Electrochemistry Communications 12 (2010) 1037–1040

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Photovoltaic performance of dye-sensitized solar cells assembled by in-situ chemical cross-linking

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ARTICLE INFO

Article history:
Received 7 April 2010
Received in revised form 17 May 2010
Accepted 18 May 2010
Available online 24 May 2010

Keywords:
Dye-sensitized solar cell
Gel polymer electrolyte
Chemical cross-linking
Long-term stability
Photovoltaic performance

ABSTRACT

Quasi-solid state dye-sensitized solar cells (DSSCs) were assembled by in-situ chemical cross-linking of a gel electrolyte precursor containing liquid electrolyte. The DSSCs assembled with this cross-linked gel polymer electrolyte showed higher open circuit voltage and lower short-circuit photocurrent density than those of DSSCs with liquid electrolyte. Addition of SiO_2 nanoparticles into the cross-linked gel polymer electrolyte significantly improved the photovoltaic performance and long-term stability of the DSSCs. The optimized quasi-solid state DSSC showed high conversion efficiency, 6.2% at 100 mW cm^{-2} with good durability.

1. Introduction

Dye-sensitized solar cells (DSSCs) have the attractive features of low cost, easy fabrication and relatively high energy conversion efficiency [1,2]. Such cells consist of a dye-sensitized nanocrystalline TiO_2 electrode, an electrolyte and a Pt counter electrode. The electrolyte usually employed in the DSSCs is an I^-/I_3^- redox couple in an organic solvent. However, this leads to major problems associated with limitations in long-term operation due to leakage or evaporation of the solvents. Therefore, many attempts have been made to replace the liquid electrolyte with polymer electrolytes, molten salts and hole transport materials [3–8]. Among these approaches, use of gel polymer electrolytes that exhibit high ionic conductivity appears to provide successful results in terms of conversion efficiency. However, such gel polymer electrolytes suffer from poor penetration of electrolyte into the porous TiO_2 electrode and poor interfacial contacts with the electrode.

To overcome this problem, we have attempted to assemble quasi-solid state DSSCs by in-situ chemical cross-linking after the penetration of electrolyte into the pores of the TiO_2 electrode. The reaction was carried out in the cell at a moderate temperature without any initiators. In this study, we present the photovoltaic performance of these DSSCs assembled with cross-linked gel polymer electrolyte containing SiO_2 particles. Also, the long-term stability of these DSSCs is compared with that of DSSCs with liquid electrolyte.

2. Experimental

2.1. Preparation of gel electrolyte precursor

A proper content of poly(ethylene imine) (PEI, $M_n = 423$) and poly (ethylene glycol) diglycidyl ether (PEGDE, $M_n = 526$) were dissolved in liquid electrolyte. The liquid electrolyte is a solution of 0.5 M lithium iodide (LiI), 0.05 M I_2 and 0.05 M 4-tert-butylpyridine dissolved in a mixed solvent of ethylene carbonate/propylene carbonate (50:50 by volume). The ratio of PEI to PEGDE in the cross-linking agent was maintained to be 50:50 by weight, and the cross-linking agents (PEI and PEGDE) were added at different concentrations (2, 4, 6, 8 wt.%) into the liquid electrolyte. Further, varying amounts (5, 10, 15, and 20 wt.%) of silanized fumed silica (Cabot Co.) were added to the gel electrolyte precursor.

2.2. Cell assembly and measurements

Nanocrystalline TiO_2 paste (Ti-nanoxide T20/SP, Solaronix) was cast onto a fluorine-doped tin oxide (FTO) glass, which was then sintered at 450 °C for 30 min. Its thickness was optimized to be 12 μm and it was sensitized overnight with a *cis*-diisothiocyanato-bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium (II) bis(tetrabutyl ammonium) (Ruthenium 535 bis-TBA, Solaronix) dye solution. The counter electrode was prepared by spin-coating 0.01 M H_2PtCl_6 in isopropanol onto the FTO glass and sintering at 450 °C. The cell was fabricated by sealing the TiO_2 electrode and Pt electrode together using a hot melting film. Then, gel electrolyte precursor was injected into the cell through a hole in the Pt electrode. The holes were then completely sealed by a sealant. Finally, the assembled cell was placed in a 50 °C

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doi:10.1016/j.elecom.2010.05.018

oven for 2 h to induce the chemical cross-linking reaction. The photovoltaic performance of DSSCs was evaluated using a xenon light source (100 mW cm^{-2}) with an AM 1.5 filter in solar simulator at ambient temperature. The light intensity was calibrated with a NREL-calibrated Si solar cell (PV Measurements Inc.). A black mask of 0.25 cm^2 aperture was placed over the cells during irradiation and an anti-reflection glass was placed on the front glass cover of the cells. We measured the performance of at least 5 cells for each electrolyte composition and confirmed that reproducible results could be obtained. AC impedance measurements were performed using an impedance analyzer (CH Instruments) over the frequency range of 10 mHz to 100 kHz at open circuit under 1 Sun illumination. The applied bias voltage and ac amplitude were set at open circuit voltage and 10 mV, respectively. The impedance spectra were analyzed by an equivalent circuit model of the DSSC [9,10].

