

A Binary Ionic Liquid Electrolyte to Achieve $\geq 7\%$ Power Conversion Efficiencies in Dye-Sensitized Solar Cells

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In the past decade considerable research and industry attention has been paid to dye-sensitized solar cells (DSCs) with a nanostructured TiO_2 film. At present, they have become a potential low-cost, efficient alternative to conventional inorganic photovoltaic devices.¹ Nanoporous film texture in these cells has a large surface area to anchor photosensitizers at a quasi-monolayer level and thus ensures efficient light-harvesting and electron injection. Additionally, the anchored dye molecules have a good contact with interpenetrated liquid or quasi-solid-state electrolytes to endow a fast dye-regeneration after photoinduced electron injection. The injected electron in the interconnected nanocrystals will be screened by some cations in the electrolytes and efficiently collected by the conducting glass matrix. The recent achievement of long-term thermostability with an amphiphilic polypyridyl ruthenium sensitizer has undoubtedly injected new momentum into this field.²

However, the sealing of volatile organic-solvent based electrolytes in large scale modules remains an issue in view of the practical application. Thus, *p*-type inorganic semiconductors,³ organic hole-transport materials,⁴ and solvent-free polymer electrolytes incorporating triiodide/iodide as a redox couple⁵ were introduced to substitute for the liquid electrolytes. On the other side, pure room-temperature ionic liquid electrolytes have been actively pursued as nonvolatile electrolytes of DSCs⁶ and the highest efficiency (6.6%) has been reached under simulated full sunlight (air mass 1.5, 100 mW cm^{-2}) very

recently using dicyanamide anion along with iodide.⁷ However, our subsequent research showed that the presence of 1-ethyl-3-methylimidazolium dicyanamide (EMIDCN) in the ionic liquid electrolyte induced an instability of the cells under visible light soaking. Hence, there is a need to replace the dicyanamide by a less reactive anion.

In this communication, a new pure ionic liquid electrolyte composed of 1-propyl-3-methylimidazolium iodide (PMII) and 1-ethyl-3-methylimidazolium thiocyanate (EMINCS) allowed us to obtain the 6.4% efficiency under simulated air mass (AM) 1.5 full sunlight which is comparable with our previous work.⁷ Furthermore, molecular-scale interface engineering of nanocrystalline TiO_2 film was performed by co-grafting an amphiphilic polypyridyl ruthenium complex and 3-phenylpropionic acid (PPA) as sensitizer and coadsorbed spacer, respectively. The molecular structures of the employed dye referred to Z-907 and PPA are shown in Figure 1. The device with the co-grafted photoanode and this new electrolyte has reached $\geq 7.0\%$ efficiencies under simulated AM 1.5 sunlight.

A screen-printed double layer of TiO_2 particle was used as photoanode. A 10- μm -thick film of 20-nm TiO_2 particles was first printed on the fluorine-doped SnO_2 conducting glass electrode and further coated by a 4- μm -thick second layer of 400-nm light-scattering anatase particles. The detailed fabrication procedure for the nanocrystalline TiO_2 photoanodes and the assembly of complete, hot-melt sealed cells has been described elsewhere.⁸ The TiO_2 electrodes were surface derivatized by immersing them in the dye solutions at room temperature for 12 h. Solution A consisted of 300 μM Z-907 in acetonitrile and *tert*-butyl alcohol (volume ratio 1:1), and solution B contained 300 μM Z-907 dye and 300 μM PPA as coadsorbent. The cells without and with PPA coadsorbent are denoted as devices A and B, respectively. The new electrolyte contained 0.2 M I_2 , 0.14 M guanidinium thiocyanate, and 0.5 M 4-*tert*-butylpyridine in the mixture of PMII and EMINCS (volume ratio 13:7). PMII was prepared according to the literature method.⁹ EMINCS ionic liquid was prepared using polymer-supported thiocyanate (Amberlite IRA 900 SCN form, Fluka). A 10-g portion of thiocyanate polymer was added to 50 mL of acetonitrile containing 1.91 g of 1-ethyl-3-methylimidazolium bromide and the mixture was stirred at room temperature for 16 h. After the polymer support was removed, the solvent was evapo-

