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Synthesis of a grafted cellulose gel electrolyte in an ionic liquid ([Bmim]I) for dye-sensitized solar cells

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ABSTRACT

The cellulose was grafted homogeneously with acrylic acid by in situ polymerization in an ionic liquid 1-butyl-3-methylimidazolium iodide ([Bmim]I) as reaction medium. This polymer is suitable for quasi-solidification of electrolytes in DSSCs by in situ synthesis because the polymerization reaction proceeds in the ionic liquid containing iodide ion. Using the matrix as polymer host, KI and I_2 as ionic conductors, an ionic conductivity of the gel polymer electrolyte was achieved 7.33 mS cm^{-1}. Based on the optimized gel electrolyte, the best result of the quasi-solid state dye-sensitized solar cell (QS-DSSC) was the light-to-electricity conversion efficiency of 5.51% under a light intensity of 100 mW cm^{-2} (AM 1.5).

1. Introduction

Owing to low production cost and high efficiency for the conversion of solar energy to electric power, Dye-sensitized nanocrystalline solar cells (DSSCs) have been attracting widespread scientific and technological interest and have evolved as potential alternatives to traditional photovoltaic devices in the past decade (Grätzel, 2001). Based on liquid electrolytes, a photoelectric conversion efficiency of 11% for DSSC has been achieved (Grätzel, 2005). However, the potential problems caused by the liquid electrolytes, such as the leakage and volatilization of liquid, are considered as some of the critical factors limiting the long-term performance and practical use of the DSSCs (Smestad, 2003). Thus, the commercial exploitation of these devices needs the replacement of the liquid electrolyte by a solid or quasi solid-state charge-transport medium (Bach, Lupo, Comte, & Grätzel, 1998; Nogueira & Paoli, 2001; O'Regan, Lenzmann, Muis, & Wienke, 2002), which not only offers hermetic sealing and stability, but also reduces design restrictions and endows the DSSCs with shape choice and flexibility (Chatzivasiloglou, Stergiopoulos, Spyrellis, & Falaras, 2005).

The potential of ionic liquids as solvents for electrolytes for dye-sensitized solar cells has been investigated during the last decade. The non-volatility, good solvent properties and high electrochemical stability of ionic liquids make them attractive solvents in contrast to volatile organic solvents (Gorlov & Kloo, 2008). Despite this, ionic liquids still cannot solve the problem of leakage for DSSCs. An alternative solution is to use iodine/iodide redox couple dissolved in polymer electrolyte (Kang et al., 2004; Nogueira, Durrant, & De Paoli, 2001; Wang, Zakeeruddin, Comte, Exnar, & Grätzel, 2003), which has the advantages of relatively high ionic conductivity and easy solidification (Li, Wang, Kang, Wang, & Qiu, 2006). Polymer electrolytes obtained from natural polymers—as cellulose derivatives like hydroxyethyl cellulose (HEC) or hydroxypropyl cellulose (HPC)—have attracted attention in recent times because of their superior mechanical and electrical properties (Dragunski & Pawlicka, 2002; Morales, Le Nest, & Gandini, 1998; Tambelli et al., 2001). Cellulose derivatives are abundant, renewable, and biodegradable natural polymers and their use offer a promising alternative for the development of new polymer electrolyte materials (Nair et al., 2009). The cellulose derivative chains can be modified by condensation (graftization) reaction of –OH groups making possible the generation of a great variety of networks (Morales et al., 1998). The ionic conductivity results show that cellulose derivatives based networks are very good candidates for solid polymer electrolyte (Regiani, Machado, Le Nest, Gandini, & Pawlicka, 2001).

In this paper, a novel gel polymer electrolyte of grafted cellulose with acrylic acid was synthesized homogeneously by in situ polymerization in an ionic liquid 1-butyl-3-methylimidazolium iodide (BMIMI) as reaction medium. Using the grafted cellulose as host polymer, a gel-electrolyte with high conductivity of 7.33 mS cm^{-1}

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was prepared. The gel-electrolyte was used to assemble quasi-solid-state dye-sensitized solar cell (QS-DSSC). The electrolyte was optimized and the photovoltaic performance of this system was also evaluated.

