



Dye-sensitized solar cells with quasi-solid-state cross-linked polymer electrolytes containing aluminum oxide

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ABSTRACT

Cross-linked gel polymer electrolytes containing aluminum oxide nanoparticles are prepared by in situ chemical cross-linking after injection of the gel precursor into the dye-sensitized solar cell (DSSC). This makes it possible to directly solidify the electrolyte in the cell and maintain good interfacial contacts between the electrolyte and the electrodes without suffering loss of performance in the DSSC. These gel polymer electrolytes exhibit high ionic conductivity and favorable charge transfer reaction at the interfaces of electrodes and electrolyte. The quasi-solid-state DSSC assembled with optimized gel polymer electrolyte exhibited remarkably high conversion efficiency, 6.34% at 100 mW cm⁻², and better long-term stability, as compared to the DSSC with liquid electrolyte.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have been considered one of the promising alternatives to conventional solar cells, because of their low cost, easy fabrication and relatively high energy conversion efficiency [1,2]. Based on a liquid electrolyte, a conversion efficiency of 11% for DSSCs has been achieved [3]. However, the potential problems caused by the liquid electrolytes, such as leakage or evaporation of the solvents, are considered critical problems that limit the long-term operation and practical use of DSSCs. Therefore, considerable efforts have been made to replace the liquid electrolyte with polymer electrolytes [4–10], inorganic p-type semiconductors [11] and organic hole transport materials [12,13]. Among these approaches, use of gel polymer electrolytes (GPEs) that exhibit high ionic conductivity at room temperature appears to provide successful results in terms of conversion efficiency. However, such GPEs suffer from poor penetration of electrolyte solution into the porous TiO₂ electrode and poor interfacial contacts with electrodes. From a practical point of view, these problems can be overcome by cross-linking after the injection of an electrolyte containing cross-linking agent into the cell.

In this work, we synthesized cross-linked GPEs containing aluminum oxide nanoparticles, which allow assembly of quasi-solid-state DSSCs by in situ chemical cross-linking after the

penetration of the gel electrolyte precursor into the pores of the TiO₂ electrode. As cross-linking agents, we used poly(ethylene imine) (PEI) with reactive amine groups and poly(ethylene glycol) diglycidyl ether (PEGDE) with reactive epoxy groups. The cross-linking reaction of PEI with PEGDE has been previously reported for applications in lithium batteries [14]. The photovoltaic performance and long-term stability of quasi-solid-state DSSCs assembled with these cross-linked GPEs are investigated and compared with those of liquid electrolyte-based DSSC. A further focus of this study is on the influence of aluminum oxide content on the photovoltaic performance of DSSCs.

2. Experimental

Gel electrolyte precursor consisting of cross-linking agents, liquid electrolyte and Al₂O₃ particles was prepared as follows. Proper quantities of PEI ($M_n = 423$, Aldrich) and PEGDE ($M_n = 526$, Aldrich) were dissolved in liquid electrolyte. The liquid electrolyte used in this study is a solution of 0.5 M lithium iodide (LiI), 0.05 M I₂ and 0.05 M 4-tert-butylpyridine (TBP) dissolved in a mixed solvent of ethylene carbonate (EC)/propylene carbonate (PC) (50:50 by volume). The ratio of PEI to PEGDE in the cross-linking agent was varied, i.e., 1:1, 1:2 and 1:3 by weight, and the cross-linking agents were added at 4.0 wt.% into the liquid electrolyte. Different amounts (0, 5, 10, 15, 20, 25 wt.%) of aluminum oxide (particle size: 2–4 nm, Aldrich) were added to the gel electrolyte precursor, and the mixture was sonicated to ensure homogeneity. Nanocrystalline TiO₂ paste (Ti-Nanoxide

