Conductive polymer–carbon–imidazolium composite: a simple means for constructing solid-state dye-sensitized solar cells†

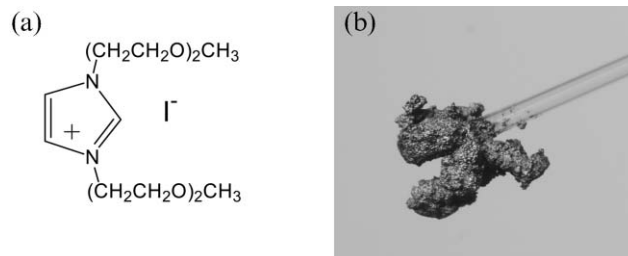**Nobuyuki Ikeda, Kenjiro Teshima and Tsutomu Miyasaka**

A clay-like conductive material comprising polyaniline-loaded carbon black particles and an ethyleneoxide-substituted imidazolium iodide was prepared. The material was sandwiched between dye-coated porous TiO$_2$ and counter-electrode to form a solid-state dye-sensitized solar cell, which works with overall conversion efficiencies of 3.48% and 4.07% for AM 1.5, 100 mW cm^{-2} and 23 mW cm^{-2} irradiation, respectively.

The dye-sensitized nanocrystalline solar cell (DSC) has established itself as a sole utility-type photovoltaic device based on the electrochemical interface. The use of flammable volatile electrolytes, which achieve the highest 11% conversion efficiency,[1] is however a hard issue to accept in the manufacture processes and for the safety of users. For the manufacture of flexible plastic DSCs,[2–4] it is desired that the electrolyte is supplied as a paste useful for coating on the semiconductor layer so that roll-to-roll processes are applied. In this respect, as well as to improve the lifetime of the DSC, replacement of the liquid electrolyte with a solid-state or quasi-solid-state charge transport layer is becoming a major goal of DSC research.[5–10] However, solidification of the DSC without the use of liquid electrolyte components raises the problems of poor penetration of solid conductive materials (p-type CuI, polymer, *etc.*) into the semiconductor mesopore[11] and low conductivity of the polymer material that limits the diffusion length of carrier. To improve such inefficiency, we have previously reported a solid-state DSC constructed on poly(*N*-vinylcarbazole) hole transporter mediated by alkali iodide; the cell attained a power efficiency of 2.4% at 1/4 sun (AM1.5) where the mediator helps to drive the carrier transport inside the mesoporous TiO$_2$.[10] In this report we show that preparation of a mostly solid-state electro-conductive material comprising polyaniline, carbon black, and ionic liquid in the form of a hard incombustible paste enables solidification of DSC and generation of high-density photocurrent with a conversion efficiency over 4% despite the small amount of iodine (conventionally used but highly oxidative electron acceptor) incorporated in the device.

F-doped SnO$_2$ (FTO) conductive glass (sheet resistance 10 ohm per square) was coated with a 7 μm thick mesoporous TiO$_2$ layer prepared by sintering a coating of nanocrystalline TiO$_2$ paste (Solaronix, SA) at 550 °C for 30 min. The TiO$_2$ 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) (Peccel Technologies). The conductive polymer–carbon composite material was prepared by mixing a solid powder of polyaniline-loaded carbon black with a hydrophilic ionic liquid compound. The polyaniline-loaded carbon black, which was supplied from Sigma-Aldrich Inc., contained 20 wt% polyaniline emeraldine salt (half oxidized and hydrogenated polyaniline doped with organic sulfonic acid). A similar polyaniline–carbon black composite, but dominant for polymer content, has been prepared by Sotzing *et al.*[12] Carbon black, contained in the composite, is generally characterized as a nano-carbon material with a primary particle size of less than 100 nm. To convert the composite powder into a paste form, 30 mg of the polyaniline–carbon black composite (PACB) was triturated on an agate mortar in the presence of 250 mg of an ionic liquid, 1,3-diethyleneoxide derivative of imidazolium iodide (EOI), as shown in Fig. 1(a). This mixing yielded PACB–EOI composite in the form of a highly viscous black paste (Fig. 1(b)), which is mostly solid-state like a clay and is free of volatile and flammable fluid components. A 90 μm thick layer of the hard paste was applied between the dye-sensitized TiO$_2$ layer and a FTO glass counter-electrode. The surface of counter-electrode (cathode) underwent no treatment for loading a catalyst, such as Pt, which is normally needed for FTO that has a high overpotential for cathodic reduction. All processes were conducted in aerated conditions. The black PACB–EOI composite layer tightly contacts the surface of the dye-coated photo-electrode and FTO counter-electrode to form a solid-state photocell with an effective electrode area of 0.24 cm^2.†

