High efficient dye sensitized solar cells using phthaloylchitosan based gel polymer electrolytes

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1. Introduction

Recent years have witnessed a tremendous rise in the development of dye sensitized solar cells (DSSCs) and efficiency as high as ~ 14% [1] has been achieved till date ever since it was first reported by Gratzel’s group 26 years ago [2]. Although this efficiency is much lower than its counterparts, silicon-based solar cells with the efficiency of 25% [3], DSSCs are still been considered as promising alternative for the silicon-based photovoltaic cells since the former are environmental friendly and low in cost compared to latter [4–6]. Among the DSSC’s components, the electrolyte can be considered as the heart since it plays a vital role as medium for charge transport. Most of the highly efficient DSSCs usually employ liquid electrolytes. However, liquid electrolytes are prone to evaporate, leak and corrode making them unstable for long run. As substitution, gel polymer electrolytes (GPEs) have been favored than solid polymer electrolytes owing to their considerably high ionic conductivity, good chemical and physical stability as well as having better contact with electrodes. Essential components in GPEs for DSSCs are (i) solvents with high dielectric constant and boiling point, (ii) polymers as gelling agents, (iii) iodide-based salts and (iv) iodine crystals which provide iodide/triiodide (I⁻/I₃⁻) redox mediator when they interacts with the salts. The ionic conductivity is an important factor for efficient charge transfer from cathode or counter electrode to photoanode and thereby may results in good performance of DSSCs. The conductivity of a GPE is dependent on several parameters. In the selection of salt, the lattice energy must be low to ensure easy dissociation of the salt. The cations and anions of the salts are significant in DSSC application. Small cations for instance lithium cation (Li⁺) has been reported to adsorb better onto photoanode surface than large cations i.e. tetrabutylammonium cation (C₁₆H₃₃N⁺) thereby resulting in fast electron injection and consequently leading to higher short current density (JSC) and fill factor (FF) [7]. The common inorganic salts particularly LiI, NH₄I and KI contained in liquid electrolytes possess limited solubility at ambient temperature [8]. On the other hand, organic salts namely tetramethylammonium iodide (TMAI), tetrabutylammonium iodide (TBAI), tetrathylammonium iodide (THTAI), pyridinium iodide and picolinium iodide which are non-volatile and stable under atmospheric environment have been chosen and used in DSSCs by many researchers [9–17]. Lee et al. [10] have prepared GPE with poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) as polymer host and TPAI salt which exhibited higher efficiency compared to PVdF-HFP-NH₄I GPE. The former also demonstrated higher JSC and Voc than the latter. TPA⁺ or C₁₆H₃₃N⁺ cation is bigger than NH₄⁺ cation and therefore possesses lower lattice energy. In PVdF-HFP-TPAI system,
it can be inferred that I\(^-\) anions are the dominant species contributing to the conductivity since the bulkier TPA\(^+\) cation may not be so mobile. With the high iodide concentration, \(J_C\) will increase and subsequently improve the DSSC efficiency. Based on the above reasons, TPAI salt is chosen in this work. With the aim to enhance the conductivity and DSSC performance in this work, blending of two polymers i.e. phthaloylchitosan and poly(ethylene oxide) (PEO) and incorporation of ionic liquid (IL) have been employed. Phthaloylchitosan has been obtained from chitosan, a biopolymer, through N-phthaloylation in order to improve its solubility in organic solvents whereas PEO is a synthetic polymer frequently used by many researchers. Blending of two different polymers is known to increase the ionic conductivity. To the best of the authors’ knowledge, there is no report on the utilization of phthaloylchitosan-PEO blended GPE in DSSCs. ILS are salts which have melted at room temperature that exists in liquid form and have unique properties including high ionic conductivity, thermally and chemically stable, non-flammable and non-volatile to name a few [18,19]. IL can act as plasticizer as well as provide additional charge carriers in GPEs. Ionic liquid 1-butyl-3-methyl-imidazolium iodide (BMIIL) is added into phthaloylchitosan-PEO/TPAIP GPEs as its ambient conductivity is higher than 1-propyl-3-methylimidazolium iodide (PMII) [20]. Other than ionic conductivity, the diffusion coefficient of triiodide ion parameter in GPEs will also affect the performance of DSSCs. Hence, the diffusion coefficient of triiodide ion has been calculated in this work using steady state current measurement.

