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Effect of Conducting Ability of Electrolytes on the Photovoltaic Performance of Quasi-Solid State Dye-Sensitized Solar Cells

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DSSCs based on quasi-solid type of electrolytes were prepared to investigate the influence of ionic mobility and recombination kinetics in electrolytes on DSSC performances. The improved ionic mobility of electrolyte in PMMA system resulted in the enhancement of J_{sc} value in DSSC which was well confirmed with the incident photon-to-current spectra and the impedance analysis. Furthermore, the retarded recombination rate from TiO_2 electrode to electrolyte in PMMA system enhanced the electron life time of DSSC in the photoanode. DSSCs based on quasi-solid type of electrolytes composed of PMMA showed a power conversion efficiency of 3.36% under AM 1.5 illumination (100 mWcm^{-2}) in an photo active area of 0.24 cm^2 , short circuit current density of 7.69 mAcm^{-2} , open circuit photo voltage of 0.69 V and fill-factor of 64%.

Keywords Dye-sensitized solar cells; ionic mobility of electrolyte; photovoltaic performances; PMMA and PEO electrolyte; quasi-solid type of DSSC

Introduction

There has been an increasing interest in the dye-sensitized solar cells (DSSCs) owing to a potential for highly efficient solar energy-to-electricity conversion efficiency, low-cost and easy manufacturing process [1–2]. Typically, DSSC could be constructed with dye-absorbed wide band gap oxide semi-conductor electrode such as TiO_2 or ZnO , liquid type of electrolyte containing I^-/I_3^- redox couples, and Pt coated counter electrode. The mechanism of DSSC is based on the injection of an electron from a photo-excited dye into the conduction band of nanocrystalline TiO_2 . The oxidized dye is reduced by the hole injection into either a hole counter or an electrolyte.

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However, the potential problems caused by liquid electrolytes such as desorption and photo-degradation of attached dyes and corrosion of the Pt counter electrode, have had the effect of limiting the long-term stability and practical use of DSSCs. Also, the presence of a liquid electrolyte demands a perfect seal to avoid leakage and evaporation of the solvent [3]. Many efforts have been investigated to solve above mentioned problems by replacing the liquid electrolyte by organic and inorganic hole-transport materials or polymer and gel-electrolytes [4–8].

In this paper, DSSCs based on quasi-solid type of electrolytes composed of polymethylmethacrylate (PMMA) and PEO (polyethyleneoxide) were executed and the photovoltaic characteristics were summarized. The photovoltaic performances of the DSSCs composed of different polymeric materials of quasi-solid electrolyte compared using I-V curves, incident photon-to-current (IPCE) efficiencies, and impedance analysis to investigate the conducting properties of electrolyte.

Experimental

Quasi-Solid Electrolyte Composed of PMMA. The PMMA (MW: 120,000; 10 wt%) was solved into the solvent (ethylene carbonate, propylene carbonate, and dimethyl carbonate mixture with the mass ratio of 4:2:1) and the solution was stirred and heated at 60°C for 24 h to dissolve PMMA, followed by cooling down to room temperature to form a polymer gel. Finally, lithium iodide (0.5 M), and iodine (0.05 M) were added into the gel system, then sonicated in 60 minutes with stirring for 24 h.

Quasi-Solid Electrolyte Composed of PEO. The PEO (MW: 1,000,000; 10 wt%) was solved in acetonitrile, the solution was stirred for 24 h to dissolve PEO in solvent. After that, lithium iodide (0.5 M), and iodine (0.05 M) were added into the gel, then the system was sonicated in 60 minutes with stirring for 24 h.

DSSC Assembly. The TiO₂ paste (solaronix, 13 nm, Switzerland) was spread on the FTO glass plate by using doctor-blade method, then sinter for 20 h at 450°C. After sintering, the TiO₂ film was treated with 40 mM TiCl₄ solution by sintering at 70°C for 30 minutes, then rinsed with ethanol and once again sintering at 450°C for 20 h. The TiO₂ electrode was immersed in the 3×10^{-4} M solution of RuL₂(NCS)₂ (Solaronix, N3 dye) for 48 h at room temperature. After that, the TiO₂ film was rinsed with acetonitrile and then immersed in a 0.5 M of 4-tert butylpyridine (TBP) in acetonitrile solution for 15 minutes, then rinsed with acetonitrile. For the counter electrodes, the Pt catalyst was deposited on the FTO glass by coating with a drop of H₂PtCl₆ solution with the repetition of the heat treatment at 400°C for 15 minutes. The dye-coated TiO₂ films and the Pt counter electrodes were assembled into sealed sandwich-type cells by heating with a hot-melt of ionomer films (Surlyn 1702, 60 μm thickness, Du-Pont).

