Effect of TiO_2 Inclusion in the Poly(vinylidene fluoride-*co*-hexafluoropropylene)-Based Polymer Electrolyte of Dye-Sensitized Solar Cell

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Since the first appearance of Grätzel cell,[1] dye-sensitized solar cells (DSSCs) have been much attracted as a promising candidate of next-generation energy source devices. The solar cells are typically consisted of a porous TiO_2 photo-anode sensitized by Ru-complex dye, a liquid electrolyte containing redox couple (I_3^-/I^-), and a Pt-coated counter-electrode. It was recently claimed that the DSSC with liquid electrolyte could give a maximum photo-electro conversion efficiency higher than 10%[2,3] under AM1.5 one sun condition. The lack of long-term stability, however, could occur by the leakage or evaporation of liquid electrolyte components. Many efforts were paid to replace the liquid electrolyte by various types of quasi-solid-state polymer electrolyte.[4] The approach of using polymer electrolytes has been attracted with high interest but usually resulted in lower conversion efficiency than conventional Grätzel cell with liquid electrolyte. Among many polymer electrolytes, the poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVdF-HFP) as polymer matrix material in DSSC has been known[5-7] to be quite useful because of its photoelectrochemical stability under potential application. The previous result of PVdF-HFP polymer electrolyte[7] presented somewhat low conversion efficiency of about 2-3%. We have considered that the low efficiency might be due to the inhibition of ion migration by the viscosity originated from polymer chain obstacles. Thus, we tried to modify the PVdF-HFP polymer electrolyte system to improve ion migration.

In the present note, we report the effect of TiO_2 inclusion into the PVdF-HFP polymer electrolyte of DSSC to obtain the same effect of liquid retention (solid solvent) as the polymer electrolyte of lithium rechargeable battery.[8,9] Through this note, the increase in conversion efficiency by the addition of TiO_2 nanoparticles is mainly observed but furthermore discussed in terms of long-term durability of DSSC. In addition, *the readers should not be confused by the TiO_2 nanoparticles in polymer electrolyte with the TiO_2 photo-anode on conducting glass*.

The PVdF-HFP and TiO_2 used were a commercial fluoro-copolymer KynarFlex 2801 (Atofina Chemicals, HFP content of 12 mol%) and nanocrystalline titanium oxide PC-101 (Japan Titan Kogyo, anatase, avg. diameter of 20 nm), respectively. A homogeneous solution of PVdF-HFP in *N*-methyl-2-pyrrolidone (NMP; Aldrich) as a solvent with a 15 : 85 weight ratio was first obtained by room-temperature stirring. Second homogeneous solution was also prepared by the further addition of redox couple source. Two systems of redox couple source were used: (i) 1 M 1-hexyl-2,3-dimethylimidazolium iodide (C_6DMI, C-Tri Co.)/0.1 M I_2 (Aldrich) and (ii) 1 M LiI (Aldrich)/0.1 M I_2. Viscous pastes were prepared by the final addition of TiO_2 nanoparticles varying the content as 0, 10, 30 wt% with a weight basis of (PVdF-HFP + TiO_2). The viscosity of paste samples ranged over 20,000-35,000 cP (1 cP = 1 mPa/s). Precise fabrication procedures of DSSC, such as TiO_2 photo-anode, dye adsorption, Pt-coated counter-electrode, and sealing with Surlyn 1702 (du Pont), could be referred to elsewhere[7,10] except the application of PVdF-HFP/TiO_2/(I_3^-/I^- sources) pastes with a thickness of about 10 mm on the TiO_2 photo-anode adsorbed by N719 dye. Photovoltaic characteristics were measured by using a solar simulator (Keithly 2400 source measure unit with a 1000 W Xe lamp, Oriel 91193 as a light source). The simulator was pre-calibrated by a reference silicon cell (Fraunhofer, C-ISE269) and the active area was about 0.156 cm^2.