2. Experimental

2.1. Materials

Chitosan, phthalic anhydride, polyethylene oxide (PEO), ethylene carbonate (EC), tetrapropylammonium iodide (TPAI), 1-butyl-3-methylimidazolium iodide (BMIIL) and triton X-100 were purchased from Sigma-Aldrich. Iodine (I\(_2\)) crystals and dimethylformamide (DMF) were purchased from from Amocochemie-Hamburg and Friedemann Schmidt Chemical, respectively. Titanium dioxide (TiO\(_2\)) with 21 nm (P25) and 15 nm (P90) particles size were obtained from Evonik Industries. Cis-diisothiocyanato-bis(2,2’-bipyridyl-4,4’-dicarboxylic acid) ruthenium(II) dye (N3) and platinum (Pt) solution were purchased from Solaronix.

2.2. Preparation of gel polymer electrolytes

Phthaloylchitosan (PhCh) was prepared by refluxing the chitosan with phthalic anhydride in DMF under nitrogen environment at \(\sim 110^\circ\)C for 6 h. The mixture of the solution was kept overnight at temperature \(\sim 60^\circ\)C and poured into ice water to obtain the N-phthaloylchitosan. The N-phthaloylchitosan was washed with ethanol and dried in vacuum for about 8 h. The phthaloylchitosan together with PEO were added and dissolved into liquid electrolyte containing TPAI, EC and DMF. The ratio of PhCh/PEO was 4:1. The reason of blending PhCh with small amount PEO is to help to improve flexibility in the polymer backbone of the gel polymer electrolyte system. Four samples of gel polymer electrolytes containing different amount of TPAI (21.7 wt.%, 22.7 wt.%, 23.6 wt.% and 24.5 wt.%): were prepared. Other materials were fixed (PhCh = 0.08 g, PEO = 0.02 g, EC = 0.50 g and DMF = 0.60 g). Small amount of iodine crystals (7.5% from the amount TPAI) was added to obtain redox couple in the gel polymer electrolyte system.

All samples were characterized using electrochemical impedance spectroscopy where the bulk resistance, \(R_b\), of the gel polymer electrolyte can be obtained from the Nyquist plot. The measurements were carried out in the frequency range from 50 Hz to 5 MHz using Hioki 3531 Z Hi Tester. The conductivity, \(\sigma\), can be calculated from the following equation:

\[
\sigma = \frac{t}{AR_b}
\]

where \(A\) and \(t\) is the area and thickness of the sample. The diffusion coefficient of triiodide ions was obtained from steady state current measurement of symmetric cell. The gel polymer electrolyte was sandwiched between two Pt electrodes (Pt/electrolyte/Pt). A spacer with 53 \(\mu\)m thickness and 0.2 cm\(^2\) hole area was used for the fabrication of symmetrical cell. The cell was characterised using linear sweep voltammetry (LSV). The applied voltage was swept from \(-0.7\) V to 0.7 V with slow scan rate of 10 mV s\(^{-1}\).

