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Dye-Sensitized Solar Cells Assembled with Composite Gel Polymer Electrolytes Containing Nanosized Al_2O_3 Particles

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Polymeric ionic liquid, poly(1-methyl 3-(2-acryloyloxy propyl) imidazolium iodide) (PMAPII) containing iodide ions is synthesized and used as a matrix polymer for preparing the composite polymer electrolytes. The composite gel polymer electrolytes are prepared by utilizing PMAPII, organic solvent containing redox couple and aluminum oxide nanoparticle for application in dye-sensitized solar cells (DSSCs). PMAPII is highly compatible with organic solvents and thus there is no phase separation between the PMAPII and organic solvents. This makes it be possible to directly solidify the liquid electrolyte in the cell and maintain good interfacial contacts between the electrolyte and electrodes. The addition of 10 wt.% Al_2O_3 nanoparticle to gel polymer electrolyte provides the most desirable environment for ionic transport, resulting in the improvement of the photovoltaic performance of DSSC. The quasi-solid-state DSSC assembled with optimized composite gel polymer electrolyte containing 10 wt.% Al_2O_3 nanoparticle exhibits a relatively high conversion efficiency of 6.51% under AM 1.5 illumination at 100 mA cm^{-2} and better stability than DSSC with liquid electrolyte.

Keywords: Composite Gel Polymer Electrolyte, Dye-Sensitized Solar Cell, Polymeric Ionic Liquid, Aluminum Oxide Nanoparticle.

1. INTRODUCTION

Photovoltaic device has received great attention as one of the environmentally sustainable energy technologies. Dye-sensitized solar cells (DSSCs) provide a promising alternative to conventional silicon-based photovoltaic cells, because of their low cost, easy fabrication and relatively high energy conversion efficiency.[1,2] The highest conversion efficiency of DSSC reported to date is 12.3% under AM 1.5 when used in conjunction with a liquid electrolyte containing the I^-/I_3^- redox couple.[3] However, the potential problems caused by the liquid electrolytes, such as leakage or evaporation of the organic solvents, are considered to be critical problems that limit the long-term operation and practical use of DSSCs. Therefore, considerable efforts have been made to replace the volatile liquid electrolyte with a solid-state hole conductor, polymer electrolyte and ionic liquid electrolyte.[4–10] Among these approaches, use of gel polymer electrolytes that exhibit high ionic conductivity at room temperature appears to provide successful results in terms of conversion efficiency. Several types of gel polymer electrolytes based on different kinds of polymers have been studied in the DSSCs, such as poly(acrylonitrile)(PAN), poly(ethylene oxide)(PEO) and poly(vinylidene fluoride-*co*-hexafluoropropylene)(P(VdF-*co*-HFP)).[11–17] Alternatively, the polymeric ionic liquids having some of the characteristics of ionic liquids, such as high ionic conductivity, wide electrochemical stability and low flammability, have been synthesized and used as the matrices for preparing the gel polymer electrolytes.[18–20] Addition of inorganic nanoparticles, such as SiO_2, Al_2O_3 and TiO_2 into the gel polymer electrolyte is an effective way to improve the photovoltaic performance of DSSCs assembled with gel polymer electrolytes.[21–23] However, reports about the photovoltaic performance of quasi-solid-state DSSCs assembled with composite gel polymer electrolytes based on polymeric ionic liquids and inorganic nanoparticles are limited.

In this work, we synthesized a polymeric ionic liquid, poly(1-methyl 3-(2-acryloyloxy propyl) imidazolium iodide) (PMAPII), as a matrix polymer for preparing the composite gel polymer electrolytes. With the polymeric ionic liquid, the composite gel polymer electrolytes containing nanosized aluminum oxide particle were prepared and characterized. The photovoltaic performances of quasi-solid-state DSSCs assembled with these composite

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gel polymer electrolytes are investigated and compared with those of liquid electrolyte-based DSSC. The influence of aluminum oxide content on the photovoltaic performance of DSSCs is also investigated.

