Good prospect of ionic liquid based-poly(vinyl alcohol) polymer electrolytes for supercapacitors with excellent electrical, electrochemical and thermal properties

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Abstract
Poly(vinyl alcohol) (PVA)/ammonium acetate (CH3COONH4)/1-butyl-3-methylimidazolium chloride (BmImCl) based polymer electrolytes were prepared by solution casting method. The ionic conductivity increased with temperature as shown in temperature dependent-ionic conductivity study. The maximum ionic conductivity of $(7.31 \pm 0.01) \text{ mS cm}^{-1}$ was achieved at 120 $\text{C}$ upon adulteration of 50 wt% of BmImCl. The samples obeyed Vogel–Tamman–Fulcher (VTF) relationship. The glass transition temperature ($T_g$) of the polymer matrix was reduced by doping it with salt and ionic liquid as shown in differential scanning calorimetry (DSC). Supercapacitor was thus assembled. Wider potential stability range has been observed with addition of ionic liquid. Inclusion of ionic liquid also improved the electrochemical behavior of EDLC. The capacitance of supercapacitor were determined by cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge–discharge tester. The cell also illustrated energy density of 2.39 Wh kg$^{-1}$ and power density of 19.79 W kg$^{-1}$ with Coulombic efficiency above 90%.

1. Introduction
As the world paces towards green technology, the implementation of environmentally friendly materials in manufacturing is an alternative way to reduce environmental issues of plastic waste disposal throughout all phases of the product life cycle. Therefore, biodegradable polymers have received an upsurge of interest nowadays in replacing those environmentally unfriendly polymers. Among biodegradable synthetic polymer, poly(vinyl alcohol) (PVA) is a multitutalented material with excellent tensile strength and high ability to form transparent film [1]. PVA has merits of being a host polymer due to its availability, good optical properties, cost effectiveness, non-toxicity, high hydrophilicity and good mechanical strength as well as high temperature resistance [2,3]. PVA also possesses some inherent characteristics, viz. biocompatible, ease of preparation, high abrasion resistance and high flexibility with superior chemical and thermal stabilities [4,5]. Other reasons for choosing PVA as host polymer are greater extent of polar groups (hydroxyl group) and high chain flexibility which promotes the salt-solvation [6]. High dielectric constant, excellent charge storage capacity and

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dopant–dependent electrical properties make PVA as a promising candidate in the development of electrochemical devices, especially EDLC and fuel cell applications [7]. Ammonium acetate is selected as doping salt in this current project. Ammonium acetate (CH$_3$COONH$_4$) is chosen due to its plasticizing effect. Besides, the acetate anion (CH$_3$COO$^-$) is preferred in salt-solvation through hydrogen bonding.

The PVA–CH$_3$COONH$_4$ polymer system has been widely investigated by G. Hirankumar and his co-workers [6–8]. However, the ionic conductivity is still too low and it is not applicable in the electrochemical devices. Therefore, several ways have been employed to improve the ionic conductivity, such as polymer blending, addition of plasticizers, impregnation of ionic liquids and doping of fillers. Among all the methods, addition of ionic liquid is the most viable technique to enhance the ionic conductivity because of its strong plasticizing effect, environmental friendly nature and high ion content. Ionic liquid is generally defined as a type of molten salt composed solely of ions. Other features of ionic liquid are excellent thermal stability, negligible vapor pressure, non-volatile, low melting point, non-flammable, low viscosity, wider electrochemical potential window and high ionic conductivity [9]. The objective of this present work is to prepare an environmentally friendly polymer electrolyte with superior electrical, thermal and electrochemical properties. Another aim is to investigate the effect of ionic liquid onto the polymer electrolytes and supercapacitors. In this paper, we report the effect of ionic liquid on the PVA–CH$_3$COONH$_4$ polymer electrolytes in supercapacitor application. Supercapacitor (or known as electrical double layer capacitor, EDLC) is fabricated using the highest conducting polymer membrane in this present work. Supercapacitor is the preferred choice compared to secondary batteries owing to the longer cycle life (>10$^4$ cycles), higher power density, higher capacitive density and faster charge–discharge rate as well as higher ability to be charged and discharged continuously without degrading [10].

2. Experimental

2.1. Materials

Polymer electrolytes containing PVA, CH$_3$COONH$_4$ and 1–butyl–3–methylimidazolium chloride (BmImCl) were prepared in this current work. Synthetic biodegradable polymer, 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 host polymer, salt and ionic liquid, respectively. All the materials were used as received.

