

# A solid-state dye-sensitized photovoltaic cell with a poly(*N*-vinyl-carbazole) hole transporter mediated by an alkali iodide

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A polymer-based dye-sensitized solar cell in dry solid state was constructed using poly(*N*-vinyl-carbazole) (PVK) as a hole-transporting layer; the cell attained the highest power efficiencies of 2.4% and 2.0% at 1/4 sun and 1 sun (AM1.5), respectively, by incorporation of a solid intermediate layer (LiI, KI) at the dye–PVK interface.

Solidification and quasi-solidification of dye-sensitized solar cells (DSC) has been the subject of intense study by various types of approaches using p-type inorganic semiconductors (CuI, CuSCN, etc.),<sup>1–4</sup> organic hole conductors,<sup>5–8</sup> and ionic polymers<sup>9,10</sup> for replacement of liquid electrolytes. Use of organic conductors or polymer layers are especially promising for fabrication of a flexible thin solar cell, which is a recent trend in advanced DSC research.<sup>11–13</sup> Grätzel's group first showed a solid-state DSC made of an organic hole conductor with a power conversion efficiency of 0.74%.<sup>5</sup> The efficiency of this system was improved to reach 3.2% (1 sun, AM1.5 illumination),<sup>7</sup> where a dye-sensitized TiO<sub>2</sub> mesopore was coated with 2,2',7,7'-tetrakis(*N,N*-di-methoxy-phenyl-amine)-9,9'-spirobifluorene (OMeTDA) as an organic hole-transporting material mixed with an ionic composition containing a 4-*tert*-butylpyridine. Polymer films have been actively studied for solidification of DSC. Quasi-solid DSCs using polymer electrolyte gels<sup>9,10</sup> have achieved high efficiencies of 3.8–4.5%. Using polymer materials, however, it has been difficult to devise a dry solid-state DSC that is free of ionic electrolyte and exhibits high performance. To construct an all solid-state polymer-based DSC, we employed in this study poly(*N*-vinylcarbazole) (PVK) as a hole-transporting layer to form a solid junction comprising nanocrystalline TiO<sub>2</sub>/dye monolayer/hole transporter at which photo-induced charge separation proceeds. It has been well investigated that the photoelectric performances of polymer-based DSCs are highly affected by the interfacial structures of the dye/hole transporter and hole transporter/counter-electrode interfaces. In particular, poor penetration of macromolecules into TiO<sub>2</sub> mesopores<sup>14</sup> and imperfect contact between the dye-adsorbed surface and the hole-transporting polymer are the main causes of low photocurrent density. Here we show that an optimized layered structure formed by incorporation of alkali iodide as an intermediate at the dye/hole transporter interface greatly improves the conversion efficiency of the polymer-based solid-state DSC.

F-doped SnO<sub>2</sub> conductive glass (sheet resistance 10 Ω per square) as an electrode substrate was pre-coated with a dense TiO<sub>2</sub> underlayer (buffer layer) by a spray pyrolysis method<sup>15</sup> to prevent direct contact between the SnO<sub>2</sub> layer and the hole-transporting polymer. This coating was made by chemical vapor deposition of [(CH<sub>3</sub>)<sub>2</sub>CHO]<sub>4</sub>Ti (1 M in acetylacetone and ethanol (2 : 1))

