3.1. Ambient temperature-ionic conductivity studies

The ionic conductivity of polymer electrolytes is determined using the following equation:

\[
\sigma = \frac{1}{R_b A}
\]

where \(I\) is the thickness of polymer electrolytes (cm); \(R_b\) is bulk resistance (\(\Omega\)) of polymer electrolytes and \(A\) is the known surface area (\(\text{cm}^2\)) of blocking electrodes. Fig. 1 shows a typical impedance plot of CL 0 at ambient temperature. The \(R_b\) is determined as shown in Fig. 1. Since the impedance plot is not starting from origin, so the series resistance \(R_s\) is appeared in the figure. The total resistance (combination of \(R_b\) and \(R_s\)) is calculated from the intercept of the spike with the extrapolation of the semicircular region on Z real axis. The \(R_s\) is computed from the deduction of the total resistance with the initial \(R_b\). On the other hand, the spike of the plot indicates the charge accumulation at the electrolyte–electrode interface. Fig. 2 depicts the ionic conductivity of proton-conducting polymer electrolytes at different mass fraction of BmImCl. Upon inclusion of ionic liquid, the ionic conductivity is increased. As expected, the ionic conductivity increases with mass loadings of ionic liquid, up to an optimum level. The ionic conductivity increases gradually when 10 wt% of BmImCl is added into the polymer electrolyte. However, the ionic conductivity is found to be increased rapidly with doping of 20 wt% of BmImCl. The highest ionic conductivity of \((5.74 \pm 0.01)\) mS cm\(^{-1}\) corresponding to addition of 50 wt% of BmImCl is observed. This conductivity has been increased by two orders of magnitude in comparison to the polymer electrolyte without impregnation of ionic liquid. The abrupt increase in ionic conductivity is due to strong plasticizing effect of ionic liquid [16,18]. Strong plasticizing effect of ionic liquid aids to soften the polymer backbone and hence increases the flexibility of polymer chain. The proton can be transported easily within the polymer matrix with highly flexible polymer...
chains. Besides, higher flexibility of polymer chains improves the mobility of polymer segments and assists the ionic transportation within polymer complexes. Consequently, the ionic conductivity is higher compared to the polymer electrolyte without doping of ionic liquid. Moreover, ionic liquid increases the amorphousness of the polymer matrix. Ionic liquid could weaken the transient coordinative bonds among the molecules in the crystalline region and thus turn the polymer chains into flexible characteristic leading to higher amorphous degree of polymer complexes. Ionic liquid also promotes the ionic conduction process by providing more conducting sites. This can be done by interacting BmIm\(^+\) with hydrogen of the side chain in the polymer backbone. This interaction not only provides more conducting sites, but it also provides more mobile proton upon the deprotonation.

In order to understand the principle in the proton-conducting polymer electrolytes, the proton hopping mechanism must be well studied. We propose a mechanism pertaining to transport of conducting ions for proton-conducting polymer electrolytes illustrated as follows. The ionic liquid: imidazolium cation (BmIm\(^+\)) and chloride (Cl\(^-\)) can be easily detached from the transient partial bonding due to the bulky size of the cation. Thus, the hydrogen at C2-position of the mobile BmIm\(^+\) is initially de-protonated to form a stabilized carbene [21,22].

This carbene could then interact with the hydrogen in hydroxyl group of PVA and result carbocation in the imidazolium ring.

