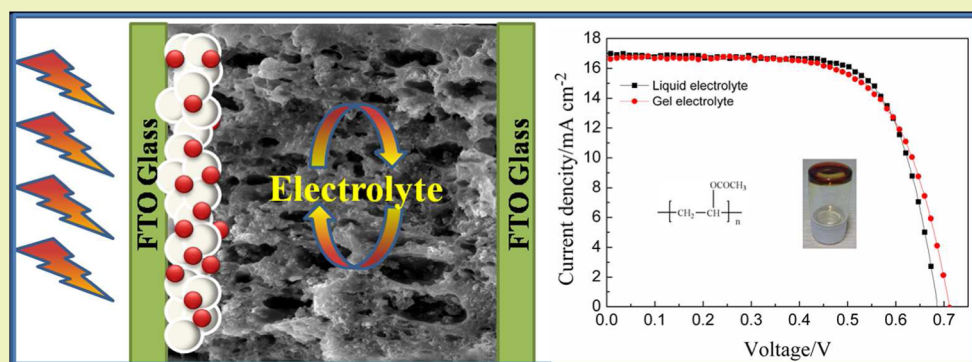


# Highly Stable Gel-State Dye-Sensitized Solar Cells Based on High Soluble Polyvinyl Acetate

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**S** Supporting Information



**ABSTRACT:** The highly soluble polyvinyl acetate (PVAc) was synthesized by simple solution polymerization, which was used to prepare the gel-state dye-sensitized solar cells (DSCs) for the first time. The values for open-circuit photovoltage ( $V_{oc}$ ), short-circuit photocurrent density ( $J_{sc}$ ), and fill factor (FF) of gel electrolyte-based DSCs were 0.712 V, 16.78 mA cm<sup>-2</sup>, and 68%, respectively, yielding an overall photovoltaic conversion efficiency (PCE) of 8.18%, which is comparable to a liquid electrolyte-based one with a value of 8.27%. The results of the electrochemical impedance spectra (EIS) revealed that the large charge transfer resistances at the TiO<sub>2</sub>/dye/electrolyte interface and the large diffusion resistances of the redox couple in the electrolyte are responsible for similar PCEs of gel and liquid electrolytes. The long-term stability test revealed that the PCE of the gel electrolyte-based DSC did not decay after 1000 h under AM1.5 simulated solar illumination at 60 °C and 40–50% humidity, which is superior to a liquid electrolyte-based DSC. This new method overcomes the degradation of DSCs arising from volatilization and leakage of the liquid electrolyte and promotes the industrialization process of DSC.

**KEYWORDS:** Highly stable, Gel-state electrolyte, Dye-sensitized solar cell, Polyvinyl acetate, High solubility

## INTRODUCTION

Dye-sensitized solar cells (DSCs) have attracted intensive interest since their breakthrough in 1991 because of their high efficiency, low-cost, and easy fabrication procedure compared with silicon solar cells, as reported by O'Regan and Grätzel.<sup>1,2</sup> This type of solar cell is commonly composed of a mesoporous TiO<sub>2</sub> electrode sensitized by a ruthenium bipyridine dye, redox electrolyte, and platinum counter electrode. Photoexcited electrons of the dye are transferred to the conduction band of TiO<sub>2</sub>, and the oxidized dye cations are regenerated by the I<sup>-</sup> in the redox couple. In turn, the I<sub>3</sub><sup>-</sup> formed is reduced in the platinum, thus completing the cycle and generating the photocurrent. Recently, a PCE of 11.18% was achieved based on the liquid electrolyte containing an I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox couple.<sup>3</sup> However, the potential problems of using a liquid electrolyte, such as leakage and volatilization of organic solvents, are considered as some of the critical factors limiting sealing, shape, and long-term stability. Therefore, many researchers focused on alternatives to the organic liquid electrolyte, such as ionic liquid, solid, or gel electrolytes, which can aid in reducing costs and

enable easier assembly of DSCs. The various alternatives, such as ionic liquid electrolytes, organic or inorganic hole conductors, polymer gel electrolytes prepared with ionic liquids, and solidification of liquid electrolytes, were attempted to resolve these problems.<sup>4–20</sup> Among them, the ionic liquid-based electrolytes possess superior properties, such as good stability, negligible vapor pressure, and high ionic conductivity. However, the efficiency based on ionic liquid electrolytes needs to be further improved. Alternatively, polymer gel electrolytes are considered as one of the most promising substitutes for liquid electrolytes. They usually exist in a quasi-solid-state, which is on the boundary between the liquid and solid states. Therefore, polymer gel electrolytes have the merits of solid-state electrolytes, such as higher long-term stability, lower leakage, and volatilization, as well as the advantages of liquid electrolytes, such as high ionic conductivity and an excellent interfacial contacting property. In preparing polymer gel electrolytes for DSCs, the

