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# Quasi-solid state dye-sensitized solar cells-based gel polymer electrolytes with poly(acrylamide)–poly(ethylene glycol) composite

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**Abstract**

A novel gel polymer electrolyte based on poly(acrylamide)–poly(ethylene glycol) composite and binary organic solvent was prepared. And the highest ionic conductivity of the gel polymer electrolyte was 1.94 mS cm$^{-1}$ under the ambient atmosphere. The polymer gel electrolyte based on the composite of poly(acrylamide)–poly(ethylene glycol), the binary organic solvent of ethylene carbonate and propylene carbonate and the additive of 4-*tert*-bytylpyridine has been employed to fabricate quasi-solid state dye-sensitized solar cell with an overall conversion efficiency of approximately 3% under irradiation of 60 mW cm$^{-2}$.

*Keywords:* Quasi-solid state dye-sensitized solar cells; Gel polymer electrolytes; Poly(acrylamide)–poly(ethylene glycol) composite; Ionic conductivity

## 1. Introduction

Dye-sensitized solar cells (DSSC) based on sensitization of $TiO_2$ nanocrystalline by photoexcited dye molecules have been investigated intensively because of its lower cost and potential alternatives to traditional photovoltaic device [1–3]. light-to-electrical energy conversion efficiencies of DSSC based on liquid electrolytes using organic compound, such as acetonitrile, propylene carbonate and ethylene carbonate as solvent and iodide/triiodide ($I^-/I_3^-$) redox couple as electrolyte have reached 10–11% under irradiation of AM 1.5 [2–7]. However, this type of liquid-junction cell remains some problems including low long-term stability which caused by organic solvent evaporation and leakage of liquid electrolytes, high temperature instability and difficulties in sealing the devices [8].

To overcome these problems, much effort has been made to replace the liquid electrolytes with solid or quasi-solid type charge transport materials [9–12]. 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 in a host matrix, good contacting and filling properties with 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 kind of polymers have already been used in quasi-solid state dye-sensitized solar cells [12–14].

Poly(acrylamide) possess carbonyl group and amine group on its molecular chain [15], also poly(ethylene glycol) have many hydroxyl group on its molecular chain. It is expected that the interaction between sensitized dye and the matrix of gel polymer can be improved based on the hydrogen bond interaction between the carbonyl group on sensitized dye and the carbonyl group, amine group and hydroxyl group on matrix of gel polymer electrolyte. On the other hand, the ionic conductivity of the gel polymer electrolyte can be enhanced according to the complexation from carbonyl group, amine group and hydroxyl group on poly(acrylamide) and poly(ethylene glycol) to $K^+$ ions in electrolyte. Consequently, the overall conversion efficiency of the DSSC can be enhanced. In this paper, using poly(ethylene glycol) as both reactant and plasticizer, a novel homogeneous poly(acrylamide)–poly(ethylene glycol) composite without phase separation was synthesized. Using the composite as matrix, and 4-*tert*-bytylpyridine as

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additive, the binary organic compounds ethylene carbonate and propylene carbonate as solvent, a gel polymer electrolyte with quasi-solid state was prepared. Further, a dye-sensitized solar cell was fabricated by sandwiching the gel polymer electrolyte.

## 2. Experimental

### 2.1. Materials

Poly(ethylene glycol) with average molecular weight 400 (PEG-400), acrylamide monomer, ammonium persulfate, potassium iodide, iodine, ethylene carbonate (EC), propylene carbonate (PC) and γ-butyrolactone (γ-BL) were all A.R. grade and all purchased from Xilong Chemicals. PEG-400 was dried at 120 °C for 12 h before used. Other reagents were used without further treating 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 on and were cut into 2 cm × 1.5 cm sheets. Sensitizing dye *cis*-[$(dcbH_2)_2Ru(SCN)_2$] was purchased from SOLARONIX, SA.

### 2.2. Synthesis of the poly(acrylamide)–poly(ethylene glycol) in situ composite

Poly(acrylamide)–poly(ethylene glycol) in situ composite was synthesized by adding 3 g PEG-400 into 6 g acrylamide monomer. The mixture was heated at 70–75 °C to melt the monomer and mix two components homogeneously. The mixture was marked as A. A polymerization initiator (ammonium persulfate, 1 wt.% of acrylamide monomer) and PEG-400 (1 g) were mixed and stirred until the mixture dissolved entirely at room temperature, and the mixture was marked as B. Under vigorous stirring and keeping a temperature at 70–75 °C on a water bath heater, the mixture B was added into the mixture A slowly, the polymerization reaction took place and a homogeneous mixture formed, the mixture was marked as C. It is noticeable that as soon as the polymerization reaction begins, the mixture C should be put out of the water bath heater and down to room temperature to prevent implosion because the reaction is exothermic reaction. When the mixture C became a viscous gel in ambient environment, it was heated again at 60–65 °C for 30 min to complete polymerization reaction. After that, the poly(acrylamide)–poly(ethylene glycol) in situ composite was synthesized.

