

Gelation of Ionic Liquid-Based Electrolytes with Silica Nanoparticles for Quasi-Solid-State Dye-Sensitized Solar Cells

Peng Wang,[†] Shaik M. Zakeeruddin,^{*,†} Pascal Comte,[†] Ivan Exnar,[‡] and Michael Grätzel^{*,†}

Laboratory for Photonics and Interfaces, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland, and NTERA Batteries, CH-1015 Lausanne, Switzerland

Received November 11, 2002; E-mail: shaik.zakeer@epfl.ch and michael.gratzel@epfl.ch

Dye-sensitized solar cells (DSSCs) with a mesoporous network of interconnected TiO₂ nanocrystals are currently attracting widespread scientific and technological interest as a high-efficiency and low-cost alternative to conventional inorganic photovoltaic devices.¹ The working principle of these devices is based on ultrafast electron-injection from a photoexcited dye into the conduction band of an oxide semiconductor and subsequent dye regeneration and hole transportation to the counter electrode. Although an impressive 10% light-to-electricity conversion efficiency has been obtained for photovoltaic devices with organic solvent-based electrolytes,² the presence of liquid electrolytes in such modules may result in some practical limitations of sealing and long-term operation. Therefore *p*-type semiconductor,³ hole-conductor,⁴ and polymeric materials incorporating triiodide/iodide as a redox couple⁵ have been attempted to substitute the liquid electrolytes for solid-state DSSCs.

Recently, growing attention has been paid to room-temperature ionic liquids (RTILs) especially those with 1,3-dialkylimidazolium cations due to their favorable properties such as thermal stability, nonflammability, high ionic conductivity, negligible vapor pressure, and a possible wide electrochemical window.⁶ They have been used as an important source for iodide-based redox couple and as a solvent in DSSCs.⁷ Among the 1,3-dialkylimidazolium iodide compounds, 1-methyl-3-propylimidazolium iodide (MPII) has the lowest viscosity, and its liquid domain extends down to -55 °C.^{7e} Combination of RTILs with polymers^{7d,8} and low-molecular weight gelators^{7c,9} can produce quasi-solid-state materials that have been employed as electrolytes for electrochemical devices and highly selective separation membranes. Very recently, RTILs have been used as media for the formation and stabilization of metal nanoparticles that are recyclable catalysts for biphasic hydrogenation.¹⁰ Additionally, submicrometer-sized anatase and graphite particles can be dispersed in these high ionic strength media to form stable colloidal solutions.¹¹ These striking and significant observations have triggered our interest to explore the use of nanoparticles as "gelator" to solidify ionic liquid-based electrolytes. Herein we communicate preliminary results on the use of photochemically and electrochemically stable silica nanoparticles to gel MPII-based liquid electrolytes for high-efficiency nanocrystalline solar cells.

A screen-printed double layer of TiO₂ particles was used as photoelectrodes. A 10-μm thick film (average pore diameter: 22 nm) of 20-nm-sized TiO₂ particles was first printed on the fluorine-doped SnO₂-conducting glass electrode and further coated by a 4-μm-thick second layer of 400-nm light-scattering anatase particles (CCI, Japan). After sintering at 500 °C and cooling to 80 °C the TiO₂ electrodes were dye-coated by immersing them into a 0.3 mM solution of an amphiphilic dye [Ru(H₂dcbpy)(dnbpy)(NCS)₂, where H₂dcbpy is 4,4'-dicarboxylic acid-2,2'-bipyridine and dnbpy is 4,4'-

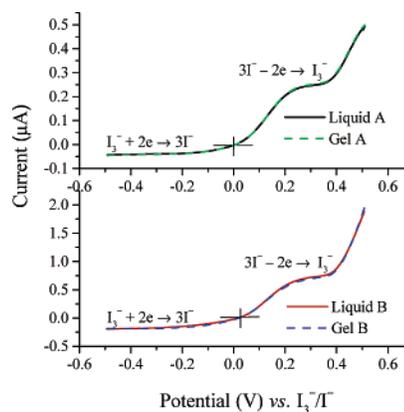


Figure 1. Steady-state voltammograms of MPII-based liquid and gel electrolytes with Pt ultramicroelectrode. Scan rate: 10 mV/s.

dinonyl-2,2'-bipyridine] referred to Z-907¹² in acetonitrile and *tert*-butyl alcohol (volume ratio: 1:1) at room temperature for 12 h and then assembled with thermally platinumized conducting glass electrodes.¹³ The electrodes were separated by a 35-μm-thick hot-melt ring (Bynel, DuPont) and sealed up by heating. Fumed silica nanoparticles (5 wt %; 3 vol %) with 12-nm primary particle size purchased from Degussa was mixed under sonication with MPII-based liquid electrolytes A or B to produce a stable gel. Liquid electrolytes A and B are composed of 0.5 M iodine and 0.45 M *N*-methyl-benzimidazole (NMBI) in either pure MPII or a mixture of MPII and 3-methoxypropionitrile (volume ratio: 13:7), respectively. The cell internal space was filled with liquid and gel electrolytes using a vacuum pump. As the used silica nanoparticles are much smaller than the pores of TiO₂ film, there is no problem for the quasi-solid-state electrolytes to enter the mesoporous film. The electrolyte-injecting hole made with a sand-ejecting drill on the counterelectrode glass substrate was sealed with a Bynel sheet and a thin glass cover by heating.