This interaction leads to the partial hydrogen bonding between oxygen and hydrogen. In addition, the de-protonated hydrogen in this step can help in accelerating the proton conduction as it is in mobile state. When the hydrogen bonding is partially bonded, the dissociated chloride and acetate anions from ionic liquid and salt will prefer to interact with the carbocation and thus break the hydrogen bond between the imidazolium cations and side chain of PVA. After the disintegration of hydrogen bonding, the oxygen atom in the hydroxyl group of PVA turns into negatively charged or forms anions. Therefore, these electron deficient oxygen anions would accept the electron from proton from the loosely bounded ammonium cations or from imidazolium cations. Two possible side products could be formed in this segment, viz. 3-butyl-2-chloro-1-methyl-4,5-dihydro-1H-imidazole and 3-butyl-1-methyl-4,5-dihydro-1H-imidazole-2-carboxylic acid methyl ester, as shown in the mechanism below.
Beyond this step, there are two possibilities of proton conduction process. The proton transportation can be generated from the hydrogen in ammonium cations or the hydrogen in BmIm cations. The dissociated proton from loosely bounded ammonium cations of doping salt would then interact with this negatively charged oxygen and result in the formation of hydroxyl group through hydrogen bonding. This partial hydrogen bonding would result in the CONH coordination bond. On the other hand, the detached chloride or acetate anions will abstract an electron from hydrogen. This hydrogen will thus leave the hydroxyl group and hence turn into anions. The adjacent hydrogen could interact with this oxygen and hence generate the proton transportation from site to another adjacent site.

Apart from that, we suggest that proton conduction can also take place at the BmIm cations. For this proton transport, BmIm cations could interact with the oxygen in PVA and form N–O bond temporarily. Similarly, the detached chloride or/and acetate anions will abstract an electron from hydrogen of another branched site and produce oxygen which is appeared as anions. As next step, the electron from the hydrogen from C2-position in BmIm cations could be donated to this electron-deficient oxygen. In order to form a stable compound, the N–O bond must be broken down. Hence, this bond detachment could lead to the formation of carbene, which is an important chemical compound in weakening the transient coordination bond within the macromolecules. Eventually, the proton conduction mechanism is repeated again with the formation of carbene. These two possible mechanisms will cause continuous ionic hopping mechanism in the polymer matrix.

Beyond adulteration of 50 wt% of BmImCl, the ionic conductivity is found to be lower in value. This is ascribed to the agglomeration of ions. Excessive ions in the polymer electrolyte could form ion pairs and ion aggregates. These ion pairs and ion aggregates might block the conducting pathway and hinder the proton from transportation, leading to lower ionic conductivity. The amount of proton for conduction is also decreased in the presence of ion pairs and ion aggregates. At high concentration of ionic liquid, NH4C to 235/C14 is due to the dehydration of water or moisture as polymer is a hydroscopic compound [23]. The insignificant weight loss in this stage is also due to the elimination of impurities in the polymer electrolytes. Small weight losses of 5%, 5% and 6% are observed for pure PVA, CL 0 and CL 6, respectively in this region. However, higher mass losses of 9% have been observed for CL 2 and CL 5. Beyond this stage, the weight of all the samples remains the same until 200 °C. Upon the dehydration, ammonium acetate could be decomposed easily into acetamide, CH3C(O)NH2.

On the contrary, two PVA polymer chains might be cross-linked as a result of water removal. This elimination could lead to the formation of ether cross-linkages [11]. Above 200 °C, an abrupt decrease in weight is observed for all the samples. Among all the samples, pristine PVA portrays the highest mass loss from 210 °C to 235 °C in this segment. Elimination of side chain in polymer backbone of PVA is the main contributor to this thermal degradation for pure PVA [14]. Apart from formation of ether cross-linkages, the polymer

### Thermogravimetric analysis (TGA)

Fig. 3 portrays thermogravimetric analysis for pure PVA, CL 0 and ionic liquid-based polymer electrolytes. Pure PVA shows three major weight losses, as described in Yang et al. [14]. However, four thermal degradation steps are observed for salt and/or ionic liquid-doped polymer electrolytes. The initial thermal degradation in the region of 25 °C–125 °C is due to the dehydration of water or moisture as polymer is a hydroscopic compound [23]. The insignificant weight loss in this stage is also due to the elimination of impurities in the polymer electrolytes. Small weight losses of 5%, 5% and 6% are observed for pure PVA, CL 0 and CL 6, respectively in this region. However, higher mass losses of 9% have been observed for CL 2 and CL 5. Beyond this stage, the weight of all the samples remains the same until 200 °C. Upon the dehydration, ammonium acetate could be decomposed easily into acetamide, CH3C(O)NH2.

