Quasi-Solid-State Dye-Sensitized Solar Cells based on Mesoporous Silica SBA-15 Framework Materials *

YANG Hong(杨红)[1], CHENG Yun-Fei(成云飞)[1], LI Fu-You(李富友)[1**], ZHOU Zhi-Guo(周治国)[1], YI Tao(易涛)[1], HUANG Chun-Hui(黄春辉)[1], JIA Neng-Qin(贾能勤)[2]

[1]*Institute of Advanced Material, Fudan University, Shanghai 200433*
[2]*Department of Chemistry, Fudan University, Shanghai 200433*

(Received 9 March 2005)

We develop a novel and efficient quasi-solid-state electrolyte based on the mesoporous silica SBA-15 as a framework material for a dye sensitized nanocrystalline TiO_2 solar cell. A solar energy-to-electricity conversion efficiency of 4.34% is achieved under AM 1.5 illumination (100 mW/cm^2).

PACS: 82. 47. Jk, 84. 60. Jt

Dye-sensitized nanocrystalline solar cells (DSSCs) have recently received considerable attention for their high-energy conversion efficiency and long-term stability.[1−3] High efficiency can be obtained using liquid electrolytes.[1,4] However, some practical problems such as leakage and evaporation of organic solvent may be the serious obstacles. This enables new electrolytes to be candidates for the DSSCs. Pure p-type semiconductors[5,6] and hole transport organic materials[7] have been reported to substitute the liquid electrolytes, whereas some problems such as low hole mobilities need to be solved.

Most of the quasi-solid-state electrolytes are based on room-temperature ionic liquids (RTILs). RTILs are used as an important iodide source and a solvent in DSSCs, for their unique physicochemical properties such as a high thermal stability, negligible vapour pressure, and relatively high ionic conductivity.[8,9] In RTIL-based quasi-solid electrolytes, a framework material is an important component, and some polymers,[10] gelators[11] and nanoparticles[12] have been introduced to solidify the liquid electrolyte. For their pore structures (2–50 nm) and large surface area, mesoporous materials may solidify liquid electrolytes and provide favourable channels for the triiodide/iodide diffusion. In this Letter, we describe, for the first time to our knowledge, a novel quasi-solid-state DSSC with a high energy conversion efficiency of 4.34% by using the mesoporous SiO_2 material SBA-15 as the framework material.

The mesoporous SiO_2 material SBA-15 with the pore diameter of 5 nm was prepared according to the reported process.[13] SBA-15 (in 3 wt.% of ionic liquid electrolyte) was mixed under sonication with an ionic liquid electrolyte (donated liquid electrolyte) to produce a stable gel electrolyte (donated gel electrolyte). The ionic liquid electrolyte was composed of 0.5-M I_2 and 0.45-M 1-methylbenzimidazole in 1-methyl-3-propyl-imidazolium iodide (MPII). Steady-state voltammograms of these ionic liquid and gel electrolytes are shown in Fig. 1. The curves of these two electrolytes are similar especially in the anodic and cathodic steady-state currents I_{ss}. The apparent diffusion coefficients D_{app} of iodide and triiodide (see Table 1) can be calculated according to the following equation:[14]

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

where n is the charge number per molecule, a is the microelectrode radius, F is the Faraday constant, and c is the bulk concentration of the electroactive species. The equilibrium potential of iodide/triiodide coupler can be clearly determined from the potentials when the currents become zero by ultramicroelectrode technique. It can be seen from Table 1 that the diffusion coefficient values of triiodide D_{app} (I_3^-) and iodide D_{app} (I^-) for the liquid electrolyte are similar to those of the gel electrolyte. A similar phenomenon was also observed in some fumed silica gel systems.[12] These facts indicate that triiodide and iodide can freely move in the open channels of the SBA-15 network.[15]

Table 1. The electrochemical properties of the ionic liquid and gel electrolytes.

Sample	D_{app} (I^-) $(10^{-7}\,\mathrm{cm}^2/\mathrm{s})$	D_{app} (I_3^-) $(10^{-7}\,\mathrm{cm}^2/\mathrm{s})$
Liquid electrolyte	0.76	1.35
Gel electrolyte	0.50	1.17

In dye-sensitized solar cells, the electron exchange should occur between I^-, I_3^-, and polyiodides (I_{2n+1}^-) through chemical bond exchanges.[16] To indicate clearly the electron exchange process, the Raman spectra of the ionic liquid and gel electrolytes were investigated and are shown in Fig. 2. The two bands around 110 and 150 cm^{-1} assigned to the symmetric

* Supported by the National High Technology Program of China under Grant No 2002AA302403, and the Shanghai Science and Technology Committee under Grant Nos 03QB14006, 03DZ12031 and 0216nm040.

** To whom correspondence should be addressed. E-mail: fyli@fudan.edu.cn

©2005 Chinese Physical Society and IOP Publishing Ltd

stretch of I_3^- and I_5^-, respectively, were observed apparently in both the electrolytes.[15] The band around 210 cm^{-1} attributed to the vibration of molecular iodine (I_2) was too small to be observed.[16] The Raman spectra analysis suggested that the charge transfer mainly belongs to the Grotthuss-type mechanism, that is, the electrons hopping and polyiodides bond exchange occur simultaneously.[17] This fact favored to the effective conductance of the electrolytes in the presence of SBA-15.