2.3. Fabrication of dye sensitized solar cells

The preparation of TiO\(_2\)/dye photoanode is similar to that reported elsewhere [21]. The TiO\(_2\) paste for nanoporous layer was prepared by mixing and grinding 0.5 g TiO\(_2\) powder (P90) with 2 mL of 0.1 mol nitric acid. The paste was then coated on top of conducting side of fluorine doped tin oxide (FTO) glass by spin coating technique and sintered at 450 °C for 30 minutes. The mesoporous TiO\(_2\) layer was prepared by coating another TiO\(_2\) (P25) paste on top of nanoporous TiO\(_2\) layer using doctor blade method and sintered at 450 °C for another 30 minutes. The paste for mesoporous TiO\(_2\) layer was prepared by grinding 0.5 g TiO\(_2\) (P25) powder with 2 mL of 0.1 mol nitric acid, 0.1 g carbowax and few drops of Triton X-100. The TiO\(_2\) layers electrode was then sensitized with N3 dye sensitizer by soaking the electrode in 0.3 mM N3 dye solution for 24 h. The Pt counter electrode of DSSC was prepared by spreading a platinum solution (platinol from Solaronix) on top of conducting side of FTO glass and sintered at 450 °C for 30 minutes. DSSC was assembled by sandwiching the prepared gel polymer electrolytes between photoanode and counter electrode. The j-V characteristics and impedance measurement of DSSC were carried out under solar simulator (Oriel LCS-100) with light intensity of 100 mW cm\(^{-2}\). The frequency range of impedance measurement for DSSC was 100 kHz to 10 mHz where the bias potential was set at open circuit voltage of DSSC.

Fig. 1. Nyquist plot of gel polymer electrolyte having 22.7 wt.% TPAI.
3. Results and discussion

3.1. Conductivity studies

Fig. 1 shows the Nyquist plot for gel polymer electrolyte containing 22.7 wt.% TPAI at room temperature (RT). The bulk resistance ($R_b$) value of the gel polymer electrolyte has been obtained from intersect between the spike and real axis as shown in Fig. 1. All the impedance plots of gel polymer electrolytes in this work exhibit a similar profile (only spike). The ionic conductivity of gel polymer electrolytes having different amounts of TPAI are shown in Fig. 2. It can be observed that the ionic conductivity is slightly varied particularly for the gel polymer electrolyte having 21.7 wt.% TPAI ($\sigma = 8.3 \pm 0.7 \text{ mS cm}^{-1}$). The conductivity of gel polymer electrolyte depends on the number density, $n$ and mobility, $\mu$ of free ions. The number density of free ions will usually increase with the amount of salt. At the same time, these free ions also tend to re-associate or to form ion pairs and ion aggregates. At high salt concentration, the number density of ion pairs and ion aggregates are higher than the number density of free ions. This leads to decrease in ionic conductivity. As can be seen in Fig. 2, the highest conducting value of gel polymer electrolyte was 11.1 $\pm$ 1.2 mS cm$^{-1}$ for 22.7 wt.% of TPAI salt. This conductivity is clearly higher as compared to the conductivity value for the gel polymer electrolyte containing 21.7 wt.% TPAI which is $8.3 \pm 0.7 \text{ mS cm}^{-1}$. No significant change in conductivity is observed when 23.6 wt.% TPAI was added as compared to 22.7 wt.% TPAI. Although the conductivity values for 24.5 wt.% TPAI and 23.6 wt.% TPAI are considered similar, the value for the former (9.3 $\pm$ 0.5 mS cm$^{-1}$) is clearly lower than that of 22.7 wt.