

Application of Thermosetting Organic Solvent Free Polymer Gel Electrolyte in Quasi-Solid-State Dye-Sensitized Solar Cell

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Received 9 July 2009; accepted 5 October 2009

DOI 10.1002/app.31564

Published online 23 December 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A kind of thermosetting organic solvent free polymer gel electrolyte with oligomer ethylene glycol as liquid phase was prepared and applied in quasi-solid-state dye-sensitized solar cell (QS-DSSC). The viscosity and the ionic conductivity of the polymer gel electrolyte are sensitive to the changed temperature. The photovoltaic performance of QS-DSSC is also improved with the

increased temperature due to the increased ionic conductivity and diffusion coefficient of iodide in polymer gel electrolyte. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1329–1333, 2010

Key words: polymer gel electrolyte; organic solvent free; dye-sensitized solar cell; ionic conductivity; viscosity

INTRODUCTION

Since the prototype of a dye-sensitized solar cell (DSSC) was reported in 1991 by O'Regan and Gratzel,¹ considerable efforts have been devoted to it. Based on liquid electrolyte, a light-to-electricity conversion efficiency of 11% for DSSC has been achieved.² However, the potential problems caused by liquid electrolytes, such as, the leakage and the volatilization of organic solvents, are considered as some of the critical factors limiting the long-term performance and practical use of DSSC. Thus, researchers have been paying attentions to find the substitutes of liquid electrolytes, such as, organic-inorganic p-type semiconductors and polymer electrolytes.^{3–5} It is found that polymer gel electrolytes can obtain moderate long-term stability and maintain highly photovoltaic performance of quasi-solid-state dye-sensitized solar cell (QS-DSSC) due to their excellent interfacial contacting property.^{6,7} In the continuous efforts, a light-to-electrical energy conversion efficiency of over 7% for QS-DSSC has

been achieved.⁸ However, QS-DSSC based on polymer gel electrolyte still contains volatile organic solvent components, which will influence the long-term stability. So some kinds of nonvolatile solvents, such as, ionic liquid, oligomers are used to fabricate organic solvent free polymer gel electrolytes.^{9,10}

QS-DSSCs based on gel electrolyte with polymer or organic molecular gelling agents containing ether groups usually show highly photovoltaic performance, which mainly due to the perfect solvate ability of ether groups with I^-/I_3^- redox couples.^{8–10} Taking into account of good performance of ether groups in polymer gel electrolytes for QS-DSSC, the oligomer ethylene glycol (O-EG) is selected as liquid phase in preparing organic solvent free polymer gel electrolyte for QS-DSSC. Due to the perfect complexing interaction between ether groups and alkali metal ions, KI and I_2 were selected as charge carriers and the source of I^-/I_3^- redox couples used in QS-DSSC. The polymer gel electrolyte shows typical thermosetting property, namely, the characteristics of polymer gel electrolyte are changed with the changed temperature. The photovoltaic performance of QS-DSSC based on this kind of polymer gel electrolyte is also sensitive to temperature. Thus, the highly photovoltaic performance of QS-DSSC can be obtained at high temperature.

EXPERIMENTAL

Materials

O-EG with average molecular weight 600, polyvinyl pyrrolidone (PVP) with average molecular weight

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Contract grant sponsor: National High Technology Research and Development Program of China; contract grant number: 2009AA03Z217.

Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: 50572030, 50842027.

Contract grant sponsor: Natural Science Foundation of Hua Qiao University; contract grant number: 09BS401.

40,000, titanium iso-propoxide, nitric acid, glacial acetic acid, terpineol, ethyl cellulose, ethanol, KI, and I₂ were all A.R. grade and all purchased from Sinopharm Chemical Reagent Co., China. All reagents were used without further treating.

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 substrates for precipitating TiO₂ porous films. Sensitized dye N-719 [RuL₂(NCS)₂, L = 4, 4'-dicarboxylate-2,2'-bipyridine] and optical diffuser paste Ti-Nanoxide 300 were purchased from Solaronix SA.