### 2.3. Preparation of gel polymer electrolyte

A mixture organic solvent was made by mixing ethylene carbonate (EC), propylene carbonate (PC), γ-butyrolactone (γ-BL). Potassium iodide [KI = 10 wt.% of total weight of the composite and the mixture solvent] and iodine ($I_2$ = 10 wt.% of KI) were dissolved in the mixture organic solvent to form a liquid electrolyte. Suitable amount of poly(acrylamide)–poly(ethylene glycol) composite was added into the liquid electrolyte under continuous stirring at room temperature to form a gel polymer electrolyte with quasi-solid state.

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

Nanoporous $TiO_2$ film was manufactured by 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 of 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 were added to form a $TiO_2$ colloid.

A conducting glass sheet (FTO) was immersed in an isopropanol solution for 48 h to remove any impurities. 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 technique. The process was done for three times to form a thick $TiO_2$ film about 6–8 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 solidified and sintered by firing the conducting glass sheet at 450 °C in air for 30 min.

After cooled to 80 °C, the $TiO_2$ film was immersed in a $2.5 \times 10^{-4}$ M absolute ethanol solution of *cis*-[$(dcbH_2)_2Ru(SCN)_2$] for 24 h to absorb the dye adequately, the other impurities were washed up with anhydrous ethanol and dried in moisture-free air. After that, a $TiO_2$ porous film electrode absorbed dye was prepared.

Quasi-solid state dye-sensitized solar cell was assembled by dropping a drop of gel polymer electrolyte into the aperture between the $TiO_2$ porous film electrode (anode electrode) and a Pt plated conducting glass sheets (cathode electrode, prepared by electrodepositing). The two electrodes were clipped together and a cyanoacrylate adhesive was used as sealant to prevent the electrolyte solution from leaking.

### 2.5. Measurements

Poly(acrylamide)–poly(ethylene glycol) composite thermal stability was measured by a SDT2960 simultaneous DSC–TGA device (USA TA Instrument) over a temperature range of 30–600 °C at a heating rate of 10 °C min$^{-1}$. The ionic conductivity of gel polymer electrolytes was measured by using model DDB-6200 digitized conductivity meter (Shanghai Reici Instrument Factory, China). The instrument was calibrated with 0.1 M KCl aqueous solution prior to experiments.

The photovoltaic test of quasi-solid state dye-sensitized solar cells was carried out by measuring the *J*–*V* character curves under irradiation of white light from a 100 W xenon arc lamp (XQ-500W, Shanghai Photoelectricity Device Company, China) under ambient atmosphere. The incident light intensity and the active cell area were 60 mW cm$^{-2}$ and 0.8 cm$^2$, respectively. The photoelectrochemical performances [i.e. fill factor (FF) and overall energy conversion efficiency ($\eta$)] were calculated by the following equations [16]:

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

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

where $J_{\mathrm{sc}}$ is the short-circuit current density (mA cm$^{-2}$), $V_{\mathrm{oc}}$ the open-circuit voltage (V), $P_{\mathrm{in}}$ is 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

### 3.1. Thermogravimetric analysis of polymer matrix

As the gel polymer matrix, the thermal stability of poly(acrylamide)–poly(ethylene glycol) composite must satisfy the requirement of the dye-sensitized solar cells in practical application. Therefore, the thermogravimetric analysis of the composite was examined.

Fig. 1 exhibits the thermogravimetric curve of polymer matrix. It shows that before thermal degradation, both the poly(acrylamide)–poly(ethylene glycol) composite and the poly(acrylamide) have weight lost, which is due to absorbent water in ambient environment. The data also shows that the weight loss in the poly(acrylamide)–poly(ethylene glycol) composite before thermal degradation (about 9 wt.%) is higher than that of pure poly(acrylamide). The total absorbent water for poly(acrylamide)–poly(ethylene glycol) composite is removed easily by heating in vacuum oven and cannot seriously influence upon photovoltaic performance of solar cells. From Fig. 1, it is observed that the temperature of the thermal degradation of the composite of 241 °C is higher than that of pure poly(acrylamide) about 218 °C, this may be caused by adding PEG-400 to poly(acrylamide). Based on TGA, the thermal stability of poly(acrylamide)–poly(ethylene glycol) composite satisfies the requirement of the dye-sensitized solar cells.