Photocurrent–voltage (*I–V*) characteristics were measured on a Keithley 2400 source meter under irradiation of AM 1.5, 100 mW cm^{-2} (1 sun) supplied by a solar simulator (Peccell Technologies). To determine the *I–V* curve, the voltage was scanned starting at 0 V with a constant rate of 20 mV s^{-1}. This operation caused an initial drop in photocurrent (Fig. 2) before current stabilisation. External

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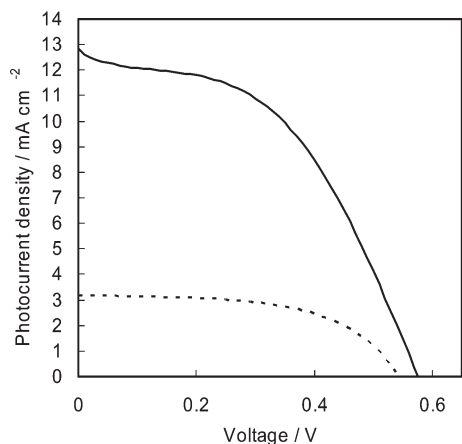

Fig. 1 (a) Molecular structure of the ethylene oxide-type ionic liquid iodide, EOI; (b) clay-like highly viscous, black paste of polyaniline–carbon black (PACB)–EOI composite.

Fig. 2 Photocurrent–voltage characteristics for the PACB–EOI-based solid-state dye-sensitized solar cells under incident intensities (AM 1.5) of 1 sun (100 mW cm^{-2}, solid line) and 1/4 sun (23 mW cm^{-2}, dashed line). The conductive composite contained 10.7 wt% of PACB.

quantum conversion efficiency (EQE, or incident photon to current conversion quantum efficiency) was determined by a monochromatic irradiation system operated at 5.0 Hz in combination with a lock-in amplifier.

Fig. 2 shows photocurrent–voltage (I–V) characteristics of the PACB–EOI-based photocell. On irradiation at 1 sun intensity (100 mW cm^{-2}), the photocell gave a short-circuit photocurrent density (J_{sc}) of 12.8 mA cm^{-2} and an open-circuit voltage (V_{oc}) of 0.56 V. Overall power conversion efficiency was 3.48%. The conversion efficiency was increased to 4.07% at 1/4 sun intensity (23 mW cm^{-2}), reflecting influence of a relatively high internal resistance against charge transfer, probably due to the high-viscosity ionic liquid. As shown in the EQE spectrum (Fig. 3), the maximum EQE at the optical absorption peak of the dye layer (540–550 nm) was 48%, which is much lower than the 80–85% of the liquid electrolyte-type cell.[13] The spectrum response lacks in intensity in the long wavelength region of 700–800 nm where light confinement by the scattering effect normally increases the intensity. This is influenced by the black PACB composite that absorbs the scattered light. Although these features of EQE and a relatively low standard of photovoltage, 0.56 V, are subjects for improvement, the conversion efficiency obtained by the present
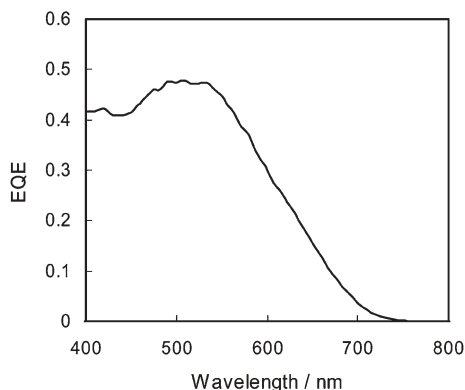
cell-making method is amply high as a solidified DSC, in particular, taking into account the simple composition of the cell that omits the use of iodine and the cathode catalyst such as platinum normally needed for the DSC fabrication.

