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# Novel and Efficient Organic Liquid Electrolytes for Dye-sensitized Solar Cells Based on a Ru(II) Terpyridyl Complex Photosensitizer

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We have developed a novel and efficient organic liquid electrolyte composed of 1-ethyl-3-methylimidazolium iodide, iodine ($I_2$), and acetonotrile solvent for a nanocrystalline $TiO_2$ solar cell sensitized with a Ru(II) terpyridyl complex. A solar energy-to-electricity conversion efficiency of 8.0% was attained under AM 1.5 irradiation (100 mW $cm^{-2}$).

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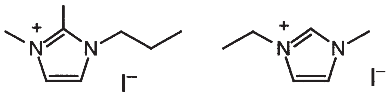
Dye-sensitized nanocrystalline $TiO_2$ solar cell (DSSC) has been intensively studied during the last decade because this unconventional solar cell demonstrates not only a high performance but also the possibility for low-cost production of such devices.[1] Ruthenium polypyridyl complexes, e.g., *cis*-dithiocyanato bis(4,4′-dicarboxy-2,2′-bipyridine)ruthenium(II) (N3 dye)[2] and trithiocyanato 4,4′4″-tricarboxy-2,2′:6′,2″-terpyridine ruthenium(II) (black dye),[3] have been intensively used as efficient photosensitizers of DSSCs. DSSC that exhibits the best solar-cell performance is the one based on the black dye, owing to its wide light absorption region, which extends to 900 nm.[3] Nevertheless, quite few papers of detailed investigations of the experimental conditions such as electrolyte composition for DSSCs based on black dye have been reported.

To improve the performance of DSSCs based on the black dye further, we have investigated in detail the effects of electrolytes on the cell performance. The electrolytes normally used in DSSCs based on Ru-complex photosensitizers contain several components to obtain high solar-cell performance: for example, 0.6 M (mol $dm^{-3}$) of 1,2-dimethyl-3-*n*-propylimidazolium iodide (DMPImI), 0.1 M of LiI, 0.1 M of $I_2$, and 0.5 M of 4-*tert*-butylpyridine (TBP) in methoxyacetonitrile.[3] In addition, several kinds of imidazolium salts have been found to play an important role in DSSCs based on both liquid electrolytes[4–8] and on quasi-solid-state electrolytes,[9–12] in order to improve the cell performance. Recently, we developed novel organic liquid electrolytes that composed of an imidazolium iodide, iodine, and acetonitrile as an organic solvent. Interestingly, they do not include LiI and TBP. These electrolytes perform better than a conventional electrolyte previously reported for use in DSSCs based on the black dye. In this paper, we report the interesting effect of counter cations of iodines in the electrolytes on the photovoltaic performance of a DSSC based on the black dye, and we also report the efficient performance of a novel electrolyte containing an imidazolium salt.



**DMPImI** **EMImI**

**Scheme 1.** Molecular structures of imidazolium iodides.

$TiO_2$ nanoparticles were prepared by the method reported by Grätzel and co-workers.[4] A nanoporous $TiO_2$ photoelectrode (area, 0.25 $cm^2$; thickness, 14 μm) was prepared by a screen-printing technique. An organic $TiO_2$ paste consisting of the $TiO_2$ nanoparticles, large $TiO_2$ particles (average diameter, 100 nm) as scattering centers, ethyl cellulose as a binder, and $\alpha$-terpineol as a solvent, was printed on a glass substrate coated with transparent conducting oxide (TCO, F-doped $SnO_2$). The coated substrate was subsequently sintered at 500 °C in air for 2 h. The black dye, purchased from Solaronix SA, and used without any further purification, was dissolved in dehydrated ethanol with a concentration of 0.2 mM. Deoxycholic acid was added to the dye solution (20 mM) as a co-adsorbate with the dye. The $TiO_2$ thin films were immersed in the dye solution, and then kept at 25 °C for at least 12 h so that the dye could be adsorbed onto the $TiO_2$ surface. Photovoltaic measurements were carried out with an open sandwich-type cell consisting of a dye-coated $TiO_2$ electrode, a Pt counter electrode, a polyethylene film spacer, and an organic electrolyte. The imidazolium iodides, DMPImI and 1-ethyl-3-methylimidazolium iodide (EMImI), used in the electrolytes were purchased from Tomiyama Pure Chemical Industries Ltd. The photovoltaic performance of the solar cells was measured with a source meter and an AM 1.5 solar simulator that produced AM 1.5 radiation (100 mW $cm^{-2}$).