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backbone of PVA could start a rapid chain stripping on the polymer backbone upon heating and hence turn into conjugated double bonds, giving rise to formation of polyene, as illustrated as below [11]:

Upon addition of salt and ionic liquid, the mass loss in this stage is significantly decreased. Besides, the starting decomposition temperature in this stage is improved. These observations deduct the contribution from the complexation between salt and/or ionic liquid and PVA. This is because higher energy would be required to break the transient coordination bond in the complexation process. Weight losses of 32%, 43%, 33% and 44% corresponding to the temperature range of 240 °C–245 °C, 245 °C–285 °C, 250 °C–305 °C, 235 °C–245 °C are attained for CL 0, CL 2, CL 5 and CL 6, respectively. The contributor of this thermal decomposition stage is suggestive of the degradation of acetamide where its decomposition temperature is around 222 °C. The chain stripping mechanism is less favorable in CL 0 when the salt is complexed with PVA. In contrast, the carbene produced from ionic liquid interacts with the hydrogen from hydroxyl group in PVA and forms the coordination bond. Therefore, the chain stripping process might also be absent in the polymer between salt and/or ionic liquid and PVA. This is because higher energy would be required to break the transient coordination bond in the complexation process. Weight losses of 32%, 43%, 33% and 44% corresponding to the temperature range of 240 °C–245 °C, 245 °C–285 °C, 250 °C–305 °C, 235 °C–245 °C are attained for CL 0, CL 2, CL 5 and CL 6, respectively. The contributor of this thermal decomposition stage is suggestive of the degradation of acetamide where its decomposition temperature is around 222 °C. The chain stripping mechanism is less favorable in CL 0 when the salt is complexed with PVA. In contrast, the carbene produced from ionic liquid interacts with the hydrogen from hydroxyl group in PVA and forms the coordination bond. Therefore, the chain stripping process might also be absent in the polymer backbone of PVA could start a rapid chain stripping on the polymer backbone upon heating and hence turn into conjugated double bonds, giving rise to formation of polyene, as illustrated as below [11]:

Final weight loss is attained at elevated temperature. Pure PVA and CL 0 show 20% and 26.8% of weight losses, along with 12% and 11% of mass residues at 575 °C, respectively. Ionic liquid-based polymer electrolytes display lower mass loss in comparison to CL 0. CL 2 exhibits 21% of weight loss from 365 °C to 570 °C with residual mass of 3%, whereas CL 5 reveals higher mass loss, which is around 25% with 6% of residue in the temperature range of 355 °C-565 °C. CL 6 starts to loss its weight around 22% with 9% of residue from 350 °C to 575 °C. This final weight loss is connected to the breakdown of the polymer backbone as reported in Yang et al. [14]. Upon further heating, the double bond of polyene would be broken down into single bond and eventually converted into aliphatic polymer chains at this stage [24]. Beyond this stage, the weight loss is limited to the breakdown of etheric cross-linkages and random chain scissoring between carbon–carbon bonds [11]. Random bond scission yields two intermediate products and thus forms methyl-terminated allylic polyene in cis and trans isomerisms via elimination process, as demonstrated as below [24].

Please cite this article in press as: Liew C-W, et al., A novel approach on ionic liquid-based poly(vinyl alcohol) proton conductive polymer electrolytes for fuel cell applications, International Journal of Hydrogen Energy (2013), http://dx.doi.org/10.1016/j.ijhydene.2013.07.092
of samples remains unchanged. This observation infers the fully decomposition of the polymer matrix. Although the residual mass of ionic liquid-based polymer electrolytes is lesser, however, CL 5 is still a promising candidate as polymer electrolyte due to its higher first decomposition temperature.

