

# High efficiency dye-sensitized nanocrystalline solar cells based on ionic liquid polymer gel electrolyte†

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An ionic liquid polymer gel containing 1-methyl-3-propylimidazolium iodide (MPII) and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) has been employed as quasi-solid-state electrolyte in dye-sensitized nanocrystalline TiO<sub>2</sub> solar cells with an overall conversion efficiency of 5.3% at AM 1.5 illumination.

Owing to their high efficiency for the conversion of solar energy to electric power and low production cost, dye-sensitized nanocrystalline solar cells (DSSCs) have been attracting widespread scientific and technological interest and have evolved as potential alternatives to traditional photovoltaic devices in the past decade.<sup>1</sup> The mesoscopic TiO<sub>2</sub> film texture in these cells significantly increases the optical path length for light harvesting by the surface-anchored ruthenium polypyridyl dyes while keeping a suitable contact with electrolytes. These modules contain organic electrolytes with dissolved triiodide/iodide as redox couple. However, the presence of organic liquid electrolytes in cells can result in some practical limitations with sealing and long-term operation. Thus hole-transporting organic materials,<sup>2</sup> *p*-type semiconductors<sup>3</sup> and polymers incorporating the redox couple<sup>4</sup> have been attempted to replace organic solvent-based liquid electrolytes. Replacing the liquid electrolyte by polymeric materials allows the assembly of flexible solid-state devices. Until now, DSSCs with polymer electrolytes have shown less than 4.0% light-to-electricity conversion efficiency and questionable UV stability due to the intrinsic photodegradation of these polymers.

Room-temperature ionic liquids (RTILs) are attractive due to their chemical and thermal stability, negligible vapor pressure, nonflammability, high ionic conductivity and a wide electrochemical window. Since the discovery of air-stable RTILs by Wilkes and Zaworotko,<sup>5</sup> various RTILs have been explored for applications as benign solvents for green synthesis and separation.<sup>6</sup> The physical and chemical properties of RTILs can be changed by varying the nature of cations and anions. Hence, they have been employed as important sources for iodide-based redox and solvents in DSSCs.<sup>7</sup> Amongst the 1,3-dialkylimidazolium iodide compounds, 1-methyl-3-propylimidazolium iodide (MPII) with a small cation has the lowest viscosity. An impressive photovoltaic performance was obtained using small gelator molecules in combination with RTILs.<sup>7d</sup> Polymer gels have been actively developed as highly conductive electrolyte materials for lithium secondary batteries and fuel cells.<sup>8</sup> RTILs consisting of a perfluorinated anion (*e.g.* BF<sub>4</sub><sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>) and 1,3-dialkylimidazolium cation have been incorporated into poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) matrix to form free standing RTIL-polymer gel electrolytes for dual intercalating cells.<sup>9</sup> It is known that fluorinated polymers are photochemically stable even in the presence of TiO<sub>2</sub> and Pt nanoparticles.<sup>10</sup> Hence MPII are combined with PVDF-HFP to form polymer gel electrolyte for solid-state DSSCs in this paper.

In the fabrication of photoelectrochemical cells, hydrophobic dye (Z907 shown in Fig. 1) coated nanocrystalline TiO<sub>2</sub>

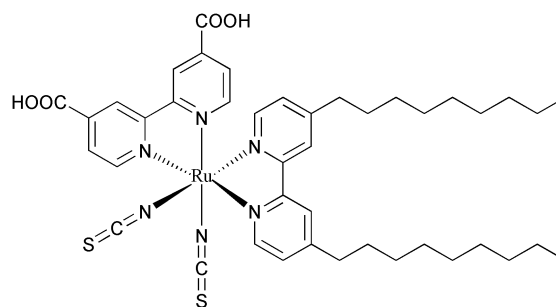


Fig. 1 Chemical structure of the hydrophobic dye Z-907.