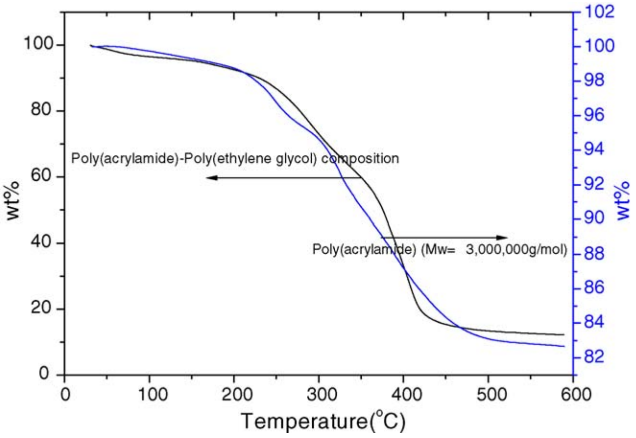

Fig. 1. TGA of poly(acrylamide)–poly(ethylene glycol) composite and poly(acrylamide) ($M_{\mathrm{w}} \geq 3{,}000{,}000$ g/mol).

### 3.2. Conductivity of electrolyte

It is said that the ionic conductivity of the polymer electrolyte can be improved by adding appropriate organic solvent, or named plasticizers [12,17–19]. Some kinds of organic solvents and binary organic solvents were selected to improve the ionic conductivity of the gel polymer electrolyte. The ionic conductivity of gel electrolytes were measured and given in Table 1.

As shown in Table 1, the ionic conductivity of the binary organic solvents EC/PC or EC/γ-BL is higher than that of single one PC or γ-BL. It is well known that EC is a high viscosity solvent with high dielectric constant. Higher dielectric constant of EC is favorable for ionization of salts and resulting in the higher ionic conductivity using EC as solvent. But when using pure EC in gel polymer electrolyte, it can’t achieve high ionic conductivity because EC has tendency to crystallize at low temperature, which causes phase disengagement between EC and composite matrix. So other organic solvents were used to form binary organic solvents with EC. When adding other organic solvents in EC, relatively higher ionic conductivity was obtained. On the binary organic solvents conditions, the tendency to crystallize of EC has been restrained and homogeneous gel polymer electrolytes are achieved, so they have relatively higher ionic conductivity.

From Table 1, it is noticeable that the ionic conductivity of the binary organic solvents of EC and PC is higher than the binary organic solvents of EC and γ-BL with the same proportion, although the conductivity of PC is lower than that of γ-BL. The molecular structure of EC, PC and γ-BL are shown in Fig. 2, it is found that the molecular structure of PC is more similar to the EC than that of γ-BL, it is easier to mix binary organic solvents to form homogenous solvents between EC and PC than EC and γ-BL, which lead to the higher conductivity of mixed solution of EC and PC than EC and γ-BL. The phenomenon provides a valuable clue to search other solvent or additive.

The ln $\sigma$ versus 1/$T$ plots for the gel polymer electrolytes with different organic solvents and binary organic solvents are shown

Table 1
The ionic conductivity of gel polymer electrolytes with different solvent[a]

| Organic solvent (w/w) | $\sigma$ (mS cm$^{-1}$) (30 °C) |
|---|---|
| PC | 1.46 |
| γ-BL | 1.61 |
| EC | 2.63[b] |
| EC:PC = 7:3 | 1.94 |
| EC:γ-BL = 7:3 | 1.80 |

[a] Based poly(acrylamide)–poly(ethylene glycol) composite [4:6 (w/w)] and containing KI (10 wt.% of gel), iodine $I_2$ (1 wt.% of gel) with different organic solvents.

[b] The date was measured at 40 °C. Since EC exists in solid state at 30 °C and EC exists in liquid state at 30 °C in mixture solution.

