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Short communication

Photovoltaic performance of dye-sensitized solar cell assembled with gel polymer electrolyte

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Abstract

A gel polymer electrolyte is prepared by soaking a porous membrane in an organic electrolyte solution containing the I_3^-/I^- redox couple. The ionic conductivity of the gel polymer electrolyte is 2.7×10^{-3} S cm^{-1} at room temperature, and encapsulates the electrolyte solution well without solvent leakage. A dye-sensitized solar cell (DSSC) employing the gel polymer electrolyte gives an open-circuit voltage of 0.72 V and a short-circuit current of 6.27 mA cm^{-2} at an incident light intensity of 100 mW cm^{-2}. This yields a conversion efficiency of 2.4%. The DSSC employing the gel polymer electrolyte shows a more stable photovoltaic performance than a DSSC assembled with liquid electrolyte.

Keywords: Dye-sensitized solar cell; Gel polymer electrolyte; Photovoltaic performance; Porous membrane; Ionic conductivity; Conversion efficiency

1. Introduction

Photoelectrochemical solar cells based on dye-sensitized TiO_2 are considered to be promising alternatives to conventional silicon solar cells because of their low cost [1–3]. Such cells consist of a dye-sensitized nanoparticulate TiO_2 electrode, an electrolyte containing a redox couple and a Pt coated counter electrode. It has been claimed [4] that dye-sensitised solar cells (DSSCs) can give conversion efficiencies of up to 10%. The electrolyte commonly used is a I^-/I_3^- redox couple in an organic solvent. The long-term durability of DSSCs is limited by leakage or evaporation of the liquid electrolyte. Therefore, efforts have been made to replace the liquid electrolyte with a polymer electrolyte, molten salt, inorganic p-type semiconductors or organic hole transport materials [5–10]. Among these approaches, use of polymer electrolyte appears to give rise to successful results in terms of conversion efficiency. Conventional poly(ethylene oxide) (PEO)-based solid polymer electrolytes exhibit ionic conductivities that range between 10^{-8} and 10^{-5} S cm^{-1} at room temperature [11,12]. This performance is not sufficient for practical application at ambient temperature. In this respect, most of the recent studies have been directed to the preparation and characterization of gel polymer electrolytes that have higher ionic conductivity at ambient temperature. Gel polymer electrolytes are prepared by incorporating liquid electrolyte into a matrix polymer such as polyacrylonitrile (PAN), poly(vinylidene fluoride) (PVdF) and poly(methyl methacrylate) (PMMA) [13]. Some of these systems have an ionic conductivity in excess of 10^{-3} S cm^{-1}. Such gel polymer electrolytes do, however, suffer from poor mechanical strength that makes cell assembly difficult and increases the incidence of shorting between electrodes. The latter disadvantage arises because impregnation of liquid electrolyte into a polar polymer results in softening of the polymer. To overcome this problem, an activation process in which a porous polymer membrane is soaked in an electrolyte solution has been investigated [14–17]. Unlike conventional methods such as solution casting and direct dissolution of the polymer in the electrolyte solution, this procedure handles the mechanically robust porous film until the liquid electrolyte is finally added.

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In this study, a highly conductive gel polymer electrolyte is prepared by using a porous membrane based on acrylonitrile (AN)–methyl methacrylate (MMA) co-polymer. MMA is useful as a co-monomer due to its ability to be gelled easily by polar solvents. To our knowledge, this is the first reported attempt to assemble, and evaluate the performance of a dye-sensitized solar cell constructed with such a gel polymer electrolyte using porous membrane.

