Photovoltaic Performance of Dye-sensitized Solar Cells assembled with Hybrid Composite Membrane based on Polypropylene Non-woven Matrix

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Hybrid composite membranes were prepared by coating poly(ethylene oxide) and SiO_2 particles onto the porous polypropylene nonwoven matrix. Gel polymer electrolytes prepared by soaking the hybrid composite membranes in an organic electrolyte solution exhibited ionic conductivities higher than 1.1×10^{-3} S cm^{-1} at room temperature. Dye-sensitized solar cell (DSSC) employing the hybrid composite membrane with PEO and 10 wt % SiO_2 exhibited an open circuit voltage of 0.77 V and a short circuit current of 10.78 mA cm^{-2} at an incident light intensity of 100 mW cm^{-2}, yielding a conversion efficiency of 5.2%. DSSC employing the hybrid composite membrane showed more stable photovoltaic performance than that of the DSSC assembled with liquid electrolyte.

Key Words: Dye-sensitized solar cell, Gel polymer electrolyte, Hybrid composite membrane, Photovoltaic performance, Polypropylene nonwoven

Introduction

Dye-sensitized solar cell (DSSC) has been considered as an alternative to a conventional silicon solar cell because of low cost, easy fabrication and relatively high conversion efficiency.[1,2] It consists of a dye-sensitized nanoparticulated TiO_2 electrode, an electrolyte containing redox couple and a Pt coated counter electrode. Such solar cells have conversion efficiencies reaching around 11%, where the electrolyte usually used in the cells is an I^-/I_3^- redox couple in organic solvents.[3] However, the long-term durability of the cell is limited by the leakage or evaporation of the liquid electrolyte. Therefore considerable efforts have been made to replace the liquid electrolyte with polymer electrolyte,[4-13] inorganic p-type semiconductors[14] and organic hole transport materials.[15,16] Among these approaches, use of the gel polymer electrolyte appears to give rise to successful results in terms of conversion efficiency. Conventional poly(ethylene oxide)(PEO)-based solid polymer electrolytes exhibit ionic conductivities ranging from 10^{-8} to 10^{-5} S cm^{-1} at room temperature, which is not sufficient for practical application at ambient temperature. In this respect, most of the recent studies have been directed to the preparation and characterization of gel polymer electrolytes which exhibit higher ionic conductivity at ambient temperature. Gel polymer electrolytes prepared by incorporating liquid electrolyte into a matrix polymer such as polyacrylonitrile(PAN), poly(vinylidene fluoride)(PVdF), poly(methyl methacrylate) (PMMA) and PEO have been employed in quasi-solid-state DSSCs. However, such gel polymer electrolytes suffer from poor mechanical strength, making assembly difficult and increasing the incidence of shorting between electrodes, because impregnation of liquid electrolyte into a polar polymer results in softening of the polymer. To overcome this problem, the porous separators such as microporous polyolefin membranes and nonwoven mats have been used as the supporting framework to make gel polymer electrolyte for lithium-ion batteries.[17-20] Here the porous separator serves as the mechanical support, while gel polymer electrolyte coated onto the separator provides the necessary ionic conductivity between electrodes. To our knowledge, no gel polymer electrolytes supported by the porous separator have been reported so far for DSSC applications.

In our work, we prepared hybrid composite polymer membranes by coating PEO and SiO_2 particles onto a porous polypropylene (PP) nonwoven matrix. PEO was useful as a coating material due to its ability to be easily gelled by the polar solvents. Highly conductive gel polymer electrolytes were then prepared by soaking the hybrid composite membrane in electrolyte solution containing I^-/I_3^- redox couple. In this paper, we report the photovoltaic performance of the dye-sensitized solar cells constructed with the gel polymer electrolyte using the hybrid composite membrane based on PP nonwoven matrix.