### 3.3. Attenuated total reflectance-Fourier Transform Infrared (ATR-FTIR)

The PVA–CH₂COONH₄ polymer electrolyte systems have been prepared and investigated. The FTIR results and the complexation between PVA and CH₂COONH₄ have been elucidated in the literature [15,20,26–32]. Therefore, the interaction between PVA and CH₂COONH₄ is not discussed in this present work. The interactions between ionic liquid and ammonium acetate-doped polymer electrolyte are also analyzed and discussed in details. Fig. 4 depicts the ATR-FTIR spectra of CL 0, BmImCl, CL 2, CL 5 and CL 6. On the other hand, the band assignment of the spectra is summarized in Table 1. The ATR-FTIR spectrum of CL 5 is investigated as it achieves the maximum ionic conducting as aforementioned in section 3.1. Upon adulteration of BmImCl, sixteen new peaks have been formed by comparing Fig. 4(a) with Fig. 3(d). These peaks are C–H vibrational mode for cyclic BmIm⁺ at 655 cm⁻¹, 693 cm⁻¹, 3109 cm⁻¹ and 3159 cm⁻¹ [33], C–H bending mode for cyclic BmIm⁺ at 752 cm⁻¹ [33], in-plane C–H bending mode of imidazolium ring at 890 cm⁻¹ [34], in-plane C–N–C bending mode at 951 cm⁻¹ [35], out-of-plane C–H wagging mode in alkyl chain at 1019 cm⁻¹ [34], CH₃–N stretching mode at 1168 cm⁻¹ [36], CH₃ asymmetrical stretching mode at 1335 cm⁻¹ [33], CH₃ asymmetrical stretching mode at 1378 cm⁻¹ [33], CH₃ symmetrical bending mode at 1428 cm⁻¹ and 1456 cm⁻¹ [36], C–N stretching mode at 1540 cm⁻¹ [37] and C–C and C–N bending modes of imidazolium ring at 1696 cm⁻¹ [33]. Some characteristic peaks of CL 0 are disappeared with doping of BmImCl. Examples of these characteristic peaks are the combinations of CHOH bending mode, CH₃ in-plane deformation and C–H wagging mode at 329 cm⁻¹, C–H deformation mode at 1414 cm⁻¹ and C=O stretching mode at 1701 cm⁻¹.

Apart from that, the C–Cl stretching mode of BmImCl at 791 cm⁻¹ is disappeared. This entails the chloride dissociation from BmIm cations. Therefore, the dissociated BmIm cations could form the carbene compound after the deprotonation process, as suggested in section 3.1. This idea is supported by the absences of out-of-plane C–H bending mode of imidazolium ring at 730 cm⁻¹ [35], C–H bending mode in methyl group at 1132 cm⁻¹ [38], C–N stretching mode of imidazolium ring at 1289 cm⁻¹ [35] and C–H stretching mode at 3091 cm⁻¹ [35]. The proton conduction in ammonium salt-doped polymer electrolyte is based on the formation of CONH bond, as explained in section 3.1. However, the proton is migrated in a different way for polymer electrolytes containing BmImCl, as suggested in section 3.1. The CONH bonding mode of CL 0 is absent in all the ionic liquid-based polymer electrolytes and further verifies the proposed mechanism.

The C–H bending mode of CL 0 is shifted to lower wavenumber from 662 cm⁻¹ to 655 cm⁻¹ due to the overlapping of C–H vibration mode for cyclic BmIm⁺. The C–H vibration mode for cyclic BmIm⁺ at 698 cm⁻¹ also exhibit downward shift to 693 cm⁻¹ by comparing Fig. 4(a) with Fig. 3(d). The sharp peak at 844 cm⁻¹ in Fig. 4(a) is designated as skeletal C–H rocking mode of PVA and shifted to 846 cm⁻¹ with doping of ionic liquid. This peak not only exhibits the change in shift, but it also undergoes the change in peak intensity. The intensity of peak is gradually reduced from 11.28% to 8.66%, in transmittance mode. A sharp peak at 844 cm⁻¹ is also collided with other peaks and further reduces the intensity of the peak. This phenomenon indicates the interaction between ionic liquid and polymer matrix. Another apparent proof to show the interaction mode of C–H and polymer matrix is the C–H wagging mode at 900 cm⁻¹ with a shoulder peak at 940 cm⁻¹. A sharp peak with its intensity of 19.12% is observed in ionic liquid spectra; however, it has been turned into a weak peak with its intensity of 0.14% in transmittance mode. Fig. 4(b) depicts a sharp peak at 900 cm⁻¹ with a shoulder peak at 940 cm⁻¹. Upon addition of the C–H wagging mode in alkyl chain with polymer matrix and further deduces the interaction between C–O bond from polymer matrix and C–H functional group from ionic liquid. This result agrees well with our proposed mechanism in section 3.1 where the hydrogen from ionic liquid will be abstracted to the adjacent electron-deficient oxygen for the proton hopping mechanism. Even though the C–O stretching mode still remains unchanged at 1236 cm⁻¹, however, the intensity of the peak is relatively reduced upon impregnation of ionic liquid. The peak reduction entails that the proton conduction could be taken place at

