

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} .

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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 proce-

dures are simple. These advantages of polymer gel electrolytes lead to broad 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:

$$Q_{le} = \frac{W - W_0}{W_0} \quad (1)$$

where W is the weight of swollen hybrid and W_0 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

TiO₂ colloidal paste and dye-sensitized TiO₂ 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 TiO₂ colloidal paste and dye-sensitized TiO₂ 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 reagent of Triton X-100 were added to form TiO₂ colloid.

The fluorinedoped SnO₂ conducting glass (FTO glass, sheet resistance 8 $\Omega \text{ cm}^{-2}$, purchased from Hartford Glass Co., USA) was first cleaned in Triton X-100 aqueous solution, washed with ethanol, and treated with 50 mM TiCl₄ aqueous solution at 70 °C for 30 min, to make a good mechanical contact between the following printed TiO₂ layer and the conducting glass matrix. The former prepared TiO₂ 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 TiO₂ film about 10 μm . The TiO₂ film was treated with 50 mM TiCl₄ aqueous solution in ambient environment for 12 h and washed with distilled water. Finally, the TiO₂ 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 TiO₂ electrode was dye-coated by immersing it into a 2.5×10^{-4} M absolute ethanol solution of *cis*-[(dcbH₂)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 TiO₂ 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 cm² (0.5 cm \times 1 cm). The fill factor (FF) and overall energy conversion efficiency (η) of the cell were calculated by the following equations:

$$FF = \frac{V_{\max} J_{\max}}{V_{oc} J_{sc}} \quad (2)$$

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

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-

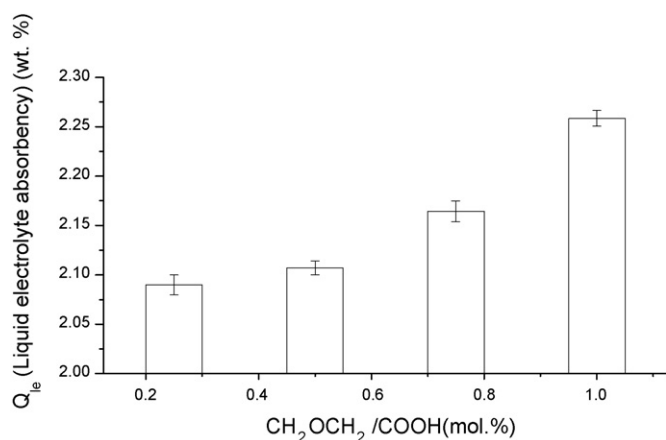


Fig. 1. Liquid electrolyte absorbency of the hybrid with various mole ratio of ether/acid groups in pure γ -butyrolactone.

ciently absorbed in the domain of PEG [19]. Therefore, the ratio of PAA and PEG in the hybrid plays a critical role in determining the absorbent ability of the hybrid for liquid electrolyte. Fig. 1 shows liquid electrolyte absorbency of the hybrid in pure γ -butyrolactone with different mol ratio of ether/acid groups ($\text{CH}_2\text{OCH}_2/\text{COOH}$). The liquid electrolyte absorbency increases with increasing mol ratio of ether/acid groups. The best value is obtained when the hybrid contains an equivalent mol ratio of ether/acid groups, and the polymer gel electrolyte shows high chemical stability. This is due to the efficient absorbent ability of PEG for liquid electrolyte. On the other hand, network can be formed in the gel through sufficient hydrogen bonding between ether and acid groups. However, the gel became unstable by further increasing the mol ratio of ether/acid groups in the hybrid. The reason is that on this condition the hydrogen bonding cannot hold all polymer chains of PEG in the network and the superabundant chains of PEG will dissolve in liquid electrolyte which causes higher liquid electrolyte absorbency (data not shown) but weaker network in the gel.

Fig. 2 illustrates liquid electrolyte absorbency dependence of ionic conductivity of polymer gel electrolyte with the hybrid matrix containing an equivalent mol ratio of ether/acid groups. As seen in Fig. 2, there exist three different change trends.

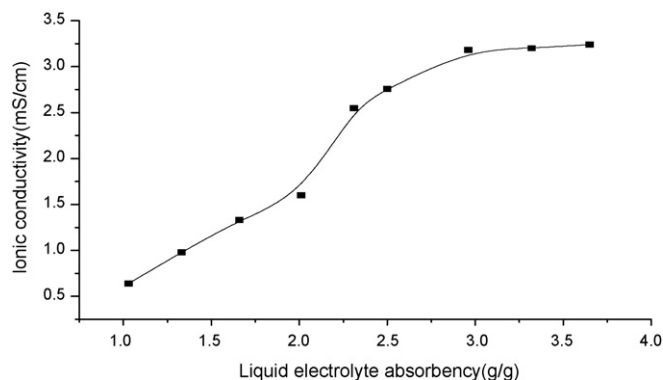


Fig. 2. Ionic conductivity of polymer gel electrolyte with the hybrid matrix containing an equivalent mol ratio of ether/acid groups as functions of liquid electrolyte absorbency.

