

## A Solvent-Free, $\text{SeCN}^-/(\text{SeCN})_3^-$ Based Ionic Liquid Electrolyte for High-Efficiency Dye-Sensitized Nanocrystalline Solar Cells

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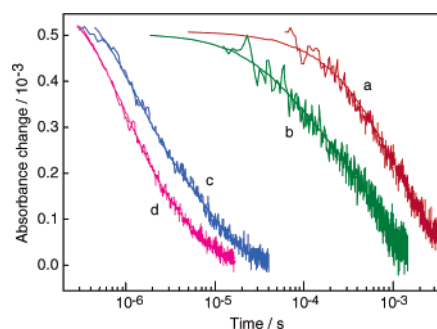
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Nanocrystalline dye-sensitized solar cells (DSCs) are attracting considerable academic and industrial interest as low-cost, high-efficiency alternatives to the conventional solid p-n junction photovoltaic devices.<sup>1</sup> A record of 10.6% total power conversion efficiency has recently been reached using a liquid organic electrolyte based on the iodide/triiodide redox couple.<sup>2</sup> The recent achievement of long-term thermal stability by molecular-scale interface engineering has undoubtedly injected new momentum into this field.<sup>3</sup> However, the sealing of volatile electrolytes in large scale modules still remains a critical issue in view of the practical application. Solid hole-transport materials<sup>4</sup> and solvent-free polymer electrolytes<sup>5</sup> incorporating iodide and triiodide have been introduced to replace the liquid electrolytes, but until now efficiencies of these devices are still relatively low. Another attractive option which is widely investigated currently is to employ room-temperature ionic liquids as nonvolatile electrolytes for DSCs.<sup>6</sup>

While considerable interest has been focused on the engineering of sensitizers and mesoporous semiconductor films, efforts to identify new electron mediators that could replace the iodide/triiodide couple have so far met only with modest success. Several polypyridyl cobalt(II/III) complexes<sup>7</sup> have shown promise to rival the iodide/triiodide couple at low light intensity. However, under standard air mass (AM) 1.5 full sunlight the conversion efficiencies dropped below 4% due to mass transport limitations of the photocurrent. Oskam et al.<sup>8</sup> tested the pseudohalides  $\text{SCN}^-/(\text{SCN})_2$  and  $\text{SeCN}^-/(\text{SeCN})_2$  as redox couples in acetonitrile by employing the standard N3 sensitizer. Their performance was found to be disappointing, the incident photon-to-current conversion efficiency (IPCE) being at most 20% compared to >80% for the iodide/triiodide-based system. This was attributed to the inefficient dye regeneration by the  $\text{SeCN}^-$  or  $\text{SCN}^-$  electron donor. Here we present results on the new and low-viscosity ionic liquid 1-ethyl-3-methylimidazolium selenocyanate (EMISeCN). When used in conjunction with a nanocrystalline  $\text{TiO}_2$  film sensitized by an amphiphilic analogue of the N3 dye, unprecedented solar to electric power conversion efficiencies have been reached for solvent-free redox electrolytes.

EMISeCN was prepared according to the procedure published for 1-ethyl-3-methylimidazolium thiocyanate (EMISCN).<sup>9</sup> The viscosity of pure EMISeCN was determined to be 25 cP at 21 °C, which is extraordinarily low for an ionic liquid. The most fluid imidazolium iodide-based analogue, i.e., 1-propyl-3-methylimidazolium iodide (PMII), has a 35 times higher viscosity, i.e., around 880 cP at room temperature. The specific conductivity of EMISeCN is 14.1 mS/cm compared to 0.5 mS/cm for PMII. Even at -30 °C it is still 1 mS/cm, whereas it becomes negligibly small for PMII. The higher conductivity of EMISeCN is mainly due to a decrease in cohesive energy, probably because the van der Waals energy associated with the highly polarizable iodide component has been removed.