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

Ionic liquid based-poly(vinyl alcohol) polymer electrolytes were prepared by means of solution casting. Table 1 shows the weight proportion of PVA, CH$_3$COONH$_4$ and BmImCl added into the polymer electrolytes and the designations of the polymer complexes. 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 weight ratio of BmImCl was thus added into the PVA–CH$_3$COONH$_4$ mixture to prepare ionic liquid-based polymer electrolyte. The resulting solution was stirred thoroughly and heated at 70 °C for few hours until a homogenous colorless solution was obtained. The solution was eventually casted on glass Petri dish and dried in an oven at 60 °C. A free-standing polymer electrolyte film was obtained and shown in Fig. 1.

2.3. Characterization of ionic liquid based-PVA polymer electrolytes

2.3.1. Temperature dependence-ionic conductivity studies

Freshly prepared samples were subjected to ac-impedance spectroscopy for ionic conductivity measurements. Digital micrometer screw gauge was used to determine the thickness of the samples. The ionic conductivity of the polymer electrolytes was measured by HIOKI 3532-50 LCR HiTESTER impedance analyzer over a frequency range between 50 Hz and 5 MHz from ambient temperature to 120 °C at a signal level of 10 mV. Polymer electrolytes were placed on the sample holder under spring pressure in the configuration of stainless steel (SS) blocking electrode/polymer electrolyte/SS electrode.

2.3.2. Differential scanning calorimetry (DSC)

DSC analysis was carried out by TA Instrument Universal Analyzer 200 which consists of DSC Standard Cell FC as main

![Fig. 1 – The image of ionic liquid–based PVA polymer electrolyte.](Image)
unit and Universal V4.7A software. The whole analysis was conducted in a nitrogen atmosphere with a flow rate of 60 ml min⁻¹. Samples weighing 3–5 mg were hermetically sealed in the aluminum Tzero pan, while an empty aluminum pan was hermetically sealed as reference cell. In order to remove any trace amount of water and moisture, the samples were heated from 25 °C to 105 °C at a heating rate of 10 °C min⁻¹. The heating process was maintained at 105 °C for 5 min to ensure the complete evaporation. Beyond this step, an equilibrium stage was achieved at 25 °C. After that, the samples were heated from 25 °C to 150 °C and followed up with a rapid cooling process to −50 °C at the pre-setting heating rate. The samples were eventually reheated to 150 °C at the same heating rate. Glass transition temperature (Tg) was evaluated using the final heating scan with the provided software.

2.4. Electrodes preparation

The activated carbon-based EDLC electrodes were prepared by dip coating technique. The carbon slurry was prepared by mixing 80 wt% of activated carbon (Kuraray Chemical Co Ltd., Japan, particle size is 5 ~ 20 μm, surface area is 1800 ~ 2000 m² g⁻¹), 10 wt% of carbon black (known as Super P) and 10 wt% of poly(vinylidene fluoride) (PVdF) binder (molecular weight of 534000 g mol⁻¹ from Aldrich) in 1-methyl-2-pyrrolidone (Purity ≥ 99.5% from Merck, Germany). This slurry was stirred thoroughly for several hours at ambient temperature until homogenous slurry with smooth surface is obtained. The aluminum electrode mesh and the slurry were then subjected to dip coater for dip coating process. The speed of lifting up and down is 90 mm s⁻¹; meanwhile the duration for the dipping process is 15 s. The coated electrodes were dried in an oven at 70 °C for drying process. The weight of electrode materials was evaluated including the binder and super P.

2.5. EDLC fabrication

EDLC cell was fabricated by sandwiching the polymer electrolyte between two symmetrical activated carbon-based electrodes. The cell was then pressed by hydraulic hand pump at 1 MPa to ensure good contact between electrolyte and electrode. The EDLC cell configuration was eventually placed in a cell kit for further electrochemical analyses.

2.6. EDLC characterization

The EDLC cell was subsequently subjected to linear sweep voltammetry (LSV), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge–discharge (GCD) tester for electrochemical characterization. The effect of ionic liquid was investigated for all of these electrochemical analyses by assembling two different EDLCs, except GCD study. The cells using the polymer electrolyte without doping of ionic liquid (denoted as CL 0) is designated as type I supercapacitor, whereas the one using the most conducting ionic liquid-based polymer electrolyte is assigned as type II supercapacitor.

