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Short communication

Quasi-solid-state dye-sensitized solar cells with a novel efficient absorbent for liquid electrolyte based on PAA–PEG hybrid

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Abstract

A novel efficient absorbent for liquid electrolyte based on poly(acrylic acid)–poly(ethylene glycol) (PAA–PEG) hybrid is prepared. The highest value of liquid electrolyte absorbency about 3.65 is achieved. The polymer gel electrolyte shows a moderate value of ionic conductivity about 3.24 mS cm^{-1} and high chemical stability. Based on the polymer gel electrolyte, a quasi-solid-state dye-sensitized solar cell was fabricated and its overall energy conversion efficiency of 3.19% was obtained under irradiation of 100 mW cm^{-2}.

Keywords: Quasi-solid-state dye-sensitized solar cell; Absorbent; PAA–PEG hybrid; Polymer gel electrolyte; Liquid electrolyte absorbency; Energy conversion efficiency

1. Introduction

Dye-sensitized solar cells (DSSCs) are one of the promising candidates for the next generation of solar cells because of their simple structure with relatively high conversion efficiencies, inexpensive fabrication procedures in contrast with amorphous silicon [1–3]. Although DSSCs based on liquid electrolytes have already been achieved a record conversion efficiency of 11% [4], they also exist some substantial problems for practical uses. For example, the high volatilities and solvent losses during long-term operations of liquid electrolytes result in decrease of the performance of DSSCs [5]. Thus, work has been done to replace liquid electrolytes with p-type semiconductors and hole-conducting materials but currently with moderate success [6–7]. Recently, the interest in quasi-solid-state dye-sensitized solar cells has risen immensely [8–12]. The advantages of using polymer gel electrolytes in dye sensitized solar cells include the following aspects: firstly, they can obtain good contacting and filling property with nanoporous TiO_2 film and counter electrode; secondly, they show high ionic conductivity by “trapping” volatile organic solvents in polymer cages formed in polymer matrix; thirdly, their fabrication procedures are simple. These advantages of polymer gel electrolytes lead to abroad application in DSSCs [11]. Up to the present, several types of polymer gel electrolytes based on different kinds of polymer materials or their hybrids have already been used in fabricating quasi-solid-state dye-sensitized solar cells [10,13–17].

In this communication, a new polymer gel electrolyte is fabricated by soaking a novel efficient absorbent for liquid electrolyte based on poly(acrylic acid)–poly(ethylene glycol) (PAA–PEG) hybrid in the conventional organic liquid electrolyte. It is well known that poly(acrylic acid) is a kind of superabsorbents which can absorb a large amount of water and maintain the absorbed water even under some pressure. However, pure poly(acrylic acid) is not a good absorbent for organic solvents used in liquid electrolytes. In order to use the property of poly(acrylic acid) superabsorbent in dye sensitized solar cells, we tried to modify poly(acrylic acid) with the amphiphilic poly(ethylene glycol). Through hydrogen bonding between polymer chains, they can form homogeneous hybrid without phase disengagement. The hybrid shows efficient absorbent ability for liquid electrolyte. By soaking it in liquid electrolyte, it can form a stable polymer gel electrolyte which can keep large amount of liquid electrolyte and shows moderate value of ionic conductivity and good chemical stability. Further a quasi-solid-state dye-sensitized solar cell was fabricated by sandwiching the polymer gel electrolyte between two electrodes.

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2. Experimental

2.1. Preparation of hybrid and polymer gel electrolyte

Poly(acrylic acid)–poly(ethylene glycol) hybrid was synthesized by the following processes. Firstly, appropriate amount of poly(ethylene glycol) (PEG, $M_w = 20{,}000$, Sinopharm Chemical Reagent Co., Ltd., China) was dissolved in 5 ml deionized water under stirring. The mixture was marked as A. Secondly, oligo(acrylic acid) was prepared by prepolymerization in water solution. 7.2 ml acrylic acid monomers were dissolved in 5 ml deionized water under stirring. Sodium pyrosulfite with an equivalent mole ratio of ammonium persulfate (2 wt% of monomers) were used as room temperature redox initiators to initiate polymerization reaction. When the mixture B became a viscous solution, the oligo(acrylic acid) marked as B was obtained. Thirdly, the mixture A was dropped into the mixture B slowly under vigorous stirring to form homogeneous hybrid at room temperature. The final hybrid was kept in the ambient environment for about 1 h to turn the oligo(acrylic acid) to poly(acrylic acid) because of the exothermic polymerization reaction. Finally, the hybrid was moved into a vacuum oven at 80 °C to remove the water in the hybrid. Polymer gel electrolyte was prepared by soaking the hybrid in liquid electrolyte. The latter was composed of 0.5 M NaI, 0.05 M I_2 and 0.5 M 4-*tert*-butylpyridine in γ-butyrolactone. The liquid electrolyte absorbency (Q_{le}) of hybrid was defined as:

$$Q_{le} = \frac{W - W_o}{W_o} \tag{1}$$

where W is the weight of swollen hybrid and W_o is the original weight of dry hybrid. The Q_{le} values of samples were calculated according to Eq. (1). Ionic conductivity was measured by using model DDB-6200 digitized conductivity meter (Shanghai Reici Instrument Factory, China). The instrument was calibrated with 0.01 M KCl aqueous solution prior to experiments.

2.2. Preparation of electrodes

TiO_2 colloidal paste and dye-sensitized TiO_2 electrode were prepared according to the method reported in our previous references [15,16]. The difference is that titanium *iso*-propoxide was used as precursor instead of tetrabutyl titanate in this communication. The details of preparation of TiO_2 colloidal paste and dye-sensitized TiO_2 electrode were described as follows: Titanium *iso*-propoxide (20 ml) was rapidly added into distilled water (200 ml) and a white precipitate was formed immediately. The precipitate was filtered with a glass frit and washed three times with 100 ml distilled water. The filter cake was added to nitric acid aqueous solution (0.1 M, 200 ml) under vigorous stirring at 80 °C until the slurry became a translucent blue-white liquid. The resultant colloidal suspension was autoclaved at 200 °C for 12 h to form milky white slurry. The resultant slurry was concentrated to 1/4 of its volume, then PEG-20,000 (10 wt% slurry) and a few drops of emulsification regent of Triton X-100 were added to form TiO_2 colloid.

The fluorinedoped SnO_2 conducting glass (FTO glass, sheet resistance 8 $\Omega\,cm^{-2}$, purchased from Hartford Glass Co., USA) was first cleaned in Triton X-100 aqueous solution, washed with ethanol, and treated with 50 mM $TiCl_4$ aqueous solution at 70 °C for 30 min, to make a good mechanical contact between the following printed TiO_2 layer and the conducting glass matrix. The former prepared TiO_2 colloid was dropped on the FTO glass plate by using a doctor scraping technique. The process was done for three times to form a thick TiO_2 film about 10 μm. The TiO_2 film was treated with 50 mM $TiCl_4$ aqueous solution in ambient environment for 12 h and washed with distilled water. Finally, the TiO_2 porous film was sintered by firing the conducting glass sheet at 450 °C in air for 30 min. After sintering at 450 °C and cooling to 80 °C, the nanostructured TiO_2 electrode was dye-coated by immersing it into a 2.5×10^{-4} M absolute ethanol solution of *cis*-$[(dcbH_2)_2Ru(SCN)_2]$ for 24 h.

2.3. Cells assembly and testing

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. The two electrodes were clipped together and a cyanoacrylate adhesive was used as sealant. Epoxy resin was used for further sealing the cell. Cell performance was evaluated with a 100 W xenon arc lamp (XQ-100 W, Shanghai Photoelectricity Device Company, China) to measure the $J-V$ character curves. The power of light intensity was measured with energy meter model LPE-1A and the active area of the cell was 0.5 cm^2 (0.5 cm × 1 cm). The fill factor (FF) and overall energy conversion efficiency (η) of the cell were calculated by the following equations:

$$\mathrm{FF} = \frac{V_{max} J_{max}}{V_{oc} J_{sc}} \tag{2}$$

$$\eta(\%) = \frac{V_{max} J_{max}}{P_{in}} 100\% = \frac{V_{oc}\, J_{sc}\, \mathrm{FF}}{P_{in}} 100\% \tag{3}$$

where J_{sc} is the short-circuit current density (mA cm^{-2}), V_{oc} the open-circuit voltage (V), P_{in} the incident light power, and J_{max} (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.

3. Results and discussion

Polymer gel electrolyte cannot function well without a sufficiently expanded organic subphase when it is used to fabricate quasi-solid-state dye-sensitized solar cells. This is due to two reasons: (1) organic subphase can form a local solvent channel for ion conduction, which is the major medium governing the ionic conductivity [18]. (2) Organic subphase can penetrate into the titania nanoporous structure and ensure electrical conduction with an optimal number of nanocrystallites. In order to obtain a sufficiently expanded organic subphase in polymer gel electrolyte, the amphiphilic poly(ethylene glycol) was used to modify poly(acrylic acid). Liquid electrolyte cannot be absorbed by pure poly(acrylic acid). However, it can be effi-