A New Ionic Liquid Electrolyte Enhances the Conversion Efficiency of Dye-Sensitized Solar Cells

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An ionic liquid electrolyte composed of 1-methyl-3-propylimidazolium iodide, 1-methyl-3-ethylimidazolium dicyanamide, and lithium iodide (LiI) was combined with an amphiphilic polypyrindyl ruthenium sensitizer to obtain a solar cell based on a solvent-free electrolyte that had an efficiency of 6.6% at an irradiance of air mass 1.5 (AM 1.5, 100 mW cm$^{-2}$) and >7.1% at lower light intensities. This is the first time such a high efficiency was obtained for dye-sensitized solar cells with pure ionic liquid electrolytes. A thin-layer electrochemical cell was used to determine the redox potential of sensitizers anchored on TiO$_2$ nanocrystalline film by square-wave voltammetry. Laser transient absorbance measurements revealed that a significant enhancement of the device efficiency, after adding LiI to the ionic liquid electrolyte, could be ascribed to an increase in the electron injection yield and dye regeneration rate.

Introduction

The rapid depletion of fossil fuels and disastrous environmental problems of their combustion are forcing us to develop renewable energy resources for growing energy demands. Fortunately, solar energy has a great potential to fulfill an important part of the sustainable energy demand of future generation. During the past decade, dye-sensitized solar cells (DSCs) have attracted much attention as low-cost alternatives to conventional inorganic photovoltaic devices.\textsuperscript{1-7} The mesoscopic TiO$_2$ film texture in these cells significantly increases the cross section for surface-anchored light harvesters while maintaining a good contact with electrolytes. In these devices, photon-to-electricity conversion is achieved by ultrafast electron injection from a photoexcited dye into the conduction band of TiO$_2$ and subsequently dye regeneration and hole transportation to the counter electrode. An impressive solar-to-electricity power conversion efficiency of 10.4% was achieved with a panchromatic dye, when used in conjunction with conventional non-aqueous electrolytes that contain the triiodide/iodide couple.\textsuperscript{8} One of the main problems of this device during long-term operation lies in the difficult encapsulation of volatile solvents, especially for DSCs with a plastic matrix. Thus, replacing an organic solvent-based liquid electrolyte with a solid-state hole conductor,\textsuperscript{9,10} $p$-type semiconductor,\textsuperscript{11,12} and solvent-free polymer electrolyte\textsuperscript{13-15} was attempted to develop all-solid-state DSCs; however, to date, no satisfactory conversion efficiencies have been achieved in all of these cases.

Room-temperature ionic liquids (RTILs) that have good chemical and thermal stability, negligible vapor pressure, nonflammability, high ionic conductivity, and a wide electrochemical window have been extensively pursued as alternative electrolytes for DSCs,\textsuperscript{16-22} and other electrochemical devices.\textsuperscript{23-28} However, the conversion yields obtained with ionic liquids at a full air mass (AM 1.5) solar irradiance have been markedly lower than those achieved with organic solvent-based electrolytes. Only recently were efficiencies of 5%-6% achieved for DSCs with pure ionic liquid electrolytes.\textsuperscript{21,22} In this paper, an ionic liquid electrolyte that consisted of 1-methyl-3-propylimidazolium iodide (PMII), 1-methyl-3-ethylimidazolium dicyanamide (EMIDCN),\textsuperscript{29} and lithium iodide (LiI) was combined with an amphiphilic light harvester, Z-907 [Ru(Hdcbp)$_2$-(dnbpy)(NCS)$_2$, where Hdcbp is 4,4’-dicarboxylic acid-2,2’-bipyridine and dnbpy is 4,4’-dinonyl-2,2’-bipyridine], to obtain a device with a solar-to-electricity efficiency of 6.6% at an irradiance of air mass of 1.5 (AM 1.5, 100 mW cm$^{-2}$) and >7% at lower light intensities.