2. Experimental

2.1. Materials

Cellulose powder, 1-butyl-3-methylimidazolium iodide ([Bmim]I), acrylic acid(AA), azodiisobutyronitrile (AIBN), potassium iodide (KI), iodine, acetic acid, and titanium iso-propoxide were all A.R. grade and all purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were used as received.

Conducting glass plates (FTO glass, Fluorine doped tin oxide over-layer, sheet resistance $8\,\Omega\,\mathrm{cm}^{-2}$, purchased from Hartford Glass Co., USA) were used as a substrate for precipitating TiO_2 porous film and were cut into $2 \times 1.5\,\mathrm{cm}^2$ sheets. Sensitizing organometallic dye *cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium (II) $[RuL_2(NCS)_2]$ was purchased from SOLARONIX, SA (Switzerland).

2.2. Preparation of grafted cellulose gel electrolytes

The synthesis of grafted cellulose with AA in the ionic liquid [Bmim]I was carried out according to the literature (Lin, Zhan, Liu, Fu, & Zhang, 2009). The cellulose powder (1.0 g) was added to [Bmim]I (25 g) in a three-neck flask. The mixture was stirred at 100 °C for 12 h to guarantee the complete dissolution. The flask was continuously purged with gaseous N_2. After completely dissolving, the temperature was lowered to 60 °C, and then AIBN (0.1 g, the initiator) and partially neutralized AA (4.0 g) were added. The polymerization reaction was conducted at 60 °C for 2 h. The products were cooled down to room temperature and stirred vigorously for 6 h. Then, the samples were dried by using a vacuum drying oven under 60 °C for 12 h.

The appropriate amounts of KI and I_2 (10 mol.% of KI) were dissolved in the above product, the resulting mixture was heated at 80 °C under vigorous stirring until a homogeneous composite was obtained, followed by cooling down to room temperature and stored in a desiccator before use.

2.3. Calculation of grafting percentage

After the graft reaction, the mixture was added to silicone oil containing a specific amount of Span 80 as dispersant at 80 °C and stirred for 30 min. Then the mixture was cooled down to room temperature and continuously stirred for 2 h. The mixture were filtered and washed several times with a mixture of methanol–water to remove unreacted monomer and the ionic liquid. The product was dried by using a vacuum drying oven under 60 °C for 6 h. Grafting percentage (GP) was calculated by the equations:

$$GP = \frac{W_b - W_a}{W_a} \times 100\%$$

where W_a is the weight of the original cellulose and W_b is the weight of the product after the graft reaction. The product was characterized by FT-IR.

2.4. Preparation of TiO_2 colloid

0.05 mol of acetic acid was added to 0.05 mol of titanium iso-propoxide under stirring at room temperature. The mixture was rapidly poured into 120 ml distilled water with vigorous stirring and a white precipitate was formed immediately. After a half hour stirring, acetic acid (12 ml) and nitric acid solution (65 wt.%, 1.2 ml) were added to the mixture. Then the mixture was heated to 80 °C and peptized for 12 h. The resultant mixture was autoclaved at 200 °C for 12 h to form a white suspension with some precipitate. The resultant suspension was concentrated to 1/4 of its volume, PEG-20000 (10 wt.% TiO_2) and a few drops of emulsification regent of Triton X-100 was added to the resultant colloidal solution with stirring. Then the colloidal solution was concentrated to form a TiO_2 paste of suitable concentration.

2.5. Fabrication of the QS-DSSCs

A quasi solid-state dye-sensitized solar cell (QS-DSSC) (active area of $0.25\,\mathrm{cm}^2$) was assembled according to the following procedure. Conducting glass sheet (FTO) was washed with ethanol and immersed in 50 mM $TiCl_4$ aqueous solution for 12 h in order to make a good mechanical contact between the following printed TiO_2 layer and conducting glass substrate. The TiO_2 electrode (TiO_2 film thickness about 6 μm) was obtained by spreading the TiO_2 paste on the conducting glass substrate using a “doctor blade method” and then sintered at 450 °C for 30 min in air. After cooling to 80 °C, the TiO_2 electrode was dye-sensitized with 0.5 mM cis-$[(dcbH_2)_2Ru(SCN)_2]$ solution in absolute ethanol for 24 h at room temperature. Afterwards, the dye-sensitized TiO_2 electrode was rinsed with absolute ethanol and dried in moisture-free air.

