

## Quasi-solid dye sensitised solar cells filled with ionic liquid—increase in efficiencies by specific interaction between conductive polymers and gelators

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**Photo-energy conversions for quasi-solid dye sensitised solar cells increased when gel electrolytes were combined with conductive polymers as counter electrodes and the conversion surpassed that for DSSCs equipped with conventional Pt counter electrodes.**

Dye sensitised solar cells (DSSC) have high energy conversion efficiencies reaching 10%, which is almost the same as that for amorphous silicon solar cells.<sup>1</sup> This enables DSSCs to be candidates for the next generation of solar cells. They usually contain highly volatile organic solvents in electrolytes. This has been reported to decrease their durability for long term operation and is one of the crucial problems to be solved before DSSCs are put into practical use.<sup>2</sup> We focused on quasi-solid DSSCs, where non-volatile ionic liquids are solidified by chemically cross-linked gelators.<sup>3–6</sup> Physically cross-linked gel electrolytes for DSSCs have been reported previously.<sup>7–11</sup> In order to decrease volatilities from the gels, ionic liquids have been combined with physically cross-linked gelators.<sup>12–15</sup> We successfully solidified the ionic liquids for the first time without losing the photo-voltaic performances by using chemically cross-linked gelators.<sup>3–6</sup> The success was brought about by considering the following factors. Electrolyte precursors (a liquid state) containing ionic liquids and gelators were injected into cells and then they were gelled in the cell directly. This made it possible to realize good physical contact between quasi-solid electrolytes and nanoporous TiO<sub>2</sub> electrodes. We employed tetrabromomethylbenzene (B4Br) and polyvinylpyridine (PVP) as the cross-linkers in order to cause micro-phase separations during gelation. Retardation of I<sub>3</sub><sup>–</sup> (ionic species to determine limiting currents) was successfully minimized by the micro-phase separation technique. In addition we found that the B4Br decreased charge transfer resistances between the gel electrolytes and Pt on the counter electrolytes. It is most likely that B4Br molecules bonded to Pt surfaces aid the charge transfer from Pt to I<sub>2</sub> molecules in gel electrolytes. This was supported by the fact that charge transfer resistances between electrolytes and the counter electrodes decreased when Pt counter electrodes were treated with B4Br molecules.<sup>5</sup> This prompted us to employ other counter electrodes for our chemically cross-linked gel electrolytes. Counter electrodes using conductive polymers have advantages over Pt, because film preparation becomes easy by using spin-coating and low temperature baking processes. Yanagida and co-workers have already reported that conductive polymers having restricted structures are effective for DSSCs filled with solvent type electrolytes.<sup>16</sup> We have found that conductive polymers exhibited characteristic behaviours when they are combined with our ionic liquid type electrolytes and gel electrolytes.

Electrolyte compositions are summarized in Table 1. Imidazolium iodides were purchased from Shikoku Kasei Co. and used without further purification. Ti-Nanoxide D paste (Solaronix SA) was coated on SnO<sub>2</sub>/F layered glasses (30 Ω/square, Nippon Sheet Glass Co. Ltd.) by using a metal mask (*t*:

30micron) and the plate was baked at 450 °C for 30 min. TiO<sub>2</sub> layers with 9 micron thickness were obtained by repeating the process three times. TiO<sub>2</sub> layers were immersed in *cis*-di(thiocyanato)-*N,N'*-bis(2,2'-bipyridyl-4,4'-dicarboxylate)-ruthenium(II) (N3) dye solutions (Kojima Kagaku Co.) in ethanol (0.1%) at room temperature over night. After TiO<sub>2</sub> electrodes were rinsed with ethanol, they were dried at room temperature in the dark. Counter electrodes were fabricated as follows. Polystyrenesulfonate doped poly(3,4-ethylenedioxythiophene) (PEDOT-PSS) (commercially available, Baytron P, Bayer AG) was spin-coated on SnO<sub>2</sub>/F layered glass plates. Pt counter electrodes were fabricated by depositing H<sub>2</sub>PtCl<sub>6</sub> solution at 400 °C and used for reference samples. Plastic sheets (Himilan 1702, 50 micron, DuPont-Mitsui Polymer Chemicals Co. Ltd) were inserted between TiO<sub>2</sub> electrodes and counter electrodes as the spacer. Gel electrolyte precursors and ionic liquid type electrolytes were injected in the cell at room temperature. In case of gel electrolytes, these cells were heated at 80 °C for 5 min. The gelation is brought about by reacting PVP (Aldrich) with B4Br (Aldrich) to make chemically cross-linked ionomer structures.<sup>3</sup> Finally, the cells were sealed with epoxy resins. The cell area was 1 cm<sup>2</sup>. Interfacial resistances were monitored by the method described in the previous literature.<sup>2</sup> Symmetrical cells sandwiched with two thermally deposited Pt or spin-coated PEDOT-PSS electrodes fabricated on SnO<sub>2</sub>/F layered glass substrates were employed. Interfacial resistances were estimated by using a Cole–Cole plot. Impedance spectra were recorded over frequency ranges of 0.01 Hz to 100 kHz by using Perkin-Elmer Model 283 Potentiostat/Galvanostat and Model 5210 Lock-in-Amplifier. Photo-electrochemical measurements were performed using solar simulator (YSS-50A, Yamashita Denso Co. Ltd.) furnished with a Xenon lamp (AM 1.5, 100 mW cm<sup>–2</sup>). The light intensity was monitored with a polysilicon illuminometer.

