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Quasi-solid-state dye-sensitized solar cells assembled by in-situ chemical cross-linking at ambient temperature

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ABSTRACT

Cross-linked gel polymer electrolytes containing aluminum oxide nanoparticles are successfully prepared using in-situ chemical cross-linking at room temperature after injection of the gel precursor into a dye-sensitized solar cell (DSSC). This makes it possible to directly solidify the electrolyte in the cell without leakage of solvent and to maintain close interfacial contact with the porous TiO_2 electrode. The quasi-solid-state DSSC assembled with gel polymer electrolyte containing 20 wt.% Al_2O_3 particles yields an overall conversion efficiency of 5.25% under AM 1.5 illumination at 100 mW cm^{-2}.

1. Introduction

Dye-sensitized solar cells (DSSCs) have been considered a promising alternative to replace conventional silicon solar cells because of their low cost, easy fabrication and relatively high energy conversion efficiency [1,2]. An impressive conversion efficiency of 11% has been achieved for a DSSC with liquid electrolyte [3]. However, the potential problems caused by the liquid electrolytes, such as the leakage or evaporation of the solvent, 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 electrolytes with polymer electrolytes [4–13]. Unfortunately, solid polymer electrolytes showed low ionic conductivity at ambient temperature and poor electrolyte–electrode interfacial contacts, which resulted in low conversion efficiency. Gel polymer electrolytes (GPEs) that exhibit high ionic conductivity provided successful results in terms of conversion efficiency. However, such GPEs suffer from poor penetration of the electrolyte into the porous TiO_2 electrode and poor interfacial contacts with the electrodes. From a practical point of view, these problems can be overcome by polymerization after the injection of the monomer and liquid electrolyte into the cell [14]. However, in-situ polymerization of a monomer in DSSCs is difficult because it is inhibited by the presence of an iodine-based redox couple [15]. In recent studies, the cross-linked GPEs were synthesized in the presence of iodine at 50 or 70 °C, which allowed the assembly of quasi-solid-state DSSCs via in-situ chemical cross-linking [10,16,17]. The viscosity of the gel electrolyte precursor was not high, and it was possible to impregnate the precursor directly into the pores of the TiO_2 electrode. No initiator was used, and hence cell degradation due to side reactions with the initiator was avoided. As a follow-up investigation, we had great interest in searching for room-temperature cross-linkable GPE systems for DSSCs. In this paper, we report for the first time that the cross-linking reactions between poly(ethylene imine) (PEI) and trimethyol propane triglycidyl ether (TMPTGE) can occur even in iodine-containing electrolyte solution at room temperature without any initiators. The photovoltaic performance of quasi-solid-state DSSCs assembled by in-situ chemical cross-linking was investigated.

2. Experimental

Gel electrolyte precursor consisting of cross-linking agents, liquid electrolyte and Al_2O_3 particles was prepared as follows. First, different amounts of aluminum oxide (particle size: 2–4 nm, Aldrich) were dispersed in liquid electrolyte. The liquid electrolyte was a solution of 1.0 M lithium iodide (LiI), 0.1 M I_2 and 1.0 M 4-tert-butylpyridine (TBP) dissolved in γ-butyrolactone. Then, appropriate quantities of PEI ($M_n = 423$, Aldrich) and TMPTGE (Aldrich) were added into the solution and the mixture was sonicated to ensure homogeneity. The ratio of PEI to TMPTGE in the cross-linking agent was fixed to be 1:3 by weight, and the cross-linking agents were added at different concentrations (2, 4, 6, 8 and 10 wt.%).

A nanocrystalline TiO_2 paste (Ti-Nanoxide 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. An active area of 0.25 cm^2

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was selected from sintered TiO_2 electrode 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 for 30 min. The cell was fabricated by sealing together the TiO_2 electrode and Pt counter electrode 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 with a sealant. Finally, the assembled cell was placed in a 25 °C oven for 24 h to induce the chemical cross-linking reaction, resulting in the formation of three-dimensional polymer networks, as shown in Fig. 1.

The photovoltaic performance of the DSSCs was evaluated using a xenon light source (100 mW cm^{-2}) with an AM 1.5 filter in a solar simulator. The light intensity was calibrated with an NREL-calibrated Si solar cell (PV Measurements Inc.). A black mask 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. A two-electrode electrochemical cell consisting of cross-linked GPE sandwiched between two identical Pt electrodes was used to estimate the diffusion coefficient of the triiodide ion from the diffusion-limited current measurements by cyclic voltammetry at a scan rate of 5 mV s^{-1}[18,19].