Experimental

Preparation of PEO-coated Composite Membrane. Appropriate amounts of PEO (MW: 100,000, Aldrich Chemical) was dissolved in an anhydrous dichloroethane. Different amounts (0, 5, 10, 15, 20 wt %) of fumed silica (particle size: 14 nm) were added to the polymer solution and uniformly dispersed by ball milling overnight. The mixture was further sonicated for 20 min to ensure complete homogeneity. The resulting solution was then coated onto both sides of a porous PP nonwoven fabric (Nippon Kodoshi Co., thickness: 29 μm, porosity: 70%). After evaporation of dichloroethane for 10 min at room temperature, the hybrid composite membrane was vacuum dried at 80 °C for 24 hr. The thickness of the hybrid composite membrane was about 31 μm.

Electrode Preparation and Cell Assembly. 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. The TiO_2 film formed on the FTO was 12 μm thick and 5 mm × 5 mm in size. It was

sensitized overnight with a *cis*-diisothiocyanato-bis(2,2'-bipy-ridyl-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 $^\circ$C for 30 min. A dye-sensitized solar cell was fabricated by sandwiching the hybrid composite membrane between a dye-coated nanoporous TiO_2 electrode and a platinum counter electrode, and sealing the perimeter of the cell while pressurizing it. The membrane was gelled by filling liquid electrolyte into the cell through the holes on the counter electrode. The organic liquid electrolyte was composed of 0.5 M lithium iodide (LiI), 0.05 M I_2 and 0.5 M 4-*tert*-butylpyridine (TBP) in ethylene carbonate (EC)/γ-butyrolactone (γ-BL)(50:50 by volume). EC and γ-BL were used as organic solvent, because they have high dielectric constant and high boiling point, which are effective for solvating inorganic iodide and iodine, and reducing the evaporation of solvent in the cells. Upon injection of liquid electrolyte, the gelation of PEO occurred and the liquid electrolyte was trapped in the membrane. The electrolyte-injecting holes on the counter electrode were sealed by a sealant.

Measurements. The surface morphologies of TiO_2 electrode, PP nonwoven fabric and hybrid composite membranes were examined using a scanning electron microscope (JEOL, JSM-6300). In order to measure ionic conductivity, the hybrid composite membrane was immersed in organic liquid electrolyte for 20 min. The gelled membrane was sandwiched between two stainless steel (SS) electrodes. AC impedance measurements were then performed to measure ionic conductivity using an impedance analyzer over the frequency range of 10 Hz to 100 kHz with amplitude of 10 mV. 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.

Results and Discussion

Scanning electron micrographs of the surface of porous PP nonwoven and hybrid composite membranes are presented in Figure 1. The PP nonwoven fabric exhibits a highly porous three-dimensional web morphology formed by the interconnected fine fibers. As PEO and SiO_2 powder were coated onto the PP nonwoven substrate, the SiO_2 particles were covered with PEO, due to the high volumetric ratio of PEO to SiO_2 powder. Due to the high porosity and large pore size of the PP nonwoven matrix, the coating materials (PEO and SiO_2) are readily impregnated into the PP nonwoven mat and fill up the uneven surface. As a result, the thickness of the hybrid composite membrane was not greatly increased after coating. Upon gelling with the liquid electrolyte, the polymer becomes a gel electrolyte and it in turn serves as an adhesive to bond the membrane and electrodes together, which meanwhile increases uptake and retention of the liquid electrolyte. In the hybrid composite membrane, PP nonwoven matrix could give enough mechanical integrity to the gel polymer electrolyte system.