3. Results and discussion

The cross linking reaction between PEGDE and PEI has been previously reported in the literature [11]. PEI has many reactive amine groups on the backbone, which allows for reaction with the epoxy groups in PEGDE to form a cross-linked network structure. The reaction was carried out at 50 °C without any initiators, which prevents the introduction of residual impurities in the gel polymer electrolyte. Before applying the gel electrolyte precursor into the cell, gel formation was confirmed by performing chemical cross-linking with different contents of cross-linking agents. Fig. 1 shows images of the cross-linked gel polymer electrolytes. Clearly, the electrolyte becomes non-fluidic due to the formation of three-dimensional polymer networks after cross-linking. However, complete gelation is not visually detected for the electrolyte system cured by 2 wt.% cross-linking agent. This result suggests that the content of the cross-linking agent should be higher than 2 wt.% in order to effectively induce chemical cross-linking.

Fig. 2 represents the photocurrent density–voltage curves of the DSSC assembled with the cross-linked gel polymer electrolytes, as a function of cross-linking agent content. For comparison, the photocurrent density–voltage curve of the DSSC with liquid electrolyte is also shown in the figure. As shown, the photovoltaic performance of the cells was dependent on the content of cross-linking agent. The value of the short-circuit current density (J_{sc}) decreases with increasing cross-linking agent content. The cross-linking reaction causes an increase in the resistance for ion migration due to the formation of three-dimensional networks, which results in a decrease in J_{sc} with increasing cross-linking density. The ionic conductivity of liquid electrolyte is 4.9 mS cm^{-1} and the ionic conductivities of the gel polymer electrolytes decreases with the content of cross-linking agent, as given in Fig. 2. On the other hand, the open circuit voltage (V_{oc}) of the cells slightly increases with increasing cross-linking agent content. When the gel electrolyte precursor is injected into the cell, it may be adsorbed onto the surface of the TiO_2 electrode. After chemical cross-linking, the cross-linked polymer networks formed on the TiO_2 electrode may suppress the back electron transfer from the conduction band of the TiO_2 to the I_3^- ion in the electrolyte, which results in an increase of V_{oc}. The overall conversion efficiency decreases with the increasing content of cross-linking agent. Because solidification of the electrolyte failed at 2 wt.% cross-linking agent, as shown in Fig. 1, the content of cross-linking agent was chosen to be 4 wt.% for further studies.

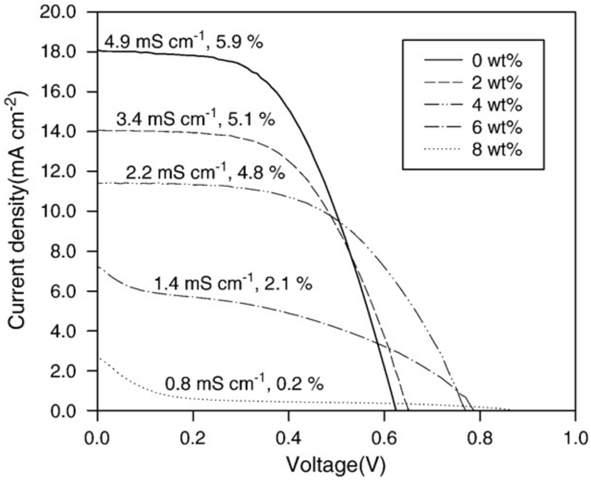

Fig. 2. Photocurrent–voltage curves for DSSCs assembled with liquid electrolyte and gel polymer electrolytes cured by different amounts of cross-linking agent. The numerical values on the curve mean the ionic conductivity of electrolyte and conversion efficiency of DSSC, respectively.