Preparation of organic solvent free polymer gel electrolyte

Organic solvent free polymer gel electrolytes were prepared by mixing suitable amount of KI, I₂, PVP, and 10 g O-EG in ethanol under continuous stirring to form homogeneous solution. Then the solution was kept in a vacuum oven at 333.15 K till the whole weight attained to a constant value. The role of PVP here is used as gelling agent to gel O-EG.

Assembling of quasi-solid state dye-sensitized solar cell

The preparation of TiO₂ colloidal paste and double-layer film was according to the method reported in our former papers.^{11,12} The TiO₂ colloidal paste was used to fabricate the transparent film about 10 μm. Then the optical diffuser film about 4 μm was printed above the transparent film by using Ti-Nanoxide 300 paste. After sintering at 773.15 K and cooling down to 353.15 K, the double-layer nanostructured TiO₂ electrodes were dye-coated by immersing them into a 2.5 × 10⁻⁴ M absolute ethanol solution of dye for 24 h. A drop of high temperature polymer gel electrolyte was sandwiched between a dye-sensitized TiO₂ electrode and an electrodeposited platinum counter electrode. The two electrodes were clipped together and a piece of cyanoacrylate adhesive (15–30 μm) was used as sealant. Bisphenol A epoxy resin (using ethylenediamine as epoxy hardener) was used for further sealing process.

Measurements

The ionic conductivity of samples was measured with model DDB-6200 digitized conductivity meter (Shanghai Reici Instrument Factory, China). The instrument was calibrated with 0.01M KCl aqueous solution before experiments. The viscosity of samples was measured with model NDJ-8S digitized viscosity meter (Cany precision Instruments Co., China). If not mentioned specially, the measure-

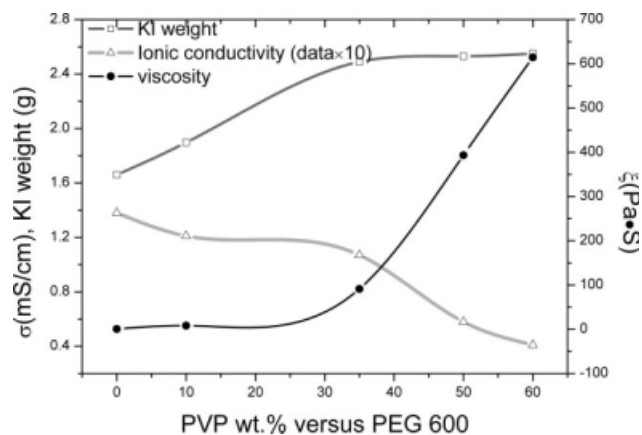


Figure 1 The influences of PVP on the saturated concentration of KI, the ionic conductivity, and the viscosity of polymer gel electrolyte.

ments were carried out at 298.15 K in ambient atmosphere.

The photovoltaic tests of QS-DSSCs were carried out by measuring the J - V characteristic curves under irradiation of white light from a 500 W xenon arc lamp (CHF-XM 500, Trusttech Co., China) with AM 1.5 G filter (Oriol, USA) under 298.15 K in ambient atmosphere and recorded with CHI 660 C electrochemical workstation (CH Instrument, China). The incident light intensity and the active cell area were 100 mW cm⁻² and 0.5 cm² (1 × 0.5 cm²), respectively. The fill factor (FF) and overall energy conversion efficiency (η) were calculated by the following equations:

$$FF = \frac{V_{\max} \times J_{\max}}{V_{oc} \times J_{sc}} \quad (1)$$

$$\eta (\%) = \frac{V_{\max} \times J_{\max}}{P_{in}} \times 100\% = \frac{P_{\max}}{P_{in}} \times 100\% \quad (2)$$

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

RESULTS AND DISCUSSION

The addition of PVP in O-EG electrolyte causes the phase state turning from liquid to gel and even solid. As shown in Figure 1, the additional amount of PVP has some big influences on the saturated concentration of KI, the maximum ionic conductivity, and the viscosity of polymer gel electrolytes. Due to the coordination interaction between PVP and KI, the addition of PVP can increase the saturated concentration of KI till it attains to 35 wt %.

