Oligomer Ethylene Glycol Based Electrolytes for Dye-Sensitized Solar Cell

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ABSTRACT: Oligomer ethylene glycol (O-EG) based electrolytes without volatile components were prepared and used in dye-sensitized solar cell (DSSC). The characteristics such as viscosity, ionic conductivity, and ionic activation energy of O-EG based electrolytes including liquid, gel and solid states were investigated and compared. It is found that the gel and solid O-EG electrolytes have two E_a values with the changed phase state by going with the increased temperature, and they can increase the onset of applied voltage for generating dark current in DSSCs as from 0.222 V with liquid O-EG electrolyte to 0.420 V with gel and solid O-EG electrolytes, which results in the enhanced light-to-electricity conversion efficiency from 1.4% with liquid to 1.82% with gel and 1.86% with solid electrolytes. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2786–2789, 2011

Key words: O-EG based electrolyte; dye-sensitized solar cell; ionic conductivity; activation energy

INTRODUCTION

As 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 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 playing attention to find some more stable electrolytes to solve the problem.[3–7] Among them, one kind of electrolyte shows similar stability as that of ionic liquid based electrolyte such as nonvolatile and high stability, which is oligomer based electrolyte.[8–11]

In this study, oligomer ethylene glycol (O-EG) is selected as liquid phase component for oligomer-based electrolyte, mainly due to its perfect complexation with alkali metal ions, which is benefit for obtaining suitable concentration of I^-/I_3^- redox couples used in DSSC through dissolving sufficient amount of alkali metal iodide and iodine. The characteristics of O-EG based electrolytes including liquid, gel and solid states are investigated and compared, their influences on the photovoltaic performance of DSSC are also studied. The states of O-EG based electrolytes can be changed with addition of gelling agent. Here, the well soluble and high viscosity polymer—polyvinyl pyrrolidone (PVP) is selected as gelling agent.

EXPERIMENTAL

Materials

O-EG with average molecular weight 600 (M), polyvinyl pyrrolidone (PVP K-30) titanium iso-propoxide, nitric acid, glacial acetic acid, terpineol, ethyl cellulose, ethanol, KI and I_2 were all A. R. grade and purchased from Sinopharm Chemical Reagent, China. All reagents were used without further treating.

Conducting glass plates (FTO glass, Fluorine doped tin oxide over-layer, sheet resistance 8 Ω/sq, purchased from Hartford Glass) were used as substrates for precipitating TiO_2 porous films. Sensitizing dye *cis*-[(dcbH_2)_2Ru(SCN)_2] and optical diffuser paste Ti-Nanoxide 300 were purchased from Solaronix SA.

Preparation of O-EG based electrolytes

O-EG based electrolytes were prepared as follows: Liquid O-EG electrolyte was obtained by mixing O-EG and KI/I_2; Gel and solid O-EG electrolytes were
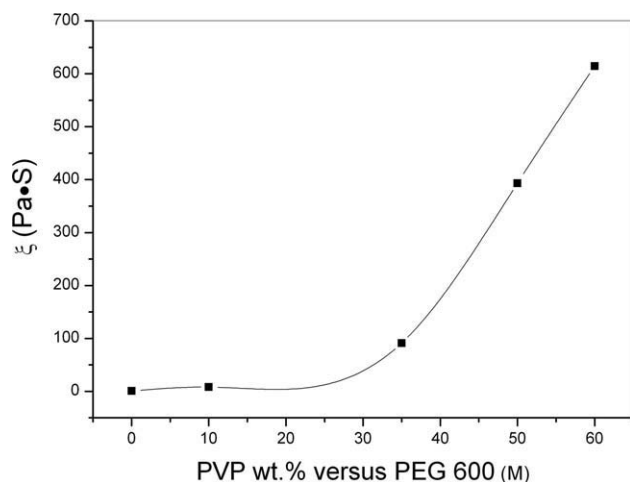
Figure 1 The viscosity of O-EG based electrolytes with different amount of PVP.

obtained by mixing suitable amount of KI, I_2, 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 attains a constant value.

