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Journal of Photochemistry and Photobiology A: Chemistry 170 (2005) 1–6

Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

A novel polymer quaternary ammonium iodide and application in quasi-solid-state dye-sensitized solar cells

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Received 10 February 2004; received in revised form 24 May 2004; accepted 13 July 2004
Available online 27 August 2004

Abstract

The characteristics of electrolytes containing novel polymer quaternary ammonium iodide, polysiloxane with quaternary ammonium side groups (PSQAS), were investigated. PSQAS exhibits a single-anionic conductivity and has special advantages over usually used iodides in dye-sensitized solar cells. Electrolytes based on PSQAS exhibited the maximum ambient conductivity (25 °C) of $4.96 \times 10^{-3}\,\mathrm{S\,cm^{-1}}$. The polymer gel electrolyte based on PAN and PSQAS has been employed to fabricate quasi-solid-state dye-sensitized solar cell with an overall conversion efficiency of 2.67% at irradiation of $100\,\mathrm{mW\,cm^{-2}}$.

Keywords: Polymer electrolyte; Polymer quaternary ammonium iodide; Polyacrylonitrile; Ionic conductivity; Quasi-solid-state dye-sensitized solar cells

1. Introduction

Due to their high energy conversion efficiency, low cost and environment-friendly photovoltaics, dye-sensitized solar cells based on nanocrystalline porous TiO_2 film have attracted widespread attention and have been investigated intensively as potential alternatives to traditional photovoltaic device [1–3]. The working principle of these cells is based on ultra fast electron injection from photoexcited dye into the conduction band of TiO_2 and subsequent dye regeneration and hole transport to the counter electrode. In these cells, organic solvent-based liquid electrolytes with inorganic triiodide/iodide as redox couple are generally used. The presence of liquid electrolytes, however, can cause the following problems: (i) the solvent evaporation and leakage of the electrolytes result in less long-term stability and decrease in cell performances; (ii) at room temperature, the solubility of inorganic salts such as LiI, KI and NaI in organic solvents is limited, while they are easily precipitated when the cells operate at lower temperature; (iii) organic solvents generally have poor compatibility with the sealing materials for the cells.

To overcome these problems, several attempts have been made to replace the liquid electrolytes with room temperature molten salts [4], p-type semiconductors [5,6], inorganic [7,8] or organic [9,10] hole transport materials, polymer electrolytes [11], polymer gel electrolytes [12,13] and addition of low molecular weight gelators to the liquid electrolytes [14,15]. The cells employing the former four electrolytes, however, show lower energy conversion efficiencies. Although the gelation of the liquid electrolytes using low molecular weight gelators has yielded quasi-solid-state solar cells with comparable energy conversion efficiency to those with liquid electrolytes, the problems of sealing and stability of the cells still remain. Using polymer gel electrolytes is favorable to overcome these problems. Therefore, they

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doi:10.1016/j.jphotochem.2004.07.016

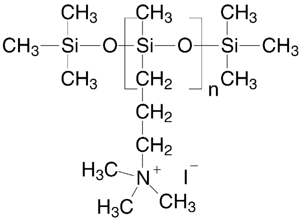

Fig. 1. The structure of PSQAS.

have been attracting intensive attention [16–19]. However, the factors that limit the compatibility between inorganic salts and polymer matrixes and the solvent retention ability of polymer gel electrolytes affect the conductive properties of electrolytes. Thus, the cells with them still exhibit lower efficiencies compared with those using liquid electrolytes.

In recent years, efforts have been made to improve the performance and efficiency of the quasi-solid-state dye-sensitized solar cells with polymer gel electrolytes. A novel polymer quaternary ammonium iodide, a polysiloxane containing quaternary ammonium groups (PSQAS), has been synthesized in our laboratory [20]. PSQAS consists of a bulky polycation and anions, as shown in Fig. 1. Different from inorganic iodide, PSQAS shows excellent compatibility with organic solvent or plasticizers such as ethylene carbonate (EC) and propylene carbonate (PC), which is beneficial to form gel-like viscous electrolyte solution at high concentration of PSQAS. On the other hand, PSQAS is also compatible very well with polymer matrixes such as polyacrylonitrile (PAN), polyethylene oxide (PEO). These favorable properties of PSQAS make it easy and convenient to form polymer gel electrolytes with polymer matrixes. The purpose of this paper is to characterize this novel polymer quaternary ammonium iodide and investigate the application of polymer gel electrolytes based on PSQAS in quasi-solid-state dye-sensitized solar cells.