A double-compartment electrochemical cell equipped with a 5.0-μm radius (*a*) Pt ultramicroelectrode as working electrode, a Pt foil as counter electrode, and a Pt wire in electrolyte A as reference electrode was used to study the equilibrium potentials (E_{eq}) of the electrolytes and the influence of silica nanoparticles on the diffusion of triiodide and iodide at 25 °C. Figure 1 shows comparative steady-state voltammograms for liquid and gel electrolytes obtained at the scan rate of 10 mV/s. The apparent diffusion coefficient (D_{app}) values of iodide and triiodide (listed in Table 1) were calculated from the anodic and cathodic steady-state currents (I_{ss}) using the following equation.¹⁴

$$I_{ss} = 4nFDCA \quad (1)$$

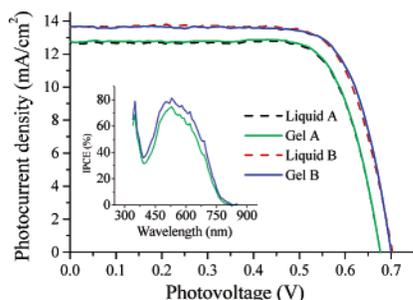
where n is the electron number per molecule, F is the Faraday

[†] Laboratory for Photonics and Interfaces.

[‡] NTERA Batteries.

Table 1. Device Efficiencies of DSSCs at Varied Sunlight Irradiation and Electrochemical Properties of MPII-Based Electrolytes

electrolyte	η (%) at different light intensities			E_{eq} (mV)	D_{app} (10^{-7} cm ² /s)	
	0.1 sun	0.5 sun	1.0 sun		I_3^-	I^-
liquid A	6.1	6.3	6.0	0	1.88	3.07
liquid B	7.0	7.2	7.0	26	8.21	14.1
gel A	6.3	6.4	6.1	0	1.89	3.09
gel B	6.9	7.1	7.0	26	8.21	13.9

**Figure 2.** Photocurrent density–voltage characteristics of DSSCs with MPII-based liquid and gel electrolytes at AM 1.5 (99.2 mW/cm²) illumination. The inset is IPCE spectra for DSSCs with MPII-based gel electrolytes. Cell active area: 0.152 cm².

constant, and C is the bulk concentration of electroactive species. Although the macroscopic viscosities of nanoparticle-gelled electrolytes are much higher than those of MPII-based liquid electrolytes, the corresponding voltammograms (Figure 1) are practically identical. This indicates that triiodide and iodide can freely move in the open channels of silica nanoparticle network. A similar phenomenon was also observed for the diffusion of electroactive species in some polymer gel systems.¹⁵ Even though the viscosity ratio of MPII^{7e} to acetonitrile^{7b} is 2162, the D_{app} of triiodide in acetonitrile is only 58 times larger than that in electrolytes A. This can be rationalized in terms of a Grotthus-like exchange mechanism and described by the Dahms–Ruff equation.¹⁶ The equilibrium potential of iodide/triiodide couple can be clearly determined from the potentials where the currents become zero by ultramicroelectrode technique. As shown in Figure 1 the equilibrium potential of liquid electrolyte B (or gel B) shifts positively 26 mV compared with that of liquid electrolyte A (or gel A). However, without considering the effect of activity coefficients, the calculated difference in E_{eq} is 19 mV by the Nernst equation.

Figure 2 presents the photocurrent density–voltage curves for DSSCs with MPII-based liquid and gel electrolytes at an irradiance of AM 1.5 sunlight, and the device efficiencies at different light intensities are listed in Table 1. Shown in the inset of Figure 2 are incident photon-to-current conversion efficiency (IPCE) curves. The maximum IPCE values are 76 and 80% at 540 nm for gel A and B, respectively, which are comparable to the value obtained for photovoltaic cells with traditional organic solvent-based liquid electrolytes. The short-circuit photocurrent density (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (FF) of the device with gel A are 12.75 mA/cm², 672 mV, and 0.709, respectively, yielding an overall energy conversion efficiency (η) of 6.1%, and for the cell with gel B the corresponding device parameters (J_{sc} , V_{oc} , FF, and η) are 13.67 mA/cm², 700 mV, 0.731, and 7.0%, respectively. This is the first time such a high efficiency was obtained for ionic liquid-based

quasi-solid-state DSSCs under full sunlight. The difference in device V_{oc} is consistent with the varied E_{eq} (Table 1) of two gel electrolytes as determined with ultramicroelectrode. Higher specific conductivity of gel B compared with that of gel A results in a better fill factor for the corresponding device. Almost identical results obtained for cells with the corresponding liquid electrolytes A and B indicate that the presence of silica nanoparticles has no adverse effect on the conversion efficiency, keeping a good consistency with diffusion coefficient test.

In summary, for the first time nanoparticles were used to solidify ionic liquids. These ionic liquid-based quasi-solid-state electrolytes were successfully employed for regenerative photoelectrochemical cells that yielded 7% efficiency at AM 1.5 sunlight in combination with an amphiphilic ruthenium polypyridyl photosensitizer. These quasi-solid-state electrolytes offer specific benefits over the ionic liquids. Thus, they will enable the fabrication of flexible, compact, laminated all solid-state devices free of leakage and available in varied geometries.

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