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T20/SP, Solaronix) was cast onto a fluorine-doped tin oxide (FTO) glass using a doctor blade and was then sintered at 450 °C for 30 min. 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. Counter electrode was prepared by spin-coating 0.01 M H_2PtCl_6 in isopropanol onto the FTO glass and sintering at 450 °C for 30 min. The cell was fabricated by sealing the TiO_2 electrode and Pt counter electrode together using a hot melting film. Then, the 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 oven for 2 h to induce the chemical cross-linking reaction. Photovoltaic performance of DSSCs was evaluated using a xenon light source (100 mW cm^{-2}) with an AM 1.5 filter in a 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. For long-term stability test, the cells were stored in a desiccator at room temperature and applied to electrochemical measurements every 24 h. A two-electrode electrochemical cell consisting of cross-linked GPE sandwiched with two identical Pt electrodes was used to measure the diffusion coefficient of the triiodide ion from the diffusion-limited current measurements [15,16]. The diffusion-limited current density was determined by cyclic voltammetry using a scan rate of 5 mV s^{-1} . In order to investigate the impedance behavior of DSSCs, 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 the open-circuit voltage and 10 mV, respectively. Impedance spectra were analyzed by an equivalent circuit model for interpreting the characteristics of the DSSCs [17–19].

3. Results and discussion

The cross-linking reaction was performed in an electrolyte solution containing iodine without harmful initiators at 50 °C, which prevents the formation of residual impurities in the GPE. After cross-linking for 2 h, the electrolyte becomes non-fluidic, due to the formation of three-dimensional polymer networks, as shown in the schematic diagram of the quasi-solid-state DSSC (Fig. 1).

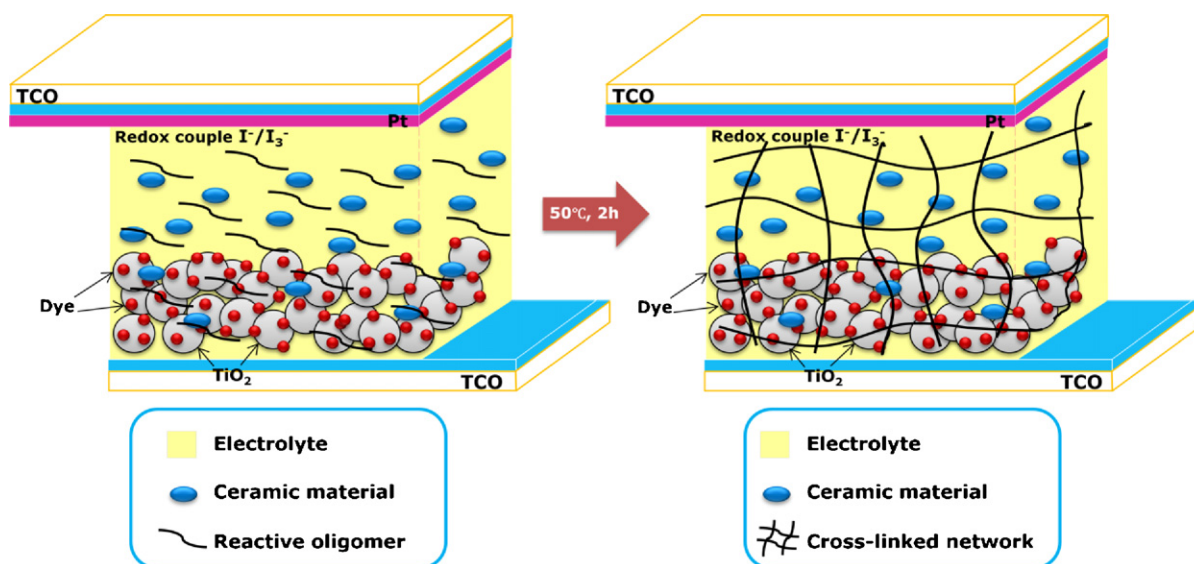


Fig. 1. Schematic diagram of DSSC before and after in situ chemical cross-linking reaction of gel electrolyte precursor containing Al_2O_3 .