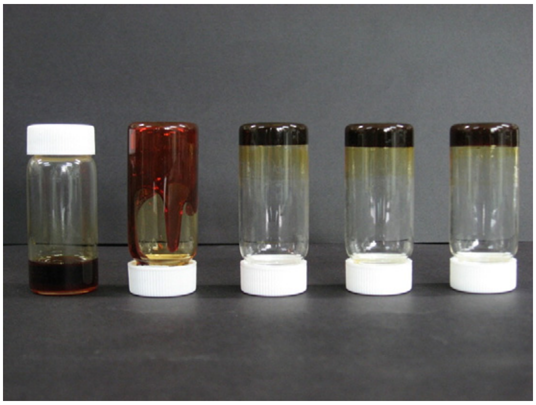

Fig. 1. Images of liquid electrolyte and cross-linked gel polymer electrolytes cured with different amounts of cross-linking agent: (a) liquid electrolyte, (b) 2 wt.%, (c) 4 wt.%, (d) 6 wt.%, (e) 8 wt.%.

It is well known that addition of nanoparticles into the electrolytes can reduce the charge recombination at the interface between TiO_2 electrode and electrolyte, and can also enhance the diffusion of I_3^- [12–14]. With the aim of improving the photovoltaic performance of the DSSCs using cross-linked gel polymer electrolyte, different amounts of silanized fumed silica were added in the gel electrolyte precursors. Table 1 lists the ionic conductivities of cross-linked gel polymer electrolytes containing SiO_2 and the photovoltaic performances of the corresponding DSSCs. J_{sc} of the DSSC increases with the addition of 10 wt.% silica and decreases with further addition. This result is related to the improvement of ionic conductivity, which arises from both the enhancement of capacity to hold liquid electrolyte and the generation of free volume at the interface [14]. On the other hand, both V_{oc} and fill factor (FF) increase with increasing content of SiO_2. From these results, the optimum SiO_2 content is believed to be about 10 wt.% to achieve the best conversion efficiency for the chemically cross-linked gel electrolyte systems under study.

In order to investigate the impedance behavior of the DSSCs assembled with different types of electrolyte, the ac impedance of the

Table 1
Ionic conductivities of cross-linked gel polymer electrolytes with different SiO_2 content and the photovoltaic performance of the DSCCs assembled with them.

SiO_2 content (wt.%)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η (%)	Ionic conductivity (S cm^{-1})
0	11.39	0.770	0.551	4.83	2.19×10^{-3}
5	13.10	0.776	0.554	5.63	2.99×10^{-3}
10	14.36	0.778	0.558	6.24	3.52×10^{-3}
15	10.57	0.791	0.561	4.69	2.13×10^{-3}
20	6.47	0.792	0.568	2.91	6.08×10^{-4}

cells was measured, and the results are shown in Fig. 3. All the spectra exhibit three semicircles, which can be assigned to electrochemical reaction at the Pt counter electrode (R_{ct1}), the charge transfer reaction at the TiO_2 electrode (R_{ct2}) and the Warburg diffusion process of I^-/I_3^- (R_{diff}) [9,10]. The electrolyte resistance (R_{el}) estimated from the intercept on the real axis at high frequency range is lowest in the DSSC assembled with liquid electrolyte. Although the electrolyte resistance increases by chemical cross-linking, it decreases again with addition of SiO_2 particle into the gel polymer electrolyte, which is consistent with ionic conductivity results in Table 1. On the other hand, R_{ct1}, R_{ct2} and R_{diff} are smallest in the DSSC assembled with cross-linked gel polymer electrolyte containing 10 wt.% SiO_2. This result suggests that the addition of SiO_2 not only reduces the Warburg diffusion resistance but also improves the charge transfer reaction at both the TiO_2 electrode and Pt counter electrode, resulting in high conversion efficiency.

The long-term stability of DSSCs assembled with different electrolyte was evaluated. Fig. 4 compares the variation in conversion efficiency (η) and J_{sc} of the DSSCs, as a function of time. Both η and J_{sc} in the liquid electrolyte-based DSSC decay continuously with time during the period of investigation. This result is related to the evaporation of liquid electrolyte, which is caused by imperfect sealing of DSSC. These photovoltaic performances (η and J_{sc}) are shown to be stabilized by using a gel polymer electrolyte. Especially, those of the DSSC assembled with gel polymer electrolyte containing 10 wt.% SiO_2 remain almost constant. The organic solution containing the I^-/I_3^- redox couple is well encapsulated in this cell, and the in-situ chemical cross-linking can promote good interfacial contact between electrolyte and electrodes, which gives a stable photovoltaic performance. Both V_{oc} and FF of all the DSSCs are hardly changed after 10 days. From these results, it is expected that the quasi-solid state DSSCs constructed with chemically cross-linked gel polymer electrolyte containing SiO_2 particles is a promising candidate for practical solar cells with good durability.