Ionic conductivity of gel polymer electrolyte prepared by
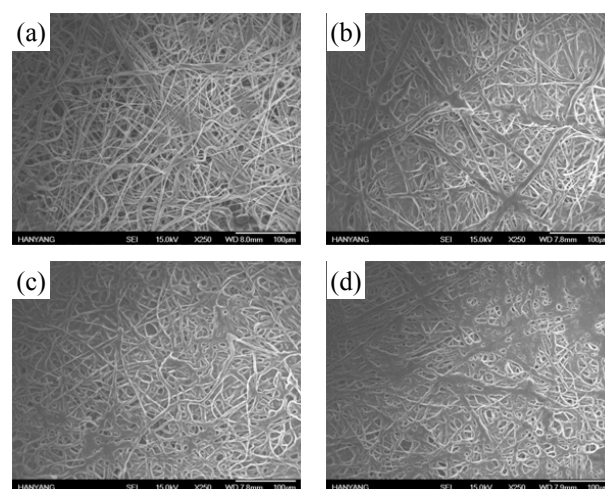
Figure 1. Scanning electron micrographs of the surface of (a) PP nonwoven and hybrid composite membranes coated by (b) PEO, (c) PEO and 10 wt % SiO_2, (d) PEO and 20 wt % SiO_2.
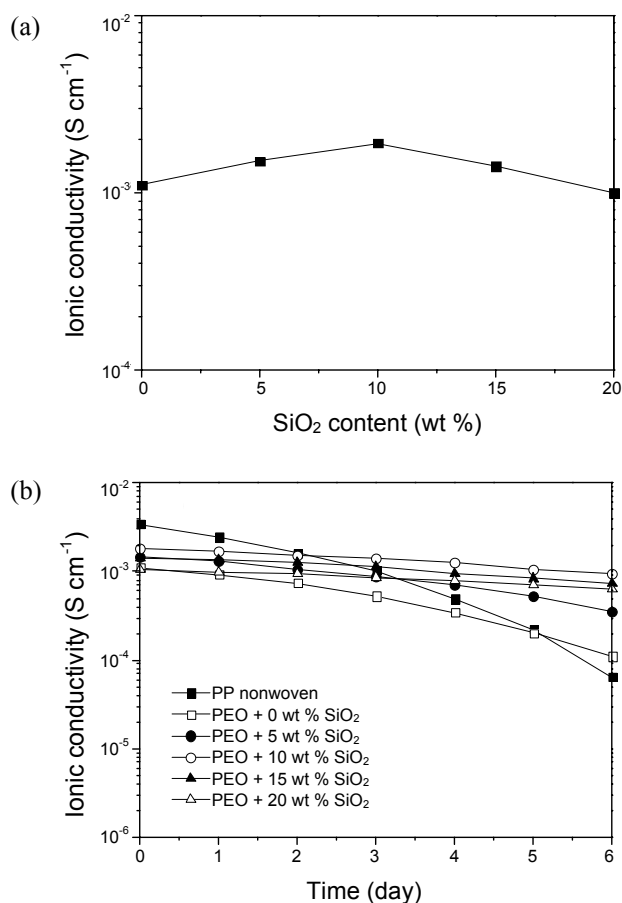
Figure 2. (a) Ionic conductivities of the gel polymer electrolytes prepared with different hybrid composite membrane, as a function of SiO_2 content. (b) Ionic conductivities of electrolyte systems prepared with different membrane, as a function of storage time at 25 $^\circ$C.

soaking the hybrid composite membrane in the electrolyte solution was measured. Figure 2-(a) shows the variation in ionic conductivities of the hybrid composite polymer electrolyte, as

(a)