Table 1 shows the photovoltaic performance of DSSCs based on a nanocrystalline $TiO_2$ photoelectrode, the black dye as the photosensitizer, and several electrolytes. The electrolytes consisted of iodide, iodine (0.05 M) and acetonitrile as a solvent. The short-circuit current density ($J_{sc}$) of electrolyte **1** (0.7 M LiI, 16.8 mA $cm^{-2}$) was larger than that of electrolyte **2** (0.7 M DMPImI, 14.5 mA $cm^{-2}$). The open-circuit voltage ($V_{oc}$) for **1** was lower than that for **2**: 0.45 V for LiI and 0.66 V for DMPImI. We speculate that the lower $V_{oc}$ for LiI was caused by a positive shift of the conduction band edge level of the $TiO_2$ electrode, due to intercalation or adsorption of Li cations reported by G. Redmond et al.[13] Kambe et al. have reported that imidazolium cation $DMHIm^+$ is strongly adsorbed on the $TiO_2$ surface.[14] Therefore, we speculate that the higher $V_{oc}$ (0.66 V) for electrolyte **2** (DMPImI) relative to that for **1** (LiI), may be due in part to suppression of the dark current (i.e., recombination between the injected electrons and $I_3{}^-$) by the strong adsorption of $DMPIm^+$ on the $TiO_2$ surface.

When the concentration of DMPImI in electrolyte **2** was increased from 0.7 to 1.5 M, both the $J_{sc}$ and the $V_{oc}$ improved, and

**Table 1.** Photovoltaic performance of dye-sensitized $TiO_2$ solar cells based on the black dye with several electrolytes

| No | Iodide | $J_{sc}$/mA cm$^{-2}$ | $V_{oc}$/V | $FF$ | $\eta$/% |
|---|---|---|---|---|---|
| **1** | 0.7 M LiI | 16.8 | 0.45 | 0.50 | 3.8 |
| **2** | 0.7 M DMPImI | 14.5 | 0.66 | 0.64 | 6.1 |
| **3** | 1.5 M DMPImI | 16.7 | 0.68 | 0.65 | 7.4 |
| **4** | 1.5 M EMImI | 17.1 | 0.67 | 0.68 | 7.8 |
| **5**[a] | 0.6 M DMPImI<br>+ 0.1 M LiI | 14.8 | 0.72 | 0.66 | 7.1 |

Electrolyte: iodide + 0.05 M $I_2$ in acetonitrile. [a]The electrolyte contained 0.5 M TBP. $TiO_2$ electrode: 0.25 cm$^2$ and 14 µm thickness. Irradiated light: simulated AM 1.5 (100 mW cm$^{-2}$).

efficiencies higher than 7% were observed (electrolytes **3**). Kambe et al. reported that adsorption of $DMHIm^+$ on the $TiO_2$ surface leads to a large increase in the diffusion coefficient of electrons in the $TiO_2$.[14] Therefore, the larger $J_{sc}$ values that we observed for electrolytes **3** might be due to an increase in the diffusion coefficient, caused by the adsorption of $DMPIm^+$ on the $TiO_2$ surface. Moreover, in the case of electrolyte **4** containing 1.5 M EMImI instead of DMPImI, the $J_{sc}$ and the fill factor ($FF$) were improved. This improved performance might be due to the slightly different molecular sizes of $DMPIm^+$ and $EMIm^+$, which affect their ionic mobility and viscosity of the electrolyte.