2.6.1. Linear sweep voltammetry (LSV)

The LSV responses of CL 0 and CL 5 were accomplished using CHI600D electrochemical analyzer. These cells were analyzed at a scan rate of 5 mV s⁻¹ with the configuration of stainless steel (SS)/polymer electrolyte/SS in the potential range of ±3 V. The sample interval was 0.001 V with 2 s as the rest time prior to the analysis.

2.6.2. Cyclic voltammetry (CV)

CHI600D electrochemical analyzer was also used to scrutinize CV measurement of EDLC. Initially, the cell was at rest for 2 s. The EDLC cell was then evaluated at 10 mV s⁻¹ scan rate in the potential range between 0 and ±1 V with sample interval of 0.001 V. The specific capacitance (Csp) of EDLC was calculated using the following equation [11,12]:

\[ C_{sp} = \frac{i}{sm} \]  (1)

where i is the average anodic–cathodic current (A), s is the potential scan rate (V s⁻¹) and m is the average mass of active materials (including the binder and super P). The average mass of electrode materials is around 0.015 g.

2.6.3. Electrochemical impedance spectroscopy (EIS)

The impedance spectroscopy was probed by HIOKI 3522-50 LCR HITESTER impedance analyzer at room temperature with a bias voltage of 10 mV. The EIS measurement was done in the frequency range of 10 mHz–100 kHz. The capacitance, C was determined from the impedance data at a frequency of 10 mHz using the following equation [13]:

\[ C = \frac{1}{\omega Z''} = \frac{1}{2\pi f Z''} \]  (2)

where \( \omega \) is angular frequency, which is represented by \( 2\pi f \) and \( Z'' \) is the imaginary part of the total impedance (Z). The specific capacitance of EDLC was calculated by dividing the capacitance with average weight of active materials (including the binder and super P). The average weight of electrode materials is 0.02 g.

2.6.4. Galvanostatic charge–discharge performance (GCD)

The charge–discharge study was performed using the Neware battery cycler. The EDLC was charged and discharged at current of 1 mA. EDLC is allowed to rest for 30 min prior to the measurement. The specific discharge capacitance (Csp) was obtained from charge–discharge curves, according to following relation [12]:

\[ C_{sp} = \frac{I}{m \Delta V} \]  (3)

where I is the applied current (A), m is the average mass of electrode materials (including the binder and super P), \( \Delta V \) represents the potential change of a discharging process excluding the internal resistance drop occurring at the beginning of the cell discharge and \( \Delta t \) is the time interval of discharging process. The \( \Delta V/\Delta t \) is determined from the slope of the discharge curve. The electrode used in this study is in 0.02 g.

Energy density (E, W h kg⁻¹), power density (P, W kg⁻¹) and Coulombic efficiency (ν, %) were assessed from the equations below [14]:

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example bigger size of anion will dissociate the cations easily [16]. In this present work, the bulky group of BmIm$^-$ also helps in improving the ionic conductivity by producing free volume for conduction [16]. Moreover, the physicochemistry of ionic liquid such as viscosity and dielectric constant also contributes to the increase in ionic conductivity. Lower viscosity of ionic liquid also enhances the polymer chain flexibility. Therefore, this flexible polymer backbone could interrupt the ion-polymer bonding and promote the ionic conducting process [16]. In contrast, high dielectric permittivity of ionic liquid plays an important role to separate the ion pairs and/or ion aggregates with high self-dissociating properties. More mobile cations are consequently produced which leads to higher ionic conductivity [16]. In addition, the ionic conductivity rises with the ionic liquid concentration, as shown in CL 2 and CL 5 plots. The same explanations as aforementioned also applied onto this increase in ionic conductivity, such as increase in amorphous region and plasticizing effect of ionic liquid. The highest ionic conductivity of $(7.31 \pm 0.01)$ mS cm$^{-1}$ has been achieved by adding 50 wt% of BmImCl at 120 °C. However, the ionic conductivity is decreased with further incorporation of BmImCl as shown in Fig. 2.