A quasi-solid-state dye-sensitized solar cell was fabricated by sandwiching a slice of polymer gel electrolyte between a dye-sensitized TiO_2 electrode and a platinum counter electrode (prepared by electrodeposition). The cell was heated at 60 °C for 30 min for complete penetration of the polymer gel electrolyte through the void of nanopores and then cooled to room temperature. The two electrodes were clipped together and a cyanoacrylate adhesive was used as sealant. Epoxy resin was used for further sealing the cell. From the above process, the polymer gel electrolyte had a good contact with the TiO_2 electrode.

2.6. Measurements

The ionic conductivity of electrolytes was measured by using a Russell RL060C digitized conductivity meter (Thermo Electron Corporation). A FT-IR spectrum sample in KBr was performed using a Nicolet Impact 410 spectrometer. Electrochemical measurements were done using a CHI-660D electrochemical work station with impedance analyzer in the dark. The frequency range is 0.005–10 kHz. The magnitude of the alternative signal is 50 mV. The photovoltaic test of dye-sensitized solar cells was carried out by measuring the *J–V* character curves (Solar Simulator 91192-SYS, NEWPORT, USA) under ambient atmosphere. The incident light intensity and the active cell area was $100\,\mathrm{mW\,cm}^{-2}$ and $0.25\,\mathrm{cm}^2$, respectively.

The photoelectronic performances were calculated by the following equations (Grätzel, 2000):

$$FF = \frac{V_{\max} \cdot J_{\max}}{V_{oc} \cdot J_{sc}} \tag{1}$$

$$\eta\ (\%) = \frac{V_{\max} \cdot J_{\max}}{P_{in}} \times 100\% = \frac{V_{oc} \cdot J_{sc} \cdot FF}{P_{in}} \times 100\% \tag{2}$$

where FF is fill factor, η is the light-to-electricity conversion efficiency, J_{sc} is the short-circuit current density ($\mathrm{mA\,cm}^{-2}$), V_{oc} the open-circuit voltage (V), P_{in} is the incident light power, and $J_{\max}$ ($\mathrm{mA\,cm}^{-2}$) and $V_{\max}$ (V) are the current density and voltage in the *J–V* curves, respectively, at the point of maximum power output.

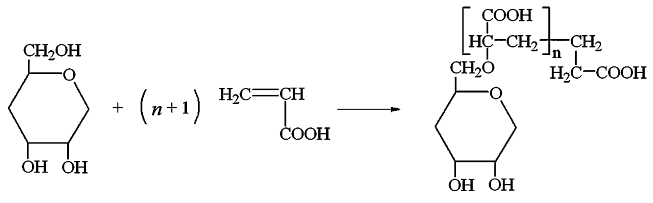

Fig. 1. Schematic reaction mode of the grafted cellulose with AA.

3. Results and discussion

3.1. FT-IR characterization of the grafted cellulose

The reaction mode of the cellulose and AA by graft copolymerization is schematically represented in Fig. 1 (Gurdag, Yasar, & Gurkynak, 1997). In this reaction, the grafting percentage could be more than 90%. After the reaction, the mixture was turned into gel from liquid state under the room temperature. Fig. 2 shows the FT-IR spectra of the cellulose (curve a) and the grafted cellulose (curve b). Compared with the spectrum of the cellulose (curve a), the FT-IR spectrum of the grafted cellulose (curve b) has all the characteristic absorbance signals of cellulose and also signature absorbance bands at 1727 cm^{-1} and 1269 cm^{-1}, which were attributed to the –C=O and C–O groups of the AA, respectively. The result confirmed the introduction of the AA side chain into the cellulose backbone via graft copolymerization (Lin et al., 2009).