In this paper, a DSSC containing Pr1 electrolyte and a Pt counter electrode is denoted as a TiO<sub>2</sub>/Pr1/Pt cell. Table 2 summarized the results when Pt or PEDOT-PSS was combined with various electrolytes. The PV performance for the TiO<sub>2</sub>/ACN1/PEDOT-PSS cell was much inferior to that for a TiO<sub>2</sub>/

**Table 1** Abbreviations and electrolyte compositions

Abbreviation	Electrolytes <sup>a</sup>			Gelator		
	Ionic liquid or solvent	LiI/mM	I <sub>2</sub> /mM	tBuPy/ mM	PV (wt% <sup>b</sup> )	B4Br (wt% <sup>b</sup> )
ACN1	MeCN	500	50	580	—	—
Pr1	MePrImI <sup>c</sup>	500	300	580	—	—
Gel1	MePrImI <sup>c</sup>	—	300	—	2	2

<sup>a</sup> MePrImI: 1-methyl-3-propylimidazolium iodide. tBuPy: *tert*-butylpyridine. MeCN: acetonitrile. B4Br: 1,2,4,5-tetrakis(bromomethyl)benzene. PV: polyvinylpyridine (*M*<sub>w</sub>: 80 000) <sup>b</sup> wt% wrt ionic liquids <sup>c</sup> Contains 5 wt% water.

**Table 2** Performances for DSSCs equipped with Pt and PEDOT-PSS<sup>a</sup>

Electrolyte	Counter electrode	$J_{sc}/\text{mA cm}^{-2}$	$V_{oc}/\text{V}$	FF
ACN1 <sup>b</sup>	Pt <sup>d</sup>	10.1	0.64	0.42
	PEDOT-PSS <sup>e</sup>	8.4	0.67	0.22
Pr1 <sup>b</sup>	Pt <sup>d</sup>	8.4	0.66	0.47
	PEDOT-PSS <sup>e</sup>	8.4	0.64	0.45
Gel1 <sup>c</sup>	Pt <sup>d</sup>	9.3	0.49	0.61
	PEDOT-PSS <sup>e</sup>	11.3	0.47	0.58

<sup>a</sup> 100 mW cm<sup>-2</sup>, AM1.5. <sup>b</sup> Exposed area, 1cm<sup>2</sup>. <sup>c</sup> Exposed area, 0.25cm<sup>2</sup>.

<sup>d</sup> Thermally deposited Pt, transparent. <sup>e</sup> Thickness, 0.3 micron.

ACN1/Pt cell. The low fill factor (FF) for the former (0.22) is responsible for the low performance. The same phenomena have been already reported by Yanagida and co-workers.<sup>16</sup> They found that, instead of PEDOT-PSS, toluene sulfonate doped PEDOT (PEDOT-Ts) was necessary to obtain the same performance as with Pt counter electrodes. They described how the low molecular weight dopant, toluene sulfonate, makes it possible for I<sub>3</sub><sup>-</sup> to penetrate into the PEDOT layers. We explain our phenomena by using charge transfer resistances between electrolyte and electrodes. The charge transfer resistance between Pt electrodes and the ACN1 electrode was 22 Ω cm<sup>2</sup>. In case of PEDOT-PSS electrodes and ACN1 electrolytes, the charge transfer resistance was about 600 Ω cm<sup>2</sup>. This was 30 times higher than that between Pt electrodes and ACN1 electrolytes. Therefore, the difference in *I*-*V* curves can be explained by the difference in charge transfer resistances between electrolytes and electrodes.