A moderate increase in ionic conductivity with a gradual increase in temperature is observed in Fig. 2. This is principally due to the fast vibration modes of the molecules in the polymer membrane upon heating. Rapid vibration mode of the macromolecules promotes the bond rotation within the polymer matrix. The cations coupling with higher polymer segmental mobility can be detached from the coordination bond with the oxygen in PVA easily at elevated temperature. Therefore, ionic transportation is enhanced with increasing temperature. In addition, the amplitude of the molecular vibration increases with temperature. Therefore, the thermal vibration improves the decoupling rate of cation from transient coordination bonding with anion. More cations can be transported within the polymer electrolytes with higher decoupling rate. Since the number of mobile cations which is responsible for ionic transportation is higher, thus more ionic conduction in the polymer electrolytes would be generated. So, as expected, higher ionic conductivity is attained in this study. Apart from that, the polymer membrane could be expanded due to higher amplitude of oscillation mode at elevated temperature. This thermal expansion creates free spaces for conduction mechanism. As a consequence, the charge carriers are decoupled and hence transported easily, contributing to increase in ionic conductivity with reciprocal of temperature.

Fig. 2 illustrates positively curved plot for all the samples where its regression value is far away from unity [17]. These non-linear variations reflect that all the polymer electrolytes exhibit Vogel–Tamman–Fulcher (VTF) theory which is associated with free volume model [17,18]. In order to interpret the result, the plots are then fitted with VTF empirical formula. Based on this volume-activated principle, the ionic conductivity is expressed as below:

$$\sigma = A_oT^{-\frac{1}{m}} \exp \left(-\frac{B}{T-T_m}\right) = A_oT^{-\frac{1}{m}} \exp \left(-\frac{E_o}{kT_T}\right)$$  \hspace{1cm} (7)

where $A_o$ is pre-exponential constant proportional to the number of charge carriers, $B$ represents a constant which is determined from the gradient of the plot (K$^{-1}$), $E_o$ is pseudo-

$$E = \frac{C_m \times (dV)^2}{2 \times 1000 \times 3600}$$  \hspace{1cm} (4)

$$P = \frac{I \times dV}{2 \times m} \times 1000$$  \hspace{1cm} (5)

$$\eta = \frac{t_d}{t_c} \times 100$$  \hspace{1cm} (6)

where $t_d$ and $t_c$ are the discharging time and charging time, respectively.

3. Results and discussion

3.1. Temperature dependence-ionic conductivity studies

Fig. 2 portrays the ionic conductivity of ionic liquid doped polymer electrolytes and ionic liquid free-based polymer electrolyte in the temperature range between ambient temperature and 120 °C. Upon addition of BmImCl, the ionic conductivity is greatly enhanced by comparing CL 0 with CL 2, CL 5 and CL 6. Strong plasticizing effect of ionic liquid is the main contributor in this phenomenon [15]. The polymer chains could be more flexible in the presence of ionic liquid. So, the flexible polymer backbone increases the segmental motion of the polymer matrix and hence assists the ionic transportation which confers with high ionic conductivity. Incorporation of ionic liquid also reduces the glass transition temperature ($T_g$). Lower $T_g$ would promote the rubbery phase formation which constrains the crystalline degree of polymer electrolytes over a wide temperature range.

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The obtained parameters from each VTF plot with the experimental glass transition temperature from DSC. This rate is hence replaced with the ratio of $E_a$ of each sample is subsequently calculated. As can be seen, the pseudo-activation energy is inversely proportional to the ionic conductivity. Among all the polymer electrolytes, CL 5 shows the highest ionic conductivity, but bears the lowest pseudo-activation energy. This observation reveals that CL 5 manifests higher flexibility of polymer backbone coupled with increased segmental mobility within the polymer chains. Hence, CL 5 requires lower activation energy for the hopping process.

3.2. Differential scanning calorimetry (DSC)

DSC is a vital analysis to determine the glass transition temperature ($T_g$) of the sample. This study signifies the phase transition of a polymer matrix in the amorphous region, from a hard glassy phase into a flexible and soft rubbery characteristic. DSC thermograms of pure PVA, CL 0, and ionic liquid-based polymer electrolytes are shown in Fig. 3. As aforementioned in introduction, ammonium acetate is a plasticizing salt. This can be proven in DSC curve profiles. Pristine PVA shows $T_g$ of 80 $^\circ$C. However, it is substantially reduced to around 47 $^\circ$C when 30 wt% of CH$_3$COONH$_4$ is complexed with 70 wt% of PVA. $T_g$ of polymer membrane should be increased upon addition of CH$_3$COONH$_4$ due to the partial coordination bonding in the complexation. Nevertheless, an oppose result is obtained. The significant decrease of $T_g$ denotes that the plasticizing effect of CH$_3$COONH$_4$ dominates the temporary interactive coordination. This plasticizing effect softens the polymer backbone and thus produces flexible polymer backbone.