Assembling of DSSC

The preparation of TiO_2 colloidal paste and double-layer film was according to the method reported in our former papers.[10,11] The TiO_2 colloidal paste was used to fabricate the transparent film about 10 μm in thickness. Then the optical diffuser film about 4 μm in thickness 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 nanostructure TiO_2 electrodes were dye-coated by immersing them into a 2.5×10^{-4} M absolute ethanol solution of cis-[(dcbH$_2$)$_2$Ru(SCN)$_2$] for 24 h. A drop of high temperature O-EG based electrolytes was sandwiched between a dye-sensitized TiO_2 electrode and an electrodeposited platinum counter electrode. The two electrodes were clipped together and a piece of cyanoacrylate adhesive (15–30 μm in thickness) was used as sealant. Bisphenol A epoxy resin (using ethylenediamine as epoxy hardener) was used for further sealing the cell.

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 0.01 M KCl aqueous solution prior to experiments. The viscosity of samples was measured with model NDJ-8S digitized viscosity meter (Cany precision Instruments, China).

The photovoltaic tests of 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, China) 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 cm^2 (1 × 0.5 cm^2), respectively.

RESULTS AND DISCUSSION

The states of O-EG based electrolytes can be changed with the addition of different amount of PVP into the system. As shown in Figure 1, liquid O-EG electrolyte shows a relatively low viscosity of 0.761 Pa S. When adding PVP into the system, the viscosity increases, especially when its amount higher than 30 wt %. The viscosity of O-EG based electrolytes with 35 and 50 wt % PVP shows 91.227 and 393.319 Pa S, which is sufficient to maintain the system in gel and solid states, respectively.[12,13] So the components of O-EG based electrolytes in liquid, gel and solid states are set as pure O-EG with 0, 35, and 50 wt % PVP.

Figure 2 presents the ionic conductivity of O-EG based electrolytes as functions of added KI concentration. It is seen that liquid O-EG electrolyte shows higher ionic conductivity comparing with the other two electrolytes with the same amount of KI, which is mainly due to the different viscosity of the O-EG based electrolytes as shown in Figure 1. The maximum ionic conductivity of gel and solid O-EG electrolytes is obtained with higher KI concentration than that of liquid O-EG electrolyte. The reason is that apart from the complexation interaction between KI and O-EG, the PVP gelling agent also can complex
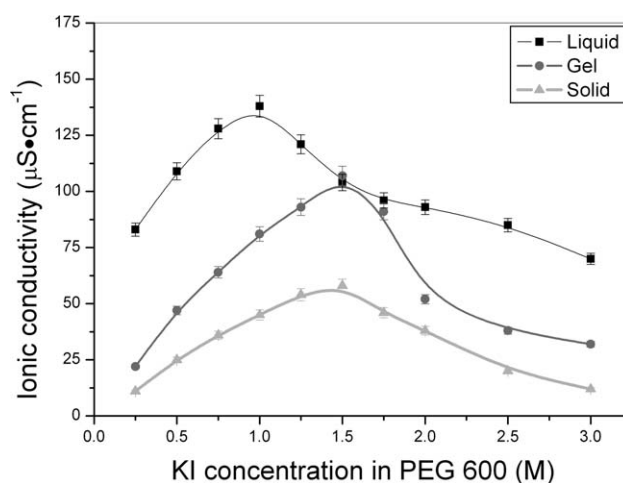

Figure 2 Ionic conductivity of O-EG based electrolytes (Liquid: O-EG; Gel: O-EG and 35 wt % PVP; Solid: O-EG and 50 wt % PVP) as functions of KI mole concentration in O-EG liquid phase at 303.15 K.
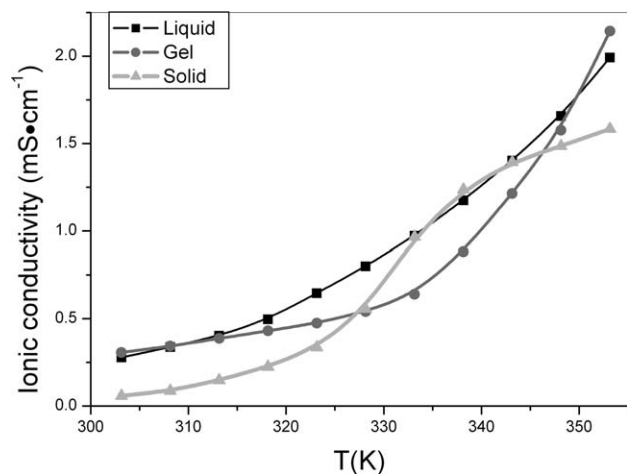
Figure 3 Ionic conductivity change tendencies of O-EG based electrolytes (Liquid: containing 1.0 M KI, 0.1 M I_2; Gel and Solid: containing 1.5 M KI, 0.15 M I_2) as functions of temperature.

with KI, which is benefit for dissolving higher amount of KI and increasing ionic conductivity. The ionic conductivity decreases with the further additional amount of KI in electrolytes due to the decreased KI diffusion ability.