We found that TiO<sub>2</sub>/Pr1/PEDOT-PSS cells exhibit almost the same photo-voltaic performance as TiO<sub>2</sub>/Pr1/Pt cells as shown in Table 2 when Pr1 electrolytes were employed. We observed the same results for other imidazolium iodides such as ethylmethylimidazolium iodide, butylmethylimidazolium iodide and hexylmethylimidazolium iodide. The charge transfer resistance between Pt electrodes and Pr1 electrolytes was 4 Ω cm<sup>2</sup> which was almost the same as that between PEDOT-PSS electrodes and Pr1 electrolytes. The concentration of I<sub>2</sub> contained in Pr1 is 6 times higher than that in ACN1. Even when 300 mM I<sub>2</sub> was added into ACN1, the increase in the photo-voltaic performance was not observed for PEDOT-PSS counter electrodes. The concentration of I<sub>2</sub> is not responsible for the difference in photo-voltaic performances.

The photocurrent  $J_{sc}$  for DSSCs with a PEDOT-PSS electrode was better than that with a Pt counter electrode when gel electrolytes filled the cells.  $J_{sc}$  for TiO<sub>2</sub>/Gel1/PEDOT-PSS cells was 11.3 mA cm<sup>-2</sup> and that for TiO<sub>2</sub>/Gel1/Pt was 9.3 mA cm<sup>-2</sup>. This is also explained by the decrease in charge transfer resistance between electrolytes and electrodes. The charge transfer resistance between Gel1 and Pt was 14.1 Ω cm<sup>2</sup> and that between Gel1 and PEDOT-PSS was 1.5 Ω cm<sup>2</sup>.

The difference in Gel1 and Pr1 was seen in the dependence of PV performances on PEDOT-PSS thickness.  $J_{sc}$  for TiO<sub>2</sub>/Gel1/PEDOT-PSS cells increased from 6.2 mA cm<sup>-2</sup> to 11.2 mA cm<sup>-2</sup> when the PEDOT-PSS thickness increased from 0.05 micron to 0.4 micron (Fig. 1). In contrast the  $J_{sc}$  increase for TiO<sub>2</sub>/Pr1/PEDOT-PSS cells was very small. The presence of gelator, B4Br, seems to be essential. I<sub>2</sub> exists as I<sub>3</sub><sup>-</sup> in electrolytes. I<sub>2</sub> is reduced after I<sub>2</sub> is dissociated from I<sub>3</sub><sup>-</sup> near counter electrodes.<sup>17</sup> We have already reported that B4Br adsorbed on Pt decreased the charge transfer resistance between I<sub>2</sub> and Pt electrodes.<sup>5</sup> The same phenomena may occur in the PEDOT-PSS counter electrodes into which gel electrolytes containing B4Br are interpenetrated.

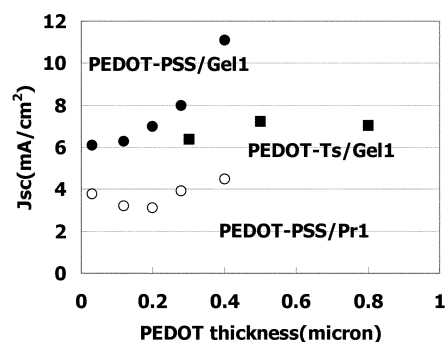
**Fig. 1** Relationship between PEDOT thickness and  $J_{sc}$ .

Fig. 1 also shows that when Gel1 was employed,  $J_{sc}$  for DSSCs equipped with PEDOT-PSS became much higher than that equipped with PEDOT-Ts (toluene sulfonate doped PEDOT) which was prepared by the same methods described in the previous paper.<sup>16</sup> The combination of Gel1 with PEDOT-PSS seems to provide particular effects on the increase in  $J_{sc}$ .

In conclusion, we found that relative performances between PEDOT-PSS and Pt counter electrodes varied, depending on electrolytes employed.  $J_{sc}$  for TiO<sub>2</sub>/ACN1/PEDOT-PSS was worse than that for TiO<sub>2</sub>/ACN1/Pt.  $J_{sc}$  for TiO<sub>2</sub>/Pr1/PEDOT-PSS was almost the same as that for TiO<sub>2</sub>/Pr1/Pt.  $J_{sc}$  for TiO<sub>2</sub>/Gel1/PEDOT-PSS cells was better than that for TiO<sub>2</sub>/Gel1/Pt cells. It appears that gelators, B4Br residues, are responsible for the  $J_{sc}$  increase.

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