3.2. Ionic conductivity of the grafted cellulose gel electrolyte

Generally, the overall light-to-electricity conversion efficiency of DSSCs is heavily dependent upon the mobility of the redox couple (I^-/I_3^-) and consequently on the ionic conductivity of the electrolyte (Kubo et al., 2001). In this regard, the ionic conductivity of the polymer electrolyte was studied.

Fig. 3 shows the ionic conductivity of the grafted cellulose gel electrolyte and the cellulose/[Bmim]I liquid electrolyte with the changed concentration of redox couple (triiodide/iodide) (the molar ratio of KI to I_2 is 10:1; the temperature is at 30 °C). The ionic conductivities of the electrolytes increase with the increased concentration of the redox couple, and there exist maximum values of ionic conductivity of both electrolytes. There are three main possible reasons for the phenomena: (1) the alkali-metal cation binds with the ether oxygens of the polyether molecules and that the viscosity increases with increasing salt concentration (Wixwat, Fu, & Stevens, 1990); (2) a high salt concentration can reduce the segmental motion of the polymer chains (Armand, 1990); (3) the larger ionic radius of I_{2n+3}^- ($n = 1, 2, 3, \ldots$) reduces the mobility of ions. From Fig. 2, it also can be seen that the ionic conductivity of the liquid electrolyte is higher than that of the gel electrolyte with the same redox couple concentration because of the higher the ions mobility of the liquid electrolyte.

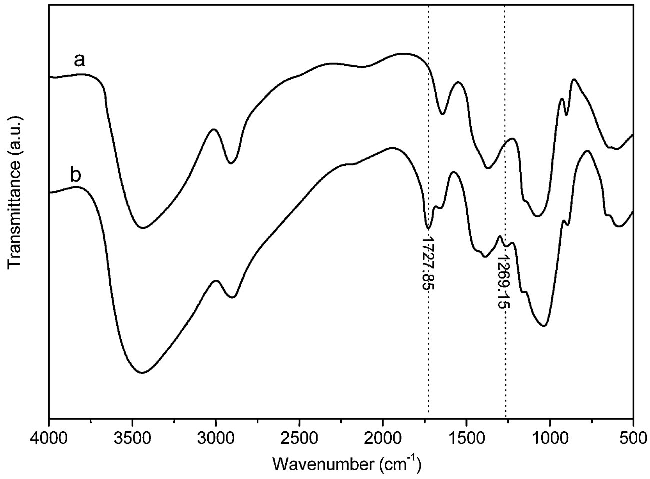

Fig. 2. FT-IR spectra of the cellulose (a) and the grafted cellulose (b).

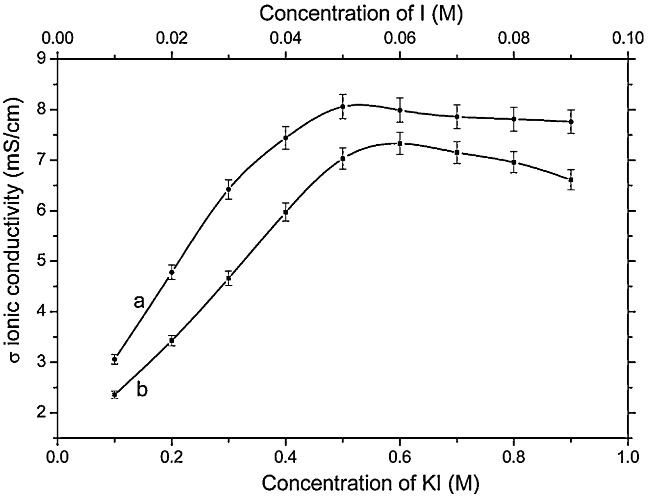

Fig. 3. Effect of redox couple ($KI + I_2$) concentration on conductivity for the liquid electrolyte (a) and grafted cellulose gel electrolyte (b).