(b)
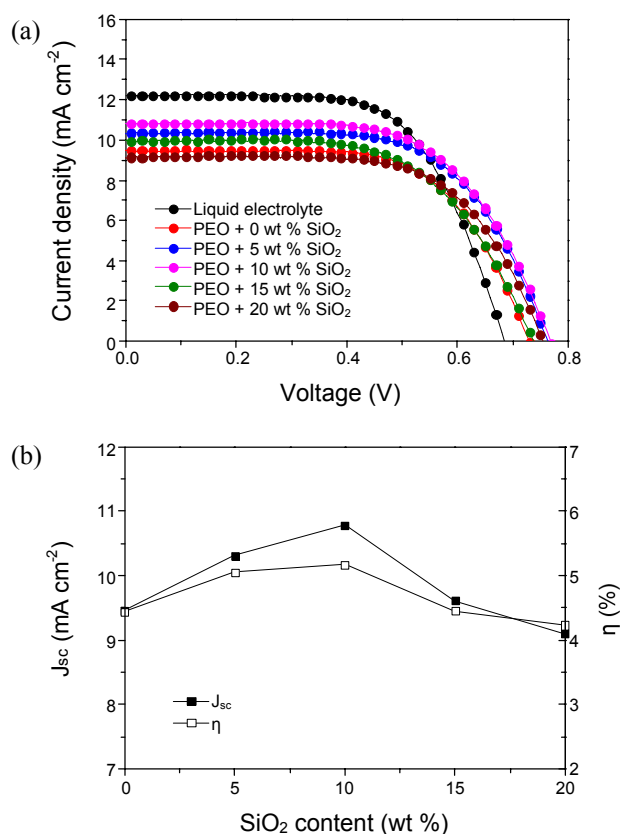
Figure 3. Effect of SiO_2 content on the photovoltaic performances of DSSCs assembled with hybrid composite membranes: (a) photocurrent-voltage curves for DSSCs (AM 1.5, 100 mW cm^{-2}), (b) J_{sc} and η *vs.* SiO_2 content.

a function of SiO_2 content. Ionic conductivity increases with increasing content of SiO_2 particle, reaching a maximum at 10 wt %, followed by a decrease. An increase in ionic conductivity with the addition of SiO_2 is related to both the generation of free volume at the interface of inorganic materials and the surface interaction between SiO_2 and inorganic iodide, as previously reported.[21,22] A decrease in ionic conductivity beyond 10 wt % SiO_2 may be attributed to the blocking effect on the transporting of charge carriers by the excessive SiO_2 particles, since the SiO_2 particle is a non-conducting material. Figure 2-(b) illustrates the time dependence of ionic conductivity for gel polymer electrolytes, as a function of storage time. It is clearly seen that the ionic conduction behavior with time is different for each membrane system. A gradual decrease in the ionic conductivity for the PP nonwoven-based electrolyte can be ascribed to the solvent exudation upon long storage, which arises from its poor compatibility with electrolyte solution due to the inherent hydrophobic properties of non-polar PP matrix. After the conductivity measurements, liquid electrolyte exuding from the PP nonwoven was observed in the cell. The PEO-coated PP membrane exhibited lower initial ionic conductivity than that of PP-based electrolyte, but its ionic conduction behavior with time was slightly improved. Moreover, as the SiO_2 powder with PEO was coated onto the PP substrate, the stability of ionic conductivity with time was significantly improved, which indicates that an electrolyte solution is well encapsulated in

the hybrid composite membrane. This result is related to the enhancement of retention capacity to hold liquid electrolyte, since SiO_2 has a high adsorption capability and subsequently enables loading of the organic solvent, as authors previously reported.[23]

The photovoltaic performance of DSSCs assembled with hybrid composite membranes was evaluated. Figure 3-(a) represents the photocurrent density-voltage curves of the DSSCs assembled with the hybrid composite membranes coated by PEO and different content of SiO_2. For comparison, the photocurrent density-voltage curve of the DSSC prepared with liquid electrolyte is also shown. The DSSCs assembled with the hybrid composite membranes exhibits a lower short circuit current density (J_{sc}) and higher open circuit voltages (V_{OC}) than the liquid electrolyte-based DSSC. Lower value of J_{SC} in the DSSC with hybrid composite membrane originates from its lower ionic conductivity. Higher resistance for ion migration reduces the supply of I_3^- to the Pt counter electrode, which causes the depletion of I_3^- and also retards the kinetics of the dye regeneration, and therefore decreasing the J_{SC}. An increase of V_{OC} in the DSSC is related to the reduction of charge recombination on the TiO_2 and electrolyte interface. The injected electron in TiO_2 is known to recombine with I_3^- in the electrolyte. If I_3^- diffuse in a slower media like gel polymer matrix, the recombination reaction will be depressed, resulting in an increase of V_{OC}. This phenomenon can be also found in literatures published elsewhere.[24-28] The increase of V_{oc} may also result from the increase of pH value of the electrolyte by addition of SiO_2, 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}.[29] With addition of SiO_2 into the electrolyte, the pH value increased from 5.94 (liquid electrolyte without SiO_2) to values ranging from 7.25 to 7.64. J_{sc} and conversion efficiency (η) of the DSSC as a function of SiO_2 content are shown in figure 3-(b). Both J_{sc} and η increased with SiO_2 content up to 10 wt % and decreased with the further increase. An increase in J_{sc} with SiO_2 content is related to improved ionic conductivity of the electrolyte, as explained in Figure 2-(a). Thus, the optimum SiO_2 content in the hybrid composite membrane to achieve the best conversion efficiency is 10 wt %. The conversion efficiency (5.17%) of the DSSC assembled with hybrid composite membrane containing PEO and 10 wt % SiO_2 is slightly lower than that of the corresponding liquid electrolyte-based DSSC (5.35%).