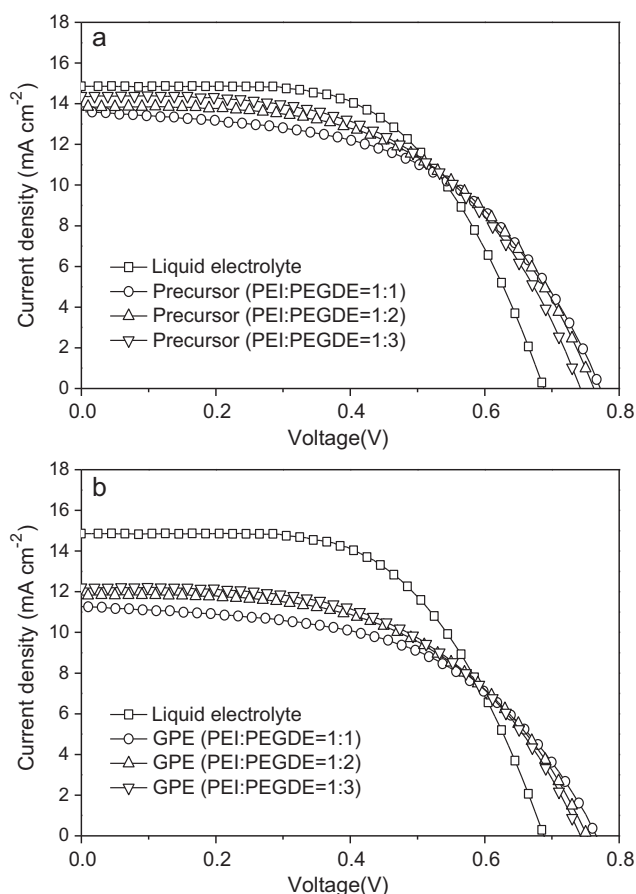


Fig. 2. Photocurrent–voltage curves for DSSCs assembled with gel electrolyte precursor before and after cross-linking reaction, as a function of ratio of cross-linking agent (PEI: PEGDE): (a) before cross-linking reaction, (b) after cross-linking reaction.

The photovoltaic performance of DSSCs assembled with gel electrolyte precursor without Al_2O_3 nanoparticles was evaluated. Fig. 2 represents the photocurrent density–voltage curves of the DSSCs with gel electrolyte precursor before and after cross-linking reaction, as a function of ratio of PEGDE to PEI in the cross-linking agents. For comparison, the photocurrent density–voltage curve of

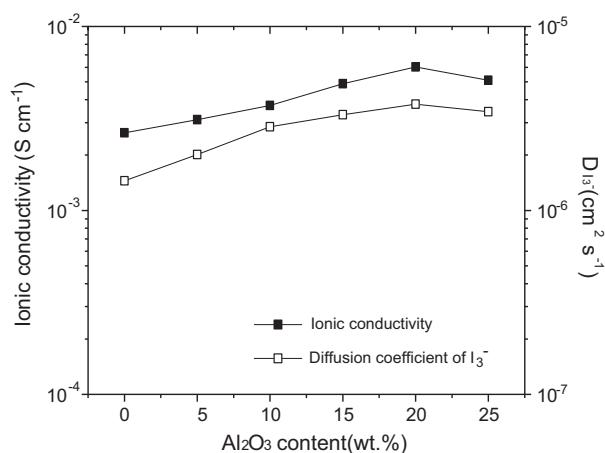


Fig. 3. Ionic conductivities and diffusion coefficients of I_3^- in the cross-linked gel polymer electrolyte (PEI: PEGDE = 1:3 by weight), as a function of Al_2O_3 content.

the DSSC prepared with liquid electrolyte is also shown in Fig. 2. In Fig. 2(a), the open circuit voltages (V_{oc}) of the DSSCs with gel electrolyte precursor are higher than that of the liquid electrolyte-based DSSC. The increase of V_{oc} may result from the basicity of PEI, because the flat band potential of TiO_2 shifts negatively with the increase of the basicity of the electrolyte, which results in an increase of V_{oc} [20]. The addition of gel electrolyte precursor into the liquid electrolyte also causes a slight decrease of short circuit current density (J_{sc}) of DSSCs, which is due to the increase in viscosity of electrolyte. After cross-linking reaction with gel electrolyte precursor, the V_{oc} values of DSSCs were hardly changed, as shown in Fig. 2(b). On the other hand, the values of J_{sc} of DSSCs decreased after cross-linking reaction. This is due to the fact that the cross-linking causes an increase in the resistance for ion migration in both the electrolyte and the electrode. It should be noted that J_{sc} slightly increases with increasing relative ratio of PEGDE to PEI. PEGDE itself has a high dielectric constant ($\epsilon = 13.7$) and a low glass transition

