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Dye-sensitized nanocrystalline solar cells based on composite polymer electrolytes containing fumed silica nanoparticles

Jong Hak Kim,[a] Moon-Sung Kang,[a] Young Jin Kim,[a] Jongok Won,[b] Nam-Gyu Park[c] and Yong Soo Kang*[a]

[a] *Center for Facilitated Transport Membranes, Korea Institute of Science & Technology, P. O. Box 131, Cheongryang, Seoul 130-650, South Korea. E-mail: yskang@kist.re.kr*
[b] *Department of Applied Chemistry, Sejong University, Seoul 143-747, South Korea*
[c] *Electronics and Telecommunications Research Institute, Daejeon 305-350, South Korea*

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We report remarkably high energy conversion efficiency (4.5% at 100 mW cm^{-2}) of a dye-sensitized solar cell in the solid state, using composite polymer electrolytes containing fumed silica nanoparticles.

Polymer electrolytes are formed by dissolving metal salts in solid polar polymer hosts. Metal salts dissolve in such polymer media because of the coordination interactions between the metal ions and the polar groups of the polymer. Polymer electrolytes have received considerable attention over the last few decades because of their potential applications in electrochemical devices such as solid-state batteries,[1] fuel cells,[2] and separation membranes.[3] Polymer electrolytes have been the subject of particular recent interest because of their use in dye-sensitized solar cells (DSSCs).[4–6]

DSSCs have generated considerable research interest because of their high-energy conversion efficiency (~11%) and low production costs.[7] The basis for energy conversion in DSSCs is the injection of electrons from the photoexcited state of the dye sensitizer into the conduction band of the TiO_2 semiconductor upon absorption of light, where the electrons necessary for regeneration of the oxidized dye are supplied by the redox reaction of the redox couple (*e.g.*, I^-/I_3^-) dissolved in the electrolyte. Thus the electrolyte containing a redox couple serves as a medium for the electrochemical redox reactions as well as for charge transport. Liquid electrolytes have commonly been used as redox media in DSSCs.[8] However, there are problems for this type of solar cell, such as leakage, evaporation of solvent, high-temperature instability, and flammability. Thus many efforts have been made to replace the liquid media with solid media, for example, polymer gel electrolytes,[9] organic hole-transport materials,[10] and solid polymer electrolytes.[4–6]

Poly(ethylene oxide) (PEO) has attracted much attention as an electrolyte medium because it is polar and chemically stable. However, its ionic conductivity is too low for solar cell applications because of its high crystallinity. There have been many attempts to modify PEO to increase its ionic conductivity, such as the incorporation of comonomer or nanoparticle fillers. Nogueira *et al*. reported that DSSCs employing poly(epichlorohydrin-*co*-ethylene oxide) ($M_w = 1.3 \times 10^6$ g mol^{-1}) with NaI/I_2 produced a high energy conversion efficiency, 2.6% at 10 mW cm^{-2}.[4a] Alternatively, nanocrystalline TiO_2 particles were introduced into a PEO ($M_w = 2 \times 10^6$ g mol^{-1})/LiI/I_2 electrolyte to prevent PEO crystal formation, resulting in a high energy conversion efficiency of 4.2% at 65.6 mW cm^{-2}.[5a] These high overall energy conversion efficiencies of solid-state DSSCs are based on the increase of both the ionic conductivity and the interfacial contact between the electrolyte and the dye-adsorbed semiconductor nanoparticles.