3. Results and discussion

The cross-linking reaction of PEI and poly(ethylene glycol) diglycidyl ether (PEGDE) with epoxy groups has been previously reported [20], and the quasi-solid state DSSCs could be assembled *via* in-situ chemical cross-linking at 50 °C [16,17]. With respect to reactivity toward the reactive amine groups in PEI, we found that TMPTGE had much higher reactivity than PEGDE, because the TMPTGE has three epoxy groups per molecule and its molecular weight (302 g mol^{-1}) is lower than that of PEGDE ($M_n = 526$). As a result, the TMPTGE was successfully used for chemical cross-linking of the electrolyte systems even at the lower temperature. Before we added the gel electrolyte precursor into the cells, gel formation was confirmed using chemical cross-linking at 25 °C. Fig. 2 shows images of the cross-linked gel polymer electrolytes without Al_2O_3 particles, which are cured with different amounts of cross-linking agent. It is clearly seen that the electrolyte becomes non-fluidic and finally solidified when the content of cross-linking agent increases, causing the formation of three-dimensional polymer networks.

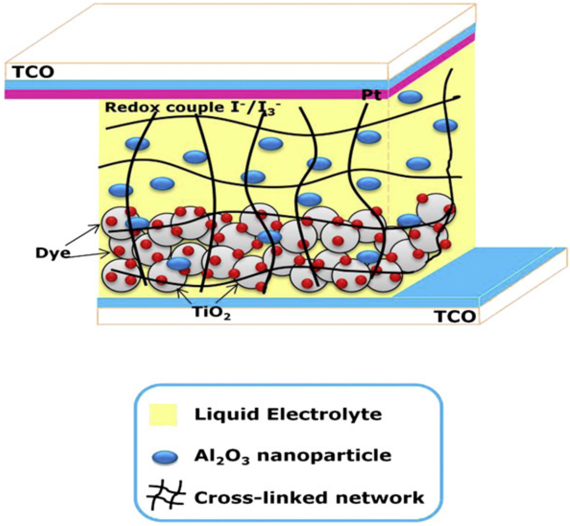

Fig. 1. Schematic diagram of DSSC assembled *via* in-situ chemical cross-linking of gel electrolyte precursor containing Al_2O_3 nanoparticles at room temperature.

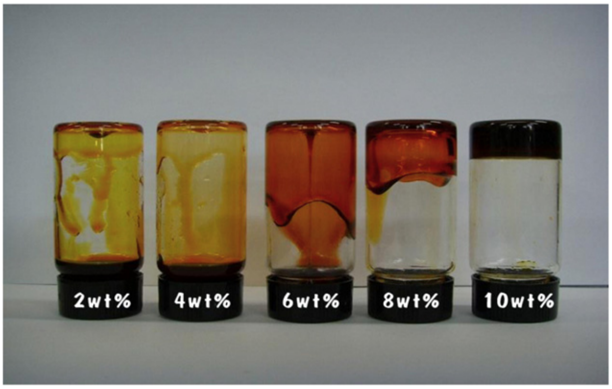

Fig. 2. Images of cross-linked gel polymer electrolytes cured with different amounts of cross-linking agent.

Fig. 3(a) shows the ionic conductivities of cross-linked GPEs without Al_2O_3 particles, as a function of cross-linking agent content. The ionic conductivity of the liquid electrolyte before chemical cross-linking was 3.2×10^{-3} S cm^{-1}, and the ionic conductivities of GPEs decrease with content of cross-linking agent. The cross-linking reaction caused an increase in the resistance for ion transport due to the formation of three-dimensional networks, which resulted in a decrease in ionic conductivity with increasing cross-linking density. The photocurrent