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polymer plays an important role in determining the efficiency of the electrolyte. To date, various polymers and copolymers have been used as gelators, such as polyacrylonitrile, poly(acrylic acid), poly(ethylene glycol), polypyrrole, poly(poly(acrylic acid)-co-ethylene glycol), and poly(vinylidene fluoride-co-hexafluoropropylene).<sup>13–16,18,19</sup>

In this study, polyvinyl acetate (PVAc) was synthesized by simple solution polymerization and was subsequently used as polymer matrix in the liquid electrolyte for the first time. PVAc has very high solubility in common organic solvents, such as acetonitrile and 3-methoxypropionitrile, thereby decreasing the organic solvent content simultaneously. This behavior means that the electrolyte is in a near-solid state and inhibits the solvent flow and evaporation by trapping the liquid electrolyte in the polymer matrix. Therefore, risk of leakage and volatilization of the electrolyte is restrained. The stability of the electrolyte has also been enhanced. The study shows that the PCE of the gel electrolyte has not dropped compared with that of the liquid electrolyte, thereby achieving a high PCE of 8.18%. The long-term stability test reveals that the gel electrolyte performs better within 1000 h under AM 1.5-simulated solar illumination at 60 °C and 40–50% humidity.

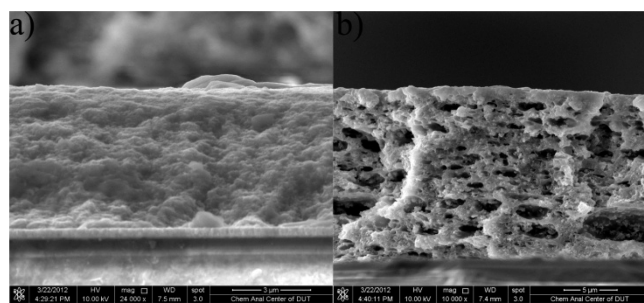
## EXPERIMENTAL SECTION

PVAc was prepared with a simple solution polymerization method. Briefly, 30 mL of vinyl acetate, 5 mL of methanol, 0.1 g of ammonium persulfate as initiator, and a certain amount of water were added to a three neck flask. The reaction was refluxed for 2 h at 70 °C. When the mixture turned viscous, 40 mL of methanol was added to this system, and the heat was stopped. The dilute reaction liquid formed a film at the deionized water surface. The obtained PVAc film was dried in the vacuum drying chamber at 40 °C for 24 h. The FT-IR spectra of PVAc was studied in Figure S1 of the Supporting Information.

The liquid electrolyte consisted of 0.1 M LiI, 0.05 M I<sub>2</sub>, 0.6 M 1-methyl-3-propyl imidazolium iodide, 0.5 M 4-tert-butyl pyridine, and 0.1 M guanidinium thiocyanate in acetonitrile. A total of 0.6 g of PVAc was added to 1 g of liquid electrolyte, and the system was stirred until the PVAc dissolved and the electrolyte became the gel state. The iodine concentration of the gel-state electrolyte was optimized (Table S1, Figure S2, Supporting Information).

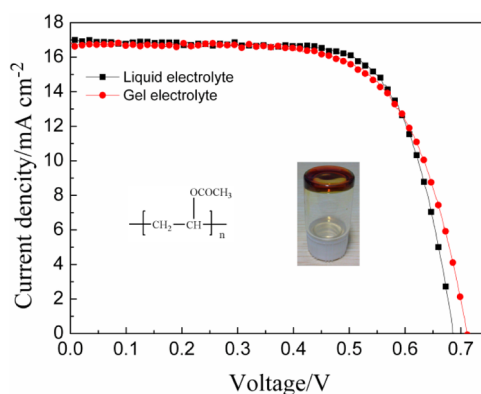
## RESULTS AND DISCUSSION

Figure 1a shows the scanning electron micrograph of the gel electrolyte on the TiO<sub>2</sub> film. As shown in the figure, the TiO<sub>2</sub>



**Figure 1.** Scanning electron micrograph showing the (a) surface and (b) cross-sectional views of the gel electrolyte on the TiO<sub>2</sub> film.

surfaces are completely covered by the gel electrolyte. The big holes are observed in the cross-sectional view in Figure 1b. The network was formed when the PVAc was dissolved in the liquid electrolyte. Thus, the liquid electrolyte can transfer freely within the polymer framework. The existence of PVAc can also suppress the volatility of the organic solvent and improve the stability of DSCs.