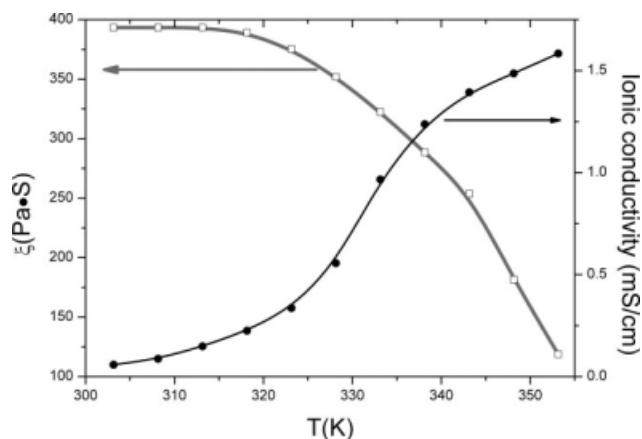


Figure 2 The ionic conductivity and the viscosity of polymer gel electrolyte as functions of temperature.

The ionic conductivity of polymer gel electrolyte decreases with the addition of PVP. When the amount of PVP is lower than 35 wt %, the values of ionic conductivity decrease slightly, whereas for further increased amount of PVP, the values of ionic conductivity decrease greatly. It is mainly due to the increased viscosity of polymer gel electrolyte with the increased amount of PVP. It is seen that the viscosity of polymer gel electrolyte increases greatly when the amount of PVP higher than 35 wt %, which causes the phase state turning from liquid to gel, and further to solid.

To keep the high stability of polymer gel electrolyte, the polymer gel electrolyte with 50 wt % PVP, 2.53 g KI, and 0.387 g I₂ [KI/I₂ = 10/1 (mol/mol)] is selected to investigate the temperature influences on its characteristics, such as, ionic conductivity and viscosity, and the photovoltaic performance of QS-DSSC. Figure 2 shows the change tendencies of the ionic conductivity and the viscosity of polymer gel electrolyte with the increased temperature. The ionic conductivity increases with the increased temperature, whereas the viscosity decreases simultaneously. Going with the decreased viscosity, the phase of polymer gel electrolyte turns from solid (400 Pa S) to gel and can keep in gel state even at high temperature (the viscosity keeps above 100 Pa S). It is known that the viscosity is an important influent factor on the ionic conductivity of polymer gel electrolyte,⁸ so the great decreased viscosity results in the increased ionic conductivity. The tendency of changed ionic conductivity presents as a reversal S-shape. The higher increased amplitude of ionic conductivity among the temperature from 323.15 to 338.15 K is mainly owing to the phase variation of polymer gel electrolyte from solid to gel, which causes the big change of ionic diffusion environment.

The viscosity and the ionic conductivity dynamic mechanism of polymer gel electrolyte can be

obtained from the plots fitted curves. As shown in Figure 3, the simplified Mcallister eq. (3) and Arrhenius relationship eq. (4) are used to fit the plots in Figure 2.

$$\ln(\xi/\xi_0) = \ln B + \frac{\Delta G^*}{RT} \quad (3)$$

$$\ln \sigma(T) = \frac{-E_a}{RT} + \ln A \quad (4)$$

where ξ and ξ_0 are the viscosity of solution and solvent, R is the molar gas constant, ΔG^* is the plastic flow free energy, and B can be considered as constant in a small temperature range, σ is the conductivity, A is a constant, E_a is activation energy, and R is the universal gas constant.