mixture) on the SnO<sub>2</sub> surface heated at 500–550 °C. A 7 μm thick mesoporous TiO<sub>2</sub> layer was formed on this layer by the conventional sintering method at 550 °C for 30 min using a commercial TiO<sub>2</sub> coating paste (Solaronix, SA). The TiO<sub>2</sub> layer was sensitized by monolayer adsorption of a ruthenium complex dye (N719), *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4-carboxylic acid-4'-tetrabutylammonium carboxylate)ruthenium(II) (Solaronix, SA). As a starting construction, the dye-sensitized TiO<sub>2</sub> layer was directly coated with a thin hole-transporting layer (0.01–0.1 μm thick) by casting a solution of PVK (Tokyo Kasei) in dichloromethane (1.0 mg mL<sup>-1</sup>). In order to modify the dye/polymer interface, an alkali halide salt (KI, LiI, and LiBr) as a dopant was added on the mesoporous surface of dye-adsorbed TiO<sub>2</sub> by allowing a dilute acetonitrile solution to dry. This treatment introduced a thin intermediate layer between the dye monolayer and PVK. The top of the PVK layer was finally covered with a 300 μm thick carbon graphite layer comprising graphite powder and polyvinylidene fluoride (19 : 1 by weight) by coating a paste dispersed in dimethylformamide and subsequent evaporation at 80 °C. All processes were conducted in aerated conditions. The graphite layer tightly contacts the surface of a Pt counter-electrode (vacuum-deposited Pt layer on conductive F/SnO<sub>2</sub> glass) to form a heterojunction solid-state cell (Fig. 1) with an effective electrode area of 0.27 cm<sup>-2</sup>.

Photocurrent–voltage characteristics were measured on a Keithley 2400 source meter under AM1.5 solar irradiation of 100 mW cm<sup>-2</sup> (1 sun) and 23 mW cm<sup>-2</sup> (1/4 sun) supplied by a Xe lamp equipped solar simulator (Pecell Technologies). External quantum conversion efficiency (EQE, or incident photon to current conversion efficiency IPCE) was determined by a monochromatic irradiation system operated at 10 Hz in combination with a lock-in amplifier (Bunkoh-keiki).

The PVK-based photocells without incorporation of the intermediate layer at the dye/PVK interface yielded a small order of dye-sensitized anodic photocurrent less than 0.05 mA cm<sup>-2</sup>. EQE was no larger than 3%. This result must reflect the difficulty

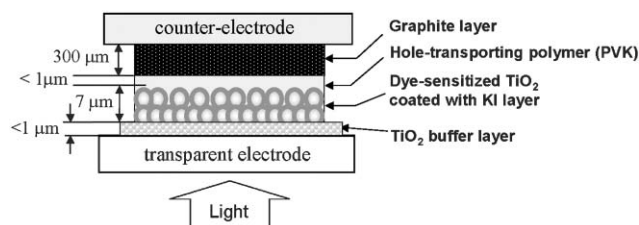
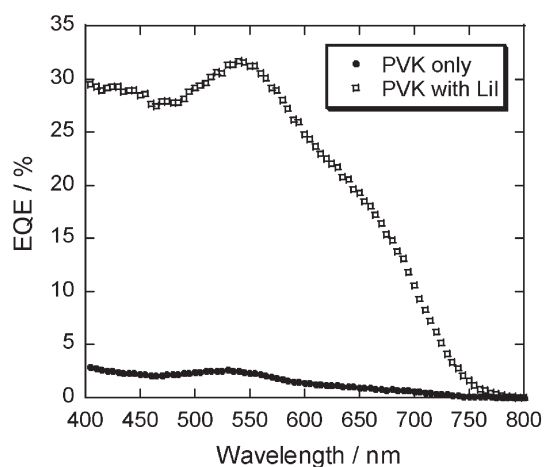


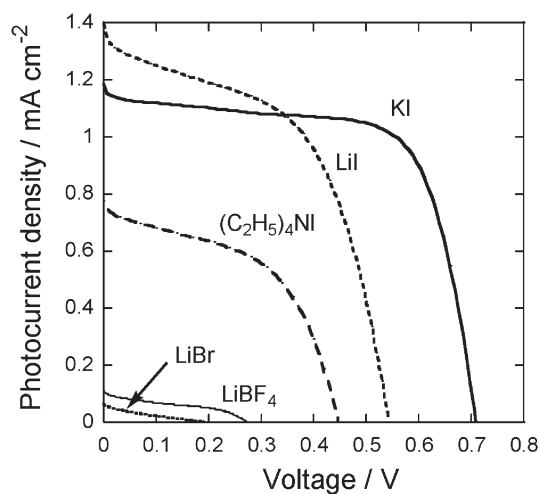
Fig. 1 Schematic structure of a solid-state dye-sensitized solar cell using PVK as a hole-transporting layer.