![Fig. 4 – ATR–FTIR spectra of (a) CL 0, (b) BmImCl, (c) CL 2, (d) CL 5 and (e) CL 6.](image)
the C–O coordination bond when the ionic liquid is complexed with polymer backbone.

The sharp peak at 1163 cm$^{-1}$ is designated as CH$_3$–N stretching mode, whereas the weak peak at 1388 cm$^{-1}$ is associated with CH$_3$ asymmetric stretching mode. The first peak exhibits upward shift to 1168 cm$^{-1}$ with reduced peak intensity of 31.11%, from 44.11% to 13% in transmittance mode. On the contrary, the latter peak shifts to lower wavenumber to 1378 where its intensity is gradually reduced from 31.11% to 0.73% in transmittance mode. The peak at 1414 cm$^{-1}$ and C–H wagging mode at 1453 cm$^{-1}$ is changed to a medium sharp peak at 1456 cm$^{-1}$ as shown in Fig. 6.

Table 1 – The assignments of the vibration modes of BmImCl, CL 0, CL 2, CL 5 and CL 6.

<table>
<thead>
<tr>
<th>Descriptions of vibration modes</th>
<th>Wavenumber (cm$^{-1}$)</th>
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<tr>
<td>C–H bending mode</td>
<td>BmImCl</td>
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<tr>
<td>C–H vibration mode for cyclic BmIm$^+$</td>
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<td>H–O stretching mode of OH group</td>
<td>3259</td>
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<tr>
<td>=C–H stretching mode</td>
<td>3091</td>
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The change in shape is suggestive of the overlap of C–H deformation mode at 1413 cm$^{-1}$, CH$_2$ asymmetric bending mode at 1434 cm$^{-1}$ and CH$_3$ symmetric bending mode at 1465 cm$^{-1}$. This can be proven using the deconvolution method. The peaks are fitted and deconvoluted as illustrated in Fig. 7. Three deconvoluted peaks are obtained in this wavenumber range. This result is in good agreement with our suggestion. Again, this signifies the interaction of hydrogen from C–H bond with polymer membrane where the proton conduction can take place at. A medium sharp peak at 1561 cm$^{-1}$ corresponding to N–H bending mode is attained in CL 0 spectra. Nevertheless, the peak has been developed into a sharp peak at 1571 with a shoulder peak at 1540 cm$^{-1}$. The intensity of the sharp peak is increased from 6.56% to 10.01% in transmittance mode. The overlapping of C=N stretching mode at 1560 cm$^{-1}$ and C=C stretching mode from ionic liquid at 1517 cm$^{-1}$ contributes to this changes of peak intensity, peak location and shape. This can be a sign of interaction between ionic liquid and CL 0. The weak peak analogous to C–H stretching mode at 1648 cm$^{-1}$ has been developed into a medium sharp peak at 1647 cm$^{-1}$. The intensity of this peak is increased from 0.43% to 5.63% in transmittance mode as observed in Fig. 4(a and d). This finding reveals the
complexation between ionic liquid and macromolecules and verifies the proton conduction. Another proof to show the proton conduction is also detected in the range of 3000 cm$^{-1}$-2800 cm$^{-1}$. Double peaks with a shoulder peak are appeared as a broad band within this region. This band is designated as C–H symmetric stretching mode in methyl group of alkyl chain. However, only a peak with a shoulder peak is observed at their respective wave-number of 2939 cm$^{-1}$ and 2870 cm$^{-1}$ upon inclusion of BmImCl. Similar phenomenon is attained for the band within the range of 3400 cm$^{-1}$-3000 cm$^{-1}$. CL 0 illustrates a broad peak at 3259 which is related to O–H stretching vibration mode of OH group in PVA. Two additional shoulder peaks are scrutinized at 3109 cm$^{-1}$ and 3159 cm$^{-1}$ in which the O–H stretching mode is shifted to 3347 cm$^{-1}$ with doping of BmImCl. These newly formed shoulder peaks are known as C–H vibration mode for cyclic BmIm$^+$ of ionic liquid. Therefore, these changes in shift and peak position can be indicative of interaction between C–H vibration mode of ionic liquid and O–H stretching mode of PVA which aids in the proton conduction.