To investigate the role of the PACB–EOI composite layer, the influence of the conductive polymer was first examined. A reference cell was made in which the PACB composite material was replaced with a carbon black powder free of polyaniline. This polymer-free reference cell was capable of producing a short-circuit photocurrent with an amplitude comparable of that with the PACB cell. In the I–V performance at 1 sun, however, its conversion efficiency was reduced to 2.69% by a significant drop in the fill factor (FF). This implies that, in the polymer-free sample, a high internal resistance exists in the carrier transport across the carbon black layer and/or at the interface of dye–TiO$_2$ and carbon. It is assumed that the presence of carbon contacting the dye–TiO$_2$ layer can cause the back electron transfer from TiO$_2$ to carbon, leading to lowering of photovoltaic performance. Thus, the doped polyaniline (a kind of p-type conductor) is considered to take part in the unidirectional carrier transport, most probably, by promoting the hole transport from the dye layer to the surface of carbon black.

An interesting fact in the present method of cell fabrication is that the cell works at high efficiency without the addition of iodine to the conductive layer. Although it is deduced that a trace amount of iodine (I$_2$) is photochemically produced from EOI at the photo-excited dye layer and involved in the redox reaction at the PACB–EOI surface, we found that incorporation of I$_2$ as an initial component of redox shuttle is not needed to drive our solid-state DSC. Table 1 compares the effects of added iodine concentrations on the parameters of I–V performance, where 1.2% I$_2$ gives a molar concentration of 0.06 mol L^{-1}. The result demonstrates that the cell works best with a minimum concentration of iodine. Fig. 4 exhibits the comparison of I–V curves for the standard I$_2$-free cell and I$_2$-added cells of various I$_2$ contents. Apparently, photovoltage itself is reduced by increased content of I$_2$. These results support that, in the absence of I$_2$, PACB–EOI itself can function as a good charge transport layer by creating a route of rectified hole transport from the dye to counter-electrode. The photocurrent amplitude was fairly stable under continuous illumination and during repeated measurements. This indicates that the iodide, EOI, is recycled in charge transfer rather than acting as a sacrificing donor to the dye.

A reference cell was also examined which did not contain PACB but used EOI alone as an ionic conductor in contact with the FTO glass or a carbon-coated FTO glass as counter-electrode. This cell

Fig. 3 EQE action spectrum for the PACB-EOI-based solid-state dye-sensitized photocell.

Table 1 Photoelectric performances of dye–TiO$_2$/PACB–EOI/FTO solid-state dye-sensitized photocells measured under simulated solar irradiation of 1 sun (AM1.5) and influence of the content of I$_2$ (wt%) added in the PACB–EOI layer on the cell performance

Iodine content	J_{sc}/mA cm^{-2}	V_{oc}/V	FF	η (%)
0%	12.8	0.58	0.47	3.48
1.2%	10.0	0.55	0.48	2.76
2.4%	9.99	0.53	0.50	2.68
3.6%	8.79	0.52	0.53	2.47
14%	6.88	0.50	0.55	1.87

