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ORIGINAL PAPER

Ionic conductivity improvement in poly (propylene) carbonate-based gel polymer electrolytes using 1-butyl-3-methylimidazolium iodide (BmimI) ionic liquid for dye-sensitized solar cell application

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Abstract Gel polymer electrolytes (GPEs) are prepared by mixing poly (propylene) carbonate (PPC) with various weight percentages of 1-butyl-3-methylimidazolium iodide (BmimI) ionic liquid. The GPEs consist of PPC host polymer, NaI iodide salt, ethylene carbonate (EC), propylene carbonate (PC), BmimI ionic liquid, and iodine (I_2). The optimum BmimI ionic liquid content was found to be 60 wt% with respect to the wt% of PPC polymer with the highest ionic conductivity of 4.79×10^{-3} S cm^{-1}. Temperature-dependent ionic conductivity studies exhibited that gel polymer electrolytes obey Arrhenius thermal-activated model. X-ray diffraction (XRD) study confirms the complexation between host polymer (PPC polymer), sodium iodide salt, and BmimI ionic liquid. Dye-sensitized solar cells are fabricated and GPEs are sandwiched between the working and counter electrodes and tested under the one Sun illumination. The highest energy conversion efficiency of 6.14% is achieved with the addition of 60 wt% of BmimI.

Keywords Gel polymer electrolytes · Ionic liquid · PPC · BmimI · DSSC

Introduction

The consumption of fossil fuels and catastrophic environment issues are the reasons why we need to build renewable energy resources for the increasing energy demand [1]. In recent years, the replacement of traditional silicon photovoltaic cells with dye-sensitized solar cells (DSSCs) has been found as an alternative way due to several advantages: low cost, simple and easy to handle, environmentally friendly, and promising an excellent photovoltaic performance [2]. By using liquid electrolytes which consist of iodide/tri-iodide ions, the conversion efficiency of DSSCs has reached ~15% [3, 4]. However, problems like leakage and volatilization limit the long-lasting stability of the cells as well as not being practical for outdoor applications. Hence, to overcome these problems, solid and gel electrolytes have been introduced as the replacement for the liquid electrolytes. In DSSCs, gel polymer electrolytes (GPEs) are commonly used due to their advantages such as high ionic conductivity, offer a good contact between the electrolyte and the electrode, as well as filling properties to solve the leakage problems. Nevertheless, the performance of GPE is usually much lower than liquid electrolytes due to the movement of ions being hindered by the presence of gel network [5]. Therefore, to overcome this drawback, there are a few ways to improve the ionic conductivity and also the photovoltaic performance of DSSC-based gel polymer electrolytes.

One of the ways to enhance the performance of the GPE is the addition of ionic liquids containing high number of ionic carriers into the system. Ionic liquids are composed of anions and cations. The main advantages of ionic liquids over organic solvents are low vapor pressure, high ionic conductivity, good chemical and thermal stability, non-flammability, as well as wide electrochemical stability window [6–8]. The imidazolium iodide-based ionic liquids are widely used in

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DSSC as it may play the roles of both conductive medium and nonvolatile plasticizers in electrolytes as well as provide better performance in dye-sensitized solar cells [9, 10].

In this paper, poly (propylene) carbonate (PPC), sodium iodide, and BmimI ionic liquid were used to prepare GPE. We propose GPE based on PPC due to its high compatibility with carbonate-based organic solvents presently used in DSSCs. PPC contains carbonate groups in the backbone which can improve the interfacial contact between electrolyte and electrode, leading to the enhancement of the photovoltaic performance in DSSCs [11]. The electrochemical impedance of the GPEs was studied using electrochemical impedance spectroscopy (EIS). XRD patterns were collected to study the structural characteristics of the GPE system. The GPE-based dye-sensitized solar cells were fabricated and analyzed under Sun illumination for photovoltaic performances.

Experimental

Materials

Poly (propylene) carbonate (PPC) polymer, ethylene carbonate (EC), propylene carbonate (PC), sodium iodide (NaI), 1-butyl-3-methylimidazolium iodide (BmimI), and di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II) dye (N719) were purchased from Sigma-Aldrich. Iodine was purchased from Friedemann Schmidt Chemical. TiO_2 nanopowder P90 (14 nm) and P25 (21 nm) were purchased from AEROXIDE.

