Hydroxypropyl Cellulose Based Non-Volatile Gel Polymer Electrolytes for Dye-Sensitized Solar Cell Applications using 1-methyl-3-propylimidazolium iodide ionic liquid

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Gel polymer electrolytes using imidazolium based ionic liquids have attracted much attention in dye-sensitized solar cell applications. Hydroxypropyl cellulose (HPC), sodium iodide (NaI), 1-methyl-3-propylimidazolium iodide (MPII) as ionic liquid (IL), ethylene carbonate (EC) and propylene carbonate (PC) are used for preparation of non-volatile gel polymer electrolyte (GPE) system (HPC:EC:PC:NaI:MPII) for dye-sensitized solar cell (DSSC) applications. The highest ionic conductivity of $7.37 \times 10^{-3}$ S cm$^{-1}$ is achieved after introducing 100% of MPII with respect to the weight of HPC. Temperature-dependent ionic conductivity of gel polymer electrolytes is studied in this work. XRD patterns of gel polymer electrolytes are studied to confirm complexation between HPC polymer, NaI and MPII. Thermal behavior of the GPEs is studied using simultaneous thermal analyzer (STA) and differential scanning calorimetry (DSC). DSSCs are fabricated using gel polymer electrolytes and J-V characteristics of fabricated dye sensitized solar cells were analyzed. The gel polymer electrolyte with 100 wt.% of MPII ionic liquid shows the best performance and energy conversion efficiency of 5.79%, with short-circuit current density, open-circuit voltage and fill factor of 13.73 mA cm$^{-2}$, 610 mV and 69.1%, respectively.

The investigations on dye-sensitized solar cells have dramatically increased in recent decades due to low cost, easy fabrication and carbon free advantage of (DSSCs)1,2. One of the big challenges for DSSC fabrication is electrolyte preparation. Among the electrolytes, liquid electrolyte is widely used for DSSC fabrication but they have some disadvantages such as liquid linkage and corrosion. One method to overcome this issue is through usage of gel electrolytes3,4. Gel polymer electrolytes (GPEs) have also been extensively investigated for DSSC fabrication5-9. Therefore, gel polymer electrolytes (GPEs) are a good alternative for DSSC applications because of advantages such as low vapor pressure, excellent contacting and filling properties between the nanostructured electrode and counter electrode, higher ionic conductivity compared to the conventional polymer electrolytes, excellent thermal stability and outstanding long-term stability10. Consequently, cellulose based polymer electrolytes are incorporated in several researches for electrochemical applications11-14 including DSSC applications due to good mechanical performance and thermal stability15.

Ionic Liquids (ILs) are good candidates as plasticizers and liquid salts for gel polymer electrolytes and electrochemical applications due to their negligible vapor pressure, non-inflammability, excellent chemical and thermal stability and high ionic conductivity16. Among the ionic liquids, imidazolium iodide based ionic liquids are widely used for dye-sensitized solar cell (DSSC) applications because of better performance17-21. Some kinds of imidazolium based ionic liquids or electrolytes synthesized by UV-cured22 procedure or in some novel ionogel forms23.
can be used in DSSCs as well. Furthermore, 1-methyl-3-propylimidazolium iodide (MPII) provides excellent efficiency and good stability in dye-sensitized solar cells.

In this work, hydroxylpropyl cellulose, sodium iodide and MPII were used to prepare gel polymer electrolytes. Ionic conductivity and temperature-dependent conductivity studies were carried out using electrochemical impedance spectroscopy (EIS). Structural characterization was performed using X-Ray diffraction (XRD). Thermal behaviors of samples were studied using simultaneous thermal analyzer (STA) and differential scanning calorimetry (DSC). The gel polymer electrolyte based dye-sensitized solar cells were fabricated and tested under Sun simulator.