temperature, which provides both generation of higher charge carriers (I^-/I_3^-) and fast ion migration in the DSSCs with high PEGDE content. As a result, the cell assembled with PEI: PEGDE = 1:3 exhibited the highest conversion efficiency (4.82%). This composition was thus chosen for assembling the quasi-solid-state DSSCs for further studies.

Addition of inorganic nanoparticles, such as SiO_2 and TiO_2 into the electrolyte is an effective way to improve the photovoltaic performance of DSSCs assembled with gel electrolytes [21–24]. In this work, we introduced nanosized Al_2O_3 particles into the cross-linked GPEs. Before applying the cross-linked GPEs into the cell, we measured ionic conductivities and diffusion coefficients of I_3^- . The diffusion coefficient of I_3^- in the cross-linked GPE was estimated by measuring the diffusion-limited current density in the steady-state current–voltage curve [15,16]. Fig. 3 shows the variation in ionic conductivities and diffusion coefficients of I_3^- in the GPEs as a function of Al_2O_3 content. Both ionic conductivity and diffusion coefficients increase with increasing content of Al_2O_3 nanoparticles, reaching a maximum at 20 wt.%, followed by a decrease. In a previous study, Huo et al. reported that the diffusion coefficient of I_3^- reached a maximum at 10 wt.% of TiO_2 in the poly(vinylidene fluoride-co-hexafluoropropylene)-based nanocomposite GPE [24]. An increase in ionic conductivity and diffusion coefficient with the addition of Al_2O_3 is related to the generation of free volume at the nanoparticle interface [23]. As also previously reported [24,25], charge can transport effectively in the channels of the nanocomposite gel network, and a special mechanism (a Grotthuss-like exchange mechanism) may contribute to the effective charge transport. A decrease in ionic conductivity and diffusion coefficient beyond 20 wt.% Al_2O_3 may be attributed to the blocking effect on the transporting of charge carriers by the aggregation of Al_2O_3 nanoparticles. The morphologies of cross-linked nanocomposite gel polymer electrolytes were analyzed by SEM images shown in Fig. 4, which were obtained after removing the electrolyte solution. It is seen that the porosity of the nanocomposite gel polymer electrolyte increases with addition of Al_2O_3 . This result indicates that the Al_2O_3 nanoparticle generates a lot of pores, which are filled