Among all the samples, we found out that the highest ionic conductivity is achieved by adding 50 wt% of BmImCl as shown in Fig. 2. One of the attributors in enhancing the ionic conductivity is correlated to lower crystalline region (or higher amorphous degree) in the polymer electrolytes. The vital feature can be proven in the ATR-FTIR spectra. C–C and C–O stretching modes of doubly H-bonded OH in crystalline region is located at 1140 cm$^{-1}$ with its intensity of 5.57% in Fig. 4(a). The intensity of this peak is gradually reduced to 3.97% corresponding to CL 2 at 1143 cm$^{-1}$ and 1.61% at 1140 cm$^{-1}$ for CL 5. Therefore, it can be concluded that CL 5 has the lowest crystalline region compared to CL 0 and CL 2. It is in good agreement with the suggestion that we proposed in section 3.1. The intensity of this characteristic peak of CL 6 is increased to 6.42% in comparison to CL 0, CL 2 and CL 5, as shown in Fig. 4(e). When the ionic liquid is added further, the crystalline phase of CL 6 becomes higher due to the ion pairing and ion aggregation as a result of excessive ion. The formation of ion pairs and ion aggregates can be further proven by the disappearance of some characteristic peaks in Fig. 4(e). These peaks are: in-plane C–H bending mode of imidazolium ring at 900 cm$^{-1}$, in-plane C–N–C bending mode at 940 cm$^{-1}$, CH$_3$–N stretching mode at 1163 cm$^{-1}$, CH$_2$ asymmetric bending mode at 1434 cm$^{-1}$, CH$_3$ symmetric bending mode at 1465 cm$^{-1}$, C=C–N stretching mode 1560 cm$^{-1}$, and C–H vibration modes for cyclic BmIm$^-$ at 3113 cm$^{-1}$ and 3152 cm$^{-1}$. The changes in peak intensity, peak position and shape establish the complexation between ionic liquid and polymer matrix.
3.4. Cell performances

In order to study the effect of ionic liquid onto the electrochemical performances of fuel cell, four fuel cells are assembled by sandwiching CL0, CL 2, CL 5 or CL 6 between anode and cathode and further analyzed. Electrolyzer is used to generate hydrogen and oxygen gases. The hydrogen gas is connected to anode, whereas the oxygen is channeled to cathode. Below are the general reactions in both electrodes.

Anode: \(2H_2 \rightarrow 4H^+ + 4e^-\)

Cathode: \(4H^+ + O_2 \rightarrow 2H_2O\)

Complete reaction: \(2H_2 + O_2 \rightarrow 2H_2O\)

Hydrogen gas which acts as fuel will be split into positively charged hydrogen (or known as proton) and negatively charged electrons in the presence of catalyst layer at anode. For next step, the polymer electrolyte membrane allows the protons to travel from anode to cathode. In contrast, the electrons are transported along the external circuit to cathode and hence create electrical current. Eventually, the combinations between proton and oxygen with the help of electrons will form water as by-product at cathode side. This by-product will be flowed out from the system.