**Results and Discussion**

The variation of the ionic conductivity with MPII ionic liquid content is exhibited in Fig. 1. The highest ionic conductivity of $7.37 \times 10^{-3}$ S/cm was achieved after addition of 100 wt.% of MPII ionic liquid (HNaP-5). Table 1 shows the ionic conductivity values for all GPEs. The results show that ionic conductivity dramatically increased after addition of MPII ionic liquid. This can be due to the increase of mobile ions after incorporation and addition of MPII ionic liquid. On the other hand, due to the high self-dissociating and ion-transporting abilities of the constituent ionic liquid, its conductivity increases with the carrier numbers in the polymer electrolytes. Besides that, the increase of the amount of the ionic liquid weakens the interaction among the polymer chains, accelerates the decoupling of the ion transport from polymer segmental motion.

Figure 1. Variation of Ionic conductivity with MPII ionic liquid content.

![Graph showing variation of ionic conductivity with MPII ionic liquid content.](image)

**Table 1. Designation and ionic conductivity of GPE system.**

| Designation | HMII ionic liquid (wt.%) | Conductivity, $\sigma$ (S cm$^{-1}$) |
|-------------|--------------------------|--------------------------------------|
| HNaP-0      | 0                        | $4.94 \times 10^{-3}$                |
| HNaP-1      | 20                       | $5.85 \times 10^{-3}$                |
| HNaP-2      | 40                       | $5.79 \times 10^{-3}$                |
| HNaP-3      | 60                       | $5.93 \times 10^{-3}$                |
| HNaP-4      | 80                       | $6.49 \times 10^{-3}$                |
| HNaP-5      | 100                      | $7.37 \times 10^{-3}$                |

where $\sigma$ is ionic conductivity, $T$ is the absolute temperature, $E_a$ is activation energy, $A$ is pre-exponential factor, $T_o$ is the reference temperature related to the equilibrium state glass transition temperature and $k_B$ is the Boltzmann constant. The regressions (R$^2$~0.99) denotes that the results are almost fitted to the VTF equation. The activation energies have been calculated and inserted in Fig. 2.

The XRD patterns of HPC:EC:PC:NaI:MPII system are represented in Fig. 3. The graph shows XRD patterns of HNaP-1, HNaP-2, HNaP-3, HNaP-4 and HNaP-5. The XRD patterns of GPEs show decrease of intensity with the addition of MPII ionic liquid content. The lowest intensity is achieved with incorporation of 100 wt.% of MPII ionic liquid.
liquid. Consequently, the variation of intensity in gel polymer electrolytes after addition of MPII can be expected as the evidence of complexation between HPC polymer and MPII ionic liquid.

Thermal behavior of HPC:EC:PC:NaI:MPII GPE system was studied using simultaneous thermal analyzer (STA) and differential scanning calorimetry (DSC). The HNaP-3, HNaP-4 and HNaP-5 GPEs were analyzed using STA and thermograms show decomposition temperature ($T_{\text{dec}}$) of 151, 154 and 155°C, respectively. The STA thermograms show a slight increase in $T_{\text{dec}}$ upon addition of MPII ionic liquid. Figure 4 illustrates the thermal analysis results of DSC for HNaP-0, HNaP-3, HNaP-4 and HNaP-5. The glass transition temperature ($T_g$) for HNaP-0, HNaP-3, HNaP-4 and HNaP-5 performed using DSC were $-107.9$, $-107.4$, $-107.7$ and $-107.1$ °C, respectively. The DSC thermographs show that the $T_g$ is almost unchanged after addition of MPII ionic liquid which is around $-107$ °C. Since the increase in ionic conductivity with addition of MPII (according to Fig. 1) may be due to increasing number of charge carriers, therefore the $T_g$ became almost unchanged in different MPII weight ratios. The thermal results show the effect of MPII ionic liquid on GPE system with complexation between HPC, NaI and MPII.