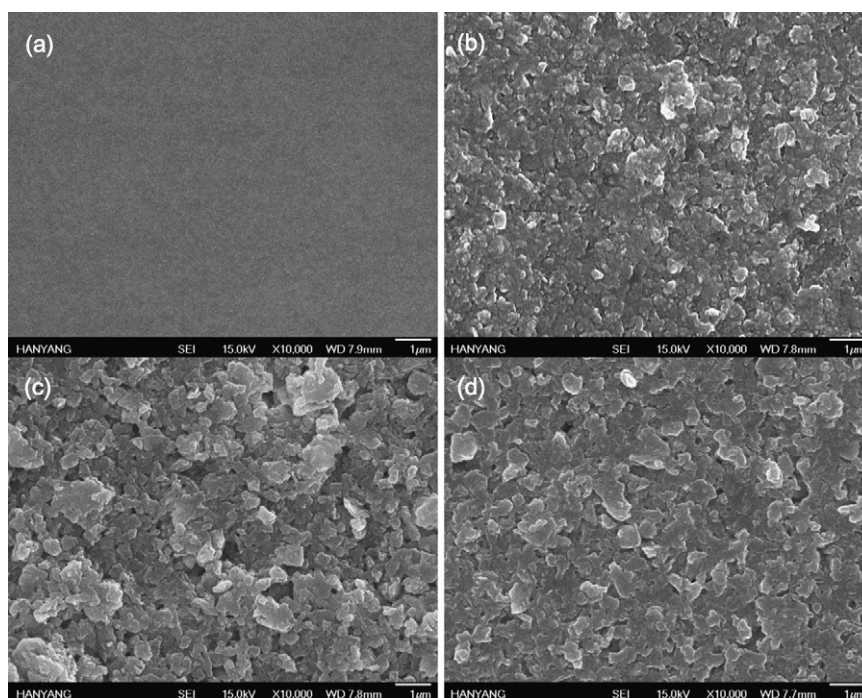


Fig. 4. Scanning electron micrographs of the surface of the cross-linked gel polymer electrolytes containing different contents of Al_2O_3 : (a) 0 wt.% Al_2O_3 , (b) 10 wt.% Al_2O_3 , (c) 20 wt.% Al_2O_3 , (d) 25 wt.% Al_2O_3 .

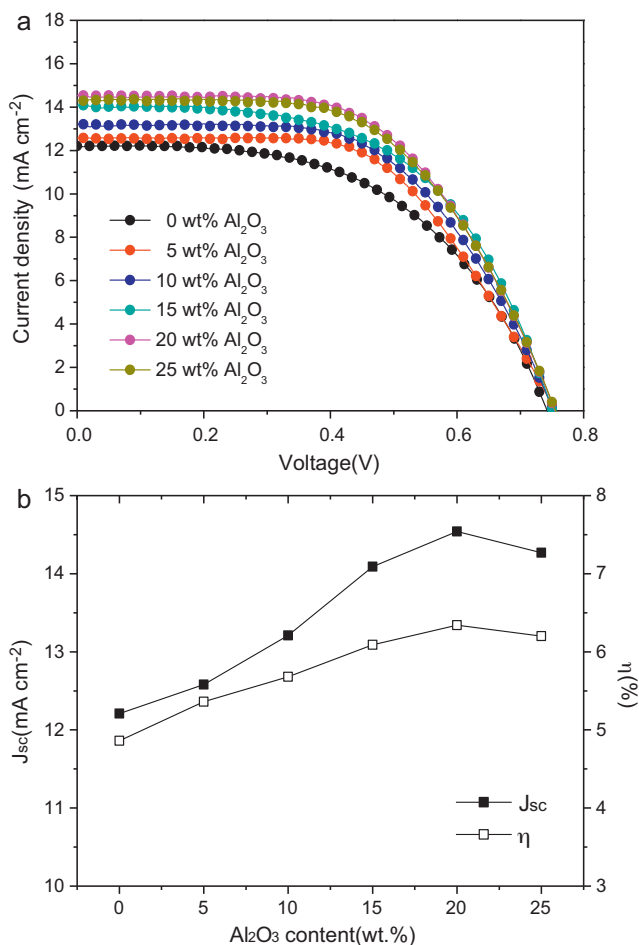


Fig. 5. Effect of Al₂O₃ content on the photovoltaic performances of DSSCs assembled with cross-linked gel polymer electrolytes: (a) photocurrent–voltage curves for DSSCs, (b) J_{sc} and η vs. Al₂O₃ content.

with liquid electrolyte solution. However, the porosity is observed to decrease at 25 wt.% Al₂O₃. From these results, it is believed that the addition of 20 wt.% Al₂O₃ provides the most desirable environment for ionic transport in the cross-linked nanocomposite GPE under study. At the optimum 20 wt.% Al₂O₃, the ionic conductivity and the diffusion coefficient of I₃⁻ are $6.0 \times 10^{-3} \text{ S cm}^{-1}$ and $3.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively.