Fig. 4 shows the ionic conductivity change tendencies of the liquid electrolyte and the grafted cellulose electrolyte as functions of temperature. The ionic conductivity increases with the increased temperature. The ionic conductivity of the grafted cellulose electrolyte is lower than that of the liquid one. The transportation of ionic conductors in the polymer gel electrolytes mainly depends on their hopping movement through solvent channels, so the Arrhenius type relationship is used to fit the data presented in Fig. 4 (Ratner, Johansson, & Shriver, 2000).

$$\sigma(T) = A\left[-\frac{E_a}{RT}\right] \tag{3}$$

where E_a is the activation energy, R is the molar gas constant, A is a constant and T is absolute temperature. The data in Fig. 4 are turn to $\ln\sigma$ versus $1000/T$ plots as shown in Fig. 5 and the Arrhenius relationship is changed as the following state:

$$\ln\,\sigma(T) = \left[-\frac{E_a}{RT}\right] + \ln A \tag{4}$$

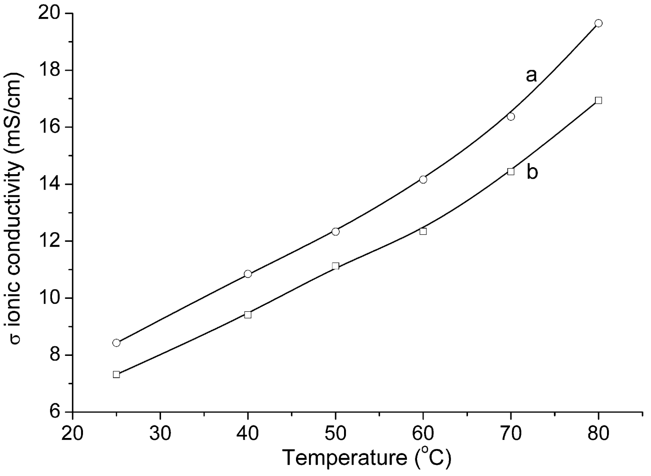

Fig. 4. Ionic conductivity of the liquid electrolyte (a) and the grafted cellulose gel electrolyte (b) as functions of temperature.

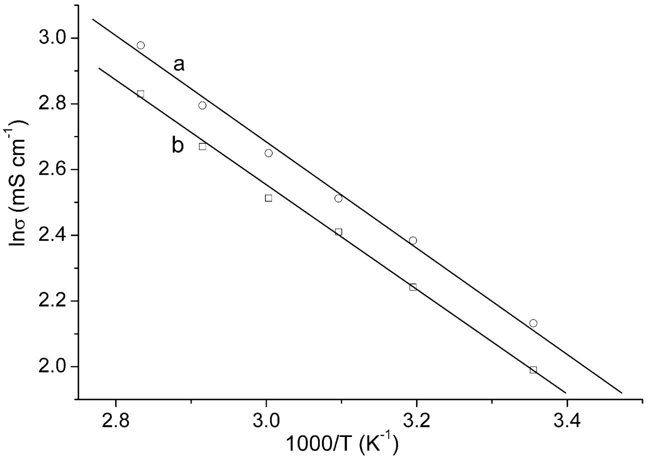

Fig. 5. Temperature dependence of ionic conductivity of the liquid electrolyte (a) and the grafted cellulose gel electrolyte (b).

As is apparent from Fig. 5, the conductivity data of all membranes showed a typical positive curvature in Arrhenius plots.

3.3. Impedance analysis of electrolytes

Fig. 6 shows the impedance spectra obtained under the same experimental conditions for two electrolytes between two Pt electrodes. The response at high frequency is related to the counter-electrode/electrolyte interface and the response at low frequency can be associated with the diffusion process of species in the electrolyte (Longo, Nogueira, & Paoli, 2002). The general behavior of the spectra was similar for both electrolytes, but the impedance of the grafted cellulose gel electrolyte was higher than that of the liquid one. It was attributed to the lower mobility of the I_3^- ions in the gel electrolyte. This result is consistent with the ionic conductivity analysis above.