The $T_g$ is decreased further with addition of ionic liquid. Sub-ambient temperature of $T_g$ is attained by adding ionic liquid. These sub-ambient temperatures divulge the rubbery state of polymer electrolytes as the surrounding temperature is much higher than $T_g$. The molecules in the polymer matrix are allowed to undergo orientation and conformational changes in the rubbery phase. So, it can be concluded that the chain flexibility of polymer electrolytes containing ionic liquid is higher than the ionic liquid-free polymer complexes which induces higher segmental mobility. The abrupt decrease in $T_g$ is assigned to the plasticizing effect of ionic liquid. Again, the plasticizing effect stimulates the flexibility of polymer backbone. As expected, the ammonium salt would form a complexation with the polymer chains. So, the charge carriers which are responsible for the ionic transportation tend to be dissociated from the native complexation owing to the flexible polymer chains. As a result, the ionic transportation is favored. In addition, $T_g$ reduces with further inclusion of ionic

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Table 2 – The obtained parameters from each VTF plot with the experimental glass transition temperature from DSC thermogram.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Regression value, $R^2$</th>
<th>Ideal glass transition temperature, $T_g$ (K)</th>
<th>Glass transition temperature, $T_g$ (K)</th>
<th>Pre—exponential constant, $A_o$</th>
<th>Constant or gradient of the plot, B (K$^{-1}$)</th>
<th>Pseudo—activation energy, $E_a$ (µev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL 0</td>
<td>0.99</td>
<td>265.07</td>
<td>315.07</td>
<td>2.3892</td>
<td>0.0900</td>
<td>7.76</td>
</tr>
<tr>
<td>CL 2</td>
<td>0.99</td>
<td>232.03</td>
<td>273.03</td>
<td>0.2941</td>
<td>0.0875</td>
<td>7.54</td>
</tr>
<tr>
<td>CL 5</td>
<td>0.99</td>
<td>203.23</td>
<td>253.23</td>
<td>1.2712</td>
<td>0.0825</td>
<td>7.11</td>
</tr>
<tr>
<td>CL 6</td>
<td>0.99</td>
<td>213.78</td>
<td>263.78</td>
<td>0.6515</td>
<td>0.0898</td>
<td>7.74</td>
</tr>
</tbody>
</table>
The $T_g$ exhibits downward shift from $-0.12^\circ C$ to $-19.92^\circ C$ corresponding to addition of 20 wt% and 50 wt% of BmImCl as portrayed in Fig. 4. The plasticizing effect becomes more apparent with increasing mass fraction of ionic liquid. Therefore, the flexibility of polymer chain in CL 5 is higher than in CL 2. The ionic hopping mechanism is more favorable in CL 5 which leads to higher ionic conductivity. The result is in good agreement with previous study. Nevertheless, different phenomenon is observed for CL 6. $T_g$ is enhanced to $-9.37^\circ C$ by adding 10 wt% of BmImCl further. The increase in $T_g$ (instead of decrease) might be due to the formation of ion pairs and ion aggregates. Ion pairing and ion aggregation could obstruct the orientation of the molecules and hence constrain the flexibility of polymer chains. Therefore, the decoupling and migration of cations are hindered by the ion pairs and ion agglomerates.

3.3. **Linear sweep voltammetry (LSV)**

The maximum operational potential for charge or energy storage in EDLCs is checked by carrying out LSV study [11]. Fig. 5(a) and (b) describe LSV responds of the EDLC cell with CL 0 and CL 5 polymer electrolytes, respectively. The CL 0-based EDLC can be operated up to 3.7 V in the potential range between $-1.9 V$ and $1.8 V$, as shown in Fig. 5(a). Upon inclusion of 50 wt% of BmImCl into the polymer electrolyte, the electrochemical stability window is expanded to 4 V, where the cathodic and anodic potentials are detected at $-1.8 V$ and $2.2 V$, respectively. Therefore, it can be concluded that impregnation of ionic liquid can improve the electrochemical stability of EDLC. Apart from that, the operational current of EDLC comprising of CL 5 is higher than that of CL 0. This is mainly assigned to high ion concentration in ionic liquid. The activated carbon layer would allow the absorption of a large extent of ions as ionic liquid provides more ions. Hence, the ion absorption forms the charge accumulation at the electrolyte–electrode interface and yields the electrical double layer. Therefore, more energy would be stored in this vicinity. More electrons will be left and transported from positive electrode to negative electrode when the ion absorption is increased. This is responsible for higher operational current in the EDLC based on CL 5 polymer membrane.