Results and Discussion

In order to investigate the influence of quasi-solid type of electrolyte system on DSSC performances, a series of solar cells were fabricated by sandwiching the electrolyte composed of PMMA and PEO containing same amounts of electrolytes of lithium iodide and iodine.

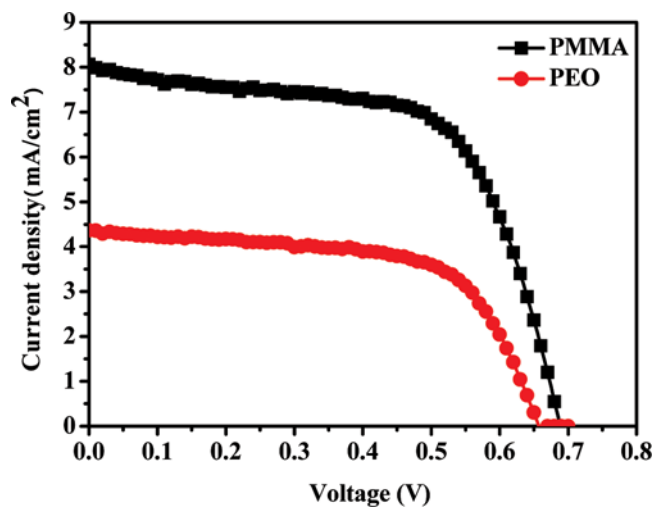


Figure 1. Current density-voltage characteristics for DSSCs composed of quasi-solid electrolytes with the illumination of simulated solar light (AM 1.5, 100 mW/cm²).

The current density-voltage characteristics of the DSSC based on the TiO₂ nanoporous electrode with quasi-solid type of electrolyte system containing PMMA or PEO are shown in Figure 1. The photovoltaic properties of DSSCs assembled with different quasi-solid type of electrolyte system are summarized in Table 1.

The incident photon-to-current efficiency (IPCE) analysis also conducted to investigate the photocurrent characteristics of quasi-solid type of electrolyte system in DSSC.

Figure 2 shows the (IPCE) spectra of the DSSCs containing PMMA and PEO quasi-solid type of electrolyte DSSCs. The DSSC fabricated with PMMA electrolyte exhibited much better IPCE of above 40% at around 500 nm in the solar response range of Ru-dye (300 nm – 750 nm) to compare with that of PEO system of 23% at 500 nm.

The enhanced IPCE in PMMA quasi-solid type of electrolyte system resulted in the high J_{sc} value and cell performances which may due to the improved ionic

Table 1. Photovoltaic performances of DSSCs composed of quasi-solid electrolytes and the electron transport properties in their photoanodes determined by impedance analysis. (Cell areas: 0.24 cm²)

| Electrolyte | J _{sc} /mA cm ⁻² | V _{oc} /V | FF | η/% | R1 (Ω) ^a | R2 (Ω) ^b | C1 | R3 (Ω) ^c | C2 | τ ^d (ms) |
|-------------|---|--------------------|------|------|------------------------|------------------------|---------------------------|------------------------|---------------------------|------------------------|
| PMMA | 7.69 | 0.69 | 63.5 | 3.36 | 15.77 | 10.02 | 1.885 × 10 ⁻⁵ | 18.75 | 1.6219 × 10 ⁻⁴ | 2.21 |
| PEO | 4.19 | 0.66 | 64.5 | 1.77 | 21.97 | 10.34 | 8.2215 × 10 ⁻⁶ | 23.86 | 4.9289 × 10 ⁻⁵ | 0.82 |

^aR1 is FTO Interface resistance.
^bR2 is due to the resistance at the interface between the counter electrode and the electrolyte.
^cR3 is possibly originated from the backward charge transfer from TiO₂ to the electrolyte and the electron conduction in porous TiO₂ film.
^dτ is life time of an electron in DSSC.

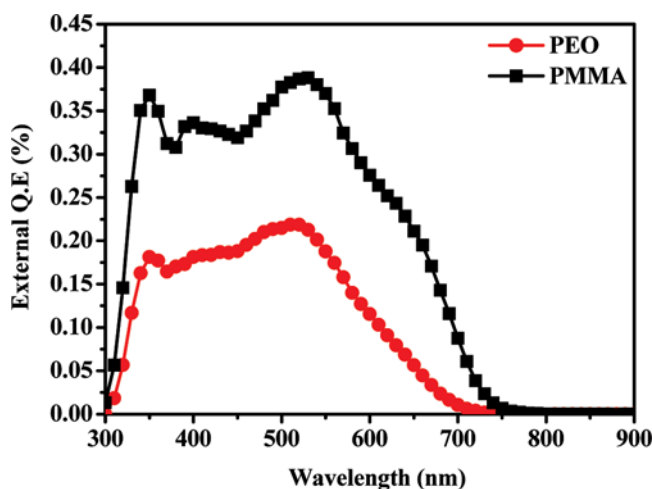


Figure 2. IPCE curves for DSSCs composed of quasi-solid electrolytes.