The GPEs were sandwiched between two anode and cathode to fabricate DSSC cell. The DSSC cells were fabricated with HNaP-1, HNaP-2, HNaP-3, HNaP-4 and HNaP-5. The GPE without MPII ionic liquid (HNaP-0) was fabricated to compare the results before and after incorporation of MPII ionic liquid. The efficiency ($\eta$) was calculated using

$$\eta = \frac{J_{\text{sc}} V_{\text{oc}} FF}{P_{\text{in}}}$$

(2)

where $P_{\text{in}}$ is incident light power, $J_{\text{sc}}$ (mA cm$^{-2}$) and $V_{\text{oc}}$ (V) are short-circuit current density and open-circuit voltage and FF is fill factor. The fill factor was calculated as

$$FF = \frac{P_{\text{max}}}{J_{\text{sc}} V_{\text{oc}}}$$

(3)
where \( P_{\text{max}} \) (mW cm\(^{-2}\)) is the maximum power of solar cell. The DSSC cell was analyzed under Sun simulator with light power of 100 (mW cm\(^{-2}\)). Figure 5 exhibits the J-V characteristic curves of DSSC cells and the inset image shows the prepared free standing GPEs. The GPEs containing MPII ionic liquid show significant enhancement of DSSC efficiency compared with GPE without ionic liquid (HNaP-0). The DSSC parameters are represented in Table 2. The energy conversion efficiencies of 3.94, 4.23, 4.27, 4.80, 5.19 and 5.79% was achieved with HNaP-0, HNaP-1, HNaP-2, HNaP-3, HNaP-4 and HNaP-5 gel polymer electrolytes, respectively. The highest energy conversion efficiency of 5.79% was achieved after incorporation of 100 wt.% of MPII with DSSC parameters namely \( J_{\text{sc}} \) (mA cm\(^{-2}\)), \( V_{\text{oc}} \) (mV), \% FF of 13.73, 610 and 69.1 in the HPC:EC:PC:NaI:MPII GPE based DSSCs. The results further indicate that the open-circuit voltage increases after addition of MPII ionic liquid. Consequently, efficiency increases dramatically after the addition of 80 and 100 wt.% of MPII ionic liquid. This can be due to

Table 2. Dye-sensitized solar cell parameters for HPC:EC:PC:NaI:MPII GPE system.
more plasticization effect after the addition of MPII ionic liquid, which results in the highest electron movement and mobility in RNaP-5 followed by increase in the current density of the solar cell. Moreover, the results reveal that open-circuit voltage (Voc) and fill factor (ff) increase with increase in the ionic conductivity which Voc and ff is the highest at HNaP-5 which has the highest ionic conductivity. There is a slight increase in Jsc values with increase in the ionic conductivity. Figure 6 shows effect of MPII ionic liquid on energy conversion efficiency, which maximizes at 100 wt.% of MPII. This work shows significant energy conversion efficiency enhancement of GPE based DSSC with incorporation of MPII ionic liquid.

In conclusion, the gel polymer electrolytes were prepared using EC, PC, NaI and MPII without solvents such as water, acetone, acetonitrile, etc. The highest ionic conductivity of $7.37 \times 10^{-3}$ S/cm was achieved with incorporation of 100 wt.% MPII ionic liquid with respect to the HPC weight. Temperature-dependent ionic conductivity study confirmed that all GPEs follow Arrhenius thermal activated model. Structural and thermal analyses confirmed complexation between HPC, NaI and MPII. XRD results indicated that the intensity of XRD patterns decrease with addition of MPII. Dye-sensitized solar cells were fabricated using HNaP-0, HNaP-1, HNaP-2, HNaP-3, HNaP-4, and HNaP-5 as gel polymer electrolytes and analyzed under Sun simulator in 100 mW/cm². The J-V graph showed energy conversion efficiencies of 3.94, 4.23, 4.27, 4.80, 5.19, and 5.79% using HNa-5, HNaP-1, HNaP-2, HNaP-3, HNaP-4 and HNaP-5 gel polymer electrolytes, respectively. The highest efficiency of 5.79% was achieved with incorporation of 100 wt.% of MPII ionic liquid.

Methods

Materials. Hydroxylpropyl cellulose (HPC) ($M_w \sim 370000$), purchased from Aldrich was used without further purification. Sodium iodide salt (NaI) was purchased from Sigma-Aldrich (assay ≥ 99%). The 1-methyl-3-pyridinium iodide (MPII) ionic liquid was purchased from Aldrich. The HPC, NaI and MPII were kept dry before use. TiO2 P90 (14 nm) and P25 (21 nm) were purchased from AEROXIDE.