The photovoltaic performance of the DSSCs assembled with cross-linked GPE containing Al₂O₃ particles was evaluated, and the results are shown in Fig. 5. The J_{sc} and conversion efficiency (η) of the DSSC increased with the addition of Al₂O₃ up to 20 wt.% and decreased with the further addition. An increase in J_{sc} with Al₂O₃ content is related to improved diffusion of I₃⁻, as explained in Fig. 3. In Fig. 5(a), the increase in V_{oc} is hardly seen with addition of Al₂O₃, indicating that the Al₂O₃ has very minor influence on V_{oc} . The optimum Al₂O₃ content to achieve the best conversion efficiency is about 20 wt.%, as shown in Fig. 5(b). Notably, the conversion efficiency (6.34%) of the DSSC assembled with cross-linked GPE containing 20 wt.% Al₂O₃ is higher than that of the corresponding liquid electrolyte-based DSSC (5.97%).

In order to investigate the effect of Al₂O₃ on the impedance behavior of the DSSCs, the ac impedance of the cells was measured. The resulting ac impedance spectra are shown in Fig. 6. For comparison purpose, the ac impedance spectrum of the DSSC prepared with liquid electrolyte is also shown. As shown, the spectra exhibit three overlapping semicircles, which can be assigned to the electrochemical reaction at the Pt counter electrode (R_{ct1}), the charge

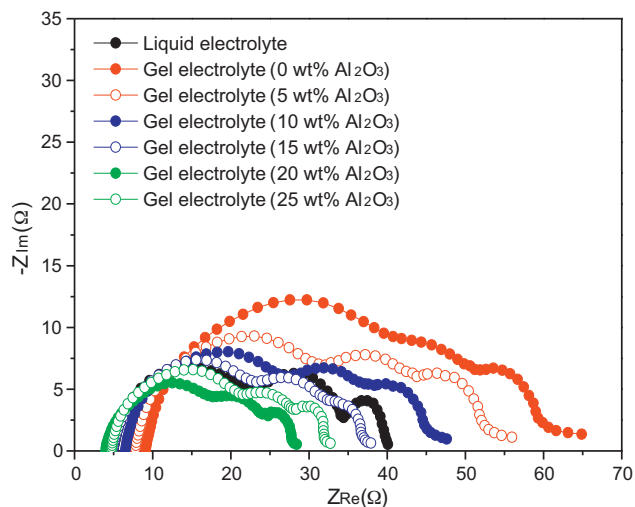


Fig. 6. AC impedance spectra of DSSCs assembled with liquid electrolyte and cross-linked gel polymer electrolyte containing different contents of Al₂O₃.