2. Experimental

2.1. Preparation of porous membrane and gel polymer electrolyte

The co-polymer used in preparing the porous membrane was acrylonitrile–methyl methacrylate co-polymer (hereafter called the AM co-polymer). The AM co-polymer was synthesized by emulsion polymerization with a small amount of potassium persulfate as an initiator, as previously reported [18]. From ^{1}H NMR spectroscopy, the molar composition of AN and MMA was determined to be 86:14. The AM co-polymer was dissolved at a concentration of 5 wt.% in dimethylformamide (DMF). After complete dissolution, the resulting viscous solution was cast with a doctor blade on a glass plate, and the film was immersed in a water bath in order to induce phase inversion. The resulting membrane was washed with running water, and then vacuum dried at 100 °C for 24 h. The water content in the membranes was confirmed to be less than 50 ppm. The gel polymer electrolyte was prepared by immersing the porous membrane in organic liquid electrolyte. The latter was composed of 0.5 M lithium iodide (LiI), 0.05 M I_2 and 0.05 M 4-*tert*-butylpyridine (TBP) in acetonitrile (ACN). The ionic conductivity was measured by means of an ac impedance analyzer over the frequency range 100–100 kHz with amplitude of 10 mV.

2.2. Preparation of electrodes

TiO_2 colloidal paste that consisted of TiO_2 powder (Degussa P25), ethylene glycol and Triton X-100 was cast on to a previously cleaned, fluorine-doped tin oxide (FTO) glass substrate by means of a glass rod. After drying in air for 15 min at room temperature, the electrode was heated to 450 °C at a rate of 5 °C min^{-1}, and then left at 450 °C for 30 min. The TiO_2 film formed on the FTO was 10 μm thick and 5 mm × 5 mm in size. The morphology of the TiO_2 electrode was examined with a scanning electron microscope. In order to sensitize the TiO_2 film, the TiO_2 electrode was immersed in a 1.5×10^{-4} M solution of the sensitizer dye, namely *cis*-bis(isothiocyanato) bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II) (ruthenium-535, Solaronix) in anhydrous ethanol, for 24 h at room temperature, and then rinsed with ethanol and dried. The counter electrode was prepared by sputtering Pt, which acts as a catalyst for the redox reaction on to glass that was coated with indium tin oxide.

2.3. Cell assembly and testing

A dye-sensitized solar cell was fabricated by sandwiching a porous membrane between a dye-coated nanoporous TiO_2 electrode and a platinum counter electrode, and then sealing the perimeter of the cell under an applied pressure. The porous membrane was gelled by filling liquid electrolyte into the cell through the holes in the counter electrode. When gelation occurs, the liquid electrolyte is completely trapped in the gelled membrane. The electrolyte-injecting holes in the counter electrode were then sealed with a Surlyn sheet and a thin glass cover by heating. Cell performance was evaluated using a xenon light source and an AM 1.5 filter. The active area of the cell was 0.25 cm^2 and the power of the incident white light from the Xenon lamp was 100 mW cm^{-2}. Photocurrent–voltage (*I*–*V*) measurements were performed with a potentiostat/galvanostat at room temperature. Each value of phothovoltaic performances was taken as the average of at least three samples.

3. Results and discussion

A typical scanning electron microscopic image of the cross-section of the porous membrane prepared with AM co-polymer by the phase inversion method is presented in Fig. 1. Microporous morphology is observed. Pores formed in the membrane result from an exchange between the organic solvent and water during immersion precipitation. The pore volume in this membrane is 51%, and the thickness of the membrane is in the range 50–60 μm. The presence of pores in the membrane can lead to an efficient uptake of the liquid electrolyte when it is immersed in an electrolyte solution. The porous membrane has an opaque appearance. After immersing the porous membrane in electrolyte solution, the pores in the membrane are barely noticeable. This suggests that an uptake of electrolyte solution into the porous membrane causes complete gelation of the membrane that results

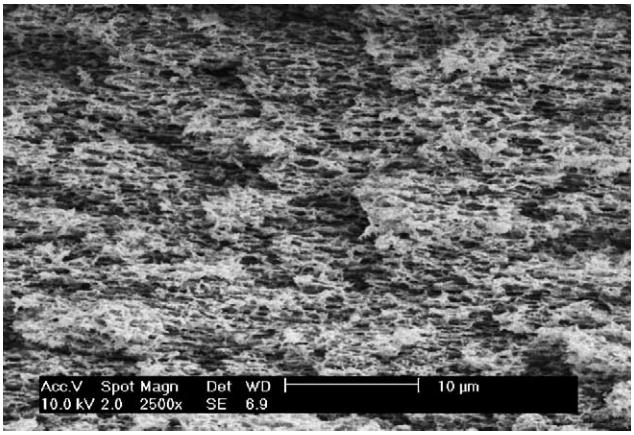

Fig. 1. Scanning electron micrograph of cross-sectional view of porous membrane.