2. EXPERIMENTAL DETAILS

2.1. Synthesis of Polymeric Ionic Liquid

PMAPII was synthesized through three steps, as depicted in Figure 1. The 3-iodo-1-propanol dissolved in tetrahydrofuran (THF) with a catalytic amount of triethylamine was fed into a glass reactor. A solution of slight molar excess of acryloyl chloride in THF was added to the reactor dropwise over a period of 1 h under N_2 atmosphere at 0 °C. After the solution was completely added, the solution was vigorously stirred for a further 24 h. The triethylamine salt was filtered off, and the product (3-iodopropyl acrylate) was obtained by removing THF in a rotary vacuum evaporator. A mixed solution of 3-iodopropyl acrylate and n-methylimidazole in ethanol was stirred at 45 °C for 12 h under N_2 atmosphere. The product was purified by precipitation with diethyl ether to obtain 1-methyl 3-(2-acryloyloxy propyl) imidazolium iodide (MAPII). The obtained MAPII monomer was polymerized with azobisisobutyronitrile (AIBN) as a free-radical initiator in dimethylsulfoxide (DMSO) at 80 °C for 12 h under N_2 atmosphere. After polymerization, the resulting solution was added drop by drop into a large excess of diethyl ether. The polymer was washed successively with diethyl ether to remove any impurities such as residual monomer and initiator. The polymer was then dried in a vacuum oven at 120 °C for 24 h. The chemical structure of PMAPII was determined by ^1H NMR spectrum using a VARIAN (Mercury 300) NMR spectrometer with DMSO-d_6 solvent.

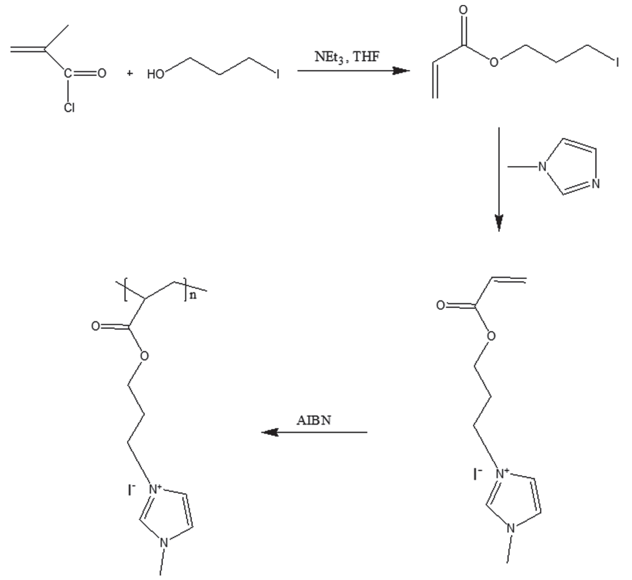


Fig. 1. Reaction scheme for synthesis of PMAPII.

2.2. Cell Assembly and Measurements

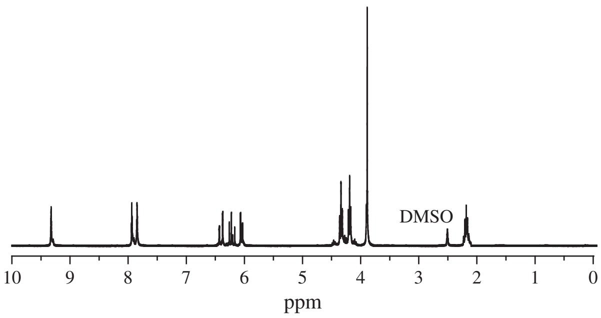
To prepare the composite gel polymer electrolyte, PMAPII was added at 40 wt.% into the liquid electrolyte. The liquid electrolyte used in this study is a solution of 0.05 M I_2 and 0.05 M 4-tert-butylpyridine (TBP) dissolved in γ-butyrolactone (γ-BL). Different amounts (0, 5, 10, 15, 20 wt.%) of aluminum oxide nanoparticle (particle size: 2–4 nm, Aldrich) were added to the polymer solution, and the mixture was sonicated to ensure homogeneity. 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. 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 sandwiching the composite polymer electrolyte between the TiO_2 electrode and Pt counter electrode, and sealing together using a hot melting film. Photovoltaic performance of DSSCs was evaluated using a xenon light source (100 $mWcm^{-2}$) 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. A two-electrode electrochemical cell consisting of composite gel polymer electrolyte sandwiched with two identical Pt electrodes was used to measure the diffusion coefficient of the triiodide ion from the diffusion-limited current measurements.[24, 25] The diffusion-limited current density was determined by cyclic voltammetry at a scan rate of 5 mV s^{-1}.