3.4. **Cyclic voltammetry (CV)**

According to the literature, there are three different techniques to find out the capacity of the electrochemical devices [24]:

i) From cyclic voltammetry
ii) From impedance spectroscopy
iii) From galvanostatic charge–discharge performance

All these experiments will be analyzed and discussed in details in this present approach. In order to verify the capacitance of the fabricated EDLC cells, the results obtained from each experiment are compared. Fig. 6(a) and (b) exemplify CV curves of type I and II cells, respectively. Type I supercapacitor shows leaf-like shape with specific capacitance of 0.02 F g$^{-1}$, whereas type II cell illustrates a voltammogram approaching ideal box-like shape with specific capacitance value of 28.36 F g$^{-1}$ [25]. This result is higher than some literatures. Pandey and his co-workers fabricated EDLC using ionic liquid-based poly(ethylene oxide) polymer electrolytes and multi-walled carbon nanotube electrodes. The result is almost 10 times lower than our current work, which is 2.6–3 F g$^{-1}$ [23]. Hybrid capacitors using PVA-sodium poly (acrylate) (PAAS)-potassium hydroxide (KOH) alkaline polymer electrolytes and nickel hydroxide (Ni(OH)$_2$)/activated carbon (AC) composite positive electrodes were also assembled by Sun et al. [27].

**Fig. 4** – DSC thermograms of pure PVA, CL 0 and ionic liquid–based polymer electrolytes from $-50^\circ C$ to $150^\circ C$.

**Fig. 5** – (a): LSV response of type I EDLC. (b): LSV response of type II EDLC.
Higher specific capacitance of 29.8 Fg⁻¹ was obtained for these hybrid capacitors. This result is expected because of the high faradic specific pseudocapacitance of Ni(OH)₂ [27].

Type I cell is deviated from the ideal rectangular shape due to the poor contact between electrode and electrolyte. So, the ions are very difficult to be absorbed onto the electrode surface with this low interfacial contact. The ill-defined rectangular shape in Fig. 6(a) is also because of the low conductivity of polymer electrolyte [10]. However, when ionic liquid is added into the polymer matrix, sticky sample is produced due to the plasticizing effect of ionic liquid. Hence, the interfacial contact is improved with this sticky behavior leading to increase in energy storage in EDLC. The improvement of interfacial contact could then induce higher capacitive performance of EDLC. In addition, the ionic conductivity is enhanced upon addition of ionic liquid which helps in improving the charge storage capacitive behavior. The capacitance of type I supercapacitor is extremely low compared with type II cell. The specific capacitance value is found to be increased about 131833% with addition of ionic liquid into the polymer matrix. Apart from better interfacial contact, the increment of specific capacitance is attributed to the main feature of ionic liquid. As aforementioned in introduction and section 3.3, ionic liquid is comprised solely of ions. Consequently, higher ion concentration favors the ion migration within the polymer electrolyte (known as separator in EDLC) and promotes the charge accumulation at the electrolyte–electrode boundary. Eventually, the formation of this electrical double layer increases the capability of energy storage in EDLC. No faradic process is detected in the figure entailing no redox reaction in the EDLC. In addition, higher operational current also observed in this study. Based on the findings, inclusion of ionic liquid is a successful way to improve the capacitive feature of EDLC.