3.4. Photovoltaic performance of DSSCs

Fig. 7 shows the photovoltaic performance of DSSCs with the optimized redox couple concentration (KI 0.60 M and I_2 0.06 M) in the liquid electrolyte (curve a) and the gel electrolyte (curve b). It is seen that the two cells have similar open-circuit voltage, while the DSSC with the liquid electrolyte shows higher short-circuit current density than the QS-DSSC with the gel electrolyte. The reason is mainly due to the ionic conductivity of the two electrolytes. Based on the grafted cellulose gel electrolyte, the QS-DSSC achieves a short-circuit photocurrent density of 12.65 mA cm^{-2}, open-circuit photovoltage of 713 mV, fill factor of 0.611 and light-to-electrical energy conversion efficiency of 5.51%. The energy conversion efficiency of DSSC based on the liquid electrolyte shows 5.75%. The energy conversion efficiency of QS-DSSC with the grafted cellulose gel electrolyte only is slightly lower than that of DSSC with the liquid electrolyte. So it is indicated that the grafted cellulose gel electrolyte with in situ synthesis in the ionic liquid ([Bmim]I) shows some advantages in preparing QS-DSSCs, such as high ionic conductivity and non-volatility.

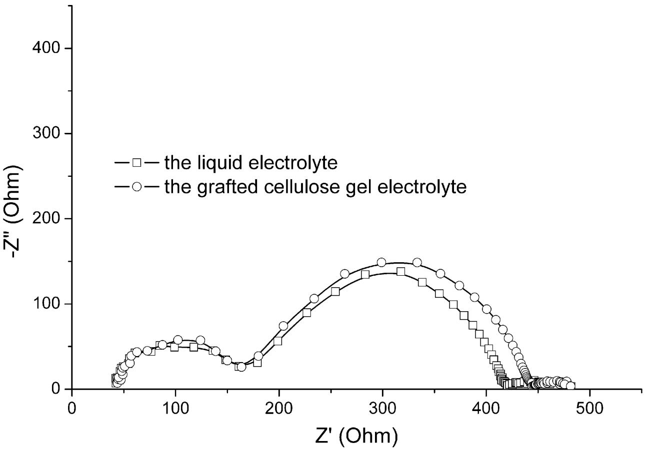

Fig. 6. Impedance spectra of the liquid electrolyte and grafted cellulose gel electrolyte.

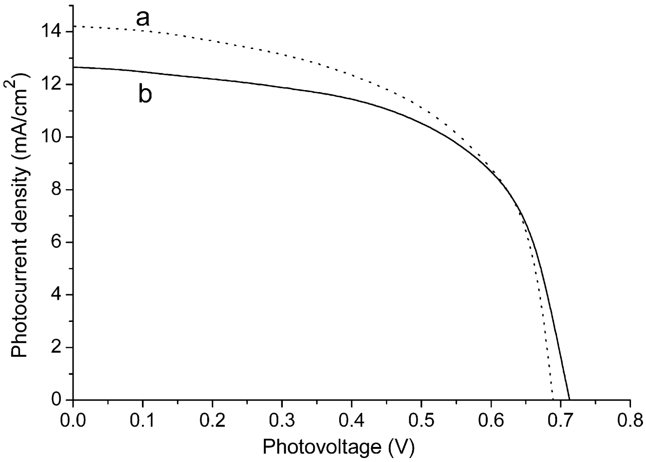

Fig. 7. Photovoltage–current density curves of DSSCs with the liquid electrolyte (a) and grafted cellulose gel electrolyte (b).

4. Conclusions

In this present work, the cellulose was grafted with acrylic acid by in situ polymerization in [Bmim]I ionic liquid. Using the grafted cellulose as host polymer, a gel-electrolyte with high conductivity of 7.33 mS cm^{-1} was prepared. Based on the optimized gel electrolyte, the best result of QS-DSSC was the light-to-electricity conversion efficiency of 5.51% under a light intensity of 100 mW cm^{-2} (AM 1.5). The grafted cellulose is promising for the development of quasi-solid-state dye-sensitized solar cells.

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