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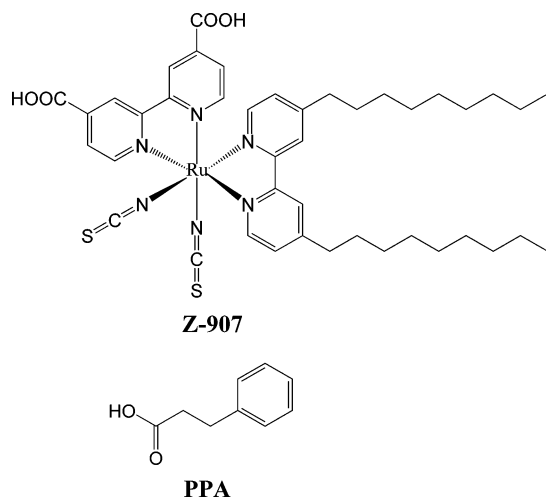


Figure 1. Molecular structures of Z-907 dye and PPA.

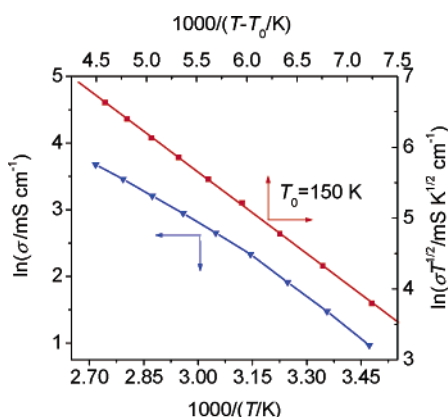


Figure 2. Plots of conductivity–temperature data in the Arrhenius and VFT coordinates for the pure ionic liquid electrolyte.

rated under vacuum to obtain 1.5 g of EMINCS ionic liquid. Its viscosity was determined to be 21 cPs. EMINCS can also be prepared with silver salt as reported by MacFarlane et al.¹⁰

The conductivity (σ) of the new pure 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–Tammann (VFT) equation.¹¹

$$\sigma(T) = AT^{-1/2} \exp[-B/(T - T_0)] \quad (1)$$

In eq 1, A and B are constants, T is the absolute temperature, and 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. 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 determination. The steady-state voltammogram for the reduction of

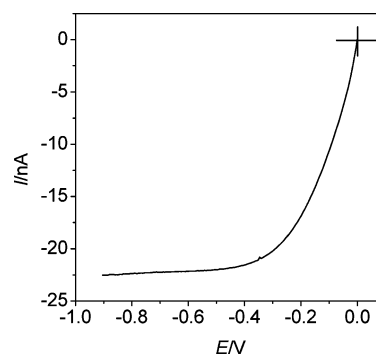


Figure 3. Steady-state voltammogram for a Pt ultramicroelectrode in the pure ionic liquid electrolyte. Scan rate: 100 mV s^{-1} .

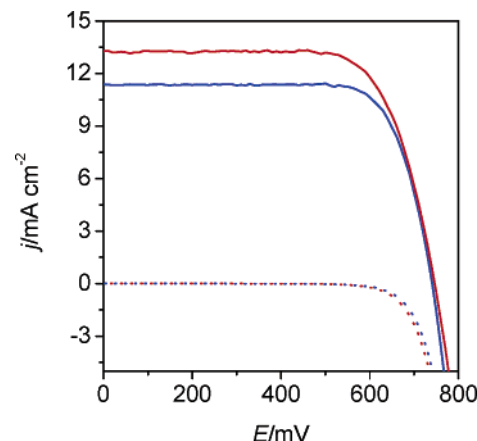


Figure 4. Photocurrent density–voltage characteristics of device A (blue curve) and B (red curve) at air mass 1.5 (100 mW cm^{-2}) illumination. Dark current–bias potential relationship is shown as dotted curves. Active area of devices with mask: 0.17 cm^2 .