2. Experimental

2.1. Synthesis of polysiloxane with quaternary ammonium groups (PSQAS)

A functional polysiloxane with tertiary amino side groups was firstly synthesized by hydrosilylation of poly-(methylhydrosiloxane) (PMHS) with *N*,*N*-dimethylallylamine (DMAA). A 0.4 M toluene solution of PMHS was reacted with a 50 mol% excess of DMAA at 90 °C for 24 h in the presence of dicyclopentadienylplatinum(II) chloride (Cp_2PtCl_2). After toluene and excess DMAA were evaporated under vacuum, the resulting functionalized polysiloxane was dissolved in ethanol and quaternized with a large excess of methyl iodide at 40 °C for 24 h. After the reaction completed, the solvent and excess methyl iodide were removed under reduced pressure. With ^{1}H NMR analysis, the degree of quaternization was determined as about 100%.

2.2. Preparation of polymer gel electrolytes

Polymer gel electrolytes were prepared with PAN and PSQAS liquid electrolytes obtained by dissolving PSQAS and iodine in a mixed solvent of EC and PC (EC:PC = 8:2 (w/w)). Under continuous stirring, appropriate amounts of PAN were added into PSQAS electrolytes. Then the resulting mixture was sealed in a bottle and heated at 80 °C until a viscous solution was obtained, followed by cooling down to room temperature.

2.3. Measurement of thermal stability and ionic conductivity

Thermal stability was determined with a thermogravimetric analyzer (Perkin-Elmer TGA7) over a temperature range of 60–650 °C at a heating rate of 20 °C/min.

The ionic conductivity of PSQAS liquid electrolytes was measured by using model DDSJ-308A conductometer (Shanghai REX Instrument Factory) in the 25–70 °C temperature range. The measurements of ionic conductivity for polymer gel electrolytes were made with HIOKI LCR 3520 Hi TESTER at 1 kHz. The sample was placed in a polytetrafluoroethylene space ring that was compressed between two stainless electrodes and sealed in a testing cell.

2.4. Fabrication of dye-sensitized TiO_2 solar cells

The dye-sensitized TiO_2 films were prepared by the following procedures [1,2]. A colloidal TiO_2 suspension was prepared by hydrolysis of titanium isopropoxide (Aldrich, 97%) precursor in a nitric acid aqueous solution of pH 1 under vigorous stirring at 80 °C. The suspension was then autoclaved at 250 °C for 12 h and concentrated in a rotary evaporator, followed by adding carbowax (*M* 20,000) and ultrasonic dispersion to give a viscous TiO_2 paste. The nanocrystalline TiO_2 electrode (crystal phase of TiO_2 particles: anatase, particle size: 13.5 nm, film thickness: 8 μm, roughness factor: 1200, porosity: 40%) was obtained by spreading the TiO_2 paste on the F-doped SnO_2 conducting glass (sheet resistance: 30 Ω square^{-1}) and sintering at 450 °C for 30 min in air. After cooling to about 80 °C, the TiO_2 electrode was immersed in 5×10^{-4} mol/L dye solution of *cis*-di(thiocyanato)-*N*,*N*′-bis(2,2′-bipyridyl-4.4′-dicarboxylic acid) ruthenium(II) complex ($[RuL_2(NCS)_2]$) in absolute ethanol, and kept for 36 h (quantity of the adsorbed dye per unit area: 1.5×10^{-7} mol cm^{-2}). Afterwards, the dye-sensitized TiO_2 electrode was rinsed with absolute ethanol and dried in air.

Dye-sensitized nanocrystalline solar cells were fabricated by sandwiching polymer electrolytes between the dye-sensitized TiO_2 electrode and a Pt plate with a clamp without any sealing.

2.5. *Measurements of photoelectrochemical characteristics*

Photoelectrochemical measurements were performed with a potentiostat/galvanostat (EG&G Princeton Applied Research, model 273) at room temperature. A 250 W tungsten halogen lamp was used as a light source. The incident light intensity and the active cell area were 100 mW/cm^2 and 0.20 cm^2, respectively.

