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Quasi-solid state dye-sensitized solar cells based on gel polymer electrolyte with poly(acrylonitrile-*co*-styrene)/NaI+I_2

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Abstract

Gel polymer electrolyte based on poly(acrylonitrile-*co*-styrene)/NaI+I_2 and binary solvent mixture was prepared. When the system contains 0.5 M NaI and 0.05 M I_2, the maximum ionic conductivity (at 30 °C) of 2.37 mS cm^{-1} was achieved. Based on a gel polymer electrolyte with 0.5 M NaI, 0.05 M I_2 and 0.5 M 4-*tert*-butylpyridine, a quasi-solid state dye-sensitized solar cell was fabricated and its overall energy conversion efficiency of light-to-electricity of 2.75% was achieved under irradiation of 60 mW cm^{-2}.

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Keywords: Quasi-solid state dye-sensitized solar cell; Gel polymer electrolyte; NaI; Poly(acrylonitrile-*co*-styrene)

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted great attention over the past decade as a low-cost alternative to traditional photovoltaic devices (O' Regan and Grätzel, 1991; Nazeeruddin et al., 1993, 2001). Light-to-electrical energy conversion efficiencies of DSSCs based on liquid electrolytes using organic compounds, such as acetonitrile, propylene carbonate and ethylene carbonate as solvents and iodide/triiodide (I^-/I_3^-) redox couple as an electrolyte have reached 10–11% under irradiation of AM 1.5 (Nazeeruddin et al., 1993, 2001; Nakade et al., 2002; Gregg et al., 2003; Diamant et al., 2003). However, the leakage and evaporation of the liquid electrolyte caused by the technical difficulty in sealing has been a critical factor for long-term practical operation and causes substantial problems to put DSSCs into practical uses.

To overcome these problems, much effort has been made to replace the liquid electrolytes with solid or quasi-solid type charge transport materials (O' Regan et al., 2002; Bach et al., 1998; Nogueira et al., 2001; Cao et al., 1995). Compared with other kinds of charge transport materials, the gel polymer electrolytes have some advantages including high ionic conductivities which are achieved by "trapping" a liquid electrolyte in polymer cages formed

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Nomenclature

FF	fill factor	V_{oc}	open-circuit voltage (V)
I	current (A)	M	mole concentration (mol/l)
J_{sc}	short-circuit current density (mA cm^{-2})	η	energy conversion efficiency
P_{in}	incident light power (mW cm^{-2})		
V	voltage (V)		

in a host matrix, good contacting and filling properties of the nanostructured electrode and counter electrode. Therefore, the gel polymer electrolytes have been attracting intensive attention. Up to the present, several types of gel electrolytes based on different kinds of polymers have already been used in quasi-solid state dye-sensitized solar cells (Cao et al., 1995; Wang et al., 2004; Matsumoto et al., 1996).

In this paper, poly(acrylonitrile-*co*-styrene) is used as a polymer matrix to trap liquid state electrolyte with NaI, I_2 and binary organic solvent mixture to form gel polymer electrolyte. Poly(acrylonitrile-*co*-styrene) is an amorphous state which is good for solvent to immerge into polymer matrix to form gel state. The system has received relatively high ambient ionic conductivity. Quasi-solid state dye-sensitized solar cells were fabricated by sandwiching front and counter electrodes. Their photovoltaic performance was also evaluated.

2. Experimental

2.1. Materials

Poly(acrylonitrile-*co*-styrene) was commercially obtained from a chemical company in China and used without further purification. Tetrabutyltitanate, titanium tetrachloride, sodium iodide, iodine, ethylene carbonate (EC), propylene carbonate (PC) and 4-*tert*-butylpyridine were all A.R. grade and purchased from Xilong Chemicals, China. All reagents were used without further treatment before using.

Conducting glass plates (FTO glass, Fluorine doped tin oxide over-layer, sheet resistance 8 Ω cm^{-2}, purchased from Hartford Glass Co., USA) were used as a substrate for precipitating TiO_2 porous film and were cut into 2×1.5 cm^2 sheets. Sensitizing dye *cis*-[$(dcbH_2)_2Ru(SCN)_2$] was purchased from SOLARONIX, SA.

2.2. Preparation of gel polymer electrolyte

The appropriate amounts of NaI and I_2 (10 mol.% of NaI) were dissolved in binary organic solvent mixture containing EC and PC (6/4, w/w) firstly. Then, 20 wt.% of poly(acrylonitrile-*co*-styrene) was added into the above liquid electrolyte. Finally, the resulting mixture was heated at 75–85 °C under vigorous stirring until a viscous gel was obtained, followed by cooling down to room temperature.

2.3. Assembling of the quasi-solid state dye-sensitized solar cell

Nanoporous TiO_2 films were manufactured by the following procedure. Tetrabutyl titanate (20 ml) was rapidly added to distilled water (200 ml) and a white precipitate was formed immediately. The precipitate was filtered using 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-20000 (10 wt.% slurry) and a few drops of emulsification regent of Triton X 100 was added to form a TiO_2 colloid.

A conducting glass sheet (FTO) was immersed in an isopropanol solution for 48 h to remove impurities. Then it was 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 TiO_2 layer and conducting glass matrix. A plastic adhesive tape was fixed on the four sides of conducting glass sheet to restrict the thickness and area of TiO_2 porous film. The TiO_2 colloid was dropped on the FTO glass plate by using a doctor scraping

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