Experimental Section

Reagents and Electrolytes. LiI, lithium bis(trifluoromethanesulfonyl)amide (LiTFSI), and ferrocene were purchased from Fluka (Switzerland) and used as received. 3-Methoxypropionitrile (Fluka) was distilled before use. N-Methylbenzimidazole (NMBI) was purchased from Aldrich (Switzerland) and recrystallized from diethyl ether. The amphiphilic Z-907 dye and standard N-719 dye [cis-Ru(Hdcbp)$_2$(NCS)$_2$(TBA)$_2$, where TBA is tetra-$n$-butylammonium] were synthesized as described in our previous papers.\textsuperscript{30,31} Ionic liquids [PMII, EMIDCN, and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amid (EMITFSI)] were prepared according to the literature methods\textsuperscript{29,32} and confirmed by $^1$H NMR spectra. The molecular structures of sensitizers (Z-907, N-719) and ionic liquids (PMII, EMIDCN) are shown in Figure 1. The compositions of electrolytes used in this study are as follows. Electrolyte A was composed of 0.1 M iodine and 0.45 M NMBI in a mixture of PMII and EMIDCN (volume ratio of 13:7), whereas electrolyte B was composed of 0.1 M iodine, 0.1 M LiI, and 0.45 M NMBI in a mixture of PMII and EMIDCN (volume ratio of 13:7). The added iodine will react with the excess iodide to form triiodide.

Preparation of Double-Layer TiO$_2$ Electrode. The fluorine-doped SnO$_2$ conducting glass was first cleaned in Triton X-100 aqueous solution, washed with ethanol, and treated with 50 mM TiCl$_4$ aqueous solution at 70 °C for 30 min, to make a good mechanical contact between the following printed TiO$_2$ layer.
and the conducting glass matrix. A 10 \textmu m-thick film of TiO₂ particles 20 nm in size was then printed on the treated conducting glass and further coated by a 4-\textmu m-thick second layer of 400-nm-light-scattering anatase particles (CCIC, Japan). For the second layer, the screen-printing paste is composed of 10 g of TiO₂ scattering particles 400 nm in size and 2 g of fine TiO₂ particles (15 nm in size) to obtain a mechanically tough layer. The screen-printed layer was gradually heated to 500 °C in an oxygen atmosphere and subsequently sintered at that temperature for 10 min. The layer thickness was determined using an Alpha-step 200 surface profilometer (Tencor Instruments, USA). After the assembly was treated with 40 mM TiCl₄ again, the layer was rinsed with water and ethanol.

**Fabrication of Dye-Sensitized Solar Cells.** After sintering at 500 °C and cooling to 80 °C, the double-layer structured TiO₂ electrode was dye-coated by immersion into a 0.3 mM solution of Z-907 or N-719 in acetonitrile and tert-butyl alcohol (volume ratio of 1:1) at room temperature for 12 h and then assembled with thermally platinized conducting glass electrodes. The electrodes were separated by a 35-\textmu m-thick Bynel hot-melt ring (DuPont, USA) and sealed by heating. The internal space was filled with electrolyte, using a vacuum pump, to produce device A, which is composed of Z-907 dye and electrolyte A. Devices B and C contain electrolyte B with Z-907 dye and N-719 dye, respectively. The electrolyte-injection hole that was made with a sand-blasting drill on the counter electrode glass substrate was sealed with a Bynel sheet and a thin glass cover by heating. The sealed cells were aged under indoor light for 5 h before electrochemical measurements.

**Electrochemical Measurements.** Voltammetric data were recorded at room temperature on an Autolab P20 electrochemical workstation (Eco-Chemie, The Netherlands). The internal space of cells described previously was filled with ionic liquid EMITFSI, which contained 20 mM ferrocene as an internal reference compound and 0.1 M LiTFSI. The resulting thin-layer electrochemical cell was used to study the redox behavior of Z-907 dye that was anchored on interconnected TiO₂ nanocrystals. The redox potential values versus ferrocene were converted to those versus a normal hydrogen electrode (NHE) by adding a constant of 0.67 V. A two-electrode electrochemical cell, which consisted of a platinum ultramicroelectrode with a radius of 5.0 \textmu m (Bioanalytical Systems, Inc., USA) as working electrode and a platinum foil as a counter electrode, was used for the diffusion coefficient measurements of triiodide in electrolytes A and B.

**Photoelectrochemical Measurements.** A 450 W xenon light source (Oriel, USA) was used to give an irradiance of 100 mW cm⁻² (the equivalent of one sun at AM 1.5) at the surface of solar cells. The spectral output of the lamp was matched in the region of 350–750 nm with the aid of a Schott K113 Tempax sunlight filter (Präzisions Glas and Optik GmbH, Germany), to reduce the mismatch between the simulated and true solar spectra to <2%. Various incident-light intensities were regulated with neutral wire mesh attenuators. The current–voltage characteristics of the cell under these conditions were obtained by applying an external potential bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter (Keithley, USA). This process was fully automated using WaveMetrics software (http://www.wavemetrics.com/).