electrodes are sandwiched with the counter electrodes and the intervening space filled with ionic liquid-based electrolytes.<sup>†‡</sup> Fig. 2 presents a typical photocurrent density–voltage curve for photoelectrochemical cells with the PVDF-HFP (10 wt%) RTIL-polymer gel electrolyte at an irradiance of AM 1.5 sunlight. As shown in the inset of Fig. 2, incident photon-to-current conversion efficiency (IPCE) curve *versus* wavelength for the polymer gel electrolyte-based DSSCs shows a maximum efficiency, around 74% at 540 nm, comparable to the values obtained for liquid electrolyte cells. The short-circuit photocurrent density ( $J_{SC}$ ), open-circuit voltage ( $V_{OC}$ ), and fill factor ( $FF$ ) of the polymer gel-based DSSCs are 11.29 mA cm<sup>-2</sup>, 665 mV and 0.712, respectively, yielding an overall energy conversion efficiency ( $\eta$ ) of 5.3%. This overall conversion efficiency does not depend much on the light intensity. Almost identical results (Fig. 2) obtained for cells with the corresponding blank liquid electrolyte (*i.e.*, one that does not contain the PVDF-HFP polymer) indicate that the presence of polymer has no adverse effect on the conversion efficiency.

Depending on the spacer thickness the photocurrents of DSSCs may become diffusion-controlled under full sunlight

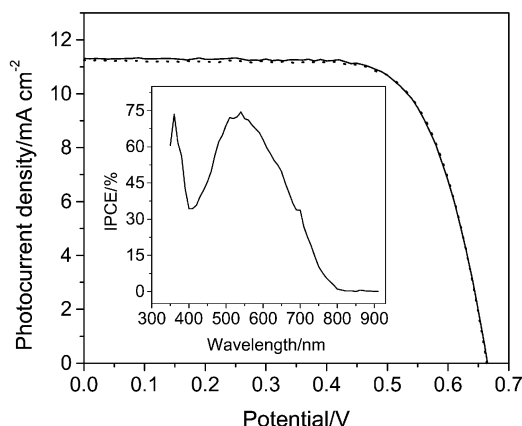


Fig. 2 Photocurrent density–voltage characteristics of DSSCs with 10 wt% PVDF-HFP RTIL-polymer gel (solid curve) and blank (dashed curve) electrolytes at AM 1.5 (100 mW cm<sup>-2</sup>) illumination. Cell active area: 0.152 cm<sup>2</sup>. The inset shows the photocurrent action spectrum for DSSCs with the polymer gel electrolyte. The incident photon-to-current conversion efficiency is plotted as a function of wavelength of the exciting light.

† Electronic supplementary information (ESI) available: fabrication procedure for the DSSCs. See <http://www.rsc.org/suppdata/cc/b2/b209322g/>

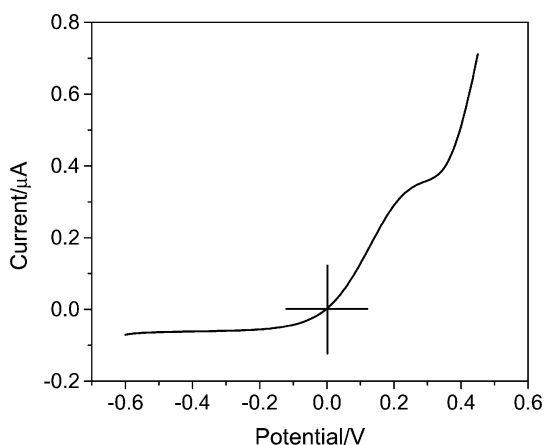
irradiation due to the higher viscosity of MPII. An Autolab P20 electrochemical workstation was used to study the diffusion of iodide and triiodide in our ionic liquid-based electrolytes and the influence of PVDF–HFP. An electrochemical cell of a two-electrode system is used, which consists of a Pt ultramicroelectrode with a radius ( $a$ ) of 6.6  $\mu\text{m}$  as working electrode and a Pt foil as counter electrode. The linear-sweep voltammogram of the RTIL-polymer gel electrolyte at the scan rate of 50  $\text{mV s}^{-1}$  is shown in Fig. 3. Anodic and cathodic currents are not affected by scan rates up to 500  $\text{mV s}^{-1}$ , suggesting that steady-state currents controlled by the diffusion of iodide and triiodide in the polymer gel electrolyte have been attained. Thus, the apparent diffusion coefficients ( $D_{\text{APP}}$ ) of iodide and triiodide can be calculated from anodic and cathodic steady-state currents ( $I_{\text{ss}}$ ) according to the following eqn. (1)<sup>11</sup>