Figure 1 shows the photocurrent-voltage profiles of the DSSCs employing PVdF-HFP/TiO_2 polymer electrolytes. Photovoltaic characteristics obtained from the profiles, such as open-circuit voltage (V_{OC}), short-circuit photocurrent density (J_{SC}), fill factor (ff), and conversion efficiency (η), are summarized in Table 1.

As shown in Figure 1, photovoltaic characteristics are improved by the inclusion of TiO_2 nanoparticles in electrolyte medium. In detail, the conversion efficiency of the PVdF-HFP/TiO_2 system with ionic liquid redox component (C_6DMI) is mainly supported by the increase in J_{SC} as the TiO_2 content increases. It can be regarded that the TiO_2 nanoparticles can interact with polymer chain to retard the crystallization of the rigid vinylidene fluoride unit and then to expand the free volume of polymer chain by its role of solid solvent.[8] The increase in free volume formed within the polymer matrix can promote the dissociation of ionic liquid species (C_6DMI) and thus the increase in J_{SC} occurs by the further activation of I^- diffusion. Meanwhile, the PVdF-HFP/TiO_2 containing LiI redox component exhibits

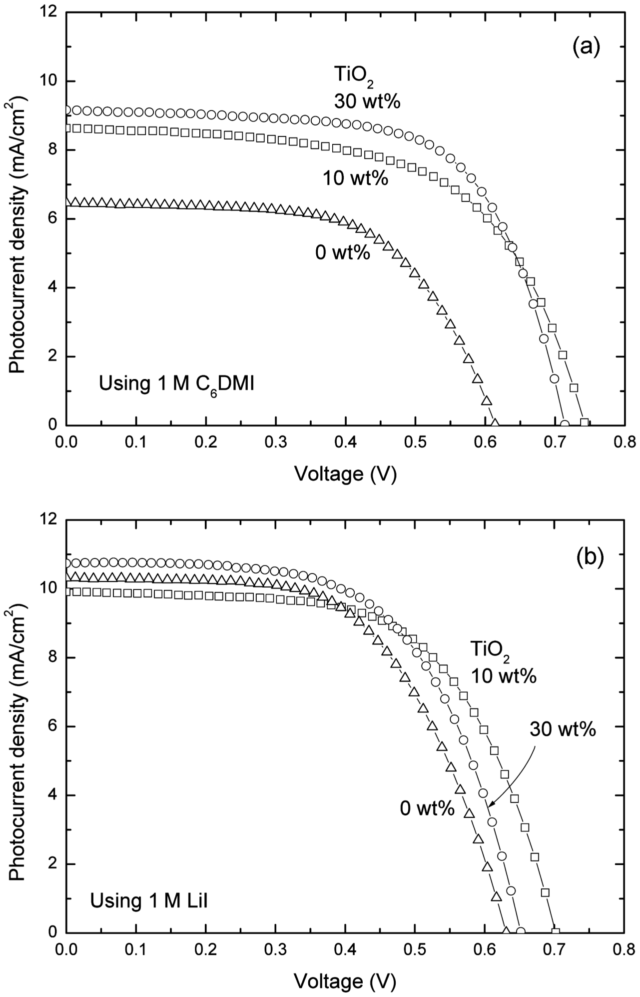


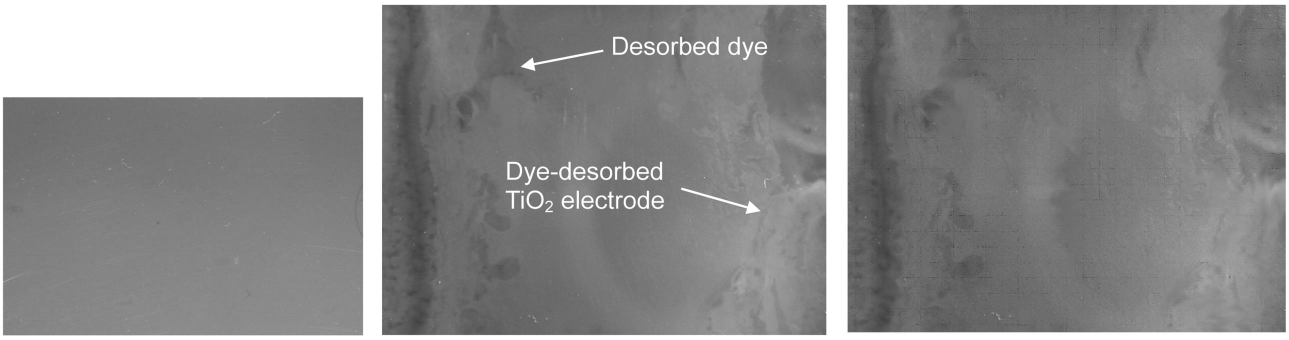
Figure 1. Photocurrent-voltage curves for the DSSCs employing PVdF-HFP/TiO$_2$ and (a) 1 M C$_6$DMI/0.1 M I$_2$ and (b) 1 M LiI/0.1 M I$_2$ as a redox couple source.

somewhat different behavior with the increase in TiO$_2$ content. The J_{SC} and V_{OC} of LiI-containing system are slightly changed up and down with increasing TiO$_2$ content. In this case, the TiO$_2$ nanoparticles do not greatly influence the ionic migration, but just play a role of trapping and maintaining liquid components to help carrier transport. Nonetheless, the increase in conversion efficiency (up to about 4.3%) by including TiO$_2$ nanoparticles has a meaning that solid solvent effect of TiO$_2$ in the polymer electrolyte can help the dissociation of ionic liquid species to enhance the photovoltaic performance of DSSC.