According to the viscosity (ξ) and the plastic flow free energy (ΔG^*) from Figure 3, the polymer gel electrolyte can be divided into three stages. Because of the high amount of PVP and extremely high viscosity, the phase state of the polymer gel electrolyte is solid in low temperature, and it turns to gel with the increased temperature. The phase transition temperature (T_p) is 342 K and the plastic flow free energy (ΔG^*) as calculated from Mcallister plots is 13.40 kJ mol⁻¹ in the solid state and 76.41 kJ mol⁻¹ in the gel state.

The ΔG^* reflects the solvent molecular mobility and the interaction between polymer host chains (PVP) and solvent molecules (O-EG).^{13,14} In low temperature range, the state of PVP host is solid, the O-EG chains are kept in the networks of PVP host, which is the main interaction between O-EG chains and PVP. The increased temperature causes the melting of PVP and the destroying of the above interaction, which result in the little decrease of viscosity. The process needs low energy, so the values of ΔG^* in low temperature range are relatively low.

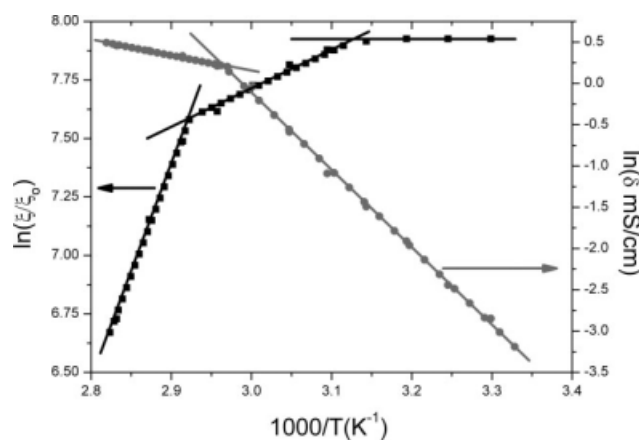


Figure 3 The temperature influences on the ionic conductivity and the viscosity of polymer gel electrolyte (the fitted curves of $\ln(\xi/\xi_0) - 1/T$ and $\ln \sigma - 1/T$).

Although in high temperature range, the polymer gel electrolyte keeps in the gel state, the main interaction between O-EG chains and PVP host chains turns to entanglement and hydrogen bond interaction, to overcome these interactions high energy is needed, so it shows relatively high ΔG^* .

Similar as the change tendencies of viscosity shown in Figure 3, the change tendencies of ionic conductivity contain three parts with different slopes. The slopes of fitted curves decrease with the increased temperature, the values of E_a also change from $77.71 \text{ kJ mol}^{-1}$ to $16.03 \text{ kJ mol}^{-1}$. The turning points in the curves signify the ionic conductivity transition temperature (T_c), which is 337 K. When the polymer gel electrolyte keeps in gel state, the ionic conductivity mainly depends on the ionic hopping frequency, which needs relatively low energy, so the value of E_a is low. However, when it keeps in solid state, the high intrinsic resistance for ionic transportation in the system causes the high value of E_a .

The photovoltaic performance of QS-DSSC with the changed temperature is shown in Figure 4. It is seen that the short-circuit current density and the maximum output power increase with the increased temperature, whereas the open-circuit voltage changes little. Because of the incident light intensity is 100 mW cm^{-2} , according to the eq. (2), the value of light-to-electricity conversion efficiency (η) is the same as the P_{\max} . The increased ionic conductivity is benefit for obtaining high short-circuit current density. Another reason is owing to the increased diffusion coefficient of iodide in polymer gel electrolyte with the increased temperature.