$$I_{\text{ss}} = 4ncaFD_{\text{APP}} \quad (1)$$

where  $n$  is the electron number per molecule,  $F$  is the Faraday constant and  $c$  is the bulk concentration of electroactive species. Since  $I_{\text{ss}}$  is directly proportional to the flux of electroactive species, the voltammetric signal is very sensitive to changes in the value of  $D_{\text{APP}}$ . The calculated diffusion coefficients of triiodide and iodide in the polymer gel electrolyte are  $1.9 \times 10^{-7}$  and  $3.1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ , respectively, which are the same as those in the blank liquid electrolyte. In fact, the macroscopic viscosity of the polymer gel electrolyte is much higher than that of the blank liquid electrolyte. This discrepancy could be attributed to an open structure of the present polymer gel system. Since the main component of the gel is MPII, liquid channels are formed in the polymeric phase and the diffusion of iodide and triiodide occurs in these channels. A similar phenomenon was also observed for the diffusion of some electroactive species in other polymer gel systems.<sup>12</sup> The  $D_{\text{APP}}$  ratio of 3  $\text{mmol l}^{-1}$  triiodide in acetonitrile to 0.5  $\text{mol l}^{-1}$  triiodide in our polymer electrolyte is 58 but the viscosity ratio of MPII<sup>7e</sup> to acetonitrile<sup>7b</sup> is 2162. A Grotthus-type electron exchange mechanism appears therefore to make a significant contribution to  $D_{\text{APP}}$ . Diffusion-controlled currents reflect the contribution from physical diffusion of triiodide and iodide to the ultramicroelectrode and electron exchange between triiodide and iodide, as described for the coupling of physical diffusion mass transport and electron-exchange by the Dahms–Ruff equation.<sup>13</sup>

$$D_{\text{APP}} = D_{\text{PHYS}} + k_{\text{EX}}\delta^2c/6 \quad (2)$$

where  $k_{\text{EX}}$  is the rate constant of electron exchange, and  $c$  and  $\delta$  are the concentration and average center-to-center distances between redox species, respectively.



**Fig. 3** Steady-state voltammogram for a Pt ultramicroelectrode in the 10 wt% PVDF–HFP RTIL-polymer gel electrolyte. Scan rate: 50  $\text{mV s}^{-1}$ .

In conclusion, for the first time we successfully employed PVDF–HFP polymer in combination with MPII ionic liquid as a polymer gel electrolyte for high efficiency dye-sensitized nanocrystalline  $\text{TiO}_2$  solar cells. Ionic liquid polymer gel electrolytes offer the same benefits as ionic liquids but with the added flexibility of having the solar cells as an all solid-state device. Thus, this is an important step towards the development of solvent free polymer gel electrolytes for flexible solar cells.

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## Notes and references

‡ MPII was prepared according to the methodology described in our previous paper<sup>14</sup> and confirmed by  $^1\text{H}$  NMR spectra. The synthesis and characterization of the hydrophobic dye referred to as Z-907 [Ru( $\text{H}_2\text{dcbpy}$ )( $\text{dnbpy}$ )( $\text{NCS}$ )<sub>2</sub>, where the ligand  $\text{H}_2\text{dcbpy}$  is 4,4'-dicarboxylic acid-2,2'-bipyridine and  $\text{dnbpy}$  is 4,4'-dinonyl-2,2'-bipyridine] will be reported elsewhere.<sup>15</sup> *N*-methylbenzimidazole (NMBI) was purchased from Aldrich and recrystallized from diethyl ether.

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