**Figure 2.** Photocurrent–voltage curves of the DSCs based on liquid electrolyte and gel electrolyte.

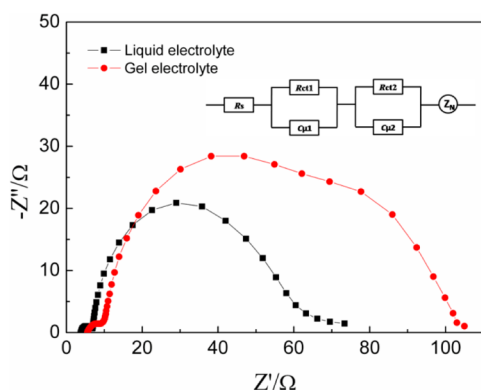
Figure 2 shows the photovoltaic performance of the DSCs based on liquid and gel electrolytes under one solar illumination (AM 1.5G, 100 mW cm<sup>-2</sup>). As shown in this figure, the values for open-circuit photovoltage (*V*<sub>oc</sub>), short-circuit photocurrent density (*J*<sub>sc</sub>), and fill factor (*FF*) of DSCs based on the gel electrolyte are 0.712 V, 16.78 mA cm<sup>-2</sup>, and 68%, respectively, yielding an overall conversion efficiency ( $\eta$ ) of 8.18%. The values (*V*<sub>oc</sub>, *J*<sub>sc</sub>, *FF*, and  $\eta$ ) for the liquid electrolyte are 0.686 V, 16.88 mA cm<sup>-2</sup>, 71%, and 8.27%, respectively. The corresponding performance parameters of the DSCs are summarized in Table 1. Comparison between the data of the gel and liquid electrolytes show that the increase in *V*<sub>oc</sub> was compensated by a slight decrease in the *FF* for the gel electrolyte.

Electrochemical impedance spectroscopy (EIS) was performed to determine the cause of the slight difference in photovoltaic parameters when the electrolyte changed from liquid to gel electrolyte. Figure 3 shows typical EIS Nyquist plots and the equivalent circuit of DSCs. The three semicircles observed in the EIS Nyquist plots of the DSCs were classified as charge transfer resistance of I<sup>-</sup>/I<sub>3</sub><sup>-</sup> on the counter electrodes in the high frequency region (*R*<sub>ct1</sub>) charge transfer resistance of the TiO<sub>2</sub>/dye/electrolyte interface in the middle frequency (*R*<sub>ct2</sub>), and the Nernstian diffusion (*Z*<sub>N</sub>) within the electrolyte in the low-frequency region. In the experiment, the overlapping of the middle- and low-frequency semicircles was observed for the liquid electrolyte, whereas three semicircles were distinctly observed in the DSC based on the gel electrolyte. Comparing the two curves, a larger charge transfer resistance (*R*<sub>ct2</sub>) and a larger diffusion resistance (*Z*<sub>N</sub>) in the gel electrolyte were evident, unlike in the liquid electrolyte, indicating that the DSC with a gel electrolyte possesses larger recombination and mass transport resistances than the DSC with a liquid electrolyte. Thus, the advantage of a large *R*<sub>ct2</sub> is balanced out with the disadvantage of a large *Z*<sub>N</sub>, and a similar PCE was obtained. The EIS fitting data are summarized in Table 1.

Polarization measurements equipped with symmetrical Pt electrochemical cells<sup>21–23</sup> are used to study the influence of polymers on the diffusion of I<sub>3</sub><sup>-</sup> at room temperature. The “symmetrical cell” was assembled using two equal Pt counter electrodes injected with the electrolyte and sealed with Surlyn film. The structure of the device can be expressed as FTO/Pt/electrolyte/Pt/FTO. The diffusion-limiting current density was measured by cyclic voltammetry using a scan rate of 2 mV/s. The apparent diffusion coefficient (*D*<sub>app</sub>) values of I<sub>3</sub><sup>-</sup> (listed in Table 1) were calculated using the following equation<sup>22</sup>

**Table 1. Photocurrent–Voltage, EIS Parameters, and  $D_{\text{app}}$  of  $\text{I}_3^-$  of DSC Based on Liquid Electrolyte and Gel Electrolyte**

