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A dye-sensitized nanoporous TiO_2 photoelectrochemical cell with novel gel network polymer electrolyte

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Abstract

A novel gel network polymer electrolyte based on polysiloxane with internal plasticizing PEO chains was applied in fabricating solid-state dye-sensitized TiO_2 photoelectrochemical cells. Ethylene carbonate (EC)/propylene carbonate (PC) and LiI/I_2 were added as liquid plasticizer to improve the performance. The cells showed open circuit voltage of 0.69 V and short circuit current density of 1.7 mA cm^{-2} under 28 mW cm^{-2} white light illumination. The energy conversion efficiencies and fill factors of the cells were 2.9% and 0.72.

1. Introduction

Dye-sensitized nanoporous TiO_2 photoelectrochemical cells with high energy conversion efficiency and low cost have been widely investigated as they offer an alternative to conventional p–n junction devices [1–5]. The porous TiO_2 electrodes in these cells greatly increase optical path length for the surface-anchored dye while maintaining contact with the electrolyte. The electrolyte usually used in these cells is a redox couple, such as I^-/I_2, in an organic solvent, such as propylene carbonate. However, the presence of liquid electrolyte in a practical cell can result in stability and performance limitation in long-term operation. In this regard, efforts have been made to fabricate solid state cells by replacing liquid electrolyte with room temperature molten salts [6], inorganic p-type semiconductors [7, 8], ionic conducting polymers [9–11] and organic hole transport materials [12–15].

To take advantage of the high surface area of the nanoporous film electrode, perfect contact is of great importance between the dye-anchored electrode and the electrolyte, that is, the electrolyte must fully penetrate into the porous network. This is the main reason that the energy conversion efficiencies of solid state cells remained low compared with the liquid version. Among the solid state cells reported, noteworthy high efficiencies of 3–5% under 30 mW cm^{-2} white light illumination have been achieved for a cell constructed with polyacrylonitrile based conducting polymer gel electrolyte [9], in which polymer electrolyte was solution cast onto a TiO_2 electrode before gelation.

Gel network polymer electrolytes are expected to have better physical stability compared to linear ones due to the improved retentivity. The disadvantage of network polymer electrolytes is the slow polymer chain motion caused by the crosslinked structure, which is detrimental to ionic conductivity. However, the presence of the internal plasticizer pendant on the network backbones can lower the glass transition temperature (T_g), improve salt solubility, accelerate free ion migration [16, 17] and thus increase ionic conductivity. In light of these considerations, we have applied a novel polysiloxane based gel network polymer with internal plasticizing poly(ethyleneoxide) (PEO) chains to dye-sensitized TiO_2 cells. The polymer electrolyte was solution cast onto the dye-coated TiO_2 film before the crosslinking reaction. The preliminary fabrication and performance of the cell are reported here.

2. Experiment details

The dye-coated nanoporous TiO_2 electrode was prepared as follows. TiO_2 nanoparticles were synthesized by adding 25 ml tetrabutyl titanate dropwise to 300 ml HNO_3 solution (pH 1) under vigorous stirring, then autoclaving the resulting sol at 230 °C for 12 h. The TiO_2 particles were redispersed under ultrasonication with addition of carbon wax with 40% of TiO_2 weight. After evaporation, a viscous TiO_2 paste was obtained. ITO conducting glass (In doped SnO_2, 20 Ω/cm^{-2}) was used as the substrate for depositing TiO_2 film. To control the film thickness and to mask electric contact strips, two edges of the ITO glass plate were covered with adhesive tape. TiO_2 paste was spread uniformly on the substrate by sliding a glass rod along the tape spacer. After drying, the sample was heated in air for 30 min at 450 °C and cooled to about 80 °C, then soaked in 0.3 mM ruthenium dye solution (*cis*-di(thiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylate) ruthenium (II) in absolute ethanol) for 10 h. Excess dye was removed by rinsing with ethanol.

The counter electrode was prepared according to a reported procedure [18]. 5 mM solution of hexachloroplatinic acid in isopropanol was spread on ITO glass at 10 μl cm^{-2}, then heated at 380 °C for 10 min.