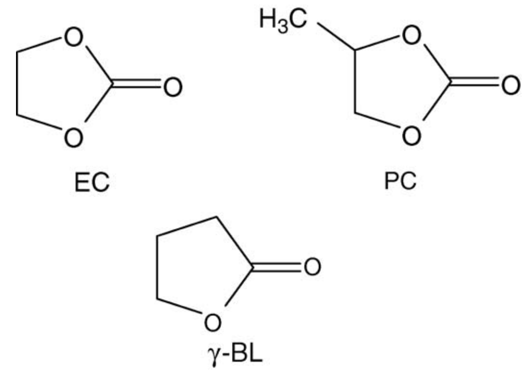

Fig. 2. The molecule structure of EC, PC and γ-BL.

in Fig. 3. Obviously, the ionic conductivity increased with the increase of temperature. The free-volume model can be used to explain this property of gel polymer electrolytes [20]. The free-volume increases with increase in temperature which enhances the mobility of polymer chains and ions dissolved in polymer matrix.

As shown in Fig. 3, although with little warp, the $\ln\sigma$ versus $1/T$ plots are almost linear. The Arrhenius equation can be used to describe the conductivity–temperature behavior of these gel polymer electrolytes

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

where $E_a$ is the activation energy, $R$ the molar gas constant, $A$ is a constant, and $T$ is the absolute temperature. Fig. 3 also shows that the temperature dependence of the ionic conductivity ($\sigma$) for gel polymer electrolytes with different organic solvents has the same change tendency and all can be described by the Arrhenius equation.

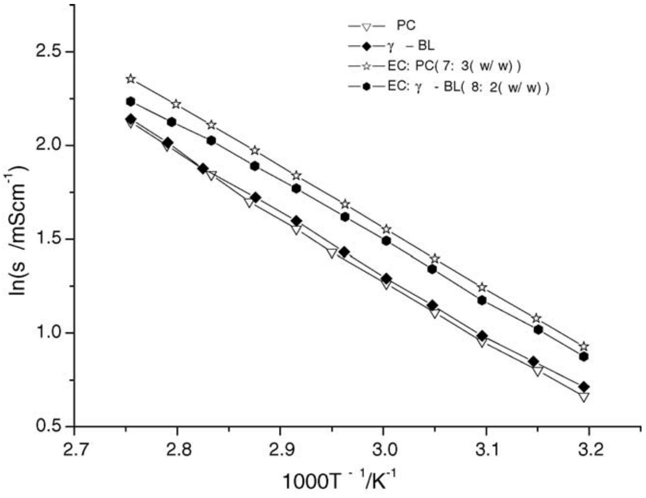

Fig. 3. Temperature dependence of the ionic conductivity ($\sigma$) for gel polymer electrolytes with different organic solvents and the same amount of KI (10 wt.%) and $I_2$ (1 wt.%).

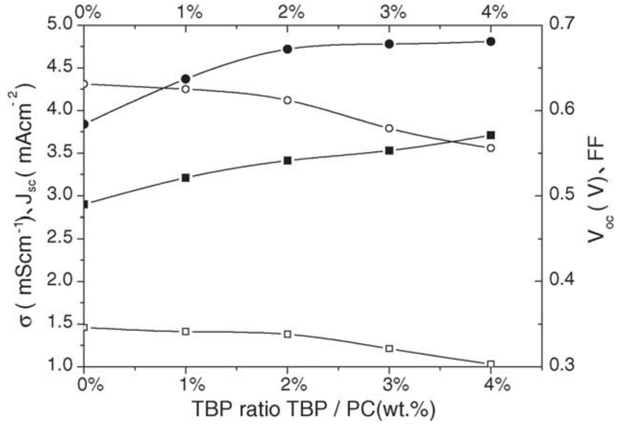

Fig. 4. TBP (4-*tert*-bytylpyridine)/PC ratio dependence of photocurrent–voltage properties: (○) $J_{sc}$; (□) $\sigma$; (●) $V_{oc}$; (■) FF.

### 3.3. *Influence of ionic conductivity on photoelectronic properties of DSSC*

In order to investigate the influence of ionic conductivity on photoelectronic properties of DSSC, a series of DSSCs were fabricated by sandwiching the gel polymer electrolyte with different amount of 4-*tert*-bytylpyridine (TBP). The *J*–*V* curves of the DSSC were measured, the fill factor (FF) was calculated, and the date is described in Fig. 4.

From Fig. 4, the open-circuit voltage ($V_{oc}$) and fill factor (FF) of DSSC increase greatly with the increase of the TBP ratio, this is because that the suppression of dark current at the semiconductor electrolyte junction through TBP blocks the surface states that are active in the charge transfer [21].