3. Results and discussion

3.1. *Thermogravimetric analysis*

Most of quaternary ammonium salts have higher hydroscopicity and poorer thermal stability than inorganic salts. As a novel polymer quaternary ammonium iodide, PSQAS must have the stabilities satisfied the requirement of the practical application in dye-sensitized solar cells. Therefore, the thermal behavior of PSQAS was examined firstly. Thermogravimetric curve depicted in Fig. 2 shows that before thermal degradation, the samples measured only have about 5% loss in weight, which is due to absorbent water from air in the keeping process, indicating that PSQAS has lower hydroscopicity. Also, it can be observed from Fig. 2 that the thermal degradation of PSQAS occurred up to 257 °C, which illustrates that this novel polymer quaternary ammonium iodide possesses excellent thermal stability.

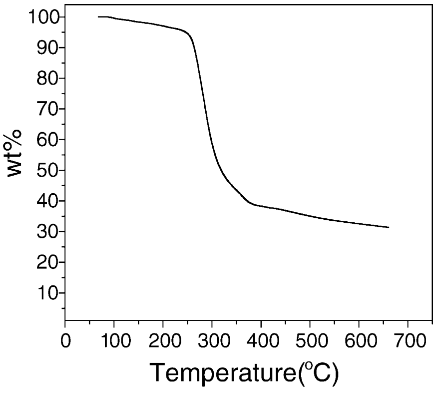

Fig. 2. TGA thermogram of PSQAS.

3.2. *Ionic conductivity measurement*

As can be seen from the chemical structure of PSQAS shown in Fig. 1, it consists of a bulky polycation with high molecular weight and anions. The migration of the polycation can be negligible and only the anions (I$^-$) are mobile, which make PSQAS to exhibit a single-anionic conductivity. In order to achieve levels of the ionic conductivity suitable for practical use, it is required to increase the number of the mobile ions in the electrolyte by enhancing ionic dissociation and promoting the transport of dissociated ions. It has been found that the ionic conductivity of the polymer electrolytes can be increased by incorporating appropriate species and amounts of suitable plasticizers into them [12,16,21,25], which would not only improve the degree of dissociation of the electrolytes, but also decrease their microscopic viscosity and form ion-transferring channels. The ambient ionic conductivity data of PSQAS electrolytes containing various plasticizers are summarized in Table 1. In these plasticized electrolytes, the concentration of PSQAS is maintained to be 0.3 M. The change in the ionic conductivity depends on the properties of plasticizers.

Table 1
The conductivity of electrolytes with different plasticizers at 0.3 M PSQAS

Plasticizers	$\sigma \times 10^{-3}$ (30 °C) (S cm^{-1})
3-Methoxypropionitrile	1.95
PC	2.13
EC:PC (5:5 (w/w))	2.18
EC:PC (8:2 (w/w))	3.23

As shown in Table 1, a binary plasticizer (EC:PC = 8:2 (w/w)) exhibits higher ionic conductivity than any other one at the given PSQAS concentration. In addition to the plasticizers list in Table 1, others such as γ-butyrolactone (γ-BL), dimethylformamide (DMF) and poly(ethylene glycol) with average molecular weight 400 (PEG400) were also examined, but their effects are less than the binary plasticizer (EC:PC = 8:2 (w/w)) with a high dielectric constant and a low viscosity. The stronger polarity of plasticizers with a high dielectric constant may contribute to the enhancement of ionic dissociation of I$^-$ from PSQAS, leading to the higher conductivity. Hence, this binary plasticizer was preferred in following experiments.

The ln σ versus 1/T plots for the electrolytes with different concentration of PSQAS were shown in Fig. 3. The influence of temperature on the ionic conductivity was measured in the range of 25–70 °C. It obviously shows that the ionic conductivity increased with the increase in temperature, especially when the concentration is at 4.5 M. This behavior can be rationalized by recognizing the free-volume model [22]. As temperature increases, the free volume increases, resulting in an increase in the overall mobility of ions and polymer

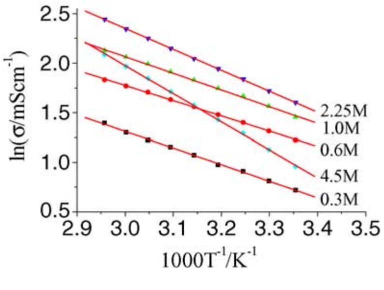

Fig. 3. Temperature dependence of the ionic conductivity for the electrolytes with different concentration of PSQAS.

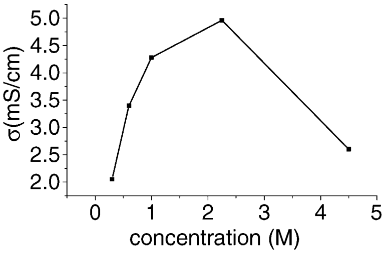

Fig. 4. Effect of PSQAS concentration on the ambient conductivity for the electrolytes containing a binary plasticizer (EC:PC = 8:2 (w/w)).