As shown in Figure 5, the steady state current of iodide in polymer gel electrolyte is increased with the increased temperature, whereas triiodide in polymer gel electrolyte changes little. It means that

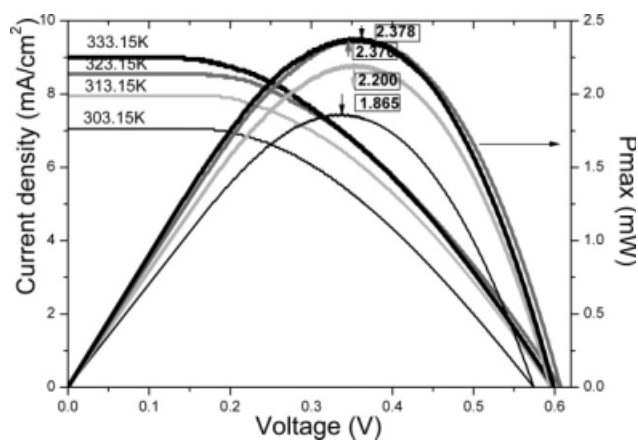


Figure 4 Photovoltage-current density curves of QS-DSSC with polymer gel electrolyte measured at different temperature.

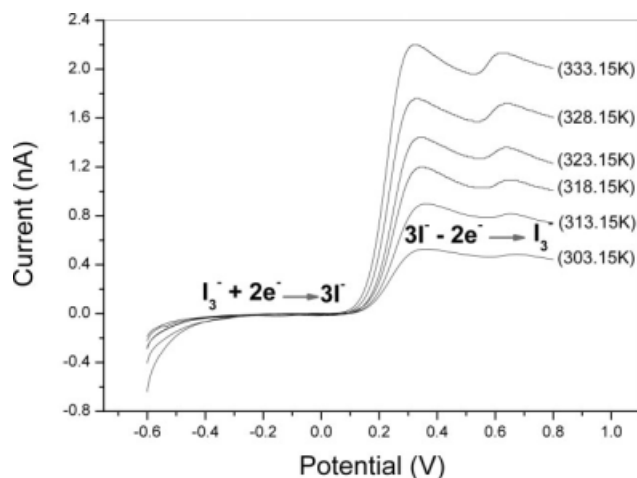


Figure 5 Steady state voltammograms of polymer gel electrolyte measured at scanning rate of 5 mV S^{-1} and different temperature.

iodide can easily diffuse in polymer gel electrolyte at high temperature and the diffusion ability of triiodide changes little,¹⁵ which is benefit for increasing short-circuit current density due to the sufficient supply of iodide for reborn of dye and maintaining the unchanged dark reaction.¹⁰ The final result is the increased photovoltaic performance of QS-DSSC. The unchanged dark reaction with the increased temperature also can be verified from the dark $I-V$ curves as shown in Figure 6, which shows that the onset of applied voltage for generating dark current in QS-DSSC changes little with the increased temperature.

CONCLUSIONS

The organic solvent free polymer gel electrolyte with O-EG as nonvolatile liquid phase was prepared and applied in QS-DSSC. The important characteristics,

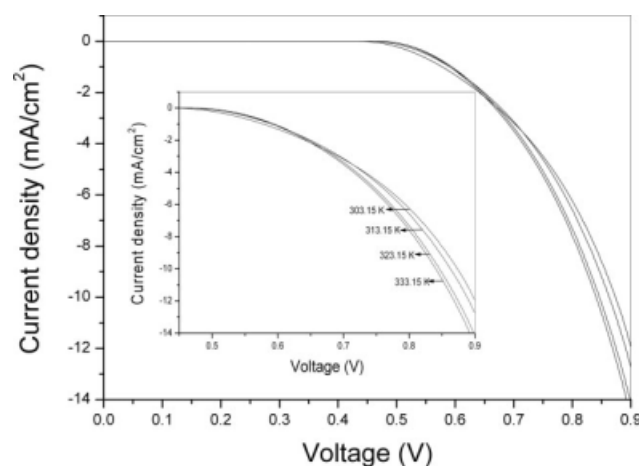


Figure 6 Dark current-voltage characteristics of QS-DSSC measured at different temperature.

such as, ionic conductivity and viscosity of the polymer gel electrolyte are changed with the changed temperature, namely, it shows typical thermosetting property, which is benefit for QS-DSSC to obtain highly photovoltaic performance at high temperature owing to the increased ionic conductivity and diffusion coefficient of iodide in the polymer gel electrolyte with increased temperature.

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