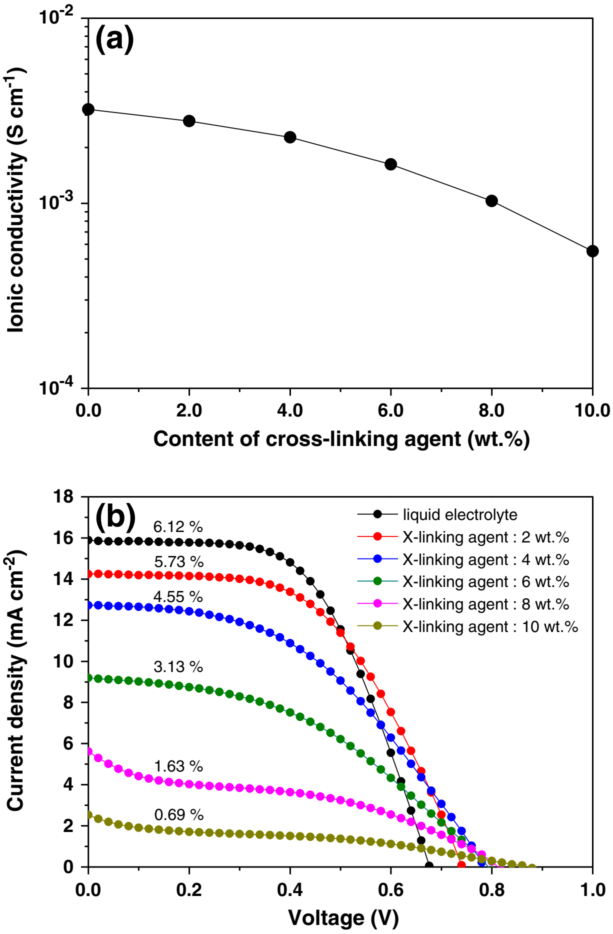

Fig. 3. (a) Ionic conductivities of the cross-linked gel polymer electrolyte as a function of cross-linking agent content, and (b) photocurrent–voltage curves for DSSCs assembled with gel polymer electrolytes cured with different amounts of cross-linking agent. The numerical values on the curve represent the conversion efficiency of each DSSC.

density–voltage curves of the DSSCs assembled with cross-linked GPEs are shown in Fig. 3(b). As shown, the photovoltaic performance of the cells was dependent on the content of cross-linking agent. Both short-circuit current density (J_{sc}) and fill factor decreased with increasing cross-linking agent content. This is due to the fact that cross-linking causes an increase in the resistance for ion migration in the cell, as explained above. The decreased ionic conductivity reduced the supply of I_3^- to the Pt counter electrode, causing a depletion of I_3^- at the electrode surface and hence decreasing the J_{sc} and fill factor of the cell [21,22]. In contrast, the open circuit voltage (V_{oc}) of the cells increased with increasing cross-linking agent content. The cross-linked polymer networks formed on the TiO_2 electrode may have suppressed the back electron transfer from the conduction band of the TiO_2 to the I_3^- ion in the electrolyte, which resulted in an increase in V_{oc}. This increase in V_{oc} may also have resulted from the basicity of PEI, because the flat band potential of TiO_2 was negatively shifted with an increase in the basicity of the electrolyte, which resulted in an increase in V_{oc}[23]. Overall, the conversion efficiency decreased with increasing content of cross-linking agent. Because of the low conversion efficiency of the DSSCs assembled with more than 6 wt.% of the cross-linking agent, the content of cross-linking agent was chosen to be 6 wt.% for further studies.