The ionic conductivity of polymer gel electrolyte shows low value and increases relatively slowly when liquid electrolyte absorbency lower than 2. While it increases greatly in the case of liquid electrolyte absorbency changing from 2 to 2.5 and then attains a stable value. This phenomenon can be explained as follows: in the case of low liquid electrolyte absorbency, liquid electrolyte can merely soak the sample, ion transport depends on the segmental motions of polymer chains which causes relatively low ionic conductivity. The segmental motions of polymer chains become easier with increasing of liquid electrolyte absorbency which results in slow increase of ionic conductivity. For further increasing liquid electrolyte absorbency, a local solvent channel for ion conduction will be built in polymer gel network. The ion transport will be easier through the solvent channel than by the segmental motions of polymer chains. On the other hand, the network of polymer gel electrolyte swells bigger than ever which destroys part of hydrogen bonding in the gel. It is known that hydrogen bonding significantly affects conductivity, so the weaker hydrogen bonding linking in the gel leads to the higher ionic conductivity. The ion transport environment keeps stable with further increasing liquid electrolyte absorbency from 3 to 3.65. Therefore, ionic conductivity attains a stable value. It also can be seen that the highest value of liquid electrolyte absorbency of the hybrid in liquid electrolyte (with the value of 3.65) is higher than that in pure γ -butyrolactone (with the value of 2.26). The reason is that there exists a dynamic force for the hybrid swelling in liquid electrolyte. The formation of the dynamic force is through the reaction given in Fig. 3. Here S represents the organic solvent. The state of ions in liquid electrolyte is solvation ions. The hybrid contains many carbonyl groups and ether groups which both have been complexation with alkali metal ions, such as potassium ions, sodium ions [20]. Therefore, when soaking it in liquid electrolyte, the above reaction will occur. The dynamic force for liquid electrolyte immersing into the hybrid will be formed and leads to higher value of liquid electrolyte absorbency.

In order to investigate the stability of polymer gel electrolyte, ionic conductivity as functions of storage time at 30°C was measured and the result is shown in Fig. 4. The ionic conductivity has slight decrease during the first 20 h, and then remains constant over the rest measured time. The liquid electrolyte in the surface layer of polymer gel electrolyte is unstable and easy to volatilize. That is the reason for the slight decrease of ionic conductivity. The highest ambient ionic conductivity of polymer gel electrolyte reaches 3.24 mS cm^{-1} , and the constant value is about 3.06 mS cm^{-1} , whereas that of liquid electrolyte (0.5 M NaI, 0.05 M I₂, 0.5 M TBP in γ -butyrolactone) is 6.7 mS cm^{-1} . So the conclusion is that liquid electrolyte is well encapsulated in

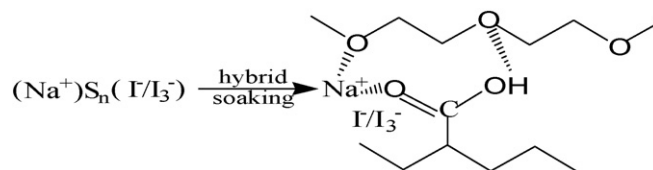


Fig. 3. The interaction between solvent and polymer host (absorbent).

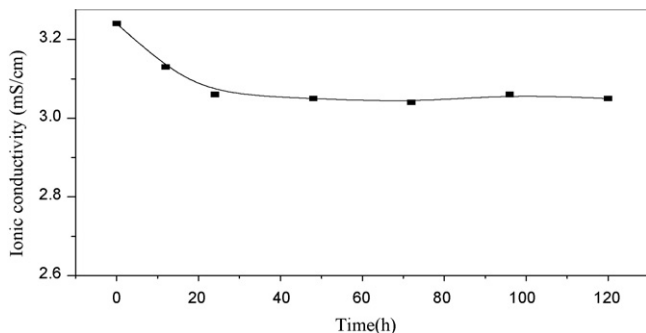


Fig. 4. Ionic conductivity of polymer gel electrolyte as functions of storage time at 25 °C.

Table 1

Parameters of photovoltaic performance of quasi-solid-state dye-sensitized solar cell assembled with polymer gel electrolyte at different light intensity

Light intensity (mW cm^{-2})	V_{oc} (mV)	J_{sc} (mA cm^{-2})	FF	η (%)
100	712	8.3	0.54	3.19
60	679	5.4	0.57	3.48
20	643	1.92	0.64	3.95

the network of the hybrid without leakage problem and obtains a moderate value of ambient ionic conductivity.