[a] J_{sc}: Short-circuit photocurrent. [b] V_{oc}: Open-circuit photovoltage. [c] FF: Fill factor. [d] η: Energy conversion efficiency.
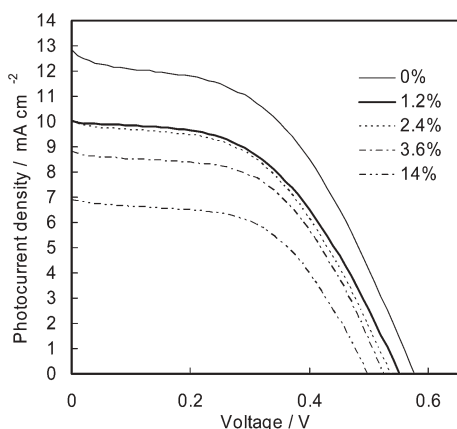
Fig. 4 Photocurrent–voltage characteristics for the PACB–EOI-based solid-state solar cells as a function of the weight content (%) of I_2 added in the PACB–EOI layer, measured under irradiation intensity of 1 sun (AM1.5).

Table 2 Photoelectric performance and conversion efficiency of dye–TiO_2/PACB–EOI/FTO solid-state dye-sensitized photocells measured under simulated solar irradiation of 1 sun (AM1.5) and influence of the content of PACB (wt%) in the PACB-EOI composition on the cell performance

PACB content	J_{sc}/mA cm^{-2}	V_{oc}/V	FF	η (%)
16.7%	12.5	0.55	0.48	3.32
10.7%	12.8	0.58	0.47	3.48
5.7%	12.0	0.57	0.29	1.96
3.8%	10.8	0.57	0.25	1.57
2.9%	2.6	0.60	0.15	0.24

[a] J_{sc}: Short-circuit photocurrent. [b] V_{oc}: Open-circuit photovoltage. [c] FF: Fill factor. [d] η: Energy conversion efficiency.

without PACB was incapable of generating a sufficient photocurrent. Therefore, the PACB–EOI composition is the key to eliciting the high-density photocurrent at the TiO_2–dye-composite interface. We consider that EOI functions as a redox shuttle, working within a minimum thickness between the dye and PACB, in which I_2 is produced in the vicinity of the PACB and immediately reduced to I^- anions at PACB. A similar attempt to create a minimum thickness for iodine/iodide organic electrolyte has been reported by Kumara et al.[14] Table 2 supports the above concept. When the PACB content is varied in the composite, best I–V performance is obtained by maximizing the PACB content and minimizing the EOI content. The efficiency showed a maximum value at 10.7–16.7 wt% of PACB. With 16.7% or more of PACB, the paste becomes too viscous and loses in coating facility. Decreasing the PACB content, which yields a low-viscosity paste, simply reduces the efficiency as shown in Table 2. It is assumed that the maximum PACB concentration creating a thinnest EOI layer and a shortest length for the I^- ion diffusion

enables the redox shuttle to work efficiently. The carbon material in this solidified system is assumed to function as a counter-electrode possessing the catalytic activity by itself. It reduces the resistance of the ionic liquid layer by closely approaching the surface of the dye layer.

The solid-state DSC invented in this study gives high conversion efficiency >4% with a simple composition. Higher efficiencies of >5% have been reported by the Grätzel's group[7] for quasi-solid DSCs using non-conductive polymer matrix holding ionic liquid with an iodide/iodine system. A significant merit of our cell is an extreme ease in making and in handling. The cell works with a counter-electrode without a catalytic coating (Pt, etc.) on the surface of electrode because the polymer–carbon composite serves as a hole transporter and a catalyst (carbon) simultaneously. Conductive electrodes such as SnO_2 and In_2O_3 are immediately useful as current-correcting substrates. The composite itself is an easy-to-make and low-cost alternative to iodine-containing liquid and quasi-solid electrolyte compositions. The ease of sealing is also noted. The extremely viscous composite paste holds together both electrodes by itself. Finally, our method of solid-state dye-sensitized solar cells can immediately be applied to the fabrication of a plastic film-type flexible photocell by way of screen-printing the composite conductive paste on the TiO_2 layer that was formed at low temperature.

Notes and references

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