The structure of the polysiloxane based network polymer with plasticizing PEO chains is shown in Figure 1 [17]. The gel network polymer electrolyte was prepared as follows. The polysiloxane precursor (the Si–H addition product of polymethylhydrosiloxane (Aldrich) and PEO (Aldrich) macromonomer) was mixed with LiI (20 wt %), ethylene carbonate (EC)/propylene carbonate (PC) (3:1 V/V, 150%) and self-made crosslinker TMP–TDI, and heated at 80 °C for 30 min. Then I_2 (5 wt %) was added. The polymer solution was cast on the dyed TiO_2 electrode under reduced pressure and pressed together with the Pt loaded counter electrode. Teflon tape (thickness ~20 μm) was placed between the two electrodes to avoid short-circuiting and ensure the thickness of the electrolyte film. Two electrodes sandwiching the gel network polymer formed a cell with dark red color. The cell was heated at 60 °C for 15 h to promote crosslinking in the gel network polymer electrolyte.

After the polymer gel was fully crosslinked, photoelectrochemical measurements were performed at room temperature, using a potentiostat (Princeton Applied Research, model 173) and a universal programmer (model 175) with a 250 W xenon lamp as light source.

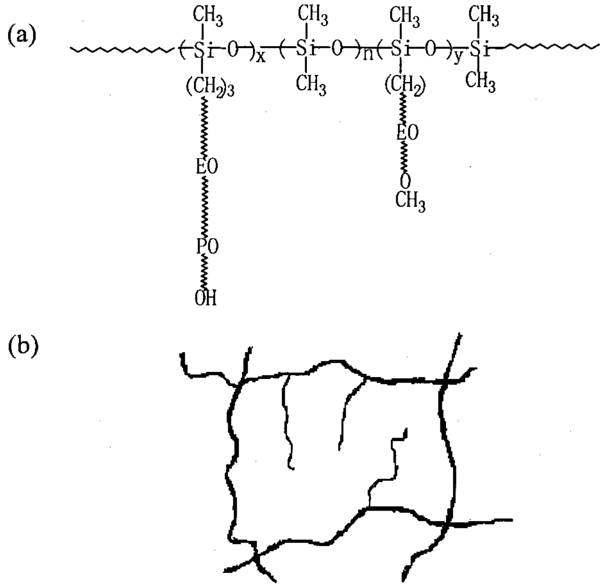

Fig. 1. (a) Formula and (b) schematic structure of the polysiloxane-based network polymer with internal plasticizing PEO chains.

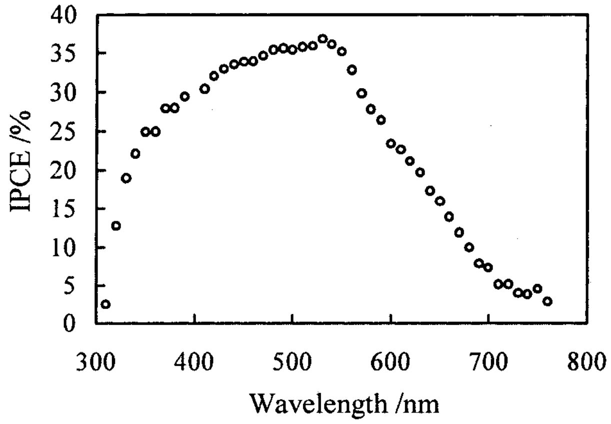

Fig. 2. Photocurrent action spectrum of the gel network polymer electrolyte cell.

3. Results and discussion

The ambient conductivity of the fully crosslinked polymer electrolyte was measured to be 1.1×10^{-3} S cm^{-1} using a HIOKI LCR 3520 Hi Tester at 1 kHz. In comparison, the conductivity of 0.5 M NaI and 0.1 M I_2 in propylene carbonate is 6.7×10^{-3} S cm^{-1} [9]. The comparable conductivity with that of the usually used liquid electrolyte indicates that the gel network polymer electrolyte used will not substantially increase the internal resistance of the cell and will be satisfactory for charge transportation between the two electrodes.