Photovoltaic performance of quasi-solid-state dye-sensitized solar cell assembled with polymer gel electrolyte at different light intensities is shown in Fig. 5. These curves were measured at light intensity of 20 mW cm^{-2} , 60 mW cm^{-2} and 100 mW cm^{-2} , respectively, and their parameters of photovoltaic performance were listed in Table 1. With the increase of light intensity power, the values of open-circuit voltage (V_{oc}) and short-circuit current density (J_{sc}) are both increased. Meanwhile, the data of fill factor and overall energy conversion efficiency (η) are decreased.

The aforementioned change tendencies can be explained by the following redox reactions and relation [21]:

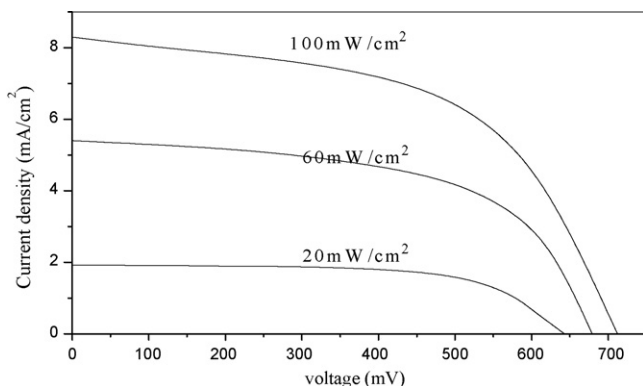
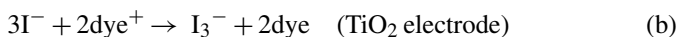


Fig. 5. Photocurrent–voltage curves for quasi-solid-state dye-sensitized solar cell assembled with polymer gel electrolyte at different light intensities.

$$V_{oc} = \left[\frac{kT}{e} \right] \ln \left\{ \frac{I_{inj}}{n_{cb} k_{et} [I_3^-]} \right\} \quad (4)$$

where k is Boltzmann constant, T the absolute temperature, e the electron energy, I_{inj} the flux of charge resulting from sensitized injection, n_{cb} the concentration of electrons at the TiO_2 surface, k_{et} the reaction rate constant of I_3^- dark reaction on TiO_2 and $[I_3^-]$ is the concentration of I_3^- in polymer gel electrolyte. An efficient transport of iodides and triiodides in the electrolyte is necessary for good performance of DSSCs. Because the oxidized state of dye (dye^+) should be regenerated by iodides efficiently after the electrons from the excited state of dye are injected into the conduction band of TiO_2 under illumination (Eq. (b)) to reduce the back reactions in the dye-sensitized solar cells and the maintain of sufficient amount of iodides needs the efficient transport of triiodides to counter electrode to regenerate iodides (Eq. (c)). Meanwhile, the electrons accumulated at counter electrode by the external circuit will lead to concentration over potentials for the electrolyte at the electrode and loss of energy of the dye-sensitized solar cells if the electrons are not transferred by iodides efficiently. However, the transport of iodides and triiodides in polymer gel electrolyte is not efficient than that in liquid electrolyte. In the case of low light intensity, the amount of excited state of dye in TiO_2 electrode is small. So the oxidized state of dye can be regenerated efficiently by the relatively low concentration of iodides. The low transport ability of iodides and triiodides in the system does not affect the photovoltaic performance and the cell shows relatively good fill factor and overall energy conversion efficiency. On the other hand, the small amount of oxidized state of dye (dye^+) and iodides in the system causes the low concentration of triiodides in the system according to Eqs. (a) and (b). Therefore, the value of V_{oc} is low according to the relation of (4). Meanwhile, the small amount of excited state of dye (dye^*) also causes the low value of J_{sc} . With the increase of light intensity, the amount of excited state of dye increases which causes the increase of V_{oc} and J_{sc} and needs higher concentration of iodide to regenerate the oxidized state of dye. On this condition, the poor transport ability of iodide and triiodide in polymer gel electrolyte will affect the light-to-electricity conversion process which causes the decrease of fill factor and overall energy conversion efficiency.

Fig. 6 shows the short-circuit current density versus light intensity of dye-sensitized solar cells made with liquid electrolyte and polymer gel electrolyte. The photocurrents are linear to the illumination intensity from 20 mW cm^{-2} to 100 mW cm^{-2} when the cell made with liquid electrolyte. However, the photocurrents of the cell employing polymer gel electrolyte begin to departure from the line at the point of 100 mW cm^{-2} . It suggests that the low iodide concentration caused by the poor ions transport ability of polymer gel electrolyte on TiO_2 electrode affects the regeneration of the oxidized dye which results in insufficient usable dye for light-to-electricity conversion at high light intensity.