% TPAI. The highest conductivity value obtained in this work is found to be slightly higher compared to that reported by Yusuf et al. [22] which is 5.27 mS cm$^{-1}$ for 19 wt.% TPAI salt. The polymer that they have used is similar (phthalalylchitosan) but excluding the small amount of PEO which has been added in this work. This shows that the PEO probably helps to improve the ionic conductivity of gel polymer electrolyte. The other possible reason is due to the presence of DMF instead of propylene carbonate (PC). The lower viscosity of DMF may contribute to the small increase in ionic conductivity. The viscosity of DMF is around 0.9 mPa s [23] while for PC it is around 2.96 mPa s [24] at temperature of 293 K. TPAI contains $PR4N^+$ cations and $I^-$ anions. According to Yusuf et al. [22], the mobility of $PR4N^+$ ions is obstructed at high salt concentration due to the bulky size and the entanglement in the polymer matrix. Hence, the contribution in ionic conductivity is mostly from the $I^-$ ions. Electrolyte using quaternary ammonium iodide salts such as tetrabutylammonium iodide and tetramethylammonium iodide have been proved to have high iodide ions transference number. Bandara et al. [25] has shown that the iodide ions transference number in polyacrylonitrile (PAN)-TPAI based quasi-solid electrolyte was 68%. This is important for DSSC since the charge transfer from cathode to photoanode is carried out by $I^-$ ions. It is known that DSSC which utilised electrolyte with high ionic conductivity can produce high short circuit current density and high overall power conversion efficiency. BMII liquid ion has been added to the highest conducting electrolyte (22.7 wt.% TPAI) to see whether the conductivity can be improved or not. The conductivity is expected to increase upon addition of BMII since BMII provides extra free ions ($BMII^+$ and $I^-$) to the gel polymer electrolytes. According to Liew et al. [26], the plasticizing effect of BMII can also contribute to the increment in conductivity by enhancing the flexibility of polymer chains thus improve the mobility of free ions. The amount of BMII has been varied from 2 wt.% to 8 wt.% and their RT conductivities have been calculated and shown in Table 1. No further addition of BMII beyond 8 wt.% as the gel polymer electrolyte has become liquid-like above that amount. From Table 1, it can be said that the ionic conductivity of gel polymer electrolytes remains unchanged or shows no significant change with the BMII concentration. Kim et al. [27] has studied the electrochemical properties of BMII ionic liquid. They found that the room temperature ionic conductivity of BMII lies within $10^{-4}$ S cm$^{-1}$. It is to be noted that even without BMII ionic liquid, the conductivity of gel polymer electrolytes obtained in this work is $10^{-2}$ S cm$^{-1}$ which is already higher than the BMII conductivity. Hence, this is probably the reason why the conductivity remains unchanged with the addition of BMII into the gel polymer electrolytes. Fig. 3 shows the temperature dependence ionic conductivity of gel polymer electrolytes. It can be observed that the conductivity-temperature relationship of both gel polymer electrolyte systems (with and without BMII) follows the Arrhenius behaviour (regression value close to 1):