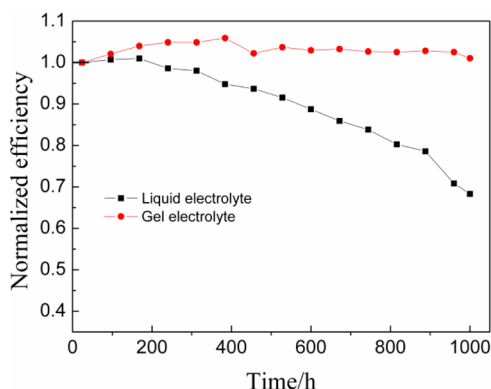
samples	$V_{\text{oc}}$ (mV)	$J_{\text{sc}}$ ( $\text{mA cm}^{-2}$ )	FF	PCE (%)	$R_s$ ( $\Omega$ )	$R_{\text{ct1}}$ ( $\Omega$ )	$R_{\text{ct2}}$ ( $\Omega$ )	$Z_N$ ( $\Omega$ )	$D_{\text{app}}$ ( $10^{-7} \text{ cm}^2 \text{ s}^{-1}$ )
gel electrolyte	$712 \pm 7$	$16.78 \pm 0.2$	0.68	$8.18 \pm 0.3$	5.80	3.16	51.20	66.20	3.30
liquid electrolyte	$686 \pm 5$	$16.88 \pm 0.2$	0.71	$8.27 \pm 0.2$	4.16	2.32	38.54	40.70	12.6

**Figure 3.** Typical Nyquist plots from impedance measurements on the DSCs based on liquid electrolyte and gel electrolyte.

$$D_{\text{I}_3^-} = \frac{i_{\text{lim}} L}{2nFc_{\text{I}_3^-}^0} \quad (1)$$

where  $n$  is the number of electrons transferred in each reaction (here  $n = 2$ );  $F$  is Faraday's constant;  $L$  is the distance between the two electrodes (here  $L = 60 \mu\text{m}$ ); and  $c_{\text{I}_3^-}^0$  is the molar concentration of  $\text{I}_3^-$  (here  $c_{\text{I}_3^-}^0 = 0.05 \text{ M}$ ). Although the  $D_{\text{app}}$  of  $\text{I}_3^-$  decreased from  $12.6 \times 10^{-7} \text{ cm}^2/\text{s}$  to  $3.30 \times 10^{-7} \text{ cm}^2/\text{s}$ , the PCE was not evidently changed, signifying that the diffusion of  $\text{I}_3^-$  into the gel electrolyte is sufficient. The diffusion can be rationalized using the Grotthus-like exchange mechanism. The diffusion tendency is consistent with the EIS measurement.<sup>5</sup>

As shown in Figure 4, the long-term stabilities of gel and liquid electrolyte-based DSCs were investigated and compared.<sup>24–27</sup>

**Figure 4.** Normalized efficiencies for the DSCs based on liquid electrolyte and gel electrolyte under 1 solar illumination at 60 °C and 40–50% humidity.

The cells used in this experiment were kept under AM 1.5 simulated solar illumination at 60 °C and 40–50% humidity. The overall efficiency was measured once every 72 h and normalized with respect to the value obtained on the first day. For the gel electrolyte-based DSC, the overall efficiency did not decrease for 1000 h compared with the initial value. For the liquid electrolyte, the efficiency decreased by 30%, which is mainly due to leakage of

the volatile solvent. In the first 450 h, the efficiency of the DSC with a gel electrolyte slightly increased because of the further penetration of the PVAc into the porous  $\text{TiO}_2$  film. Long-term stability was obtained with the high polymer concentration of 60 wt % occupied by the liquid electrolyte. A larger amount of polymer molecules would provide more “cages” for solvent molecules. Furthermore, the hydrophilic ester groups on the polymer molecule tightly bound the polar solvent molecules via van der Waals attraction. Thus, any solvent loss can be highly suppressed by PVAc.

In summary, the high soluble PVAc was synthesized by simple solution polymerization. The polymer-based gel electrolyte was successfully employed in DSC for the first time. The gel electrolyte-based DSC yielded a high efficiency of 8.18%, which was comparable to the liquid electrolyte with a value of 8.27%. Furthermore, superior long-term stability was obtained for the gel electrolyte DSC. The gel-state electrolyte possesses the advantages of high efficiency, low-cost, easy fabrication, environmental friendliness, and low risk of leakage. Thus, the stability of DSC can be improved. Further studies on this field are ongoing.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

FT-IR analysis on PVAc, optimization of concentration of iodine in gel electrolyte, and preparation of gel electrolyte and  $\text{TiO}_2$  photoanode and characterization of DSCs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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