Table 1. Photovoltaic properties of DSSCs employing PVdF-HFP/TiO$_2$ polymer electrolyte

Electrolyte constituent		V_{OC} (V)	J_{SC} (mA/cm^2)	ff	η (%)
TiO$_2$ (wt%)	I$_3^-$/I$^-$ source				
0	1 M C$_6$DMI/0.1 M I$_2$	0.615	6.46	0.609	2.42
0	1 M LiI/0.1 M I$_2$	0.631	10.31	0.585	3.81
10	1 M C$_6$DMI/0.1 M I$_2$	0.743	8.63	0.595	3.82
10	1 M LiI/0.1 M I$_2$	0.702	9.91	0.611	4.25
30	1 M C$_6$DMI/0.1 M I$_2$	0.714	9.15	0.652	4.26
30	1 M LiI/0.1 M I$_2$	0.653	10.73	0.600	4.20

On the other hand, a problem of long-term instability may occur in this polymer electrolyte system, mainly due to the usage of solvent NMP which is soluble[11] to the N719 dye adsorbed on TiO$_2$ photo-anode. Dye desorption by NMP leads to gradual decay of J_{SC} and eventually to the malfunction of DSSC. Figure 2 shows the image evolution of DSSC employing PVdF-HFP/TiO$_2$ (30 wt%) and 1 M C$_6$DMI/0.1 M I$_2$. Even after 1-day exposure to air, the dye desorption and the exposure of TiO$_2$ photo-anode are observed with the decrease in J_{SC} (not presented) to a certain extent, as shown in Figure 2(b). However, the tendency of dye desorption is getting saturated with small traces after 10 days, as shown in Figure 2(c). Conversion efficiency decreases from 4.26 (as-prepared) to 3.2% for the case of aging 1 day, and its decreasing trend diminishes after 10 days (the efficiency of about 3.0%). The small traces may be observed by slightly blotted dyes near the desorbed boundaries. This result can be supported by the fact that the improvement of stabilization by the gel-like layer between PVdF-HFP and NMP suppresses the dye desorption from TiO$_2$ photo-anode.[7] Spectroscopic study for the dye desorption will be further carried out with the development of



(a) Pristine (b) After 24h (c) After 240h

Figure 2. The images of the DSSC employing a PVdF-HFP/TiO$_2$ (30 wt%) and 1 M C$_6$DMI/0.1 M I$_2$: (a) as prepared, (b) 24 h, and (c) 240 h after the fabrication.

novel solvent system.

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