triiodide is shown in Figure 3. The apparent diffusion coefficients (D_{app}) of triiodide can be calculated from the steady-state current (I_{ss}) according to the following equation.¹²

$$I_{\text{ss}} = 4ncaFD_{\text{app}} \quad (2)$$

where n is the electron-transfer number per molecule, F is the Faraday constant, and c is the bulk concentration of electroactive species. The calculated diffusion coefficient of triiodide in this electrolyte was determined to be $2.95 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, which is about 1.6 times larger than that in the solvent-free, PMII-based ionic liquid electrolyte^{6g} due to the lower viscosity.

Figure 4 presents the photocurrent–voltage curves measured in full AM 1.5 sunlight (intensity of the solar simulator: 100 mW cm^{-2} , spectral mismatch corrected) and Table 1 lists the overall conversion efficiencies at different light intensities. The short-circuit photocurrent density (J_{sc}), open-circuit photovoltage (V_{oc}), and fill factor (ff) of device A are 11.4 mA cm^{-2} , 740 mV, and 0.76, respectively, yielding an overall conversion efficiency (η) of 6.4%. The corresponding parameters (J_{sc} , V_{oc} , ff , and η) of device B are 13.3 mA cm^{-2} , 746 mV, 0.72, and 7.0%, respectively. The increase in the short-circuit photocurrent density may appear surprising

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Table 1. Device Efficiencies of DSCs at Varied Sunlight Irradiation

| device | η (%) at different light intensities ^a | | |
|--------|--|---------|---------|
| | 0.1 sun | 0.5 sun | 1.0 sun |
| A | 6.7 | 6.8 | 6.4 |
| B | 7.7 | 7.6 | 7.0 |

^a The spectral distribution of the lamp mimics air mass 1.5 solar light. 1.0 Sun corresponds to an intensity of 100 mW cm⁻². Active area of devices with mask: 0.17 cm².

because UV-vis absorption measurements showed that the presence of PPA resulted in a 15% decrease of uploaded dye amount, which should decrease the light harvesting capacity of the mesoporous films and hence decrease the J_{sc} value. ATR-FTIR measurements further confirmed that PPA has been co-grafted with the Z-907 dye molecules onto the surface of TiO₂ nanocrystals. However, the mixed Z-907/PPA monolayer appears to be more robust to impair the escape of photoinjected electrons into the electrolyte.^{2b} In addition, co-grafting of Z-907 dye with PPA may also increase the mobility of electron transport in nanocrystalline film and thus improve the current collecting efficiency. Recently, pulsed-laser-induced current transient measurements have revealed that dye adsorption onto nanoporous TiO₂ electrode can increase the electron diffusion coefficient compared with that of bare electrode.¹³

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Importantly, device B showed a good stability in power conversion efficiency under continuous light soaking at 55–60 °C in a solar simulator (100 mW cm⁻²) equipped with a UV filter. After 720 h aging, device efficiency of a tested cell only changed from 6.78% to 6.60%. It should be noted that a 70 mV drop of V_{oc} did happen while its J_{sc} increased from 12.83 to 13.95 mA cm⁻².

In conclusion, we have demonstrated that the use of a co-grafted monolayer of an amphiphilic polypyridyl ruthenium dye and 3-phenylpropionic acid as coadsorbent enhances the efficiency of dye-sensitized solar cells. For the first time $\geq 7\%$ power conversion efficiencies under AM 1.5 full sunlight have been achieved for photovoltaic devices with solvent-free ionic liquid electrolytes. This finding will enable the fabrication of high-efficiency, flexible devices free of leakage and available in varied geometries due to the high endurance of the polymer matrix to ionic liquids.

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