A similar data acquisition system was used to control the incident photon-to-current conversion efficiency (IPCE) measurement. Under full computer control, light from a 300 W xenon lamp (ILC Technology, USA) was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd., UK) onto the photovoltaic cell that was being tested. The monochromator was incremented through the visible spectrum to generate the IPCE-λ, as defined below.

$$\text{IPCE}(\lambda) = \frac{J_{sc}}{J_{\infty}} \left( \frac{\lambda}{\phi} \right)^{12400}$$

where \( \lambda \) is the wavelength, \( J_{\infty} \) the short-circuit current photocurrent (in units of mA cm⁻²), and \( \phi \) the incident radiative flux (in units of mW cm⁻²).

**Laser Transient Absorbance Measurements.** Transparent TiO₂ mesoporous layers (8 \textmu m thick) that had been deposited on front glass sensitized with Z-907 were used for transient absorbance measurements. Nanosecond pulsed laser excitation was applied, using a GWU-355 broadband optical parametric oscillator pumped with a Continuum Powerlite 7030 frequency-tripled Q-switched Nd:YAG laser. The oscillator output (repetition rate of 30 Hz, pulse width at half-height of 5 ns) was tuned at a wavelength of 495 or 510 nm and attenuated by filters. To irradiate a large cross section of the sample, it was kept at a 30° angle to the excitation beam and the beam was expanded by a planoconcave lens. Laser fluence on the sample was kept at a very low level (30 \mu J cm⁻² per pulse), to ensure that, on average, less than one electron is injected per nanocrystalline TiO₂ particle upon pulsed irradiation. The probe light from a continuous-wave xenon arc lamp was passed through a first monochromator, various optical elements, the sample, and a second monochromator before being detected by a fast photomultiplier tube.Transient absorbance measurements of the oxidized-state dye were performed at a probe wavelength of 630 nm. Ground-state bleaching was monitored at a wavelength of 530 nm.

**Results and Discussion**

Efficient sensitization of TiO₂ nanocrystalline electrodes to visible light relies on the fact that the excited state of a dye is a stronger reducer than that in the ground state. Knowledge of the formal redox potential of the excited state (\( \phi^0(S^*/S'^*) \)) of a dye, relative to the energy level of the TiO₂ semiconductor,
allows a priori determination of the direction of current flow. An approximate value of $\phi^0(S^+/S^0)$ of a dye can be extracted from the formal potential of the ground state [$\phi^0(S^+/S^0)$] and its excitation energy ($E_{0-0}$), according to eq 2:

$$\phi^0(S^+/S^0) = \frac{E_{0-0}}{F}$$

where $F$ is the Faraday constant. Quasi-reversible electrochemical behavior of polypyridyl ruthenium complexes anchored on mesoporous TiO$_2$ film has been studied with a conventional three-electrode electrochemical cell by cyclic voltammetry. In the present work, a thin-layer electrochemical cell composed of a Z-907-sensitized TiO$_2$ nanocrystalline electrode as the working electrode and a platinized conducting glass as the counter electrode was used to study the redox property of the sensitizer. Because of the steady-state behavior of normal linear sweep voltammograms of a thin-layer electrochemical cell, square wave voltammetry with inherently high analytical sensitivity and strong immunity to capacitive effects was used to obtain accurate $\phi^0(S^+/S^0)$ values of the Z-907 dye. As shown in Figure 2, a well-defined redox wave is observed for the Ru$^{III}$/Ru$^{II}$ couple (+0.83 V vs NHE). The wave centered at +0.67 V is ascribed to the direct electron transfer between ferrocene (20 mM) and the conducting glass electrode. Because the equilibrium potentials of electrolytes A and B (derived approximately by the Nernst expression$^{42}$) are 0.463 and 0.461 V, respectively, there will be a large thermodynamic driving force for regeneration of the Z-907 dye by iodide in these electrolytes. The $E_{0-0}$ value was estimated to be 1.64 eV by the method reported in our previous paper. Thus, the $\phi^0(S^+/S^0)$ of the Z-907 dye is derived to be $-0.82$ V vs NHE by eq 2 and is comparable to that reported for the N3 dye [Ru(IIc52cy)$_2$(NCS)$_2$], which was confirmed to be an efficient sensitizer of DSCs. The detailed comparisons of absorption, luminescence, and redox properties of amphiphilic ruthenium(II) dyes and the standard N3 dye in solutions have been described in our previous paper.