3. RESULTS AND DISCUSSION

Figure 2 shows the ^1H NMR spectra of MAPII monomer and PMAPII, respectively. The vinyl proton peaks ($CH_2{=}CH$–) in MAPII monomer are observed at 6.24, 6.36 and 6.41 ppm, as shown in Figure 2(a). After polymerization of MAPII monomer, the peaks are clearly disappeared and the new proton peaks (–CH_2–CH–) corresponding to polymer backbone are observed at 2.98 and 3.42 ppm, shown in Figure 2(b), indicating that MAPII monomer was polymerized to PMAPII. The protons (–$CH_{\text{imidazole}}$–) in the imidazole unit appeared at 7.87, 7.98 and 9.55 ppm, as reported erlier.[26] The methylene protons (–CH_2–) in side acryloyloxy propyl unit are observed at 2.12, 4.28 and 4.32 ppm. The ^1H NMR spectrum of PMAPII is well consistent with the expected chemical structure.

Figure 3 shows the ionic conductivities and diffusion coefficients of I_3^- in the composite gel polymer

(a) MAPII monomer



(b) PMAPII

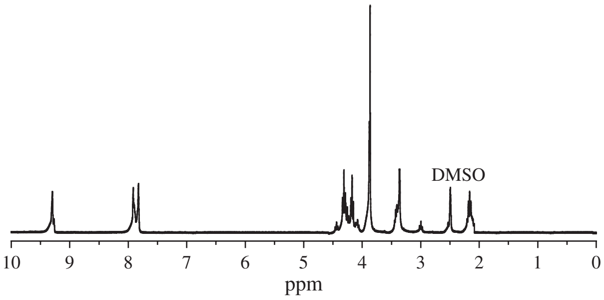


Fig. 2. ^1H NMR spectra of (a) MAPII monomer and (b) PMAPII in DMSO-d_6.

electrolytes, as a function of Al_2O_3 content. The gel polymer electrolyte without Al_2O_3 nanoparticle exhibits an ionic conductivity of 2.0×10^{-3} S cm^{-1} at room temperature. There was no phase separation between the PMAPII and liquid electrolyte, because the polymeric ionic liquid was highly compatible with γ-BL. Both ionic conductivity and diffusion coefficient increase with increasing content of Al_2O_3 nanoparticles, reaching a maximum at 10 wt.%, followed by a decrease. An increase in ionic conductivity and diffusion coefficient with the addition of Al_2O_3 nanoparticle is related to the generation of free volume at the nanoparticle interface.[22] A decrease in ionic conductivity and diffusion coefficient beyond 10 wt.% Al_2O_3 nanoparticle may be attributed to the blocking effect on charge carrier transport since the Al_2O_3 nanoparticle is an insulator for ionic transport by nature. From these results, it is believed that the addition of 10 wt.% Al_2O_3 provides the most desirable environment for ionic transport in the composite gel polymer electrolyte under study. At the optimum 10 wt.% Al_2O_3, the ionic conductivity and the diffusion coefficient of I_3^- are 3.1×10^{-3} S cm^{-1} and 2.1×10^{-6} cm^2 s^{-1}, respectively.

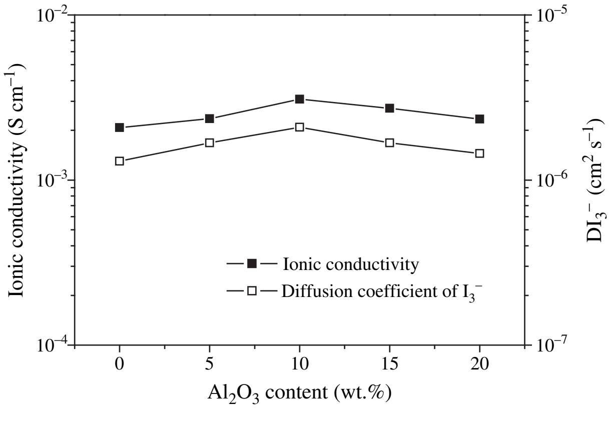


Fig. 3. Ionic conductivities and diffusion coefficients of I_3^- in the composite gel polymer electrolytes, as a function of Al_2O_3 content.

The photovoltaic performance of the DSSCs assembled with composite gel polymer electrolytes containing Al_2O_3 nanoparticles was evaluated. Figure 4 represents the photocurrent density–voltage curves of the DSSCs with composite gel polymer electrolyte containing different content of Al_2O_3 nanoparticles. As shown in figure, the short-circuit current density (J_{sc}) of DSSC increases with the addition of Al_2O_3 nanoparticles up to 10 wt.% and decreases with the further addition. An increase in J_{sc} with Al_2O_3 content is related to improved diffusion of I_3^-, as explained in Figure 3. On the other hand, the addition of Al_2O_3 nanoparticles hardly affects the open circuit voltage (V_{oc}), indicating that the Al_2O_3 has very minor influence on V_{oc}. As a result, the optimum Al_2O_3 content to achieve the highest conversion efficiency is about 10 wt.%. The DSSC assembled with composite gel polymer electrolyte containing 10 wt.% Al_2O_3 nanoparticles yields open circuit voltage of 0.69 V, short-circuit current density of 17.92 mA cm^{-2} and conversion efficiency of 6.51 %, which is 87.9 % of conversion efficiency of the corresponding liquid electrolyte-based DSSC (7.41%).