The open-circuit voltage \((V_{oc})\) is determined when no current flows into the fuel cell. This is known as the initial voltage prior to the cell voltage measurement. Figs. 8 and 9 depict the cell potential and power density of the electrochemical cells with different current density at room temperature, respectively. The \(V_{oc}\) of CL 0, CL 2, CL 5 and CL 6 are 0.27 V, 0.37 V, 0.66 V and 0.56 V, respectively as illustrated in Fig. 8. As can be seen in current density-potential curves, the cell potential of ionic liquid-based polymer electrolytes are higher than that of polymer electrolytes without inclusion of ionic liquid. This is mainly attributed to the strong plasticizing effect of ionic liquid. The plasticizing effect of ionic liquid not only helps in promoting the proton conduction by weakening the transient bonds, but it also produces sticky samples. The sticky feature of the sample can improve the contact between the cathode and anode. Therefore, the proton can be traveled easily. All the curves manifest the same pattern with respect to current density. The cell potential of fuel cell decreases with increasing the current density. The result is same as the findings that other researchers have reported previously [3–6]. Ionic liquid-based polymer electrolytes possess better electrochemical performance than CL 0 by showing higher current density at the end of the curve. This occurrence indicates that fuel cell comprising of ionic liquid-based polymer electrolytes can withstand higher current before the complete degradation process. CL 0 has been fully decomposed when 620 mA of current (or equivalent with current density of 38.75 mA cm\(^{-2}\)) is applied into the cell. Upon inclusion of 20 wt % of ionic liquid into the polymer electrolyte, the membrane is degraded at the current of 660 mA (or corresponding to 41.25 mA cm\(^{-2}\)). On the other hand, the fuel cell consisting CL 5 stops the function at the current 950 mA or current density of 59.34 mA cm\(^{-2}\). However, the electrochemical properties of fuel cell are decreased when BmImCl is further added into the polymer matrix. Comparing CL 5 and CL 6, CL 6 is decomposed at lower current that is 700 mA with current density of 43.75 mA cm\(^{-2}\).

Power density of fuel cell is also determined. The power density of fuel cell increases with current density, up to a maximum level, as depicted in Fig. 9. The inset of figure portrays the peak obtained for fuel cell based on CL 0, CL 2 and CL 5 in a smaller scale. Beyond the highest value, the power density of fuel cell is found to be decreased gradually. This decrement of power density is correlated to the degradation of polymer electrolytes at higher current supply. The doping of ionic liquid can enhance the electrochemical properties of fuel cell as explained above. The same conclusion can also be drawn using the power density result. Fuel cell based on CL 2
polymer membrane exemplifies higher power density than CL 0. The maximum power density of 0.73 mW cm$^{-2}$ is observed at 0.05 V with a peak current density of 15.63 mA cm$^{-2}$. This peak is shifted to higher current with a higher power density with addition of 20 wt% of BmImCl. Fuel cell comprising of CL 2 displays a maximum power density of 1.13 mW cm$^{-2}$ at a maximum potential of 0.06 V with a peak current density of 18.13 mA cm$^{-2}$. Among all the ionic liquid-based polymer electrolytes, the fabricated fuel cell using CL 5 offers excellent electrochemical characteristics, where the power density of 18 mW cm$^{-2}$ at a maximum operational potential of 0.38 V is observed in Fig. 9. The increase in power density of fuel cell as increases the mass loading of ionic liquid into the polymer matrix is strongly due to the higher ionic conductivity of ionic liquid-based polymer electrolytes. Numerous protons with higher mobility are allowed to be transported from anode to cathode if the polymer electrolyte is conductive. Therefore, higher conductive characteristic of polymer electrolyte promotes the conversion of the fuel into electricity through a redox process in a fuel cell system and thereby increases the power density of the electrochemical cell. Nevertheless, the further inclusion of ionic liquid alters the electrochemical properties of fuel cell. Fuel cell based on CL 6 exhibits the maximum power density of 2.96 mW cm$^{-2}$ at a maximum potential of 0.25 V with a peak current density of 11.88 mA cm$^{-2}$ is observed in Fig. 9. Upon addition of 60 wt% of BmImCl not only decreases the power density of cell, but it also reduces the peak current density, as depicted in the inset of Fig. 9. In other words, excessive ionic liquid concentration in the polymer electrolyte could produce the ion aggregation which inhibits the conducting routes within the polymer chains. As a result, this proton conducting-polymer electrolyte possesses lower ionic conductivity and hence leads to lower electrochemical performance of fuel cell.