for the polymer hole transporter to permeate into the depths of the mesoporous interior. When the mesopore was treated with a LiI solution to incorporate a thin solid LiI layer (calculated thickness of  $<1$  nm) as an intermediate undercoating for the PVK layer, the maximum value of EQE was greatly increased to 32%. The EQE action spectrum reflects the optical absorption of the absorbed dye peaking at 540–550 nm (Fig. 2). On irradiation at 1/4 sun intensity, this LiI-incorporated solid cell with a hetero-junction structure, anode/TiO<sub>2</sub>/dye/LiI/PVK/graphite/cathode, gave a short-circuit photocurrent density ( $J_{sc}$ ) over  $1 \text{ mA cm}^{-2}$  and an open-circuit voltage ( $V_{oc}$ ) of 0.54 V (Fig. 3), yielding a power conversion efficiency of 1.67%. With 1 sun intensity, however, the cell gave a lower efficiency of 1.35% by a drop in the fill factor (FF). This reflects a high electric resistance of the cell structure, presumably due to the solid polymer layer.

Knowing that the addition of alkali halide is effective for enhancement of photocurrent, we investigated the role of the alkali cation and halogen anion as a dopant in promoting the



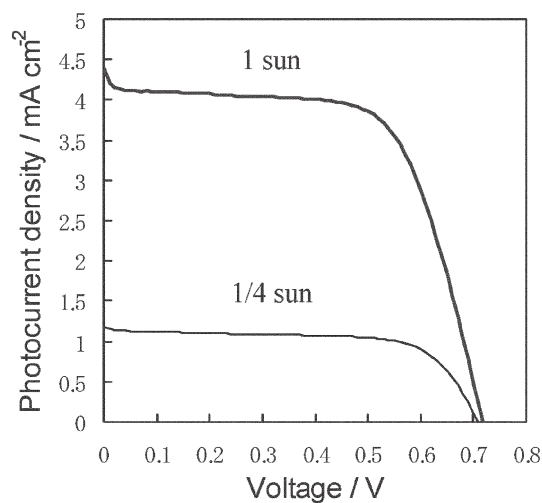
**Fig. 2** EQE action spectra for the PVK-based solid-state dye-sensitized photocells. Black circle: a cell with sole PVK layer; open square: a cell with LiI-incorporated PVK layer.



**Fig. 3** Photocurrent–voltage characteristics for PVK-based solid-state dye-sensitized solar cells using various salts as dopants, compared under irradiation intensity of 1/4 sun (AM1.5).

hole-transporting activity of PVK. These comparative experiments were performed with an incident intensity of 1/4 sun. The results are compared in Fig. 3. Replacing LiI with LiBr significantly reduced the photocurrent to a level comparable with the LiI-free PVK layer. Use of the electrochemically inactive BF<sub>4</sub><sup>−</sup> anion in place of the halogen anion caused a similar result. These results indicate that the iodide anion plays an essential role in development of sensitized photocurrent. As for the role of the Li cation, (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NI, in which Li is substituted with an inert cation, could sustain a sufficient amplitude of photocurrent. Although this substitution lowered  $V_{oc}$  ( $<0.5$  V) significantly, the Li cation is not crucial for the enhancement of photocurrent. Exchange of LiI with KI showed a noticeable effect. An essential change was found in  $V_{oc}$ , which increased to 0.71 V from 0.54 V accompanied by improvement of FF. The KI-incorporated cell exhibited the best cell performance as shown in Fig. 3. The cell yielded the highest overall conversion efficiency of 2.42% at 1/4 sun, two orders of magnitude higher than the efficiency of the dopant-free PVK cell. With an incidence intensity of 1 sun, the cell gave an efficiency of 1.97% with  $V_{oc}$  of 0.72 V.  $I$ – $V$  characteristics for 1/4 sun and 1 sun are exhibited in Fig. 3 and in Fig. 4, where the initial drop occurring in photocurrent density near 0 V is caused by the influence of the voltage scanning, which was started at 0 V without pre-scanning from negative voltage, and is not an intrinsic behaviour of the cell.

