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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.

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 TiO_2 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 TiO_2 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 Al_2O_3 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 I_2 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 TiO_2 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).

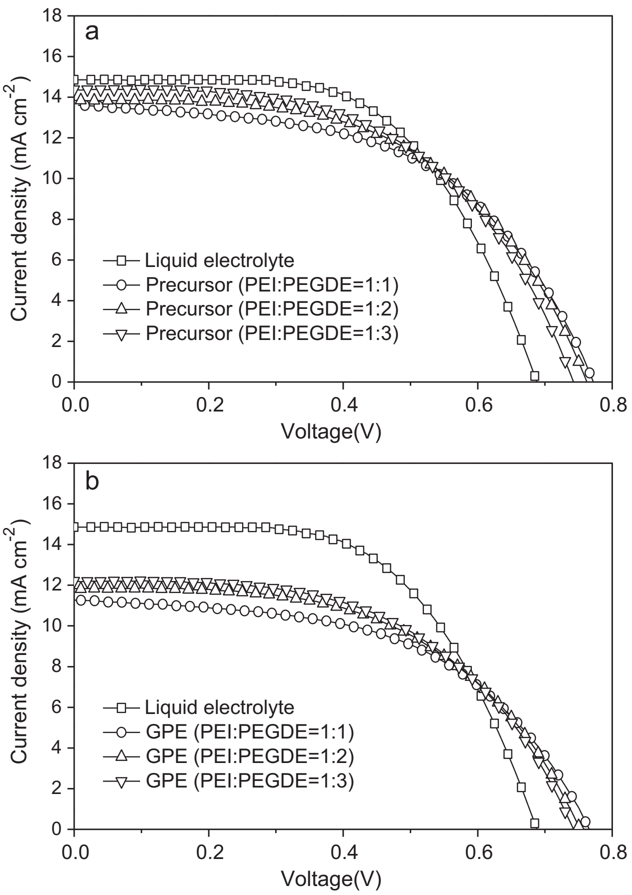

Fig. 2. Photocurrent–voltage curves for DSSCs assembled with gel electrolyte precursor before and after cross-linking reaction, as a function of ratio of cross-linking agent (PEI: PEGDE): (a) before cross-linking reaction, (b) after cross-linking reaction.

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

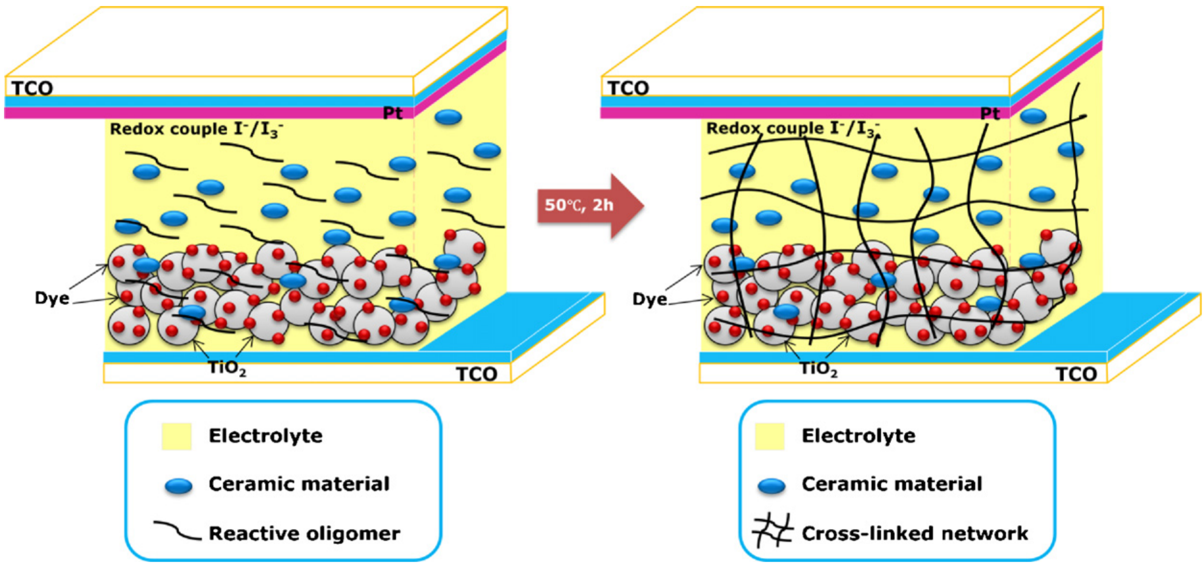

Fig. 1. Schematic diagram of DSSC before and after in situ chemical cross-linking reaction of gel electrolyte precursor containing Al_2O_3.