Preparation of gel polymer electrolytes

GPE was prepared using PPC polymer, NaI salt, BmimI ionic liquid, iodine (I_2), ethylene carbonate (EC) and propylene carbonate (PC). The mixture of gel polymer electrolytes follow the equation of PPC/EC/PC/NaI/[X]BmimI, where X is 20, 40, 60, 80, and 100 wt% of PPC polymer. The amount of PPC, EC, PC, and NaI was fixed to 1.0, 1.25, 1.25, and 0.6 g, respectively. The amount of NaI was optimized before starting the BmimI-based system. The iodine amount was one tenth of the molar ratio of the NaI. Appropriate amount of EC, PC, NaI, I_2, and BmimI ionic liquid were blended in a closed bottle and then continuously stirred at 100 °C until all the chemicals dissolved. Subsequently, PPC was added slowly in the mixture while stirring at 100 °C for 2 h to get a gelatinized and homogenous mixture. The resulting electrolyte was then cooled down at room temperature. This method was repeated for different compositions of the gel polymer electrolytes as shown in Table 1.

Fabrication of dye-sensitized solar cell

The working electrode was fabricated by coating two layers of TiO_2 on fluorine-doped tin oxide (FTO) glass; spin coating for the first layer followed by doctor-blading for the second layer [12]. At the first layer, the mixture of 0.5 g of TiO_2 (P90) and 2 ml of nitric acid (HNO_3) (pH = 1) were grounded for 30 min using agate mortar and then spin coated at: (i) 1000 rpm for 2 s and (ii) 2350 rpm for 60 s on the FTO glass and sintered at 450 °C for 30 min. While for the second layer, the mixture of 0.5 g of TiO_2 (P25), 2 ml of nitric acid (HNO_3), 1 drop of Triton X-100, and 0.1 g carbowax were grounded for 30 min and coated on the first layer using doctor blade method. Then, the electrode was sintered again at 450 °C for 30 min and then the substrate was allowed to cool down at room temperature. Lastly, the electrode was immersed in N719 dye for 1 day. Counter electrode was assembled by dropping an aqueous solution of chloroplatinic acid (H_2PtCl_6) and isopropyl alcohol (C_3H_7OH) with the ratio 1:1 on the FTO glass and then air dried. The electrode was then sintered at 100 °C for 5 min followed by 500 °C for 30 min. The resulting Pt electrode was washed using ethanol and the steps were repeated twice. Finally, the prepared GPE was sandwiched between the working and counter electrodes as represented in Fig. 1 and then tested under 1 sun illumination or for fabrication of DSSCs.

Characterization

The GPEs were studied using electrochemical impedance spectroscopy (EIS), HIOKI, 3532-50 LCR HiTESTER for ionic conductivity and temperature-dependent studies. Using PANAalytical Empyrean diffractometer (45 kV, 40 mA) with Cu-Kα radiation and wavelength of

Table 1 The ionic conductivity and activation energy of gel polymer electrolyte system

Designation	BmimI ionic liquid Composiion, (wt%)	Conductivity, σ (S cm^{-1})	Activation energy, E_a (eV)
BMIM-0	0	2.01×10^{-3}	–
BMIM-1	20	2.22×10^{-3}	0.202
BMIM-2	40	2.71×10^{-3}	0.185
BMIM-3	60	4.79×10^{-3}	0.144
BMIM-4	80	4.61×10^{-3}	0.169
BMIM-5	100	4.45×10^{-3}	0.224

λ = 1.540600 Å for 2θ range of 5–80°, the XRD patterns were obtained at ambient temperature.

Results and discussion

EIS studies of GPEs

Figure 2 illustrates the comparison of ionic conductivities between different BmimI ionic liquid contents. The ionic conductivity values for all GPEs were tabulated in Table 1. The optimum BmimI ionic liquid content was found to be 60 wt.% with the highest ionic conductivity of 4.79×10^{-3} S cm^{-1}. Figure 3 shows that the bulk resistance for sample BMIM-3 is lower compared to other samples indicating its highest ionic conductivity. This is due to the increasing number of mobile carriers in the presence of BmimI ionic liquid, which helps to improve the dissociation of NaI. Besides, one of the roles of ionic liquid is as plasticizer. Free movement of charge carriers in the BmimI ionic liquid provides more conducting pathway and could soften the polymer backbone as well as enlarge the spaces between the polymer network [13]. Moreover, the enhancement of ionic conductivity is also due to the amorphousness of the PPC polymer [14]. However, after further addition of ionic liquid, the ionic conductivity decreased because of the agglomeration of extra mobile ions. This causes the ions to pair among themselves, leading to the limitation of free charge carriers movement [14–16].