Photocurrent action spectra are shown in Figure 3. The maximum IPCE values at 550 nm are 66% and 76% for devices A and B, respectively. Figure 4 presents the photocurrent density–voltage curves for devices A–C at an AM 1.5 irradiance of 100 mW cm$^{-2}$, and the device efficiencies at different light intensities are listed in Table 1. The short-circuit current photocurrent ($J_{sc}$), open-circuit voltage ($V_{oc}$), and fill factor (FF) of device A without lithium salt in its electrolyte are 10.4 mA cm$^{-2}$, 742 mV, and 0.740, respectively, yielding an overall power conversion efficiency ($\eta$) of 5.7%. For device B, which has 0.1 M LiI in its electrolyte, the corresponding device parameters ($J_{sc}$, $V_{oc}$, FF, and $\eta$) are 12.8 mA cm$^{-2}$, 707 mV, 0.727, and 6.6%, respectively. This is the first time such a high efficiency was obtained for DSCs with pure ionic liquid electrolytes under full sunlight. As shown in Figure 5, the addition of 0.1 M LiI to electrolyte A does not influence the limiting current of the cathodic reduction of triiodide but efficiently improves the value of $J_{sc}$ (device B). This clearly indicates that the relatively low $J_{sc}$ value of device A is not limited by the slow diffusion of triiodide in electrolyte A. The apparent diffusion coefficient of triiodide in electrolytes A and B was derived to be $4.4 \times 10^{-7}$ cm$^2$ s$^{-1}$, which is 2.3 times greater than that in pure PMII, because of the lower dynamic viscosity of EMIDCN, compared with PMII. Indeed, the substitution of LiI in device B by the same concentration of LiTFSI produced...
a device with almost identical $J_{sc}$ and $V_{oc}$ values, confirming that the enhanced performance of device B, compared with device A, was mainly caused by the Li$^+$ ion, rather than by a small increase in the concentration of iodide. Although in darkness, the $V_{oc}$ value of DSCs is zero, upon illumination, electron injection from the excited dye into the TiO$_2$ leads to the quasi-Fermi level splitting that is the origin of the photovoltage of DSCs.\textsuperscript{44} Because of the negligible difference (2 mV) in equilibrium potentials of electrolytes A and B, the 35 mV difference in the $V_{oc}$ values of devices A and B should be ascribed to the difference in the flat-band potential ($\Phi_0$) of nanostructured TiO$_2$ films that can be controlled by the specific adsorption of Li$^+$ cations. In addition, compared to device B, device C (prepared with the standard N-719 dye and electrolyte B) showed lower total conversion efficiencies, because of the enhanced back transfer of injected electrons from the conduction band of the TiO$_2$ film to the triiodide. The undesirable back electron transfer is also responsible for the lower $V_{oc}$ value (675 mV). Obviously, the use of an amphiphilic dye, Z-907, markedly suppressed this problem. The most likely reason for the suppression of the back electron reaction is that the long hydrocarbon chains of the Z-907 dye interacts laterally to form an aliphatic network, thereby increasing the distance between the triiodide and electrons trapped on the TiO$_2$ surface and thus hindering the back-electron-transfer process. This has been indicated by the dark current measurements shown in Figure 4.