On the other hand, $J_{sc}$ decreases with increase of TBP concentration in TBP/PC mixed solvent from Fig. 4. This is because that $J_{sc}$ is depended on the ionic conductivity of electrolyte. TBP is a substance with higher viscosity, with the increase of amount of TBP, the viscosity of the mixed system increases, which result in the decrease of ionic conductivity shown in Fig. 4, and inducing the decrease of the $J_{sc}$. Considering the influence of the amount of TBP on both $J_{sc}$ and $V_{oc}$, the optimized quantity of TBP is about 2 wt.% of organic solvent.

Table 2 lists the photoelectronic data of the cells sandwiching gel polymer electrolyte with different organic solvents (adding 2 wt.% of TBP). It can be seen in Table 2, the highest photoelectronic values were obtained by using the highest ionic conductivity gel polymer electrolytes containing binary organic solvents EC and PC, and the change trend of photoelectronic values (short-circuit current density, open-circuit voltage, fill factor and overall energy conversion efficiency) of DSSCs accord with

Table 2
Photoelectronic values of the DSC with gel polymer electrolytes

| Electrolytes | $\sigma$ (mS cm$^{-1}$) | $J_{sc}$ (mA cm$^{-2}$) | $V_{oc}$ (V) | FF | $\eta$ (%) |
|---|---|---|---|---|---|
| PC | 1.46 | 4.12 | 0.672 | 0.541 | 2.50 |
| γ-BL | 1.61 | 4.30 | 0.715 | 0.535 | 2.74 |
| EC:PC [7:3 (w/w)] | 1.94 | 4.61 | 0.694 | 0.558 | 2.98 |
| EC:γ-BL [8:2 (w/w)] | 1.86 | 4.53 | 0.703 | 0.543 | 2.88 |

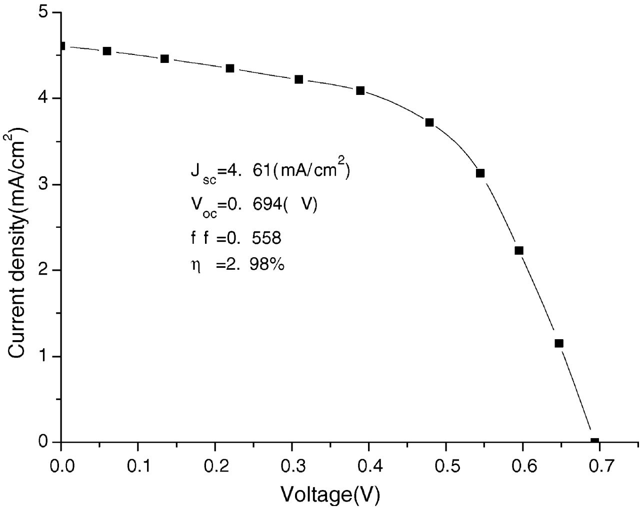

Fig. 5. Photocurrent–photovoltage curve for the quasi-solid state solar cell fabricated using the gel polymer electrolyte containing EC and PC [7:3 (w/w)].

the ionic conductivity, which reveal the important role of ionic conductivity of gel polymer electrolyte in DSSC.

### 3.4. Photovoltaic characterization of quasi-solid state dye-sensitized solar cells

Fig. 5 shows the photocurrent versus photovoltage characteristics for the cell based on the gel polymer electrolyte containing binary organic solvents EC and PC under irradiation of 60 mW cm$^{-2}$. The open-circuit voltage ($V_{oc}$) and short-circuit current density ($J_{sc}$) are 0.694 V and 4.61 mA cm$^{-2}$, respectively. The fill factor (FF) and overall energy conversion efficiency ($\eta$) of the cell were calculated to be 0.558 and 2.98%.

## 4. Conclusions

Gel polymer electrolyte based on the composite poly(acrylamide)–poly(ethylene glycol) and binary organic solvent was prepared successfully. The thermal stability, ionic conductivity of the gel polymer electrolyte, as well as the influence on the photoelectronic properties of DSSC were investigated, it is found that thermal stability of the composite satisfy the requirement of DSSC. The compositions and structure of solvent and additive affect the ionic conductivity of the gel polymer electrolyte, consequently, affect the photoelectronic properties of DSSC. Based on above study, the maximum ionic conductivity (at 30 °C) for the gel polymer electrolyte of 1.94 mS cm$^{-1}$ was obtained by using the composite of poly(acrylamide)–poly(ethylene glycol) as matrix, ethylene carbonate and propylene carbonate (7:3 (v/v)) as binary solvent, and 4-*tert*-bytylpyridine (2 wt.%) as additive. Further, a quasi-solid state dye-sensitized solar cell was fabricated and its overall conversion efficiency was approximately 3% under irradiation of 60 mW cm$^{-2}$.

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