The long-term stability of the quasi-solid-state DSSC assembled with composite gel polymer electrolyte containing Al_2O_3 nanoparticle was evaluated. Figure 5 represents the variation in the conversion efficiency of DSSC as a function of time. For comparison, the conversion efficiency of the DSSC with liquid electrolyte is also shown. Though the DSSC assembled with liquid electrolyte exhibits high conversion efficiency after being assembled, the conversion

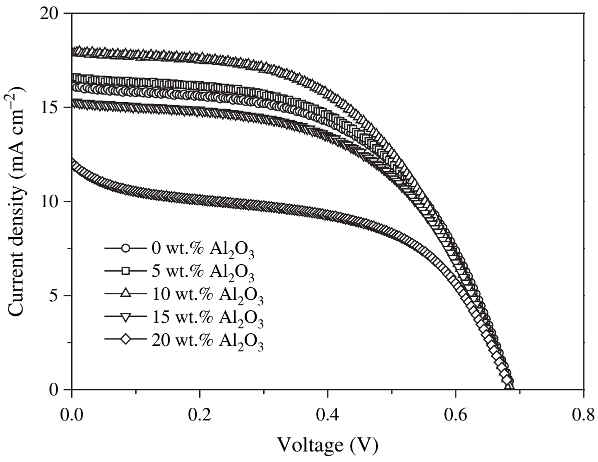


Fig. 4. Photocurrent–voltage curves of the DSSCs assembled with composite gel polymer electrolyte containing different content of Al_2O_3 nanoparticles.

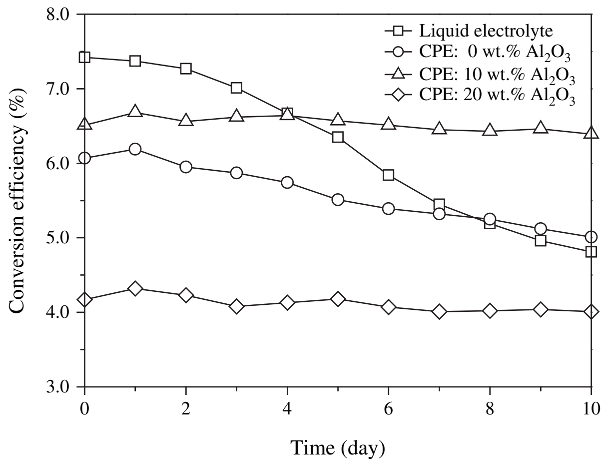


Fig. 5. Variation of conversion efficiency as a function of time for DSSCs assembled with liquid electrolyte and composite gel polymer electrolytes.

efficiency decays continuously with time during the period of investigation. The cell lost 35% of its initial conversion efficiency after 10 days. Gradual decrease of 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 DSSCs with composite gel polymer electrolyte reached a maximum value after one day, and then remained almost constant over 10 days. An initial increase of conversion efficiency may be due to the fact that the interfacial properties between electrodes and composite gel polymer electrolyte are improved at earlier stage. The organic solvent containing a redox couple is well encapsulated in the quasi-solid-state DSSC due to the physical gelation of electrolyte solution in the cell. The adhesive properties of composite gel polymer electrolyte can also promote favorable interfacial contact between a dye-adsorbed TiO_2 electrode and a platinum counter electrode, which give more stable performance than the DSSC assembled with liquid electrolyte.

4. CONCLUSIONS

Poly(1-methyl 3-(2-acryloyloxy propyl) imidazolium iodide) (PMAPII) was successfully synthesized and used as a matrix polymer for preparing the composite polymer electrolytes. The composite gel polymer electrolytes consisted of PMAPII, Al_2O_3 nanoparticles and liquid electrolyte were prepared and applied to the quasi-solid-state DSSCs. The quasi-solid-state DSSC assembled with the composite gel polymer electrolyte containing 10 wt.% Al_2O_3 nanoparticles exhibited a relatively high conversion efficiency of 6.51% at 100 mW cm^{-2} and better stability compared to the DSSC with liquid electrolyte.

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