The addition of inorganic nanoparticles into the gel electrolyte is an effective way to improve the photovoltaic performance of DSSCs [24–27]. As such, different amounts of Al_2O_3 nanoparticles were added to the gel electrolyte precursors containing 6 wt.% cross-linking agent. The photovoltaic performance of the DSSCs assembled with cross-linked GPE containing Al_2O_3 particles is shown in Fig. 4(a). Almost no variation in V_{oc} was seen with addition of Al_2O_3, indicating that the Al_2O_3 has little influence on V_{oc}. This result suggests that the addition of Al_2O_3 particles into the cross-linked GPE hardly affect the back electron transfer and the flat band potential of TiO_2. However, the J_{sc} and conversion efficiency of the DSSC increased with the addition of Al_2O_3 up to 20 wt.% and decreased with further addition. An increase in J_{sc} with Al_2O_3 content is related to the improved diffusion of I_3^-, as depicted in Fig. 4(b). The diffusion coefficients increased with increasing content of Al_2O_3 nanoparticles, reaching a maximum at 20 wt.%. An increase in diffusion coefficient with the addition of Al_2O_3 is related to the generation of free volume at the nanoparticle interface [26]. Also, as previously reported [27,28], charges can be transported effectively in the channels of the nanocomposite gel polymer network. A decrease in diffusion coefficient beyond 20 wt.% Al_2O_3 may be attributed to the blocking effect on the transport of charge carriers by the aggregation of Al_2O_3 nanoparticles. The optimum Al_2O_3 content to achieve the best conversion efficiency was about 20 wt.%. The photo inset in Fig. 4(b) shows the image of cross-linked GPE containing 20 wt.% Al_2O_3. As compared to the image of cross-linked GPE without Al_2O_3 (the 6 wt.% image in Fig. 2), complete gelation with no fluidity can be observed. This suggests that the physical interactions between the Al_2O_3 nanoparticles and polymers as well as chemical cross-linking cause solidification of the electrolyte. The quasi-solid-state DSSC assembled with an optimized GPE system exhibited an overall conversion efficiency of 5.25% at 100 mW cm^{-2}. The conversion efficiency of the cell is relatively lower than that of the cell assembled with PEI and PEGDE, when comparing to the previous results reported by us [17]. This is due to the fact that both the higher content of cross-linking agent and the higher reactivity of TMPTGE lead to the GPE with higher degree of cross-linking, which results in a decrease of short-circuit current density. More detailed studies to improve the cell performance by optimizing the composition of the chemically cross-linked GPE are in progress.

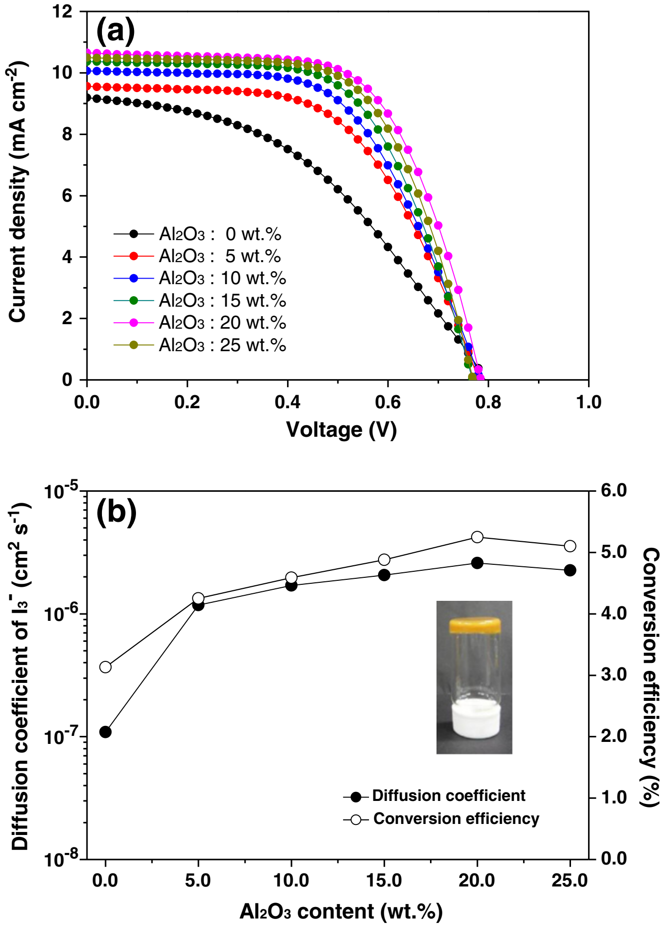

Fig. 4. Effect of Al_2O_3 content on the photovoltaic performances of DSSCs assembled with cross-linked gel polymer electrolytes: (a) photocurrent–voltage curves for DSSCs, and (b) diffusion coefficients of I_3^- and conversion efficiency *vs.* Al_2O_3 content.

4. Conclusions

We demonstrated room-temperature cross-linked GPEs achieved *via* in-situ chemical cross-linking through the reaction of PEI and TMPTGE in the presence of iodine. The quasi-solid-state DSSC assembled with the cross-linked GPE containing 20 wt.% Al_2O_3 nanoparticles exhibited a relatively high conversion efficiency of 5.25% at 100 mW cm^{-2}. Thus, we have shown that it is possible to use a room-temperature cross-linking process that could be applied to the industrial manufacture of DSSCs without the need for thermal curing at high temperatures.

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