mobility of electrolyte in DSSCs. Thus, we observed and evaluated the performance of DSSCs containing quasi-solid type of electrolyte system by measuring their impedance spectra and Bode-phase plots under light illumination condition as shown in Figure 3 and the results are also summarized in Table 1. Both of impedance spectra consist of two well defined semicircles in high frequency region and middle frequency region. The resistance (R_1) corresponds to the electrolyte and electrical contacts in the DSSC, and the resistance R_2 and R_3 correspond to the charge transfer process occurring at the Pt counter electrode and the TiO_2 /dye/electrolyte interface, respectively. The quasi-solid type of electrolyte containing PMMA system showed the lower resistance (R_1) and smaller semi-circle (lower diffusion resistance) to compare with that of PEO electrolyte, resulting in a higher J_{sc} value in DSSCs. Most importantly, decreasing diffusion resistance of PMMA electrolyte system means increasing ion mobility, which may improve the cell efficiency.

In general, V_{oc} value is quite sensitive to the electron life time (τ) in the conduction band of TiO_2 [9–10]. The observed electron life time from the Bode-phase spectral results in different electrolyte system are also shown in Table 1, which revealed the much enhanced electron life time in PMMA electrolyte system (2.21 ms) to compare with that of PEO electrolyte system (0.82 ms). Thus, the recombination rate of electrons on the TiO_2 surface in PMMA electrolyte system decreases significantly which extends the electron life time on the TiO_2 surface which can well explain the higher V_{oc} value in PMMA based DSSC to compare with that of PEO electrolyte.

Conclusions

DSSCs based on quasi-solid type of electrolytes composed of PMMA and PEO were successfully prepared and characterized by using I-V curves, incident photon-to-current (IPCE) efficiencies, and impedance analysis, precisely. The quasi-solid type of electrolyte composed of PMMA showed the higher J_{sc} and V_{oc} values and cell performances due to the improved ionic mobility of electrolyte and the enhanced

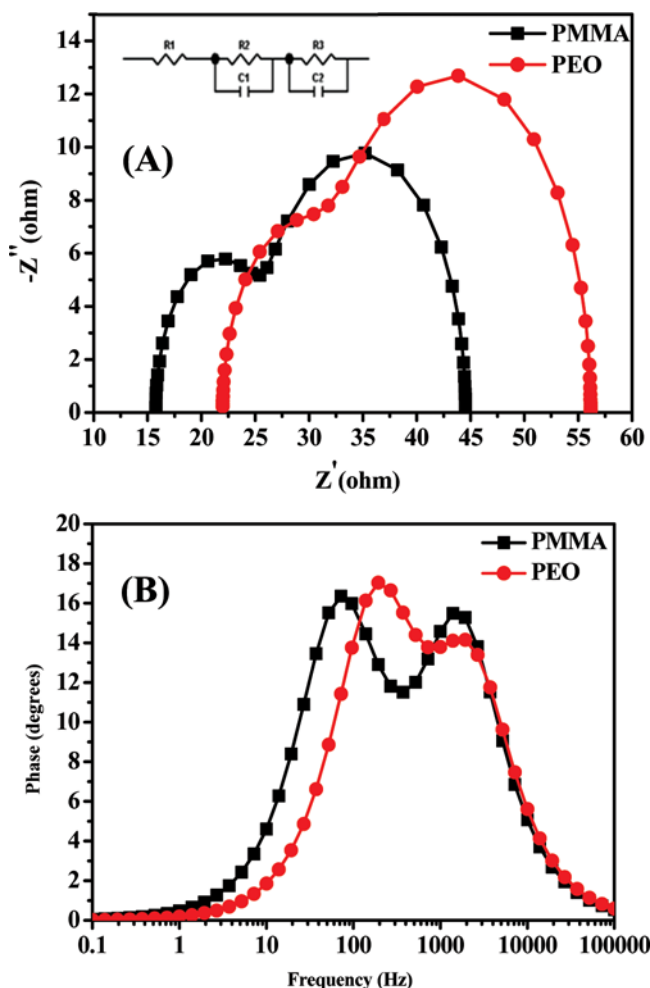


Figure 3. The impedance spectrum (A) and Bode-phase plots (B) for DSSC composed of quasi-solid electrolytes at forward bias applied condition under illumination.

electron life time in DSSCs, respectively. The stability tests of DSSCs with quasi-solid type of electrolyte system are now in progress.

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