Gel polymer electrolyte (GPE) preparation. The gel polymer electrolytes were prepared through heating and stirring process to gelatinize the HPC. Ethylene carbonate (EC) and propylene carbonate (PC) as plasticizer and iodine (I2) as redox mediator were used. The gel polymer electrolytes follow the equation HPC:EC:PC:NaI:xMPII, where x is 20, 40, 60, 80 and 100 wt.% with respect to the HPC weight. Table 1 shows designation of the system. The weights of HPC, EC, PC and NaI were kept at 0.5, 5.0, 5.0 and 0.5 g respectively. The ratio of NaI was optimized before starting the MPII based system. To begin with, the EC and PC was mixed and stirred in a glass bottle and heated at about 100 °C. Subsequently, NaI salt was added into the solution and stirred continuously. MPII ionic liquid was added into the mixture as well. To provide I⁻/I₃⁻ redox mediator, iodine was added to the mixture where molar ratio of NaI salt and iodine (NaI:I₂) is 10:1. The mixture was further heated and stirred and HPC was added slowly to the mixture during stirring. The stirring was continued to get a homogenous and gelatinized mixture. After the gel polymer electrolyte was formed, the sample was cooled to room temperature and immediately subjected to electrochemical impedance spectroscopy.

Dye-sensitized solar cell (DSSC) fabrication. Photo-electrode layer was prepared with two TiO2 layers on the FTO substrate. The first layer was prepared using the spin coating technique. At the first layer which was spin coated, 0.5 g of TiO2 (P90) was grounded for 30 minutes with 2 ml HNO3 (PH = 1) in agate mortar and spin coated on FTO at 1000 rpm for 2 seconds followed by 2350 rpm for 60 seconds. Finally, the substrate was sintered at 450 °C for 30 min. For the second layer, 0.5 g of TiO2 (P25) was grounded for 30 minutes with 2 ml HNO3 (PH = 1) in an agate mortar with 1 drop of Triton X-100 and 0.1 g carbowax. The solution was then doctor bladed on the first layer and sintered at 450 °C for 30 min. After the substrate cooled down to room temperature, the photo-electrode was soaked in N719 dye solution for 24 hrs. Counter electrode was prepared using commercial platinum solution and coated on FTO substrate and sintered at 450 °C for 30 min. The prepared GPEs were sandwiched between two electrodes and analyzed under Sun simulator.

Characterization. For ionic conductivity and temperature-dependent conductivity study, the GPEs were studied using electrochemical impedance spectroscopy (EIS), Hioki, 3532-50 LCR HiTESTER. The XRD patterns
of GPEs were recorded using PANalytical Empyrean diffractometer (45 kV, 40 mA) with Cu-Kα radiation and wavelength of λ = 1.54060 Å for 2θ range of 3–80° at ambient temperature. The GPEs were subjected to thermal studies using simultaneous thermal analyzer (STA) PERKIN ELMER (STA 6000). The Nitrogen flow rate was 20 ml/min. The samples were heated with ramping rate of 10 K/min from 25 to 600 °C to obtain decomposition temperature (T_d). Gel polymer electrolytes were further analyzed using differential scanning calorimetry (DSC) using NETZSCH DSC 200 F3 with liquid nitrogen cooling system. The experiment was performed under a nitrogen flow rate of 50 ml/min. The GPEs were sealed in the aluminum pan and analyzed in heat-cool-heat process within 4 cycles with heating and cooling rate of 10 K/min. In the first cycle, the sample was cooled from room temperature to −140 °C. In cycle 2, the heating process was performed from −140 °C to 130 °C. In cycle 3, the cooling process was applied from 130 °C to −140 °C. In Cycle 4, the final cycle, heating process was applied from −140 °C to 130 °C. At the end of each cycle, an isothermal process was applied for 1 minute. Cycle 2 was used to measure glass transition temperature (T_g).

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