Table 2
The photoelectrochemical data of the dye-sensitized solar cells assembled with electrolytes of PSQAS/I_2/EC + PC

PSQAS concentration (M)	J_{sc} (mA cm^{-2})	V_{oc} (V)	η (%)	ff
0.3	9.7	0.59	3.92	0.69
0.6	11.7	0.59	4.57	0.68
1.0	17.4	0.64	6.83	0.62
2.3	16.7	0.66	6.49	0.59
4.5	15.0	0.51	6.21	0.64

chains. The $\ln \sigma$ versus $1/T$ plots are linear, suggesting that the temperature dependence of ionic conductivity may obey the "Arehenius" equation:

$$\sigma = A \exp(-E_a/RT)$$

where E_a is the activation energy, R the molar gas constant, A a constant, and T the absolute temperature. Fig. 3 also shows that the alteration of the concentration of PSQAS has a dramatic effect on the slopes of the plots, which was attributed to the variation of E_a caused by the increase of the concentration of PSQAS. From the slopes of the plots, each E_a of the electrolytes containing different concentration of PSQAS was evaluated. E_a changes in turns from 13.74, 14.69, 14.04, 17.59 to 23.60 kJ mol^{-1}, when the concentration of PSQAS varies from 0.3, 0.6, 1.0, 2.3 to 4.5 M.

Variation of the ambient conductivity (25 °C) as a function of PSQAS concentration is shown in Fig. 4. The ionic conductivity initially increases and attains a maximum. After the maximum conductivity of 4.96×10^{-3} S cm^{-1} is reached at the PSQAS concentration of 2.3 M, the conductivity gradually decreases with increase in the concentration. This tendency can be rationalized by the variations of charge carriers and the viscosity of the electrolytes. With the accretion of the PSQAS concentration, the viscosity of the electrolytes increases, which decreases the mobility of the charge carriers hence intends to reduce the ionic conductivity. At low PSQAS concentration, the initial increase in the ionic conductivity is attributed to the build-up of charge carriers [23]. At high PSQAS concentrations, the build-up of charge carriers is offset by the retarding effect of ionic clouds and the viscosity of the electrolytes rises up largely, resulting in the decrease in ionic conductivity [24].

For comparison, we also measured the ionic conductivity of the liquid electrolytes based on inorganic or organic iodides commonly used in dye-sensitized solar cells. The ambient (25 °C) conductivities of three different liquid electrolytes consisting of tetrabutyl ammonium iodide ($Bu_4N^+I^-$), KI or methylethylimidazolium iodide (MEImI) of same concentration (0.3 M) in a mixture solvent of EC and PC (EC:PC = 8:2 (w/w)) are 4.86×10^{-3}, 6.06×10^{-3} and 6.86×10^{-3} S cm^{-1}, respectively. It was clear that the maximum ambient conductivity for PSQAS-based electrolytes is substantially at the similar order with these three electrolytes. This indicates that the electrolytes with suitable PSQAS concentration have a good conductive performance, and when used in dye-sensitized solar cells, it will not increase the internal resistance of the cell and thus impede the charge transport between the electrodes. Therefore, it may be very useful in dye-sensitized solar cells, especially in quasi-solid-state solar cells based on polymer gel electrolyte.

3.3. *Photoelectrochemical property measurement*

In order to investigate the photoelectrochemical properties of the dye-sensitized solar cells with electrolytes based on PSQAS, a series of cells were fabricated using the electrolytes with different concentration of PSQAS, I_2 and EC:PC (8:2 (w/w)). The concentration of I_2 was maintained to be 0.05 M.