The ionic conductivity of electrolytes is sensitive to changed temperature. As shown in Figure 3, the ionic conductivity of O-EG based electrolytes all increases with incremental temperature. In the case of gel O-EG electrolyte, the change tendency is the same as that of liquid O-EG electrolyte, while that of solid O-EG electrolyte shows the reversal S shape, namely, the gradient of ionic conductivity versus temperature changes from low to high then attains to low again. Going with the increased temperature, the state of solid O-EG electrolyte turns from solid to gel. The phase transition process causes the high gradient of ionic conductivity versus temperature.
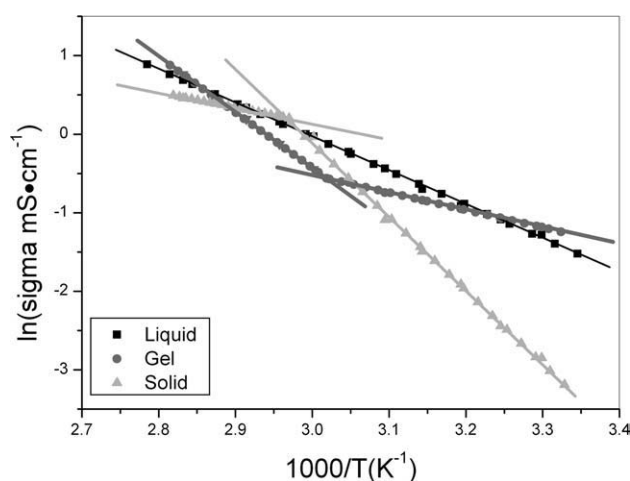
TABLE I
E_a **values of O-EG Based Electrolytes Calculated from Figure 4**

O-EG based electrolyte	Liquid	Gel	Solid
T_c (K)	–	331	337
E_a ($T < T_c$) (kJ mol^{-1})	35.78	18.51	77.71
E_a ($T > T_c$) (kJ mol^{-1})	35.78	58.67	16.03

Although in high temperature range, the viscosity of solid O-EG electrolyte decreases largely, but it still shows high values, so the gradient of ionic conductivity versus temperature is relatively low.

The activation energy of diffusion ions in O-EG based electrolytes can be calculated through the Arrhenius type relationship (1). The data in Figure 3 are turn to $\ln\sigma$ versus $1/T$ plots as shown in Figure 4, and the Arrhenius relationship is also changed as the eq. (2).[14]

$$\sigma(T) = A_{\exp}\left[\frac{-E_a}{RT}\right] \tag{1}$$

$$\ln \sigma(T) = \frac{-E_a}{RT} + \ln A \tag{2}$$

Where σ is the conductivity, A is a constant, E_a is activation energy and R is the universal gas constant. The E_a values of O-EG based electrolytes calculated from Figure 4 are summarized in Table I.

The ionic diffusion environment is different when the electrolyte keeps in different state, so the E_a values are different with the changed state of electrolyte by going with the changed temperature. The liquid O-EG electrolyte keeps in liquid state with the changed temperature, so the fitted curve has only one slope and only one calculated E_a value with the changed temperature. For the gel and solid O-EG
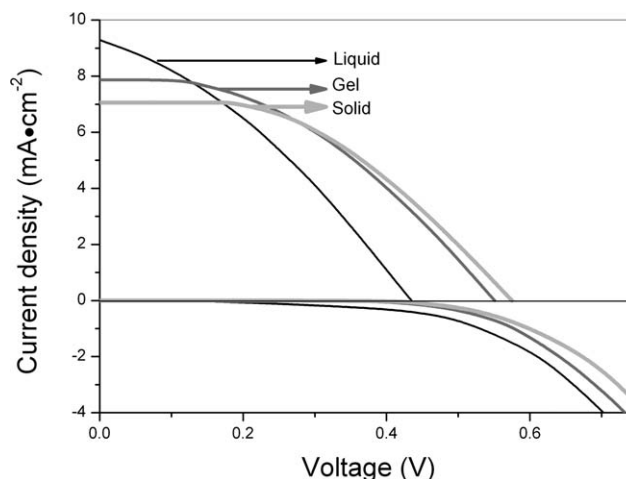

Figure 4 $\ln\sigma$ versus $1/T$ plots of data in Figure 3.