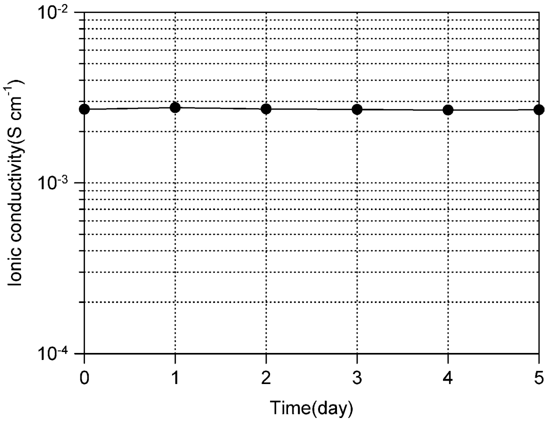

Fig. 2. Ionic conductivities of gel polymer electrolyte as function of storage time at 25 °C.

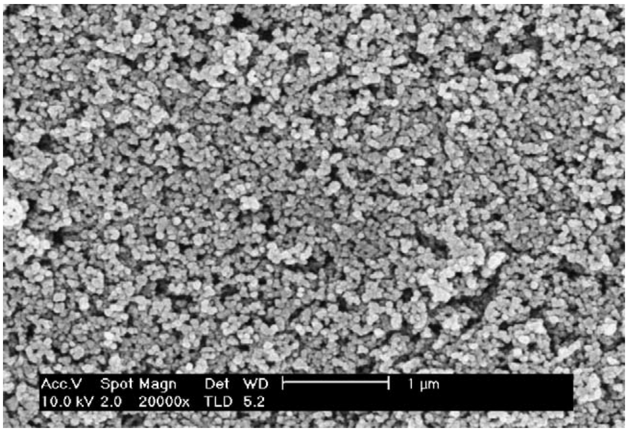

Fig. 3. Scanning electron micrograph of TiO_2 electrode used in dye-sensitized solar cell.

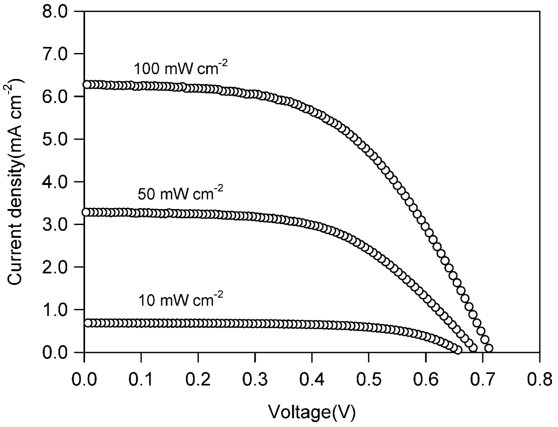

Fig. 4. Photocurrent–voltage curves for dye-sensitized solar cells assembled with gel polymer electrolytes. Curves obtained at different light intensities.

in the formation of a gel polymer electrolyte that is transparent. Gelation of the porous membrane is attributed to its high affinity for the electrolyte solution. The amount of electrolyte solution absorbed is about 2.3 times the weight of the polymer. The ability of the porous membrane to accommodate a large amount of electrolyte solution is due to the good compatibility between the polar functional group $–COOCH_3$ in the methyl methacrylate unit and the liquid electrolyte.

The time dependence of the ionic conductivity of the gel polymer electrolyte is shown in Fig. 2. The ionic conductivity remains constant over the time measured, which suggests complete gelation of the porous membrane with the electrolyte solution. After ac impedance measurements, no exuding of the solvent from the gel polymer electrolyte could be observed on the electrodes. From these results, it is believed that the electrolyte solution is well encapsulated in the matrix polymer by the physical gelation, and thereby, poses no leakage problems in the system. The ambient ionic conductivity of the gel polymer electrolyte reaches $2.7 \times 10^{-3}\,S\,cm^{-1}$, whereas that of the liquid electrolyte (0.5 M LiI/0.05 M I_2/0.05 M TBP in ACN) used for preparation of gel polymer electrolyte is $2.1 \times 10^{-2}\,S\,cm^{-1}$.