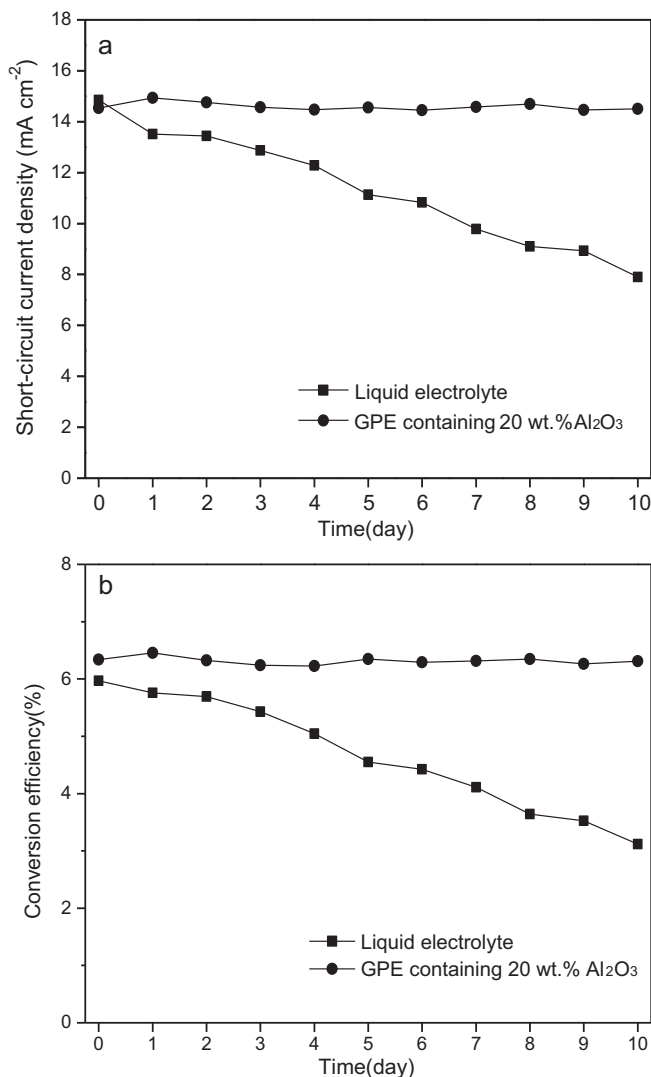


Fig. 7. Variation of short-circuit current density and conversion efficiency as a function of time for the DSSCs assembled with liquid electrolyte and cross-linked gel polymer electrolytes containing 20 wt.% Al₂O₃: (a) short-circuit current density vs. time, (b) conversion efficiency vs. time.

transfer reaction at the TiO₂ electrode (R_{ct2}) and the Warburg diffusion process of I^-/I_3^- (R_{diff}), respectively. The electrolyte resistance (R_e) can be estimated from the intercept on the real axis in the high-frequency range. After cross-linking reaction without Al₂O₃, all of the resistances increased as compared to liquid electrolyte-based DSSC. As mentioned earlier, this result arises from the increase in the resistance for ion migration in both the electrolyte and the electrode after cross-linking reaction. In the DSSCs assembled with the cross-linked GPE containing Al₂O₃, the electrolyte resistance is decreased with addition of Al₂O₃ and shows the lowest value at 20 wt.% Al₂O₃, which is consistent with the ionic conductivity results in Fig. 3. Total interfacial resistance estimated from R_{ct1} and R_{ct2} also reached a minimum at 20 wt.% Al₂O₃. The presence of nano-sized Al₂O₃ in the GPE increases the interfacial area and thus enhances the charge transport at the interface between the electrolyte and the electrode. These results indicate that the addition of proper amount of Al₂O₃ leads to an improvement in the charge transfer reaction at both the TiO₂ electrode and the Pt counter electrode, as well as enhancement of transport of I^-/I_3^- ions in the electrolyte, which results in better cell performance.

The long-term stability of the quasi-solid-state DSSC assembled with cross-linked GPE containing 20 wt.% Al₂O₃ was evaluated. Fig. 7 represents the variation of J_{sc} and conversion efficiency of the quasi-solid-state DSSC as a function of time. For comparison, the J_{sc} and conversion efficiency of the DSSC with liquid electrolyte are also shown. The conversion efficiency in the liquid electrolyte-based DSSC decays continuously with time during the period of investigation. After 10 days, the cell lost 48% of its initial conversion efficiency. Gradual decrease of J_{sc} and conversion efficiency in the DSSC assembled with liquid electrolyte is related to the evaporation of liquid electrolyte, which is caused by the imperfect sealing of the DSSC. On the other hand, the conversion efficiency of the quasi-solid-state DSSC assembled with cross-linked GPE remains almost constant. In the case of the DSSC assembled with chemically cross-linked GPE, the organic solvent containing the I^-/I_3^- redox couple is well encapsulated in the cell, and the in situ chemical cross-linking can also promote good interfacial contact between a dye-adsorbed TiO₂ electrode and a platinum counter electrode, which give more stable performance than that of the DSSC assembled with liquid electrolyte.

4. Conclusions

Quasi-solid-state DSSCs were fabricated by in situ chemical cross-linking of gel electrolyte precursor containing Al₂O₃ nanoparticles, and their photoelectrochemical performance was evaluated. The addition of an appropriate amount of Al₂O₃ nanoparticles into the cross-linked gel polymer electrolyte improved the conversion efficiency of DSSCs. The quasi-solid-

state DSSC assembled with the gel polymer electrolyte containing 20 wt.% Al₂O₃ nanoparticles exhibited remarkably high conversion efficiency, 6.34% at 100 mW cm⁻² and better long-term stability, as compared to the DSSC with liquid electrolyte. From these results, it is expected that the quasi solid-state dye-sensitized solar cell constructed with chemically cross-linked gel polymer electrolyte containing Al₂O₃ particles is a promising candidate for a practical solar cells with good durability.

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