A LOW VISCOSITY IONIC LIQUID ELECTROLYTE FOR DYE SENSITIZED SOLAR CELLS WITH ≥7.4% EFFICIENCIES

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ABSTRACT

A new binary ionic liquid electrolyte composed of 1-ethyl-2-methylimidazolium tricyanomethanide and 1-methyl-3-propylimidazolium iodide at a volume ratio of 1:1 was used in nanocrystalline dye sensitized solar cells, yielding a power conversion efficiency of 7.4 % under the air mass 1.5 full sunlight.

INTRODUCTION

Room-temperature ionic liquids (RTILs) are attractive due to their chemical and thermal stability, negligible vapour pressure, nonflammability, high ionic conductivity, and a possible wide electrochemical window (1). In the search for highly stable, non-volatile electrolytes for the nanocrystalline dye-sensitized solar cells (DSC) developed in our group, we have screened a series of ionic liquids as they are benign alternatives to conventional organic solvents. As the iodide/triiodide redox couple is still the best electron mediator for nanostructured DSCs in view of efficiency, stability, and low toxicity, we selected 1-methyl-3-propylimidazoliumiodide (PMII) as an iodide carrier due to its low viscosity in the family of ionic liquids with iodide as anion. Although the viscosity (880 cp) of PMII is much higher compared with some widely used ionic liquids, in combination with an amphiphilic polypyridyl ruthenium sensitizer we achieved an impressive, 6% power conversion efficiency under full sunlight by doping pure PMII with iodine and a solid Lewis base (2). This work should be considered as the breakthrough in dye sensitized solar cells with non-volatile electrolytes.

However, electrolytes based on low viscosity solvents like acetonitrile allowed over 10% efficiency with a state-of-art mesoporous TiO₂ film and sensitizer (3). Hence, the ionic liquid based electrolytes device performance may be enhanced by decreasing the viscosity of electrolytes. Unfortunately, many binary ionic liquid electrolytes employing PMII and some other ionic liquids (viscosities higher than 50 cp) did not produce better device performance than pure PMII although the diffusion coefficients of iodide and triiodide have been enhanced. Nevertheless a 6.6–7% efficiency under the (AM 1.5) full sunlight were reached by taking advantage of the very low viscosities of 1-ethyl-3-methylimidazolium dicyanamide (25 cp) and 1-ethyl-3-methylimidazolium thiocyanate (21 cp) ionic liquids (4,5). It must be noted that the introduction of dicyanamide anion in electrolytes resulted in poor device stability whereas the thiocyanate salt did not affect device stability under light-soaking tests.
Here, we report a new binary ionic liquid electrolyte containing 1-ethyl-3-methylimidazolium tricyanomethanide (EMITCM, Figure 1; viscosity: 18cP) and PMII which gave over 7.4% power conversion efficiency at AM 1.5 sunlight.

Figure 1. Molecular structure of EMITCM.

EXPERIMENTAL

Materials

Chemicals: N-methylbenzimidazole (NMBI) was purchased from Aldrich and recrystallized from diethyl ether. 3-phenylpropionic acid was obtained from Aldrich. The amphiphilic Z-907 dye and PMII were synthesized as described in our previous papers (6,7). EMITCM ionic liquid was prepared with a modification to the reported procedure (8). The electrolyte is composed of 0.2 M iodine and 0.45 M NMBI in a mixture of PMII and EMITCM (volume ratio: 1:1).

Synthesis of EMITCM. Solutions of Potassium tricyanomethanide (5.56 g, 43 mmol) in 50 ml acetonitrile and EMIBr (5.48 g, 29 mmol) in 10 ml acetonitrile were mixed and stirred at room temperature for 18 h. The precipitated potassium bromide was filtered off and the solvent was removed under reduced pressure. 50 ml of dichloromethane was added to the residue and kept at +2 °C for 16 h. The separated solid was filtered off, the filtrate was washed with 5 ml of water and evaporated on a rotary evaporator. Traces of water were removed by an azeotropic distillation with toluene. EMITCM was dried under reduce pressure (0.01 Torr). Yield: 4.49 g (77 %). C_{10}H_{11}N_{5}(201.23) calc.: C, 59.69; H, 5.51; N, 34.80; Br, 0.00 (%). Found: C, 60.05; H, 5.45; N, 34.44; Br, 0.00 (%).