In this communication, we report another novel method for increasing both the interfacial contact and the ionic conductivity in DSSCs, with a view to improving their overall efficiency. A high level of interfacial contact between the electrolyte and the dye-adsorbed semiconductor layer is achieved by deep penetration of the electrolyte into the nanopores of the semiconductor layer. The penetration of the electrolyte depends on the coil size of the polymer host and the pore size of the semiconductor layer. We observed that the average size of the nanopores was approximately 11.1 nm, as determined by the Brunauer–Emmett–Teller (BET) method, from the N_2-desorption isotherm. The coil size of a polymer is commonly represented by the radius of gyration (R_g), $R_g = C(M_w)^{1/2}$, where M_w (g mol^{-1}) is the molecular weight of the polymer and C is a constant depending on the properties of the solvent. It has previously been determined that C is 0.063 nm (g mol^{-1})$^{-1/2}$ for PEO in a good solvent.[11] Low molecular weight poly(ethylene oxide dimethyl ether) (PEODME, $M_w = 500$ g mol^{-1}, $R_g = 1.4$ nm) was employed in this study to achieve high interfacial contact and ionic conductivity. Further, fumed silica nanoparticles (amorphous, surface area 255 ± 15 m^2 g^{-1}, density 4.5 ± 0.5 lb ft^{-3}, 3.5–4.5 OH groups μm^{-2}) were introduced into the system to create a three-dimensional network that prevents the viscous flow of low molecular weight PEODME and consequently provides mechanical strength. In addition, fumed silica nanoparticles have been reported to improve the ionic conductivity of polymer electrolytes.[12] We have therefore prepared composite polymer electrolytes consisting of PEODME/MI (M = K^+, imidazolium$^+$)/I_2/fumed silica for use in solid-state DSSCs.

The ionic conductivities of the polymer electrolytes were measured using a galvanostatic four-probe method to investigate the mobility of the redox couple. The ionic conductivity determined by four-probe method is higher to some degree but more accurate than that by the two-probe method, due to the minimization of contact impedance, as reported by Cahan and Wainright.[2b] The mole ratio of ether oxygen to iodide salt was fixed at 20 and the iodine content was fixed at 10 wt% with respect to the salt. The maximum ionic conductivity of these electrolytes reached ~10^{-3} S cm^{-1} at room temperature. It was also observed that the ionic conductivities of polymer electrolytes containing MPII are always higher than those of polymer electrolytes containing KI for all concentrations of fumed silica, implying the ionic liquid is more effective than the metal salt in making the polymer chains flexible.

DSSCs with an active area of 0.126 cm^2 were fabricated on glass covered with tin oxide (SnO_2). Nanocrystalline TiO_2 paste (Ti-Nanoxide D, Solaronix) was cast onto the glass using the doctor-blade technique and then sintered at 450 °C for 30 min. The TiO_2 nanoparticles were sensitized overnight with $Ru(dcbpy)_2(NCS)_2$ (dcbpy = 2,2′-bipyridyl-4,4′-dicarboxylato) dye solution (1×10^{-4} mol dm^{-3}) (535-bisTBA, Solaronix), while the Pt counter-electrode was prepared by spin-coating H_2PtCl_6 solution (0.05 mol dm^{-3} in isopropyl alcohol) onto the conductive glass and then sintering at 400 °C. Finally, the polymer electrolyte solution was cast onto the TiO_2 electrode, covered by the Pt electrode. The *J*–*V* curves were measured at AM 1.5 illumination using a Keithley Model 2400 source measure unit. A 1000 W xenon lamp (Oriel, 91193) served as the light source. The light was homogeneous up to 8 × 8 in, and its intensity (or radiant power) was adjusted with an Si solar cell (Fraunhofer Institute for Solar Energy System; Mono-Si+KG filter; Certificate No. C-ISE269) for 1 sunlight intensity that was double-checked with a NREL-calibrated Si solar cell (PV Measurements Inc.). The cell performances were evaluated after vacuum drying for two days, without any special sealing.

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The *J–V* curves of the two DSSCs (KI and MPII) were measured at 100 mW cm^{-2} and are presented in Fig. 1. The silica nanoparticles' concentration was fixed at 9 wt% of the total polymer electrolyte, at which concentration a mechanically stable solid polymer electrolyte is formed with an ionic conductivity of ~ 10^{-3} S cm^{-1}. The maximum energy conversion efficiency was as high as 4.5% at 100 mW cm^{-2} for DSSC employing PEODME/MPII/I_2/fumed silica. Although a similar approach for DSSC employing a silica nanocomposite, *i.e.* PEG200/KI/I_2/SiO_2 (tetramethoxysilane) has been reported previously,[6b] the solar cell performance was low, *i.e.* V_{oc} = 4.3 mA cm^{-2}, J_{sc} = 0.47 V at 96 mW cm^{-2}. The remarkably improved solar cell efficiency in the present study is presumably due to the use of fumed silica nanoparticles and the two-step casting method. The two-step method is carried out by casting a dilute solution (2 wt%) of polymer electrolyte onto a dye-adsorbed TiO_2 electrode as a first step, and then successively casting a concentrated solution (20 wt%). In addition, the currents increase monotonically with an increase in the light intensity, indicating that the photocurrent is not significantly limited by the diffusion of the redox couple in the polymer electrolyte.