In order to evaluate the durability of photoelectrochemical performance for dye-sensitized solar cell, we measured the conversion efficiency with time. The cells were stored in a desiccator at ambient temperature and measured once a day under AM 1.5 irradiation. Figure 4 represents the variation of conversion efficiency as a function of time. The conversion efficiency in the liquid electrolyte-based DSSC decays continuously with time during the period of investigation. After 10 days, the cell lost 30% of its initial conversion efficiency, and it was lower than those exhibited by the DSSCs prepared with hybrid composite membranes. Gradual decrease of η in the DSSC assembled with liquid electrolyte is related to the slow evaporation of liquid electrolyte. On the other hand, the conversion efficiencies of the DSSCs assembled with hybrid composite memb-
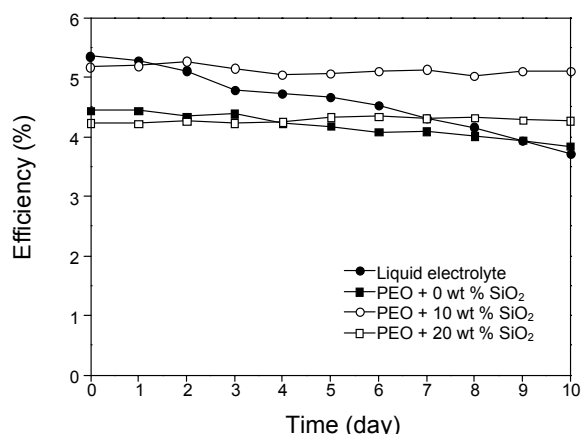
Figure 4. Variation of conversion efficiency as a function of time for the DSSCs assembled with liquid electrolyte and hybrid composite membranes.

rane coated by PEO and SiO_2 remained almost constant. The cells kept more than 98% of their initial conversion efficiencies after 10 days. In the DSSC assembled with hybrid composite membrane, the organic solvent containing I^-/I_3^- redox couple is well encapsulated in the membrane, and the gel polymer formed in the membrane can promote strong interfacial contact between a dye-adsorbed TiO_2 electrode and a platinum counter electrode, which give more stable performance than that of the DSSC assembled with liquid electrolyte.

Conclusions

Gel polymer electrolyte based on hybrid composite membrane coated by PEO and SiO_2 particle was prepared by soaking the membrane in an organic electrolyte solution containing I_3^-/I^- redox couple. It encapsulated the electrolyte solution well in the cell and showed stable ionic conduction behavior that allowed application in the dye-sensitized solar cell. The addition of an appropriate amount of SiO_2 particle into the hybrid composite membrane improved ionic conductivities. The optimum SiO_2 content in hybrid composite membrane to achieve the highest conversion efficiency is 10 wt %. Dye-sensitized solar cell employing the hybrid composite membrane coated by PEO and 10 wt % SiO_2 exhibited an open circuit potential of 0.77 V and a shirt circuit current of 10.78 mA cm^{-2} for an incident light intensity of 100 mW cm^{-2} yielding a conversion efficiency of 5.17%, and better stability as compared to the DSSC with liquid electrolyte.

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