Device Fabrication. The photovoltaic performance of the binary ionic liquid electrolyte was tested using state of the art mesoscopic titania films. The detailed fabrication procedure for the nanocrystalline photoanodes and the assembly of complete,
hot-melt sealed cells have been described elsewhere (6). A 10 µm thick film of 20 nm sized TiO₂ particles was first screen-printed on a fluorine-doped SnO₂ (FTO) conducting glass electrode and a second 4 µm thick second layer of 400 nm-sized light scattering anatase particles was subsequently coated onto the first one. The surface of the TiO₂ electrode was derivatized with the sensitizer by immersing it into the dye solution composed of 300 µM Z-907 and 300 µM 3-phenylpropionic acid as co-adsorbent in acetonitrile and tert-butanol (volume ratio: 1:1) at room temperature for 12 h. A platinized FTO conducting glass was used as counter electrode.

Measurements

**Electrochemical Measurements.** Voltammetric data were recorded at room temperature on an Autolab P20 electrochemical workstation (Eco Chimie, Netherlands). A two-electrode electrochemical cell, consisting of a 5.0 µm radius Pt ultramicroelectrode (Bioanalytical Systems, Inc., USA) as working electrode and a Pt foil as counter electrode, was used for the diffusion coefficient measurements of triiodide in the new electrolyte.

**Conductivity Measurements.** A CDM210 conductivity meter (Radiomater Analytical, SAS, France) was used to measure conductivities of the binary ionic liquid electrolyte. The CDC749 conductivity cell (Radiomater Analytical, SAS, France) with a nominal cell constant of 1.70 cm⁻¹ was calibrated with 0.1 M KCl aqueous solution prior to the experiments.

**Photoelectrochemical Measurements.** A 450 W xenon light source (Oriel, USA) was used to give an irradiance of 100 mW/cm² (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 & Optik GmbH, Germany) so as to reduce the mismatch between the simulated and true solar spectra to less than 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 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.

\[
\text{IPCE (λ)} = \frac{12400}{\lambda} \frac{\text{J}_{\text{sc}}}{\phi} 
\]  

where λ is the wavelength, Jsc is short-circuit current photocurrent density (mA/cm²), and ϕ is the incident radiative flux (mW/cm²).
RESULTS AND DISCUSSION

The conductivity ($\sigma$) of the new ionic liquid electrolyte was first examined. As is apparent from the inset of Figure 2, the Arrhenius equation cannot be used to describe the conductivity-temperature behavior of the electrolyte. A better fit to the data (Figure 1) is obtained by the Vogel–Fulcher–Tamman (VFT) equation.

$$\sigma(T) = AT^{-1/2} \exp\left(-\frac{B}{T-T_0}\right)$$

In eqn. (2), $A$ and $B$ are constants; $T$ is the absolute temperature while $T_0$ is the thermodynamic Kauzmann temperature. In this expression, $T_0$ represents the temperature at which ionic mobilities would appear to fall to zero. From the conductivity-temperature relationship it can be seen that the activation energy in the ionic liquid electrolyte is small.

![Figure 2. Plots of conductivity-temperature data in the Arrhenius and VFT coordinates for the binary ionic liquid electrolyte.](image)

A two-electrode-system electrochemical cell equipped with a Pt ultramicroelectrode (radius: 5 μm) as working electrode and a Pt foil as counter electrode was employed for diffusion coefficient determinations. The steady-state voltammogram for the redox of iodide and triiodide is shown in Figure 3. The apparent diffusion coefficients ($D_{app}$) of iodide and triiodide can be calculated from the anodic and cathodic steady-state currents ($I_{ss}$) according to the following equation.