$$\sigma = \sigma_0 \exp \left( -\frac{E_a}{k_B T} \right)$$  \hspace{1cm} (2)

Where $\sigma_0$ is pre-exponential factor, $E_a$ is activation energy, $k_B$ is Boltzmann constant and $T$ is temperature. From Fig. 3 and Eq. (2), the $E_a$ value of each gel polymer electrolyte can be obtained. The $E_a$ value is found to be the same (around 0.1 eV) for all gel polymer electrolytes having different TPAI and BMII concentration as stated in Fig. 3. This may be due to their very close ionic conductivity values. Another possible explanation is because the characteristics of PhCh based gel polymer electrolyte in this work is more likely similar to the liquid type electrolyte where the co-solvent used is the only factor determining the activation energy instead of the amount of salt [28].

3.2. j-V characteristics of DSSCs

Fig. 4 shows the j-V characteristics of DSSCs with gel polymer electrolytes having different amounts of TPAI and BMII. Their

![Fig. 2. Conductivity of gel polymer electrolytes having different TPAI salt concentration.](image-url)
performance parameters are shown in Table 2. It can be clearly seen that the $J_{sc}$ and efficiency follow the conductivity trend. For gel polymer electrolytes having different amounts of TPAl salt, the highest conducting gel polymer electrolyte (22.7 wt.% TPAl) also exhibits the highest $J_{sc}$ of 16.76 mA cm$^{-2}$ and an efficiency of 7.10%. The $J_{sc}$ and efficiency values drop to 14.38 mA cm$^{-2}$ and 6.36%, respectively for DSSCs with gel polymer electrolytes having 24.5 wt.% TPAl which is similar to the conductivity trend. It is clear that the highest $J_{sc}$ and efficiency of DSSC having highest conducting PhCh-TPAl electrolyte obtained in this work are higher than those reported by Yusuf et al. [22]. They reported a $J_{sc}$ of 7.38 mA cm$^{-2}$ and an efficiency of 3.50% for DSSC with PhCh based gel polymer electrolyte having 19 wt. % of TPAl. An efficiency of 4.30% has been reported by Bandara et al. [25] for DSSC having TPAl salt in PAN based gel polymer electrolyte. Among the quaternary ammonium iodides salts, they have reported that TPAl gives the highest $J_{sc}$ and efficiency. Although the iodide transference number of TPAl is not the highest among the other quaternary ammonium iodide salts, but its conductivity is the highest [25]. The mechanism and working principle of DSSC can be explained as follows; the incident photons ($h\nu$) were absorbed by dye molecules ($D$), get excited ($D^*$) when gain enough energy and release electrons ($D^*$) to conduction band of TiO$_2$ (called injection) as shown in Eqs. (3) and (4).

\[ h\nu + D \rightarrow D^* \]  

(3)

\[ D^* + TiO_2 \rightarrow D^+ + e_{cb}(TiO_2) \]  

(4)

The injected electrons will be then transferred to Pt counter electrode through TiO$_2$ network and external circuit. The arriving electrons at Pt counter electrode will be transferred back to the dye molecules at photoanode through the diffusion of iodide ($I^-$) ions in gel polymer electrolyte.

\[ I_3^- + 2e^- (Pt) \rightarrow 3I^- \quad \text{(diffuse to photanode)} \]  

(5)

\[ 2D^+ + 3I^- \rightarrow I_3^- + 2D \]  

(6)

$I_3^-$ in gel polymer electrolyte will accept electrons from Pt counter electrode and reduced to $I^-$ ions (Eq. (5)). These $I^-$ ions will be oxidized back to $I_3^-$ when it is diffused to photoanode and release electrons to highest occupied molecular orbital (HOMO) of dye molecule to complete the circuit (Eq. (6)). Apparently, $I^-$ and $I_3^-$ ions in gel polymer electrolyte are the determining factor in DSSCs’ performance since the other components are same. When BMII is added to gel polymer electrolyte, the $J_{sc}$ increases up to 19.55 mA cm$^{-2}$ for 8 wt.% of BMII. Meanwhile, $V_{oc}$ value slightly increases from around 0.65 V for the electrolytes without BMII to around 0.70 V for the electrolytes added with BMII. The higher value of $V_{oc}$ shows that the Fermi level of TiO$_2$ for DSSCs with gel polymer electrolytes having BMII is shifted to more negative energy. The highest efficiency of 9.61% is obtained for the DSSCs with electrolyte D. Since the conductivity of gel polymer electrolytes added with various BMII content is considered to be the same for all four electrolytes, the diffusion coefficient of $I_3^-$ is worthy to investigate.

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**Table 2**: Conductivity and efficiency values for DSSCs with TPAl, BMII and BMII-TPAl gel polymer electrolytes (wt.%).

- **TPAl (1)**: Conductivity = 11.1 ± 1.2 mS cm$^{-1}$, Efficiency = 7.10%.
- **BMII (2)**: Conductivity = 13.5 ± 1.2 mS cm$^{-1}$, Efficiency = 6.36%.
- **TPAl + BMII (3)**: Conductivity = 9.61 ± 1.5 mS cm$^{-1}$, Efficiency = 3.50%.
- **TPAl + BMII + TPAl (4)**: Conductivity = 7.38 ± 1.2 mS cm$^{-1}$, Efficiency = 4.30%.