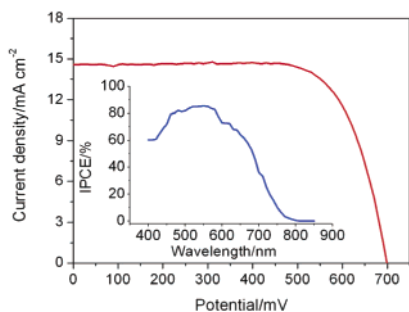


**Figure 1.** Transient absorbance decay kinetics of the oxidized state of Z-907 dye anchored on a nanocrystalline  $\text{TiO}_2$  film in the presence of various pure ionic liquids (a, EMIDCN; b, EMISCN; c, PMII; d, EMISeCN). Absorbance changes were measured at a probe wavelength of 650 nm, employing 532 nm pulsed laser excitation (10 ns fwhm pulse duration, 40  $\mu\text{J}/\text{cm}^2$  pulse fluence).

These trends are corroborated by the results from electrochemical measurements of the diffusion coefficients of  $\text{SeCN}^-$  and  $(\text{SeCN})_3^-$ . The composition of the ionic liquid employed was the same as that used in the photovoltaic experiments described further below. Apart from EMISeCN it contained 0.15 M  $\text{K}(\text{SeCN})_3$ ,<sup>10</sup> 0.1 M guanidinium thiocyanate, and 0.5 M *N*-methylbenzimidazole. The diffusion coefficients of  $\text{SeCN}^-$  and  $(\text{SeCN})_3^-$  in this electrolyte, determined by ultramicroelectrode voltammetry<sup>6b</sup> are  $2.80 \times 10^{-6}$  and  $1.28 \times 10^{-6}$   $\text{cm}^2/\text{s}$ , respectively. These values are about 9 and 7 times higher than the respective values for iodide and triiodide in the pure PMII ionic liquid.<sup>6b</sup>

These intriguing properties prompted us to investigate whether EMISeCN could replace iodide-based ionic liquids in dye-sensitized solar cells. Transparent nanocrystalline  $\text{TiO}_2$  films of 8  $\mu\text{m}$  thickness were deposited on glass and derivatized with  $\text{Ru}(\text{H}_2\text{dcbpy})(\text{dnbpy})-(\text{NCS})_2$  dye,<sup>11</sup> where  $\text{H}_2\text{dcbpy}$  is 4,4'-dicarboxylic acid-2,2'-bipyridine and dnbpy is 4,4'-dinonyl-2,2'-bipyridine. This amphiphilic sensitizer, coded as Z-907, was adsorbed onto the  $\text{TiO}_2$  film from a 300  $\mu\text{M}$  solution in a mixture of acetonitrile and *tert*-butyl alcohol (volume ratio: 1:1) by overnight dipping. Charge injection from the excited state of Z-907 into the conduction band of  $\text{TiO}_2$  occurs within the picosecond time scale.<sup>12</sup> In the absence of electrolyte the injected conduction band electrons are recaptured by the oxidized Z-907 dye molecules ( $\text{S}_{907}^+$ ) in the microsecond–millisecond domain.<sup>11</sup> Time-resolved laser photolysis in conjunction with transient absorption spectroscopy was performed to examine whether  $\text{SeCN}^-$  could intercept the back electron-transfer reaction.

Shown in Figure 1 are results illustrating the temporal behavior of the 650 nm absorption of the  $\text{S}_{907}^+$  in the presence of four imidazolium-based ionic liquids containing different anions. Curve A refers to an ionic liquid containing the redox-inactive dicyanamide (EMIDCN).<sup>13</sup> Here the 650 nm absorption decay with  $t_{1/2} = 1$  ms reflects the dynamics of recombination of injected conduction band



**Figure 2.** Current density–voltage characteristic under AM 1.5 illuminations of  $99.7 \text{ mW/cm}^2$ . The inset is its photocurrent action spectrum. Cell active area tested with mask:  $0.152 \text{ cm}^2$ .