The incident-photon-to-current conversion efficiency (IPCE) is defined as the ratio of collected electrons to incident photons. The inset of Fig. 1 shows the IPCE curves for the two DSSCs. An IPCE value as high as *ca*. 60% was obtained at 530 nm, which is comparable to that typically observed for DSSCs employing gel or liquid electrolytes.[8a] The photocurrent action spectrum matches the absorption characteristics of the Ru535 dye and goes to zero at long wavelengths.

The interfacial contact between the dye-adsorbed semiconductor nanoparticles and the electrolyte is dependent on the penetration of the electrolyte into the nanopores of the semiconductor layer. The penetration of the polymer electrolyte into the TiO_2 nanopores was investigated using field-emission scanning electronic microscopy (FE-SEM). The SEM photomicrographs of the cross-sections of a DSSC before and after employing PEODME/MPII/I_2/fumed silica electrolyte are shown in Fig. 2. Before casting the polymer electrolyte solution, the TiO_2 nanoparticles are distinguishable with a size of 30–40 nm. When the polymer electrolyte, consisting of low molecular weight PEODME with an R_g of 1.4 nm was added, the TiO_2 particle size apparently increased and the image of the nanoparticles became indistinct. This may be because the TiO_2 nanoparticles are covered by the polymer electrolyte, indicating excellent contact between the dye-adsorbed TiO_2 particles and the polymer electrolyte. This better penetration of the electrolyte into the nanopores and thus better interfacial contact are possible because the coil size of the electrolyte is much smaller than the pore size of the nanopores of the TiO_2 layer.

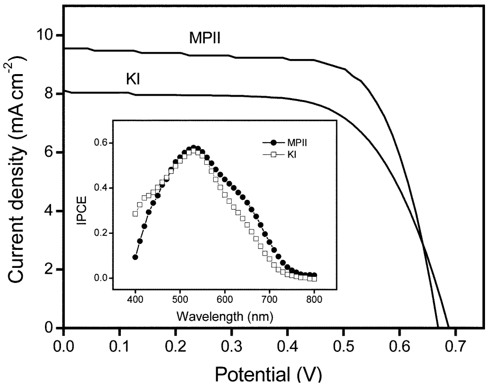

Fig. 1 *J–V* Curves of the DSSCs employing PEODME/MI (KI, MPII)/I_2/fumed silica electrolytes, measured at 100 mW cm^{-2}. The inset shows the IPCE spectra of the DSSCs as a function of the wavelength of the light.

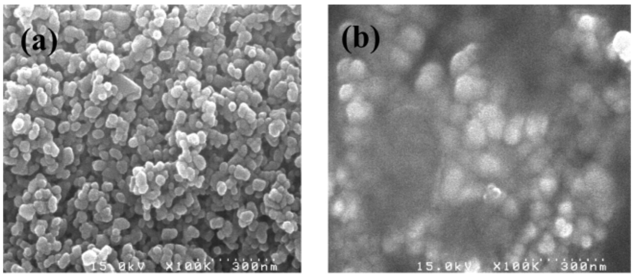

Fig. 2 Cross-sectional FE-SEM images of nanocrystalline TiO_2 layers (a) before and (b) after casting a PEODME/MPII/I_2/fumed silica electrolyte.

In conclusion, we have demonstrated that composite polymer electrolytes consisting of PEODME, fumed nanosized silica, iodide salt and iodine provide improved DSSC performance at the solid state. The DSSC exhibited remarkably high conversion efficiency, 4.5% at 100 mW cm^{-2}, which is one of the highest values ever reported for DSSCs employing solid polymer electrolytes.

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