Laser flash photolysis experiments were performed to understand the action mode of the Li$^+$ ion in enhancing the power conversion efficiency of the aforementioned devices. The concentration of oxidized-state dye molecules produced upon electron injection into the conduction band of the TiO$_2$ film is directly monitored with nanosecond transient absorbance measurements. In Figure 6, the decay of absorption signal (curves a and b) in pure EMIDCN is attributed to the recombination between electrons trapped in the mesoporous TiO$_2$ film and the oxidized-state dye. In the presence of electrolytes, signal decay (curves c and d) is essentially due to the reduction of oxidized-state dye molecules by iodide. The pulsed laser intensity was kept at a very low level, to ensure that less than one charge-separated pair (injected electron/dye cation) was produced, on average, per TiO$_2$ particle. Although measurements were performed without the application of an external bias, such a condition is still believed to be similar to that which prevails for the photovoltaic device that is functioning under natural sunlight. Figure 6 shows that interception of the oxidized-state dye by iodide (dye regeneration) competes efficiently with the recombination process. The addition of Li$^+$ ions caused the half-reaction time ($t_{1/2}$) for recombination to increase typically from 0.2 ms to 0.8 ms. Dye regeneration in the presence of iodide was observed, in all cases, to be virtually complete after 50 $\mu$s, whereas charge recombination was practically negligible within the same time frame.\textsuperscript{45,46} On the other hand, the presence of Li$^+$ ions accelerated the dye regeneration, with $t_{1/2}$ decreasing from 6 $\mu$s to 3 $\mu$s. A somewhat stronger effect of the Li$^+$ cations in the dye regeneration rate (~3–4 times) by iodide was observed in conventional solvents, which was attributed to electrostatic interactions.\textsuperscript{47} In ionic liquid electrolytes, such interactions are expected to be weaker, because of the high ionic strength, which screens the surface charge that is due to any lithium adsorption onto the surface. Hence, the effect of Li$^+$ ions on the kinetics of dye regeneration by iodide cannot fully rationalize an increase in the power conversion efficiency of device B.

The enhancement in device efficiencies may be attributed to an improved electron injection from the excited-state dye into the conduction band of the oxide. Direct determination of the absolute injection quantum yield ($\Phi_i$) can be achieved by monitoring the ground-state bleaching signal of sensitizers upon nanosecond laser flash photolysis. At 530 nm, absorption by the conduction-band electrons and the excited and oxidized states of the sensitizer is negligible.\textsuperscript{49} Thus, the transient absorption signal measured at this probe wavelength is mainly due to the bleaching and repopulation of the ground state of the dye. Photoexcited dye molecules that do not inject electrons into TiO$_2$ are deactivated to their ground-state within 10 ns. On the other hand, dye cations produced by the photoinduced electron-transfer process recapture the injected electron only in the microsecond-millisecond time domain. These two reaction channels are easily discriminated by the large difference in rate constants. Because the laser pulse duration (5 ns) is shorter than the time constant of the fastest deactivation process (~10 ns), the amplitude of the signal bleaching measured at the end of the laser excitation is proportional to the initial concentration of produced excited states. Quantitative evaluation of the amplitude of the fast and slow kinetic components of the ground-state repopulation allow direct assessment of the proportion of dye excited states decaying through natural deactivation and charge injection, respectively. Figure 7 shows that, in the presence of Li$^+$ ions, a fast recovery of the ground-state population was not observed, meaning that the injection quantum
yield $\Phi$ was similar to unity. Without the addition of Li$^+$ ions, the amplitudes of the fast and slow kinetic components were determined as being $\sim$10% and $\sim$90% of the initial bleaching signal, respectively, yielding only $\Phi = 0.90$.

Specific adsorption of small cations onto oxide semiconductors is known to possibly modify surface charge, band-edge positions, and the energy-level distribution of surface states. The flat-band potential of the semiconductor in a dry aprotic electrolyte can be shifted to considerably more positive values upon the adsorption of potential-determining ions such as the Li$^+$ ion. Such an improvement of the driving force for electron injection by several hundred millielectronvolts is expected to increase the rate and yield of the primary charge separation process considerably. With another Ru(II) complex as a sensitizer, Meyer et al. indeed showed that the adsorption of Li$^+$ cations onto the surface of TiO$_2$ increases the quantum yield of electron injection with no apparent influence on the rate of the back electron transfer. In our case, a similar effect is likely to be the primary cause of the 16% efficiency difference between devices A and B.

Conclusions

In summary, a thin-layer electrochemical cell has been conveniently used to study the redox potential of sensitizers that are anchored on a mesoporous film, in conjunction with square-wave voltammetry. For the first time in dye-sensitized nanocrystalline solar cells with pure ionic liquid electrolytes, an efficiency of 6.6% was obtained at an illumination of air mass (AM 1.5) sunlight. The addition of lithium iodide to pure ionic liquid electrolytes, an efficiency of 6.6% was obtained at an illumination of air mass (AM 1.5) sunlight. The addition of lithium iodide to pure ionic liquid electrolytes, an efficiency of 6.6% was obtained at an illumination of air mass (AM 1.5) sunlight. The present findings should foster widespread application of flexible dye-sensitized solar cells.

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References and Notes

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