A scanning electron micrograph of a typical TiO_2 film deposited on FTO glass is given in Fig. 3. The TiO_2 spherical nanoparticles are well distributed and the film has a porous structure in which the nanoparticles are all bonded together through a sintering process. Such a porous structure permits not only the adsorption of a greater number of dye molecules, but also better wetting of the film by electrolyte. Together, these features result in a perfect penetration of the I^-/I_3^- redox couple into the TiO_2 film.

The photocurrent density–voltage curves for a dye-sensitized solar cell that employs the gel polymer electrolyte are shown in Fig. 4. These curves were measured at light intensities of 10, 50 and 100 mW cm^{-2}. The values of the open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), fill factor (FF) and conversion efficiency (η) obtained from these curves are summarized in Table 1. The fill factor can be calculated from the following relationship:

$$\mathrm{FF} = \frac{P_{\max}}{I_{SC} V_{OC}} \tag{1}$$

where $P_{\max}$ is the maximum electrical power obtained; I_{SC} and V_{OC} are the short-circuit current density and open-circuit voltage, respectively. The conversion efficiency of the dye-sensitized solar cell is obtained from the following equation:

$$\eta = \frac{P_{\max}}{IA} = \frac{I_{SC} V_{OC} \mathrm{FF}}{IA} \tag{2}$$

where I is the intensity of incident light; A is the cell area that is illuminated.

Table 1
Open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), fill factor (FF) and conversion efficiency (η) of DSSC assembled with gel polymer electrolyte at different light intensities

Intensity (mW cm^{-2})	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	η (%)
10	0.66	0.69	0.65	2.9
50	0.69	3.28	0.54	2.5
100	0.72	6.27	0.53	2.4

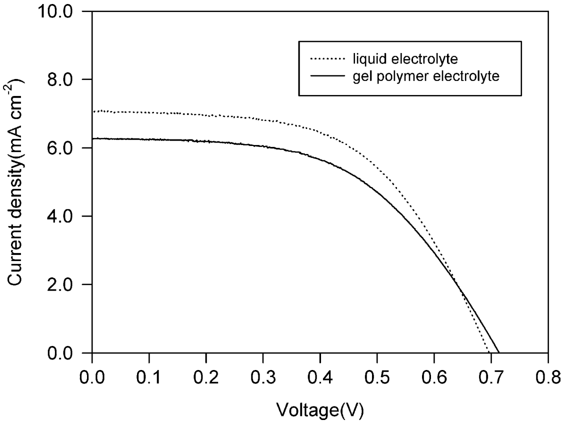

Fig. 5. Photocurrent–voltage curves for dye-sensitized solar cells, assembled with gel polymer electrolyte (—) and liquid electrolyte (···), at 100 mW cm^{-2}.

The best conversion efficiency obtained is $\eta = 2.9\%$ at 10 mW cm^{-2}. At an irradiance of 100 mW cm^{-2}, which approximates to the standard AM 1.5 irradiance, the values of J_{SC} and V_{OC} are increased to 6.27 mW cm^{-2} and 0.72 V, respectively, but the conversion efficiency is reduced to 2.4%. The reduction in conversion efficiency when the light intensity is increased may be due to a limitation in mass transport between the electrodes in the DSSC, since a large current passes through the cell at high light intensity.