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**Fig. 3**: Temperature dependence conductivity for different (a) TPAl concentration (E1 = 21.7 wt.%, E2 = 22.7 wt.%, E3 = 23.6 wt.%, and E4 = 24.5 wt.%) and (b) BMII concentration (A = 2 wt.%, B = 4 wt.%, C = 6 wt.%, and D = 8 wt.%).
produced constant anodic current systems measure could be achieved. The characteristic diffusion-limited current will be increased with the increment of voltage until a constant or steady state current is achieved. Fig. 5 shows the characteristic linear sweep voltammetry curves for the electrolytes systems containing different compositions of (a) TPAI and (b) BMII. The anodic and cathodic limiting current plateaus are quite similar which indicates the equilibrium steady state condition. It is to be noted that the limiting current is for triiodide ions (I$_3^-$) as the iodide concentration (I$^-$) is more than the concentration of I$_3$. Hence, limiting current ($J_{lim}$) can only be used to determine the apparent diffusion coefficient of triiodide ions, $D_{I_3^-}$ according to the following relation [29]:

$$D_{I_3^-} = \frac{J_{lim}}{2nF} \frac{2\delta}{C_{I_3^-}}$$  \hspace{1cm} (7)

where $n=2$ is the number of electron required for the reduction of triiodide to iodide (Eq. (5)), $C_{I_3^-}$ is the concentration of $I_3^-$ ions per unit volume and $F$ is the Faraday constant. $\delta$ is half of the thickness of the electrolyte. The $D_{I_3^-}$ values for TPAI and BMII varying GPE

![Fig. 4. j-V characteristics of DSSCs with (a) Electrolyte E1, E2, E3 and E4 (b) Electrolyte A, B, C and D.](image)

### Table 2

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
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<tr>
<td></td>
<td>Mean</td>
<td>Best</td>
<td>Mean</td>
<td>Best</td>
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<tr>
<td>E1</td>
<td>13.49 ± 0.13</td>
<td>13.58</td>
<td>0.63 ± 0.01</td>
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<tr>
<td>E2</td>
<td>16.37 ± 0.42</td>
<td>16.56</td>
<td>0.65 ± 0.01</td>
<td>0.66</td>
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<tr>
<td>E3</td>
<td>14.95 ± 0.30</td>
<td>15.15</td>
<td>0.65 ± 0.01</td>
<td>0.66</td>
</tr>
<tr>
<td>E4</td>
<td>14.33 ± 0.05</td>
<td>14.38</td>
<td>0.67 ± 0.01</td>
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</tr>
<tr>
<td>A</td>
<td>17.24 ± 0.15</td>
<td>17.34</td>
<td>0.71 ± 0.01</td>
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</tr>
<tr>
<td>B</td>
<td>17.81 ± 0.15</td>
<td>18.02</td>
<td>0.71 ± 0.01</td>
<td>0.71</td>
</tr>
<tr>
<td>C</td>
<td>18.66 ± 0.30</td>
<td>18.87</td>
<td>0.72 ± 0.01</td>
<td>0.73</td>
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<tr>
<td>D</td>
<td>19.61 ± 0.07</td>
<td>19.68</td>
<td>0.71 ± 0.01</td>
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3.3. Diffusion coefficient of $I_3^-$