Composite polymer electrolytes-based direct methanol fuel cells (DMFCs) were also prepared by Yang group. The maximum power density of 6.77 mW cm$^{-2}$ was reported in the literature. Another type of DMAFC using crosslinked PVA/SSA was also prepared by Yang. This DMAFC generates the highest power density of 4.13 mW cm$^{-2}$ at 60 °C and 1 atm [39,40]. The power density of PEMFC obtained in this present work is higher than these two literature and the literature that we further proved the complexation within the polymer electrolytes. Fuel cells were eventually fabricated using the electrolyzer and fuel cell membrane kit. Ionic liquid also helped in enhancing the electrochemical properties of fuel cells. The open-circuit voltage and power density of fuel cell have been greatly improved with doping of ionic liquid. The maximum power density of 18 mW cm$^{-2}$ was achieved in the fuel cell containing the most conducting polymer electrolyte at room temperature, along with operational current of 750 mA.

Acknowledgment

This work was supported by the High Impact Research Grant (J-21002-73851) from University of Malaya and eScienceFund (16–02–03–6031) from Ministry of Science, Technology and Innovation (MOSTI), Malaysia. Gratitude also goes to “Peruntukan Penyelidikan Pascasiswa Phd (PPP), Universiti Malaysia”. One of the authors, Chiam Wen Liew gratefully acknowledges the “5kim Bright Sparks Universiti Malaya” (SBSUM) for scholarship award.

4. Conclusion

Ionic liquid-based proton conducting polymer electrolytes were prepared by solution casting method. The ionic conductivity of these polymer electrolytes is greatly increased with doping of ionic liquid due to the strong plasticizing effect. The ionic conductivity also increased with mass fraction of ionic liquid, up to a maximum level, which corresponds to inclusion of 50 wt% of BmImCl. Upon addition of 50 wt% of BmImCl, the highest ionic conductivity of ($5.74 \pm 0.01$) mS cm$^{-1}$ is achieved at ambient temperature. This most conductive polymer membrane exhibited better thermal properties than other polymer electrolytes as it is stable up to 250 °C. The temperature of first thermal degradation stage is shifted to higher temperature with doping of salt and ionic liquid due to the complexation. ATR-FTIR showed the interactions between PVA, ammonium acetate and BmImCl and further proved the complexation within the polymer electrolytes. Fuel cell comprising of CL 5 is the promising candidate for use in fuel cells. Nevertheless, the further inclusion of ionic liquid alters the electrochemical properties of fuel cell. Fuel cell based on CL 6 exhibits the maximum power density of 2.96 mW cm$^{-2}$ at a maximum potential of 0.25 V with a peak current density of 11.88 mA cm$^{-2}$ is observed in Fig. 9. Upon addition of 60 wt% of BmImCl not only decreases the power density of cell, but it also reduces the peak current density, as depicted in the inset of Fig. 9. In other words, excessive ionic liquid concentration in the polymer electrolyte could produce the ion aggregation which inhibits the conducting routes within the polymer chains. As a result, this proton conducting-polymer electrolyte possesses lower ionic conductivity and hence leads to lower electrochemical performance of fuel cell.

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Please cite this article in press as: Liew C-W, et al., A novel approach on ionic liquid-based poly(vinyl alcohol) proton conductive polymer electrolytes for fuel cell applications, International Journal of Hydrogen Energy (2013), http://dx.doi.org/10.1016/j.ijhydene.2013.07.092