The photocurrent density versus voltage curves of dye-sensitized solar cells with liquid electrolyte and polymer gel electrolyte at a light intensity of 100 mW cm^{-2} are presented in Fig. 7. The quasi-solid-state dye-sensitized solar cell shows a

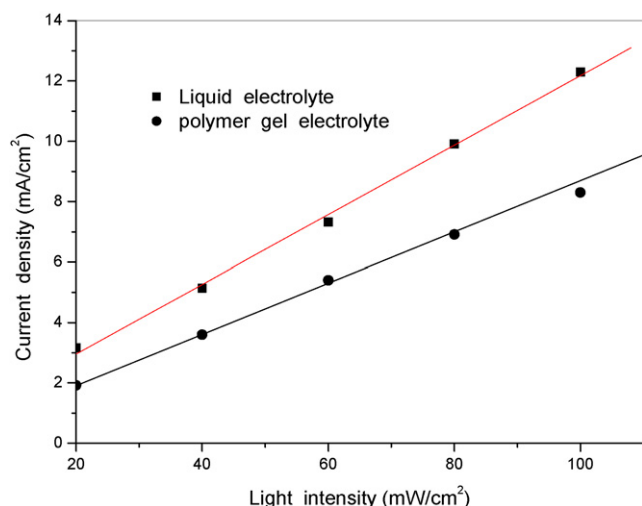


Fig. 6. Dependence of short-circuit current density on illumination intensity. The lines were drawn by fit linear of data from 20 mW cm^{-2} to 100 mW cm^{-2} and from 20 mW cm^{-2} to 80 mW cm^{-2} for liquid electrolyte and for polymer gel electrolyte, respectively.

Table 2
Parameters of photovoltaic performance of dye sensitized solar cells assembled with liquid electrolyte and polymer gel electrolyte at 100 mW cm^{-2}

Electrolyte	V_{oc} (mV)	J_{sc} (mA cm^{-2})	FF	η (%)
Liquid	680	12.3	0.55	4.6
Gel	712	8.3	0.54	3.19

lower short-circuit current density and higher open-circuit voltage than that of liquid electrolyte. The lower value of J_{sc} in the dye-sensitized solar cell assembled with polymer gel electrolyte is due to its lower ionic conductivity. The poor iodide–triiodide transport ability retards the kinetics of dye regeneration which is proved in Fig. 7, and therefore, decreases the J_{sc} . The higher value of V_{oc} for the cell with polymer gel electrolyte is related to the reduction of back electron-transfer reaction by polymer chains covering the surface of TiO_2 electrode. On the other hand, the layer of polymer gel electrolyte between two electrodes is thicker than that of liquid electrolyte, which affects the diffusion length of iodide–triiodide ions and results in lower overall energy conversion efficiency as shown in Table 2.

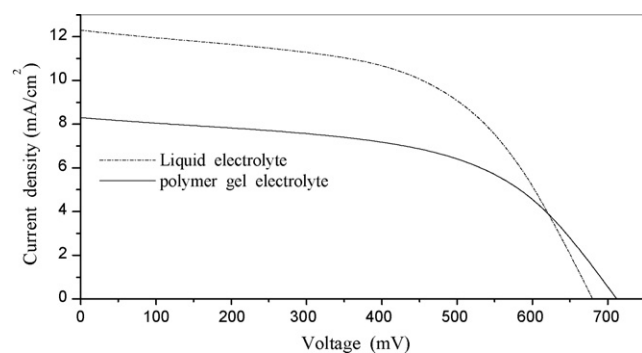


Fig. 7. Photocurrent–voltage curves for dye-sensitized solar cells assembled with liquid electrolyte and polymer gel electrolyte at a light intensity of 100 mW cm^{-2} .

4. Conclusions

A novel efficient absorbent for liquid electrolyte based on PAA–PEG hybrid polymer gel electrolyte is prepared. The mole ratio of PAA/PEG and ions in liquid electrolyte play critical roles in determining liquid electrolyte absorbency of the hybrid. The polymer gel electrolyte shows high stability and a moderate value of ambient ionic conductivity about 3.24 mS cm^{-1} . The affection of the poor ion transport ability of polymer gel electrolyte compared with that of liquid electrolyte on the photovoltaic performance of the cell is investigated and the conclusion is that it shows little affection on the performance of the cell on the condition of low light intensity, while it affects the performance of the cell seriously when the cell illuminated at high light intensity and results lower energy conversion efficiency than that of liquid electrolyte.

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