4. Conclusions

Quasi-solid state DSSCs were fabricated by in-situ chemical cross-linking of gel electrolyte precursors containing liquid electrolyte. The conversion efficiency of DSSCs with cross-linked gel polymer electrolyte decreased with cross-linking density. The addition of the proper amount of SiO_2 nanoparticles into the gel polymer electrolyte improves both the conversion efficiency and the long-term stability of DSSCs. The DSSC with the optimized gel polymer electrolyte exhibited a short-circuit photocurrent density of 14.4 mA cm^{-2}, an open circuit voltage of 0.78 V and an overall conversion efficiency of 6.2% under 100 mW cm^{-2}.

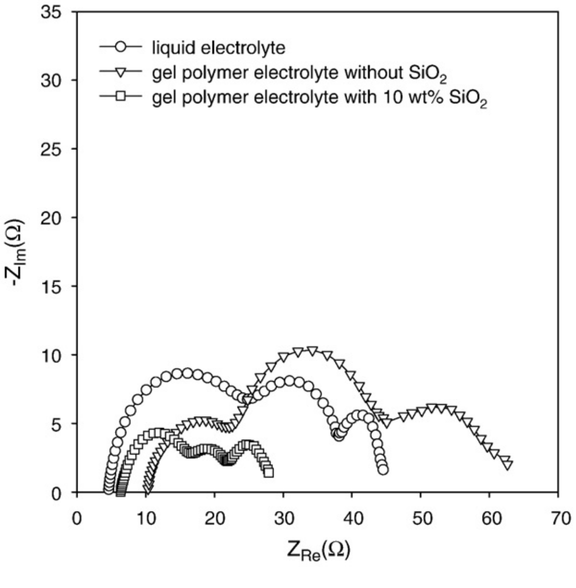

Fig. 3. AC impedance spectra of DSSCs assembled with liquid electrolyte and cross-linked gel polymer electrolyte with and without SiO_2 (10 wt.%).

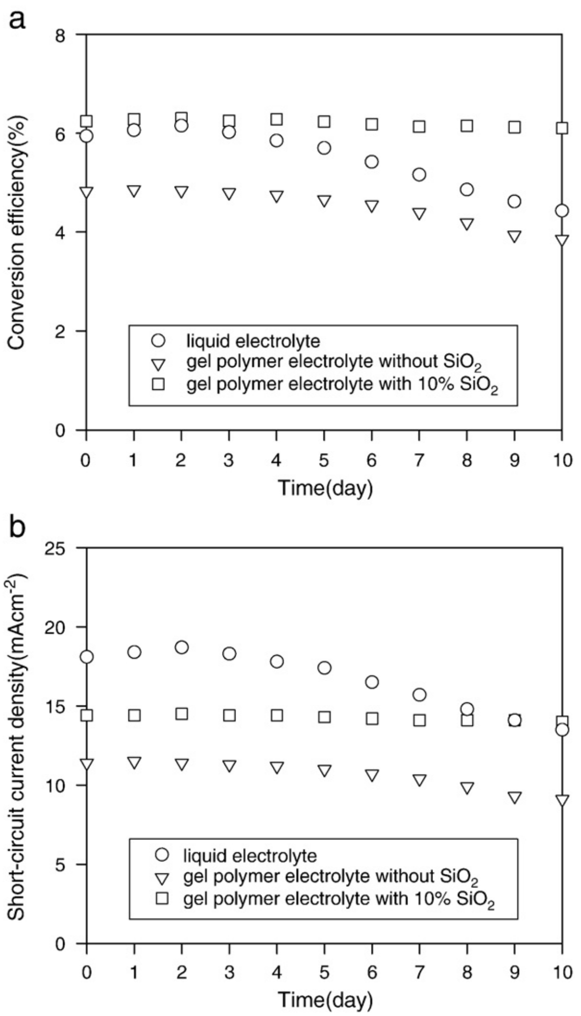

Fig. 4. Variation of conversion efficiency and short-circuit current density as a function of time for the DSSCs assembled with different electrolyte: (a) conversion efficiency *vs.* time, (b) short-circuit current density *vs.* time.

Acknowledgement

This work was supported by Basic Science Research Program through the National Research Foundation of Korea grant (No. 2010-0001842) and the Korea Center for Artificial Photosynthesis funded by the Ministry of Education, Science, and Technology (MEST) through the National Research Foundation of Korea (NRF-2009-C1AAA001-2009-0093879).

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