$$I_{ss} = 4ncaFD_{app}$$

where $n$ is the electron transfer number per species, $F$ is the Faraday constant, and $c$ is the bulk concentration of electroactive species. The calculated diffusion coefficients of iodide and triiodide in this electrolyte was $5.5 \times 10^{-7}$ and $4.6 \times 10^{-7}$ cm$^2$ s$^{-1}$, respectively. These values are larger than those in the solvent-free, PMII based ionic liquid electrolyte due to the lower viscosity of the binary electrolyte.
A typical photocurrent action spectrum of devices with the new ionic liquid electrolyte is shown in Figure 4A. The incident photon to current conversion efficiency (IPCE) exceeds 70% in the spectral range from 460 to 600 nm reaching its maximum of above 75% at 550 nm. Figure 4B presents the current density-voltage characteristics under the illumination of AM 1.5 sunlight at 100 mW/cm². The photovoltaic parameters (Jsc, Voc, ff, and η) were measured to be 12.81 mA/cm², 752 mV, 0.764, and 7.4%, respectively. Such a high efficiency has been achieved so far under AM 1.5 sunlight by solvent-free ionic liquid electrolytes based on the iodide/triiodide couple. It is comparable to the excellent device performance obtained with an ionic liquid electrolyte with the SeCN⁻/(SeCN)₃⁻ as an alternate redox couple (9). As shown in Table 1, at lower light intensities the power conversion efficiency reaches over 7.5%.
Figure 4. (A) Typical photocurrent action spectrum of devices with the binary ionic liquid electrolyte. (B) Current density-potential curves of devices (a) under the AM 1.5 full sunlight and (b) in the dark. Cell area (tested with mask): 0.158 cm$^2$.

Table 1. Detailed photovoltaic parameters of device C with the new ionic liquid electrolyte under different incident light intensities.

| $P_{in}$/mW cm$^{-2}$ | $J_{sc}$/mA cm$^{-2}$ | $V_{oc}$/mV | $P_{max}$/mW cm$^{-2}$ | $ff$ | $\eta$/% |
|-----------------------|-----------------------|-------------|------------------------|------|---------|
| 30                    | 4.11                  | 722         | 2.3                    | 0.784 | 7.6     |
| 52.0                  | 7.08                  | 734         | 4.0                    | 0.775 | 7.6     |
| 100                   | 12.81                 | 752         | 7.4                    | 0.764 | 7.4     |

Devices with the binary ionic liquid electrolyte showed a good photostability when submitted to accelerate testing in a solar simulator at 100 mW/cm$^2$ intensity. After one month of light soaking at 60 °C the drop of device efficiency is less than 10% (Fig. 5) for cells covered with a UV absorbing polymer film. In the first two weeks the performance of the cell increases, the small drop in photovoltage and fill factor being...
compensated by an increase in photocurrent. During the second phase of the light soaking process a 2% decline of the fill factor and a 10% decrease of the short circuit photocurrent was witnessed while the open circuit photovoltage remained stable. The overall efficiency declined by ca 10% over the whole illumination period.

![Graph showing device parameters evolution](image)

Figure 5. Evolution of device parameters during the one sun visible light soaking at 60 °C.

CONCLUSIONS

In conclusion, for the first time a 7.4% power conversion efficiency at full sunlight has been achieved for photovoltaic devices based on solvent-free ionic liquid electrolytes with the iodide/triiodide redox couple. Lowering the viscosity of ionic liquid electrolytes while keeping a suitable iodide concentration is critical to obtain high efficiency. This finding will foster the fabrication of high-efficiency, flexible devices free of leakage and available in varied geometries due to the high endurance of polymer matrix to ionic liquids.

ACKNOWLEDGMENT

We are grateful to T. Koyanagi (CCIC, Japan) for providing the 400 nm TiO₂ particles and P. Comte for the film preparation. The Swiss Science Foundation, Swiss Federal Office for Energy (OFEN), and the European Office of U.S. Air Force under Contract No. F61775-00-C0003 have supported this work.

Electrochemical Society Proceedings Volume 2004-24

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