3.5. Electrochemical impedance spectroscopy (EIS)

EIS is a versatile method to assess the electrical behavior of the assembled cells. Fig. 7(a) and (b) show the complex impedance spectra of different capacitor cells at ambient temperature. Both impedance responses illustrate a spike at low frequency range which is associated with a semicircle at high frequency region [26]. The semicircular feature is not so clear in Fig. 7(a), so the scale of the plot is enlarged and shown in inset of the figure. The linearly rising pattern (or spike) in the impedance plot reveals the ion absorption at the electrode–electrolyte boundary and hence indicates the capacitive behavior of EDLC. From both impedance plots, it can be seen that there are two resistances appearing in the whole frequency regime. Both resistances are determined from the intercepts on x-axis of the complex impedance plot of EDLCs. The resistance at low frequency range is known as the combination of charge transfer resistance (Rₜ) and bulk resistance (Rₑ), whereas the bulk resistance (Rₑ) is located at high frequency end, as shown in both figures. The high frequency intercept (bulk resistance) reflects the bulk properties of polymer electrolyte [11,23]. Type I cell displays high bulk resistance that is around 3400 Ω, however, this resistance is significantly reduced to 5 Ω with doping of ionic liquid into polymer electrolyte for type II supercapacitor. Strong plasticizing effect of ionic liquid is an important contributor in decreasing the bulk resistance of polymer membrane as discussed in section 3.1. The ionic mobility and transportation could be enhanced with this low bulk resistance, resulting in higher ionic conductivity. This result is in good agreement with the previous findings in section 3.1. On the contrary, the charge transfer resistance is one of the bulk behaviors of electrode–electrolyte interface. It is defined as a resistance that the charge carriers required to overcome during the charge transfer process from the electrolyte to surface of electrode. It is noteworthy that the charge transfer resistance of type II EDLC is radically improved from 1100 Ω to 4 Ω upon addition of ionic liquid into the polymer electrolyte. This observation indicates the effective role of ionic liquid in improving the interfacial contact between the electrode and electrolyte. The specific capacitance of the cells is then evaluated using equation (2). As expected, the specific capacitance of type II cell is higher than type I cell. The specific capacitances of 0.03 Fg⁻¹ and 27.76 Fg⁻¹ are obtained for type I and type II EDLCs, respectively. The results are comparable with the CV findings. Again, the abrupt increase in specific capacitance of type II EDLC is suggestive of the high ion concentration and good adhesion of the electrolyte to electrode, as explained in previous study. Superior electrochemical properties in conjunction with excellent interfacial contact are
Fig. 7 – (a): Nyquist impedance plot of type I EDLC at room temperature from 10 mHz to 100 kHz with close-up view of the plot in high frequency region (inset). (b): Nyquist impedance plot of type II EDLC at room temperature from 10 mHz to 100 kHz.
observed in EDLC comprising of ionic liquid-based polymer electrolyte.

3.6. Galvanostatic charge-discharge performance

Galvanostatic charge-discharge experiment can also be done to inspect the electrochemical property of EDLC upon the charge and discharge processes and execute the cyclic durability test. The GCD result of type II supercapacitor is shown in Fig. 8. The symmetrical pattern of the charge and discharge behavior in Fig. 8 implies the superior capacitive nature of EDLC [12]. As can be clearly seen in Fig. 8, the potential range of inclined part for charging is between 0.2 V and 1 V. The cell starts to be charged at 0.2 V instead of 0 V because of the internal resistance of the supercapacitor. Beyond charging process, it is followed with a cell discharge curve. The small drop in the initial part of discharge curve is assigned to the internal resistance of electrochemical capacitors. This ohmic loss arises from resistances between electrode and electrolyte, such as charge transfer resistance and bulk resistance of polymer electrolyte [11,13]. According to Pandey et al., the ohmic loss is also attributed to the depletion of polymer electrolyte [26]. The ion migration and accumulation in the electrical double layer could reduce the amount of mobile charge carriers in the polymer membrane causing the depletion. The depletion of polymer electrolytes could increase the cell resistance. This phenomenon is supported by Fig. 8. The internal resistance of the cell for both charging and discharging curves increase slightly with increasing cycle number. When the cycle number is increased, some ions are more preferred to be paired up rather than be transported into the electrolyte-electrode interface as a result of rapid charge accumulation in the region. This causes the depletion of polymer electrolyte and thereby rises up the internal resistance.

The principle of charging and discharging processes involving ion absorption and desorption is further described in Fig. 9. When an external electric field is applied, the electrons would be given out and be transferred from positive electrode to negative electrode. The poles that the electrons leave from the activated carbon are considered as positively-charged. The anions from the polymer electrolyte (i.e. acetate anion, CH$_3$COO$^-$ and chloride, Cl$^-$ in this current project) could be drawn to this positively charged surface at the positive electrode through ion absorption process when the voltage is applied across the cell. On the other hand, the hydrogen cations (H$^+$) in the polymer electrolyte are attracted to the negative electrode simultaneously. We suggest that 1-butyl-3-methylimidazolium cation (BmIm$^+$) is very hard to be attached to the electrode due to its bulky size with low ionic mobility. Therefore, only H$^+$ is available for the charge accumulation at the surface of negative electrode. The cations and anions are thus distributed relative to each other over the distance of the polymer matrix. Eventually, upon the completion of charging electricity process, the accumulation of the charge carriers at both electrodes will lead to the formation of electrical double layer and thereby create the energy storage in EDLC. Conversely, the ions will move away in the discharging process.