Linear sweep voltammetry (LSV) technique was applied to measure diffusion-limited current where the steady state current could be achieved (Fig. 5). When voltage is applied, current will be produced due to the diffusion of $I^-$ and $I_3^-$ in the electrolyte. The current will be increased with the increment of voltage until a constant or steady state current is achieved. Fig. 5 shows the characteristic linear sweep voltammetry curves for the electrolytes systems containing different compositions of (a) TPAI and (b) BMII. The current attain saturations for both polarities at about 0.3 V. The anodic and cathodic limiting current plateaus are quite similar which indicates the equilibrium steady state condition. It is to be
systems are tabulated in Table 3. The values of $D_{i_3}$ slightly decrease with the increase of TPAl concentration from $2.0 \times 10^{-7}$ cm$^2$s$^{-1}$ for electrolyte E1 to $1.9 \times 10^{-7}$ cm$^2$s$^{-1}$ for electrolyte E2. This behaviour was not observed in the conductivity of these electrolytes. Although the $D_{i_3}$ value of electrolyte E2 is slightly lower than that of electrolyte E1, it does not clearly affect the conductivity of the electrolyte and DSSC performance which probably due to the higher number density of $I^-$ ions that resulting in higher conductivity and $J_{sc}$. The $D_{i_3}$ value further decreases in electrolytes E3 and E4. One may interpret the phenomena as after a certain concentration of $I_3^-$, the distance between anion and cation might not be sufficient to overcome completely the electrostatic force of attraction among the ions and results in lower diffusion rate of $I_3^-$. ions, i.e. the lowering of the dissociation of the salt. The $D_{i_3}$ value increases with the addition of BMII and reaches the highest value at $3.9 \times 10^{-7}$ cm$^2$s$^{-1}$ in electrolyte D. With addition of BMII ionic liquid, the total volume of the sample was increased almost 2 times as compared to that without BMII. This will lead to decrease in viscosity of gel polymer electrolytes and hence increases the diffusion coefficient of triiodide ions. This explains why the $J_{sc}$ value increases with the addition of BMII. Hauch and Georg [30] has determined the diffusion coefficient of $I_3^-$ ions in acetonitrile using steady state current measurement and obtained the value of $1.4 \times 10^{-7}$ cm$^2$s$^{-1}$. The $D_{i_3}$ values obtained for gel type polymer electrolytes in this work are comparable with that reported in the literature [31]. The $I_3^-$ diffusion coefficient of $3.32 \times 10^{-7}$ cm$^2$s$^{-1}$ in PAN based gel polymer electrolyte has been reported by Wanninayake et al. [31].

### Table 3

$D_{i_3}$ obtained from steady state current measurement for different gel polymer electrolytes.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$J_{lm}$ (mA cm$^{-2}$)</th>
<th>$D_{i_3}$ ($\times 10^{-7}$ cm$^2$s$^{-1}$)</th>
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<tbody>
<tr>
<td>E1</td>
<td>10.9</td>
<td>2.0</td>
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<tr>
<td>E2</td>
<td>10.9</td>
<td>1.9</td>
</tr>
<tr>
<td>E3</td>
<td>10.0</td>
<td>1.7</td>
</tr>
<tr>
<td>E4</td>
<td>9.6</td>
<td>1.5</td>
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<tr>
<td>A</td>
<td>7.9</td>
<td>2.9</td>
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<tr>
<td>B</td>
<td>8.3</td>
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</tr>
<tr>
<td>C</td>
<td>9.3</td>
<td>3.3</td>
</tr>
<tr>
<td>D</td>
<td>10.7</td>
<td>3.9</td>
</tr>
</tbody>
</table>

*Steady state current method (Eq. (7))*

3.4. Electrochemical impedance spectroscopy of DSSCs

Other important factor for the DSSCs is the impedance of TiO$_2$- dye/electrolyte interface [30] which can be obtained from the impedance measurement of DSSCs. Fig. 6 shows the Nyquist plots of DSSCs with gel polymer electrolytes having different (a) TPAl and (b) BMII concentrations. A typical three semicircles in impedance spectrum of DSSC can be observed. First semicircle at high frequency region corresponds to the charge transfer resistance, $R_{ct}$ and double layer capacitance, $Q_{dl}$ at Pt counter electrode/electrolyte interface. Second semicircle at intermediate
frequency region is associated to the charge recombination resistance, $R_{CT}$ and chemical capacitance, $Q_{CT}$ at TiO$_2$ electrode/electrolyte interface whereas the third semicircle region corresponds to the diffusion in gel polymer electrolyte ($Z_D$). The impedance plots of the DSSCs seem not to start with zero impedance at the real axis which is attributed to the series resistance, $R_s$ in the cells. Due to the imperfect semicircle (imperfect capacitor), the constant phase element, CPE was used ($CPE_{Pt}$ and $CPE_{CT}$). Thus, the equivalent circuit of the impedance plots is shown in Fig. 6 (c) which can be represented as [32–34]:

$$Z_{DSSC} = R_s + \frac{R_{Pt}}{1 + (j\omega)^m R_{Pt}CPE_{Pt}} + \frac{R_{CT}}{1 + (j\omega)^n R_{CT}CPE_{CT}} + \frac{D_3}{j\omega d^2} - \delta$$  

where $n_{Pt}$ and $n_{CT}$ are the CPE index at the Pt counter electrode/electrolyte and TiO$_2$ electrode/electrolyte interface, respectively. $R_D$ is related to the Warburg diffusion resistance, $\delta$ is the effective diffusion length (half of the thickness of the sample as mentioned earlier). From Fig. 6 (a) and (b), it can be observed that all the impedance plots are well-fitted.

The charge transfer parameters of DSSCs obtained from the fitted impedance plots are tabulated in Table 4. The average series resistance of DSSCs using electrolytes with and without BMII content was $14.4\ \Omega$ and $14.8\ \Omega$, respectively. By reducing $R_s$ value, the DSSC performance can probably be improved. However, the main contribution to the series resistance in DSSC is the sheet resistance of FTO glass and by lowering the sheet resistance, the transmittance will also be reduced [35]. Liu et al. [36] reported that the $R_s$ value can be reduced by implementation of silver grid lines on the transparent conducting oxide (TCO) glass. They have reported that the $R_s$ value decreased from about $48\ \Omega$ to 3 $\Omega$. In this work, the value of $R_s$ is only slightly varied and thus can be negligible. From Table 4, it is clear that the charge recombination resistance, $R_{CT}$ is higher in DSSCs with gel polymer electrolytes having BMII. Therefore, the combination of higher diffusion coefficient of $I_3^-$ ions in gel polymer electrolytes having BMII together with lower recombination rate gives the higher efficiency of DSSCs. The values of diffusion coefficient of $I_3^-$ ions obtained from fitting in Fig. 6 are also tabulated in Table 4. It can be observed

![Fig. 6. Impedance plots of DSSCs with electrolytes having different (a) TPAI concentration (b) BMII concentration and (c) their equivalent circuit.](image-url)
that the $D_{1}$ values are comparable with the $D_{1}$ values obtained from the steady state measurement. The capacitance values of TiO$_2$-electrolyte and counter electrode/electrolyte interface lie within $10^{-3}$ F.

4. Conclusions

The highest conductivity obtained for phthalocyanitosh based gel polymer electrolyte without BMII ionic liquid was 11.1 $\pm$ 1.2 mS cm$^{-1}$ for electrolyte having 22.7 wt. % TPAl. No significant increment in conductivity value has been observed when BMII was added (13.5 $\pm$ 1.2 mS cm$^{-1}$ for electrolyte having 8 wt. % BMII). Temperature studies of ionic conductivity shows that the gel polymer electrolytes behave like liquid electrolyte where the activation energy has not changed with the amount of salt. Although the ionic conductivity of gel polymer electrolytes shows no major change in value with BMII addition, the diffusion coefficient of triiodide ions obtained from steady state measurement method increases. The highest triiodide diffusion coefficient of 3.9 $\times$ 10$^{-6}$ cm$^2$ s$^{-1}$ was obtained for gel polymer electrolyte having 8 wt. % BMII. The optimized phthalocyanitosh based gel polymer electrolyte exhibited the highest $J_{sc}$ of 19.68 mA cm$^{-2}$ and efficiency of 9.61%.

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References