In the case of one of conventional electrolytes used for DSSCs, which contains 0.5 M TBP in addition to 0.6 M DMPImI and 0.1 M LiI (electrolyte **5**), the highest $V_{oc}$ was obtained (0.72 V), whereas the $J_{sc}$ was smaller than those for electrolytes **3** and **4**. The higher $V_{oc}$ is due to the suppression of the dark current by adsorption of TBP on the $TiO_2$ surface.[2] The decreased $J_{sc}$ is probably caused by a negative shift of the conduction band edge level of the $TiO_2$ electrode, and the consequent low electron-injection yield. When the concentration of DMPImI in electrolyte **5** increased from 0.6 to 1.5 M, the $J_{sc}$ was decreased, in contrast to the case of electrolyte **3**. This indicates that the behavior of the increasing concentration of imidazolium iodides depend strongly on the presence of other electrolyte components, such as LiI and TBP.

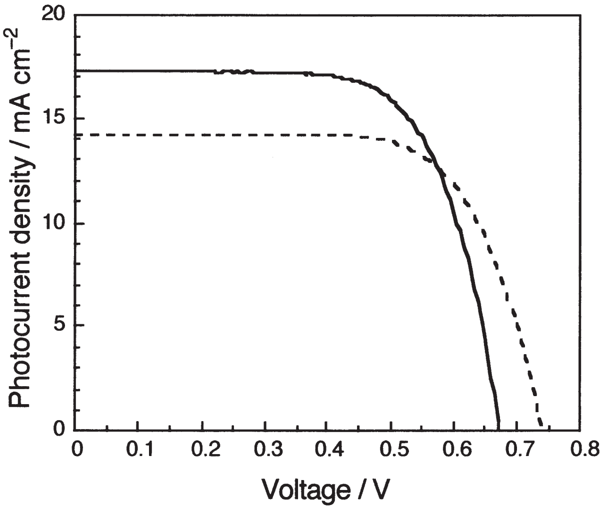


**Figure 1.** Photocurrent density vs voltage curve for the best performance obtained by a dye-sensitized $TiO_2$ solar cell based on the black dye with electrolytes **4** under AM 1.5 (100 mW cm$^{-2}$): (—) **4**, $\eta = 8.0\%$, $J_{sc} = 17.3$ mA cm$^{-2}$, $V_{oc} = 0.67$ V, $FF = 0.68$; and (- - -) **5** as a reference, $\eta = 7.2\%$, $J_{sc} = 14.2$ mA cm$^{-2}$, $V_{oc} = 0.74$ V, $FF = 0.69$. The condition of $TiO_2$ electrode differs from that for the data in Table 1.

Figure 1 shows the I–V curve for the black-dye-sensitized $TiO_2$ solar cell with electrolyte **4**, which exhibited the best performance: The condition of $TiO_2$ electrode differs from that for the data in Table 1. In this experiment, we obtained the highest conversion efficiency, $\eta = 8.0\%$ ($J_{sc} = 17.3$ mA cm$^{-2}$, $V_{oc} = 0.67$ V, and $FF = 0.68$). By comparison, the efficiency for a conventional electrolyte **5** was 7.2% ($J_{sc} = 14.2$ mA cm$^{-2}$, $V_{oc} = 0.74$ V, and $FF = 0.69$) under the same measurement conditions. The usual electrolyte components, LiI and TBP, were not required for electrolyte **4** to produce high efficiency. Our results strongly suggest that detailed study of electrolytes and fine-tuning of the electrolyte composition would improve the performance of DSSCs. When we uses electrolyte **4** for a DSSC based on ruthenium bipyridyl complexes (N3 or N719 dye), we never obtained a performance better than that of electrolyte **5**. The electrolyte performance seems to depend strongly on the nature of the other materials present, such as the photosensitizers. We are now further investigating the detailed mechanisms for the effect of the electrolyte on photovoltaic performance of DSSCs.

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