The cycle life test is a vital characterization to determine the stability of EDLC in terms of electrochemical performances after charging and discharging processes. Fig. 10 represents the specific discharge capacitance and Coulombic energy storage in EDLC.
efficiency of supercapacitor over 500 cycles. The energy and power densities are thus calculated using equations 4 and 5, respectively. The result obtained over 500 cycles is then plotted in Fig. 11. The initial specific discharge capacitance of 31.28 F g\(^{-1}\) with Coulombic efficiency of 90% is observed for type II cell in Fig. 10. This capacitance value is similar with the result obtained in CV and impedance spectroscopy. However, the capacity of cell decreases with cycle number. The energy and power densities also possess the same pattern. The decreases in the electrochemical performance might be due to the depletion of polymer electrolyte. The amount of charge carriers within the polymer membrane is reduced with increasing cycle number. The internal resistance of cell is increased with cycle number as explained as aforesaid. So, the ions requires higher amount of energy to be transported towards the surface of electrode with higher internal resistance. These ions have to overcome this barrier in order to form the electrochemical performance might be due to the depletion of polymer electrolyte. The amount of charge carriers within the polymer membrane is reduced with increasing cycle number. The internal resistance of cell is increased with cycle number as explained as aforesaid. So, the ions requires higher amount of energy to be transported towards the surface of electrode with higher internal resistance. These ions have to overcome this barrier in order to form the electrochemical performance might be due to the depletion of polymer electrolyte. The amount of charge carriers within the polymer membrane is reduced with increasing cycle number. The internal resistance of cell is increased with cycle number as explained as aforesaid. So, the ions requires higher amount of energy to be transported towards the surface of electrode with higher internal resistance.

It has been observed that the specific capacitance, energy density and power density become almost constant above 400th cycles. This signifies that the cell can remain in its electrochemical stability without any abrupt changes in electrochemical performances upon charge and discharge for 400 cycles, suggesting that the ionic liquid-based polymer electrolyte is a best choice as separator in supercapacitor. The most conducting ionic liquid-based polymer electrolyte is also a promising candidate by maintaining its Coulombic efficiency above 90% in 500 cycles of charging and discharging. According to the findings, CL 5 is very suitable to be applied in EDLC application as the electrochemical performance has been greatly improved.

4. Conclusion

PVA-based polymer electrolytes were prepared by solution casting method. The ionic conductivity increased with temperature due to the polymer expansion effect. Polymer electrolyte containing 50 wt% of BmImCl offered the maximum ionic conductivity of \((7.31 \pm 0.01)\) mS cm\(^{-1}\) at 120 °C. The samples obeyed non-Arrhenius VTF rule as convex upward curved profiles were shown in temperature dependence-ionic conductivity studies. This principle stated that the ion transportation mechanism is coupled with highly flexible polymer chain which promotes the ion hopping process. Upon impregnation of BmImCl, the \(T_g\) of polymer electrolytes is lowered down to sub-ambient value. The decrease in \(T_g\) helped in softening the polymer backbone. EDLC containing the most conducting polymer electrolyte was assembled. The fabricated EDLC can be charged up to 4.8 V, as illustrated in LSV study. Doping of ionic liquid into polymer electrolyte also increased the capacitive nature of EDLC. The specific capacitance of 28.36 F g\(^{-1}\) was achieved with better electrochemical characteristic in cyclic voltammogram. The specific capacitance value obtained from impedance spectra and galvanostatic charge–discharge test are also comparable with the result from CV study. The inclusion of ionic liquid not only improves the interfacial contact between electrode and electrolyte, but also increases the electrochemical property of supercapacitors. Doping of ionic liquid into PVA-based polymer electrolyte is a good prospect for improving the electrochemical performance of an energy storage device.

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REFERENCES

[1] Dasenbrock CO, Ridgway TH, Seliskar CJ, Heineman WR. Evaluation of the electrochemical characteristics of a