Figure 2 shows the photocurrent action spectrum, that is, the IPCE (incident photon-to-current conversion efficiency) versus wavelength for the gel network polymer electrolyte cell. IPCE is the ratio of produced electrons to incident photons, determined by measuring the short circuit photocurrent at various excitation wavelengths. The photocurrent spectrum peaks at 530 nm and resembles the ruthenium dye absorption spectrum in visible light region (Figure 3). This confirms that the photocurrent arises from the electron injection of the dye. The difference below 350 nm is due to the

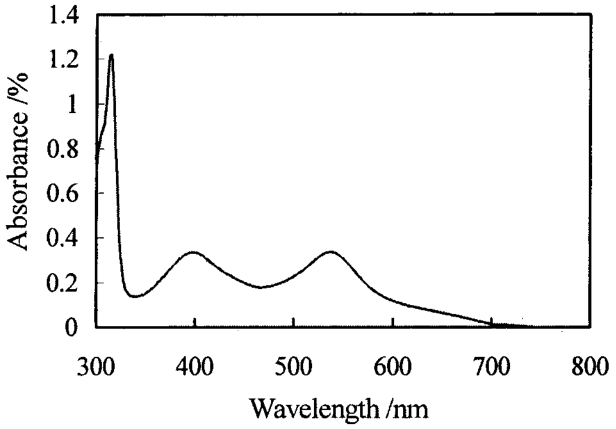

Fig. 3. Absorption spectrum of 0.03 mM ruthenium dye in ethanol.

direct photoresponse of TiO_2. Continuous photocurrent flow shows that oxidized dye can be regenerated after electron injection, that is, charges can transfer through the polymer electrolyte successfully between two electrodes. The maximum IPCE value is 37%, about a factor of 2 lower than the best values usually obtained for cells with liquid electrolyte, but it is considerable for a solid state cell [15].

Figure 4 shows current–voltage curves for the polymer gel electrolyte cell in dark and under white light illumination at an intensity of 28 mW cm^{-2} (with a 10 cm water filter and a 350 nm cut-off filter, 15% transmission loss in ITO glass was corrected). The current–voltage curves were obtained at a scan rate of 2 mV s^{-1} in a two-electrode arrangement, which is identical with loading a variable resistor. The open circuit voltage and the fill factor of the cell are 0.69 and 0.72 V, respectively, good enough to compare with cells with liquid electrolyte. The short circuit current density is 1.7 mA cm^{-2}, and the overall energy conversion efficiency is 2.9%. The dark current–voltage curve shows cathodic current at the onset potential of about −0.4 V, due to iodine reduction. The current–voltage curves show little leakage current and a steep rise in the high voltage part. This good rectification behavior suggests that surface combination and short-circuiting is insignificant in the cell. There is room for further improvement, as many parameters of the cell setup have not been optimized. A preliminary stability test was carried out after the unsealed cell was stored in a desiccator for 60 h. No decrease in open circuit voltage and a slight decrease in short circuit current (within 10%) was observed, showing that the gel network polymer electrolyte was physically stable. Stability investigation in long term operation is in progress.

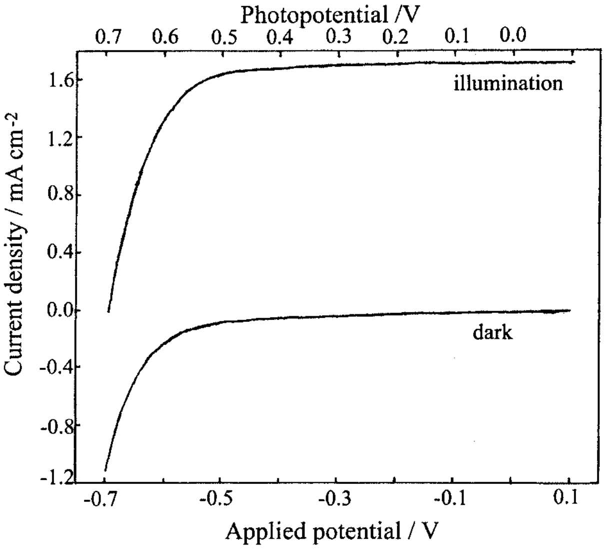

Fig. 4. Current–voltage curves for a gel network polymer electrolyte cell in the dark and under 28 mW cm^{-2} white-light illumination. The curves were obtained in a two-electrode arrangement at a scan rate of 2 mV s^{-1}.

4. Conclusions

A novel polysiloxane based gel network electrolyte with internal plasticizing PEO chains was applied successfully in fabricating solid-state dye-sensitized photoelectrochemical cells for the first time. The cells had an energy conversion efficiency of 2.9% under white light illumination, with open circuit voltage and fill factor comparable with the liquid version. Preliminary results showed the gel network polymer electrolyte was physically stable and quite retentive to the organic solvent PC and EC (liquid plasticizer).

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