electrons with  $S_{907}^+$ . For EMISecN or PMII the disappearance of  $S_{907}^+$  is greatly accelerated, the  $t_{1/2}$  values being 1.5 and  $3 \mu\text{s}$ , respectively. This shows that, contrary to the results of Oskam et al.<sup>8</sup> obtained with acetonitrile, the  $\text{SeCN}^-$  ions in the EMISecN ionic liquid intercept the back electron transfer very efficiently. Electron donation from the  $\text{SeCN}^-$  to the oxidized Z-907 dye is even faster than from iodide ions in the PMII ionic liquid, despite that the former has a more positive redox potential of 190 mV than the latter<sup>8</sup> and hence is more difficult to be oxidized. However, for the EMISecN ionic liquid containing thiocyanate instead of selenocyanate anions, the  $S_{907}^+$  decay has a much longer half-lifetime of  $200 \mu\text{s}$  indicating inefficient interception of charge recombination. Insufficient thermodynamic driving force is the probable reason for slow electron donation from  $\text{SCN}^-$  to the  $S_{907}^+$  as the replacement of selenium by sulfur results in a 270 mV increase of the standard redox potential,<sup>8</sup> bringing it closer to that of the Z-907 sensitizer.<sup>14</sup>

The photovoltaic performance of an EMISecN-based ionic liquid 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.<sup>14</sup> A thick film of 20 nm sized  $\text{TiO}_2$  particles was first screen-printed on a fluorine-doped  $\text{SnO}_2$  (FTO) conducting glass electrode and a second  $4 \mu\text{m}$  thick second layer of 400 nm-sized light scattering anatase particles was subsequently coated onto the first one. The surface of the  $\text{TiO}_2$  electrode was derivatized with the sensitizer by immersing it into the dye solution composed of  $300 \mu\text{M}$  Z-907 and  $300 \mu\text{M}$  3-phenylpropionic acid as coadsorbent in acetonitrile and *tert*-butyl alcohol (volume ratio: 1:1) at room temperature for 12 h. A platinumized FTO conducting glass was used as counter electrode.

A typical photocurrent action spectrum obtained with the new ionic liquid electrolyte is shown in the inset of Figure 2. The incident photon to current conversion efficiency (IPCE) is very high, exceeding 80% in a spectral range from 470 to 580 nm and reaching its maximum of 85% at 550 nm. Considering the light absorption and scattering loss by the conducting glass, the conversion of photons to current is practically quantitative over this spectral range. Figure 2 presents the photocurrent–voltage curve measured under an air mass (AM) 1.5 illumination of  $99.7 \text{ mW/cm}^2$ . The short-circuit photocurrent density ( $J_{\text{sc}}$ ), open-circuit photovoltage ( $V_{\text{oc}}$ ), and fill factor (ff) of the above device are  $14.56 \text{ mA/cm}^2$ , 699 mV, and 0.735, respectively, yielding an overall conversion efficiency ( $\eta$ ) of 7.5%. At the intermediate light levels of 9.5, 30, and  $51.7 \text{ mW/cm}^2$ , the device efficiencies are 8.3%, 8.3%, and 8.1%, respectively. This is the first time such high efficiencies have been

reached for dye-sensitized solar cells with pure ionic liquid electrolytes. While detailed stability tests on this system are on going, we noticed that the efficiency of the cell under room light storage varied by less than 10% for eight weeks. Apart from the high efficiency, the high conductivity of EMISecN below  $0^\circ\text{C}$  allows for the realization of photovoltaic devices having a broader operational temperature than iodide-based ionic liquids. In addition, this new ionic liquid electrolyte has the advantage over the iodide/triiodide-based analogues of having considerably less light absorption in the visible region and thus reducing optical losses due to optical attenuation by the electrolyte.<sup>6</sup>

In summary, we have demonstrated that ionic liquids based on the  $\text{SeCN}^-/(\text{SeCN})_3^-$  redox couple can be employed as mediators for high-efficiency dye-sensitized solar cells. For the first time an alternative redox couple has been identified that can rival and even exceed the performance of the iodide/triiodide couple even at full sunlight. Unprecedented 7.5–8.3% power conversion efficiencies under AM 1.5 sunlight have been achieved for photovoltaic devices with pure ionic liquid electrolytes. Work is in progress to further improve the performance of this promising system.

**Acknowledgment.** We are grateful to Marlene Rodlert (LTC, EPFL) for the viscosity measurement, P. Comte for the film fabrication, and CCIC (Japan) for a free sample of the 400 nm sized light scattering anatase particles. This work was supported by the Swiss Science Foundation, the Swiss Federal Office for Energy, and the European Office of the U.S. Air Force under Contract No. F61775-00-C0003.

**Supporting Information Available:** Synthetic procedure and data on additional conductivity, voltammetric,  $I$ – $V$ , and UV–vis measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA048472R