The effect of iodide, KI and LiI, is interpreted to be due to their involvement in the electronic reduction of the photo-oxidized dye. They are incorporated into the depths of the TiO<sub>2</sub> mesopore, making close contact with the dye monolayer on the TiO<sub>2</sub> surface. This deep contact is hardly made for the polymer hole conductor alone with a bulky structure. Alkyl iodide salt covering the surface of the mesoporous network may play a role by capturing the dye hole first and transporting it to PVK at a much high efficiency compared to the case of direct transport from the dye hole. Vacuum drying treatment of the LiI-incorporated cell showed high photoelectric performance while exposure of the cell to ambient humidity for several hours caused deterioration of the photocurrent. This fact shows that LiI and KI function in the solid state



**Fig. 4** Photocurrent–voltage characteristics of KI-incorporated solid-state dye-sensitized solar cells under irradiation intensity of 1 sun and 1/4 sun (AM1.5).

**Table 1** Photoelectric performances and conversion efficiency of TiO<sub>2</sub>/dye/intermediate/PVK/graphite/Pt sandwich-type solid-state dye-sensitized photocells measured under simulated solar irradiation of 1/4 sun (23 mW cm<sup>-2</sup>, AM1.5)

Intermediate	$J_{sc}/\text{mA cm}^{-2}$	$V_{oc}/\text{V}$	FF	$\eta(\%)$
PVK	0.048	0.25	0.018	0.009
LiI-PVK	1.39	0.54	0.51	1.67
KI-PVK	1.18	0.71	0.66	2.42
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NI-PVK	0.78	0.45	0.49	0.73
LiBr-PVK	0.065	0.20	0.18	0.010
LiBF <sub>4</sub> -PVK	1.09	0.27	0.034	0.044

<sup>a</sup>  $J_{sc}$  : short-circuit photocurrent.  $V_{oc}$  : open-circuit photovoltage. FF : fill factor.  $\eta$  : energy conversion efficiency.

rather than by releasing solvated I<sup>-</sup> anions in the presence of trace contamination of liquid or water from ambient humidity. As a solid-state reaction mechanism, iodine (I<sub>2</sub>) or radical (I<sup>•</sup>) produced by the reduction of the dye hole may be trapped by the hole transporting PVK. Here I<sub>2</sub> can be involved in the hole injection reaction in the gas phase at the junction of PVK. Although the low EQE of our cell shows that the permeation of PVK into the TiO<sub>2</sub> pore is imperfect, KI must be playing an important role for the hole injection at the interface where PVK contacts with the pore surface. The hole injected into PVK transfers to the graphite carbon layer in contact with the counter-electrode interface where electron-hole recombination occurs. Based on the hole conduction mechanism, on the other hand, it is also probable that iodine is involved in the doping of PVK to increase its intrinsic hole conductivity.

Table 1 summarizes the photoelectric performance of PVK-based solid-state dye-sensitized cells in the incident 1/4 sun condition for various compositions of salt incorporated as dopants. The maximum efficiency attained by KI-PVK, 2.42%, is backed up by a high  $V_{oc}$  of 0.71 V, which is close to the voltage range of the dye-sensitized liquid-junction cells of highest performance.<sup>16</sup> A possible reason why KI is superior to LiI may be related to the high hydrophilicity of LiI. Contamination of water brought about by LiI at the dye/PVK interface is assumed to reduce  $V_{oc}$  and the overall efficiency.

With the KI-PVK system, the cell performance is durable for a sufficiently long time even under exposure of the electrode materials to ambient air. For further enhancement of efficiency, interfacial nano-processing to reinforce the KI-PVK connection is considered most important along with minimizing the PVK layer thickness to reduce the internal resistance. In this study, we could design a solid DSC of relatively high conversion efficiency with a

simple composition for hole-transport layer and a cheap polymer material (PVK). Our method for manufacture of solid-state dye-sensitized cells can be applied directly to the fabrication of a plastic-based flexible photocell using our low-temperature TiO<sub>2</sub> coating method,<sup>12,13</sup> which is now underway.

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