Figure 5 I-V curves (light and dark) of DSSCs with O-EG based electrolytes (Liquid: containing 1.0 M KI, 0.1 M I_2; Gel and Solid: containing 1.5 M KI, 0.15 M I_2).

TABLE II
Parameters of Photovoltaic Performance of QS-DSSCs as Shown in Figure 6

O-EG based electrolyte	V_{OC}(V)	J_{SC}(mA/cm^2)	FF	η (%)
Liquid	0.435	9.29	0.346	1.398
Gel	0.551	7.87	0.420	1.823
Solid	0.575	7.05	0.460	1.863

electrolytes, the states are changed with the increased temperature, namely, the gel O-EG electrolyte changes from gel to high viscosity sol state, and the solid O-EG electrolyte changes from solid to gel, so the fitted curves have two slopes and two calculated E_a values. The turning points in the curves signify the ionic conductivity transition temperature (T_c), the values of T_c are at 331 and 337 K for gel and solid O-EG electrolytes, respectively, as shown in Table I.

The gel and solid O-EG electrolytes have similar E_a values when they keep in gel state (18.51 kJ mol^{-1} and 16.03 kJ mol^{-1}). While the solid O-EG electrolyte keeps in solid state or the gel O-EG electrolyte keeps in sol state, the systems show high E_a values (77.71 kJ mol^{-1} and 58.67 kJ mol^{-1}). The reasons can be illustrated as follows: When the gel or solid O-EG electrolytes keep in gel state, the ionic conducting mainly depends on the frequency of intermolecular ionic hopping, which needs relatively low energy, so the E_a values are low. When the solid O-EG electrolyte keeps in solid state, the intrinsic high resistance for ionic transportation in the system causes the high value of E_a. While when the gel O-EG electrolyte maintains in sol state, the ionic conductivity depends on the frequency of intermolecular ionic hopping, the speed of ionic diffusion and the wriggling motion of solvent molecules. It needs high energy for O-EG doing wriggling motion in the high viscosity sol state, so the system shows high E_a value.

The photovoltaic performance of DSSCs with O-EG based electrolytes are shown in Figure 5. Due to the high viscosity and low ionic conductivity of O-EG based electrolytes, DSSCs show relatively low photovoltaic performance. It is seen that the short-circuit current density is moderate, while the open-circuit voltage and fill factor are much lower comparing with DSSCs containing organic solvents, which results in low overall light-to-electricity conversion efficiency. DSSCs with the gel or solid O-EG electrolytes show high photovoltaic performance than that of DSSC with liquid O-EG electrolyte owing to their high open-circuit voltage and fill factor. Another reason is the PVP component, which can restrain the dark reaction in DSSCs. As shown in Figure 5, the onset applied voltage for generating dark current in DSSCs increases from 0.222 to 0.420 V with the addition of PVP into O-EG based electrolytes. At the same applied voltage, the dark currents of DSSCs with gel and solid O-EG electrolytes are lower than that of DSSC with liquid O-EG electrolyte. The quasi-solid-state DSSC (QS-DSSC) performance is summarized in Table II.

CONCLUSIONS

O-EG based electrolytes without volatile organic solvents were prepared and used in DSSC. Due to the large increased viscosity, the addition of PVP can turn the liquid O-EG electrolyte to gel and even solid. The gel and solid O-EG electrolytes show relatively low ionic conductivity due to the increased viscosity, and they have two E_a values with the changed phase state by going with the increased temperature. The photovoltaic performance of DSSCs with gel and solid O-EG electrolytes is better than that of DSSC with liquid O-EG electrolyte, which is owing to the function of PVP for suppressing dark reaction.

While the light-to-electricity conversion efficiency of DSSCs with O-EG based electrolytes is still much lower than that of DSSCs with organic liquid or gel electrolytes. The main reason is owing to the high viscosity and low ionic conductivity of O-EG based electrolytes. So the further work will be focused on the increasing the ionic conductivity of O-EG based electrolytes by substituting KI salts with other kinds of iodide salts such as organic iodide, organic–inorganic iodide hybrid and ionic liquid, and improving the interfacial contacting properties among the electrolyte, photo electrode and counter electrode in DSSC.

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