The photocurrent density–voltage curves of DSSCs with liquid and gel polymer electrolyte at a light intensity of 100 mW cm^{-2}, are presented in Fig. 5. The DSSC assembled with the gel polymer electrolyte reports a lower J_{SC} and higher V_{OC} than the DSSC with a liquid electrolyte. The lower value of J_{SC} in the DSSC with gel polymer electrolyte may originate from its lower ionic conductivity. A higher resistance to ion migration reduces the supply of I_3^- to the Pt counter-electrode. This causes depletion of I_3^- and also retards the kinetics of dye regeneration, and therefore, decreases the J_{SC}. The slight increase of V_{OC} for the DSSC with gel polymer electrolyte is related to the reduction of the back electron-transfer reaction that decreases the V_{OC} [19]. When a gel polymer electrolyte is used in the DSSC, the polymer contacted on the surface of TiO_2 suppresses the back electron-transfer from the conduction band of TiO_2 electrode to the I_3^- in the gel polymer electrolyte, which results in high value of V_{OC}. On comparing the conversion efficiency of the two types of DSSC, it is found that the cell with a liquid electrolyte exhibits a slightly higher efficiency ($\eta = 2.8\%$) than that of the cell assembled with gel polymer electrolyte ($\eta = 2.4\%$).

In order to evaluate the durability of the photoelectrochemical performance of the DSCCs, measurements of the short-circuit current density (J_{SC}) were recorded with time, as shown in Fig. 6. The short-circuit current density of the DSSC assembled with gel polymer electrolyte remains almost constant; 99% of the initial value is retained after 6 days. On the other hand, the J_{SC} for the liquid electrolyte-based DSSC decays continuously with time and is lower than that exhibited by the DSSC prepared with gel polymer electrolyte after 6 days. This gradual decrease of photocurrent is related to evaporation of the highly volatile liquid electrolyte, which is caused by imperfect sealing of the DSSC. In the DSSC assembled with gel polymer electrolyte, the organic solvent containing the I^-/I_3^- redox couple is well encapsulated in the gel polymer electrolyte. Moreover, the electrolyte can promote a strong interfacial contact between the dye-adsorbed TiO_2 electrode and the platinum counter electrode. This gives a more stable performance than that of the DSSC assembled with liquid electrolyte. From these findings, it is expected that the solid-state dye-sensitized solar cell constructed with gel polymer electrolyte is a promising candidate for a practical solar cell with good durability. Further studies on the long-term stability and efforts to improve the cell efficiency are currently in progress.

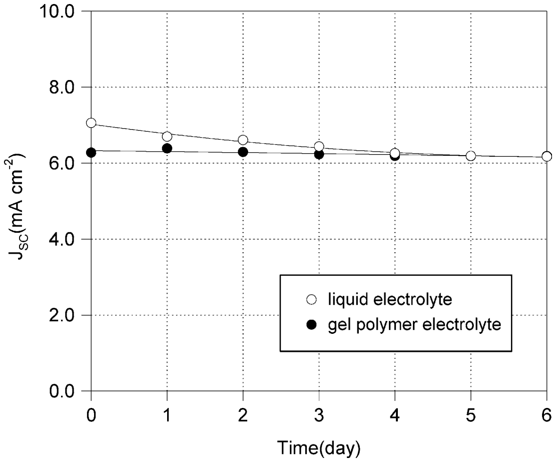

Fig. 6. Variation of short-circuit current density for dye-sensitized solar cells assembled with gel polymer electrolyte or liquid electrolyte as function of time. Measurements taken under simulated sun light (AM 1.5, 100 mW cm^{-2}).

4. Conclusions

A gel polymer electrolyte based on an acrylonitrile–methyl methacrylate co-polymer has been prepared by soaking a porous membrane in an organic electrolyte solution that contains a I_3^-/I^- redox couple. The ambient ionic conductivity of the gel polymer electrolyte reaches 2.7×10^{-3} S cm^{-1}. The gel polymers encapsulated the electrolyte solution well without solvent leakage and maintains good mechanical properties that allowed application in the dye-sensitized solar cell. A dye-sensitized solar cell employing the gel polymer electrolyte gives an open-circuit voltage of 0.72 V and short-circuit current of 6.27 mA cm^{-2} for an incident light intensity of 100 mW cm^{-2}. This yields a conversion efficiency of 2.4%. Use of the gel polymer electrolyte in the DSSC improves cell stability by suppressing solvent evaporation, but gives a slightly lower short-circuit current.

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