Table 2 lists the measured photoelectrochemical data of the above cells. From Table 2, it can be clearly concluded that the photoelectrochemical performance of the cells was deeply dependent on the PSQAS concentration in the electrolytes. Although with the increase of the PSQAS concentration, the ionic conductivity of the electrolyte increased and reached the maximum value at 2.3 M (see Fig. 4), the viscosity of the electrolyte also increased greatly. This increase in the viscosity can reduce the diffusion rate of I_3^- in the electrolyte and hence affect the performance of cells, especially short circuit density (J_{sc}) [25]. Therefore, comprehensively influenced by both the conductivity and viscosity of PSQAS solution, the optimum photoelectrochemical performance was achieved at PSQAS concentration of 1.0 M, yielding a short circuit current density (J_{sc}) of 17.4 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 0.64 V, an overall efficiency (η) of 6.83% and a fill factor (ff) of 0.62. Such performance was close very much to the one obtained from the cell assembled by the liquid electrolyte containing KI at the same measuring conditions (J_{sc} of 18.5 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 0.65 V, an overall efficiency (η) of 6.6% and a fill factor (ff) of 0.55), which further illustrated that PSQAS can be used as I^- anionic conductor to replace the iodides usually used in dye-sensitized solar cells and be adequate to the needs of these cells.

PAN-based polymer gel electrolytes have been used in quasi-solid-state dye-sensitized solar cells by solution casting technique [12,26]. In these cells, inorganic or organic iodides such as NaI, LiI or tetrapropyl ammonium iodide ($Pr_4N^+I^-$) and iodine were usually used as redox couple. On our study, novel polymer quaternary ammonium iodide, PSQAS, was

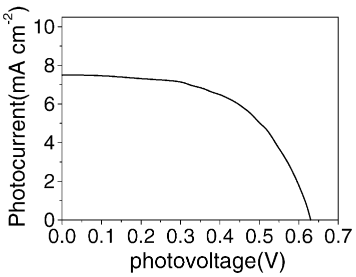

Fig. 5. Photocurrent–photovoltage curve for the quasi-solid-state solar cell fabricated using the electrolyte of PAN/PSQAS/I_2/EC/PC.

employed to substitute the above iodides and to compose polymer gel electrolytes with PAN. Out of various electrolyte compositions studied, the electrolyte containing 10 wt.% of PAN was preferred to assemble the quasi-solid-state cell with higher performance in terms of both ionic conductivity and the contact between the polymer electrolytes and nanoporous TiO_2 electrode. The polymer gel electrolyte with composition of PAN (10 wt.%)/PSQAS (1.0 M)/I_2 (0.05 M) in a mixture of EC and PC (EC:PC = 8:2 (w/w)) exhibited the ionic conductivity (30 °C) of 2.97×10^{-3} S cm^{-1}. After assembling the cell (assembling time: less than 2 min), retarded photocurrent increase with illumination time was not observed in the experiments, indicating the polymer gel electrolyte used penetrate completely into the pores of the porous TiO_2 electrode for less than 2 min.

Fig. 5 shows the photocurrent versus photovoltage characteristics for the cell based on the PAN-PSQAS quasi-solid polymer electrolyte under irradiation of 100 mW cm^{-2}. The open-circuit voltage (V_{oc}) and short-circuit photocurrent density (J_{sc}) are found to be 0.63 V and 7.5 mA cm^{-2}, respectively. The fill factor (ff) and overall energy conversion efficiency (η) of the cell were calculated to be 0.57 and 2.67%. The performance of this cell can be further improved by optimizing the electrolyte composition and the fabrication of the cell. Long-term stability investigation of the cell is in progress.

4. Conclusion

A novel polymer quaternary ammonium iodide, PSQAS, has been presented. Thermogravimetric result revealed that it has thermal stability up to 257 °C. PSQAS-based electrolytes exhibited a good anionic (I^-) conductive performance. The maximum ambient (25 °C) conductivity of the electrolyte with suitable concentration of PSQAS was 4.96×10^{-3} S cm^{-1}, which is close to commonly used liquid electrolytes with inorganic or organic iodides. The dye-sensitized solar cells assembled with the electrolyte composition of PSQAS (1.0 M)/I_2 (0.05 M)/EC + PC exhibits a comparable photoelectrochemical performance to cells with liquid electrolyte based on KI. A quasi-solid dye-sensitized solar cell employing the polymer gel electrolyte composed of PAN/PSQAS/I_2/EC/PC was successfully fabricated. The J_{sc}, V_{oc}, and FF of the cell are 7.5 mA/cm^2, 0.63 V and 0.57, respectively, yielding 2.67% efficiency at irradiation of 100 mW/cm^2. Further optimization of the electrolyte composition and the cell assembly is expected to enhance the efficiency of the cell.

Acknowledgements

This work was supported by National Research Fund for Fundamental Key Project (G2000028205), Hi-Tech Research and Development Program of China (2002 AA 302403), Innovative Foundation of Chinese Academy of Sciences (KGCX2-303-02) and the National Natural Science Foundation of China (No. 50221201).

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