Figure 4 demonstrates temperature-dependent ionic conductivity results for all the GPEs. The ionic conductivity was measured between 30 and 100 °C. The almost straight line with the average regression value of ~0.97 was obtained which indicates that the system follows Arrhenius model. The Arrhenius model is represented by the following equation;

$$\sigma(T) = A\exp\left[\frac{-E_a}{kT}\right] \qquad (1)$$

where E_a is the activation energy (eV), k is the Boltzmann constant, A is pre-exponential constant, and T is absolute temperature. Using Eq. (1), the calculated activation energy is 0.144 eV for BMIM-3. The activation energy for all GPEs is listed in Table 1. The highest ionic conductivity of GPE is expected to have the lowest activation energy. This can be explained by the less energy needed by ions to hop from one allocation to another allocations [17]. Thus, greater ion transportation was achieved leading to the enhancement of ion conduction [5].

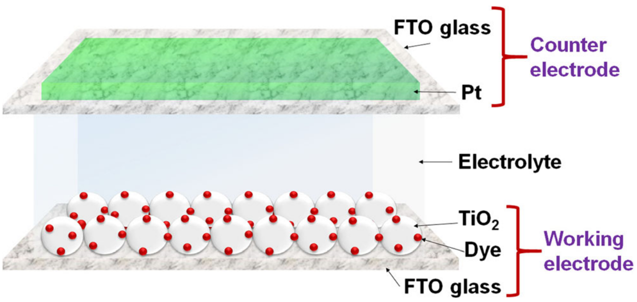

Fig. 1 Illustration of cell assembly of the DSSC

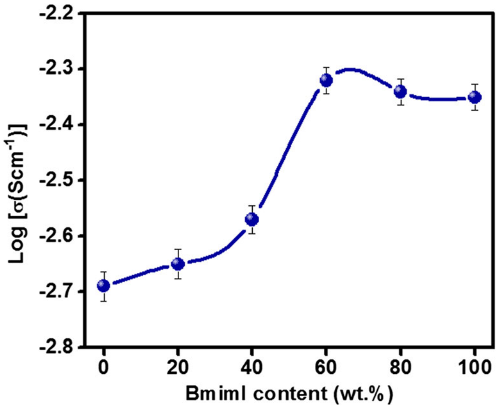

Fig. 2 Variation of ionic conductivity as a function of BmimI ionic liquid content in GPEs

X-ray diffraction

X-ray diffraction (XRD) patterns are demonstrated in Fig. 5 where Fig. 5a represents the XRD patterns for pure PPC polymer, pure NaI salt [18], and pure BmimI ionic liquid, respectively, while Fig. 5b demonstrates the XRD patterns of BMIM-2, BMIM-3, and BMIM-4, respectively. Apparently, the intensity of XRD patterns of GPEs was decreased after the addition of BmimI ionic liquid. With the addition of BmimI, the lowest intensity was achieved at 60 wt%. In addition, the peak of pure PPC was broader after the incorporation of BmimI ionic liquid and NaI salts indicating its higher amorphous structure. This confirms that the complexation between PPC polymer, NaI salt, and BmimI ionic liquid has occurred.

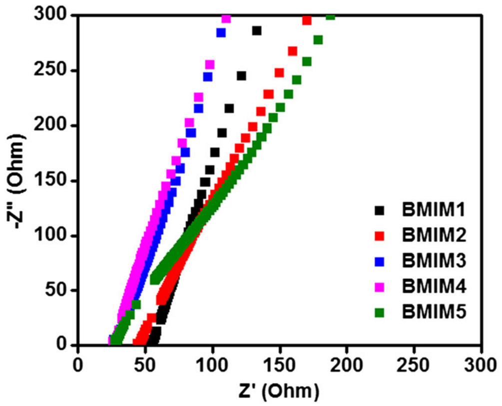

Fig. 3 Cole-Cole plot of GPE samples

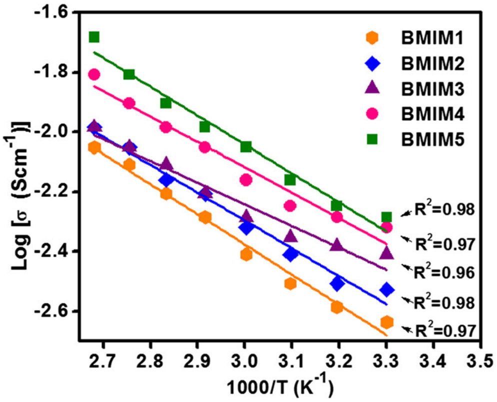

Fig. 4 Temperature-dependent ionic conductivity results of the GPEs

Dye-sensitized solar cells

Figure 6 illustrates the J-V results of the fabricated DSSC. The graph shows the highest energy conversion efficiency of 6.14%, exhibited by BMIM-3. The J-V parameters are shown in Table 2. The J-V results show the decrease in efficiency achieved by BMIM-4 which can be due to the decreased in ionic conductivity after the addition of 80 wt% BmimI. As for J_{sc}, it can be seen that there is a similar trend of J_{sc} with ionic conductivity. This is because in general J_{sc} is directly related to the mobility of charge carriers where the mechanism is similar to ionic conduction. The increment of J_{sc} is mainly due to the accumulation of the mobile charge from the ionic liquid. It can be noted that the obtained efficiency was lower than other related work which the efficiency was 6.42% [19] where the electrolyte used was liquid electrolyte which has fast ion diffusion due to its viscosity. It is worth mentioning that our work with efficiency up to 6.14% is comparable to other works using GPEs which achieved highest efficiencies of 5.41% [20], 5.0% [21], and 4.75% [22] in fabrication of DSSC.

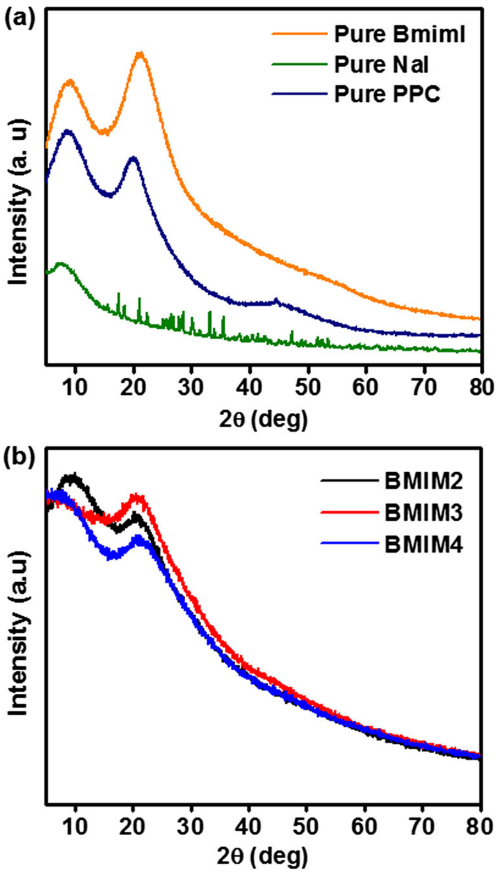

Fig. 5 **a** XRD patterns of pure PPC polymer, Pure NaI salt, and pure BmimI ionic liquid. **b** XRD patterns of GPEs for BMIM-2, BMIM-3, and BMIM-4

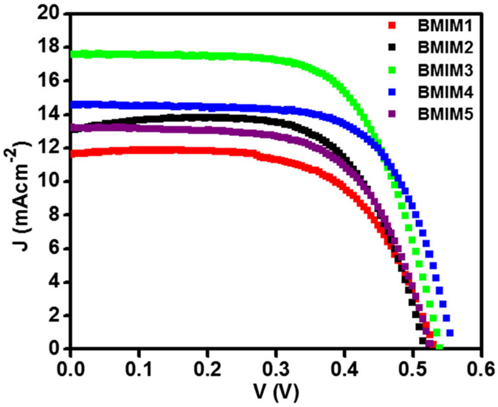

Fig. 6 Photocurrent density versus cell potential (J-V) for DSSC fabricated using BMIM-1, BMIM-2, BMIM-3, BMIM-4, and BMIM-5

Conclusion

New GPEs based on PPC complexed with NaI and BmimI ionic liquid was prepared. The ionic conductivity of the GPE was augmented with the incorporation of BmimI and the maximum value of ionic conductivity of 4.79×10^{-3} S cm^{-1} was achieved at 60 wt% of BmimI ionic liquid. The GPE system followed Arrhenius model with the activation energy of 0.144 eV for the highest ionic conductivity with incorporation of 60 wt% of BmimI ionic liquid. The XRD patterns show the successful complexation between pure PPC and BmimI ionic liquid. In addition, the highest energy conversion efficiency

Table 2 Dye-sensitized solar cell parameters for PPC/EC/PC/NaI/BmimI system

Electrolyte	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	Efficiency, η (%)
BMIM-1	11.625	0.529	62.9	3.87
BMIM-2	13.069	0.514	68.7	4.61
BMIM-3	17.560	0.539	64.9	6.14
BMIM-4	14.557	0.554	67.5	5.44
BMIM-5	13.221	0.524	63.4	4.39

of 6.14% is achieved after the addition of 60 wt% of BmimI ionic liquid.

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