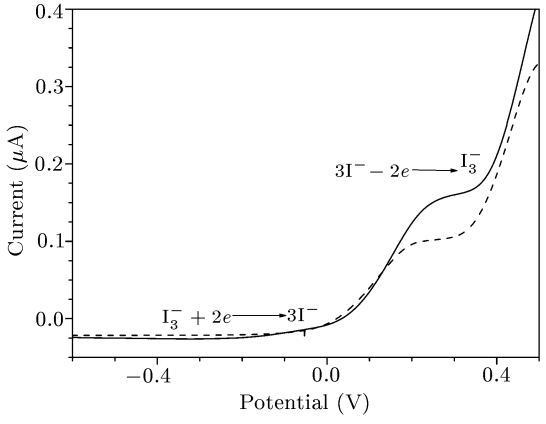


Fig. 1. Steady-state voltammograms of the ionic liquid (solid) and gel (dashed) electrolytes with Pt ultramicroelectrode for the scanning rate of 10 mV/s.

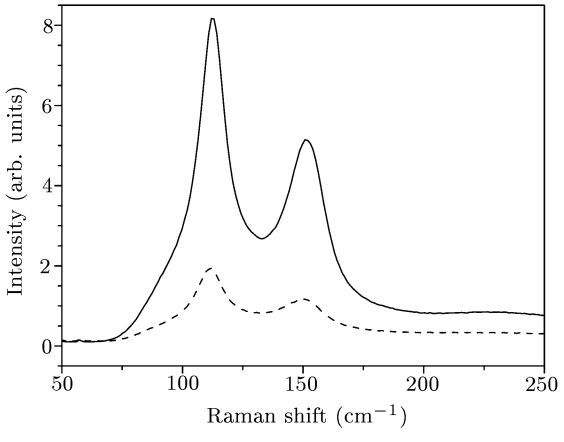


Fig. 2. Raman spectra of the ionic electrolyte (solid) and gel electrolyte (dashed).

The 9 μm-thick TiO_2 films were prepared according to the literature[1] and sensitized by N_3 dye. Photovoltaic measurements were carried out with a sandwiched cell consisting of the dye-coated TiO_2 electrode as a working electrode, a Pt counter electrode, a polyethylene film spacer, and an electrolyte. Figure 3 shows the photocurrent-voltage curves for DSSCs with an ionic liquid and gel electrolytes under AM 1.5 illumination (100 mW/cm^2). Compared with the ionic-liquid-electrolyte-based solar cell, a decrease (1.6 mA/cm^2) of the short circuit photocurrent density and slight increases of the open circuit voltage (V_{OC}) and the fill factor (FF) were observed for the gel-electrolyte-based solar cell. As a result, the energy conversion efficiency (η = 4.34%) of the gel-electrolyte-based solar cell are close to that (η = 4.65%) of the ionic-liquid-electrolyte-based solar cell (see Table 2).

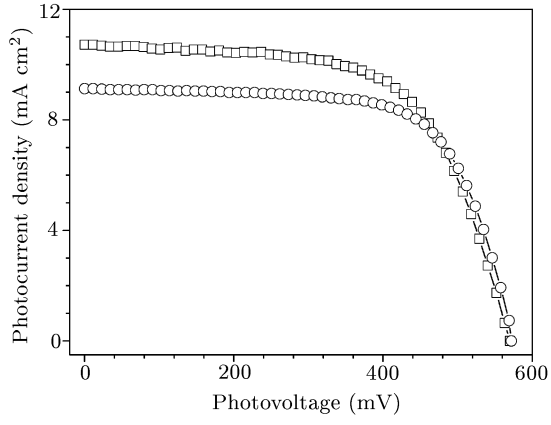


Fig. 3. Photocurrent-voltage curves of the cells based on the ionic liquid (squares) and gel electrolyte (circles) under AM 1.5 irradiation.

Table 2. The parameters of the cells based on the ionic liquid and gel electrolytes under AM 1.5 irradiation (cell active area: 0.188 cm^2).

Electrolyte	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF (%)	η (%)
Liquid electrolyte	563.01	10.72	61.66	4.65
Gel electrolyte	569.00	9.13	66.90	4.34

The stabilities of these solar cells sealed with thermal adhesive films (surlyn 1702) were investigated. The energy conversion efficiency was measured once per two days after being stored under dark at room temperature. The conversion efficiencies of the gel-electrolyte-based solar cell were kept constant, but that of the ionic-liquid-electrolyte-based solar cell decreased to 70% after 700 h, indicating that the introduction of the mesoporous SBA-15 is beneficial to long stability of the solar cell.

In summary, we have developed a novel quasi-solid-state electrolyte by using mesoporous silica SBA-15 as the framework material. The energy conversion efficiency of this quasi-solid-state DSSC reaches 4.34%, and the stability of the cell is improved by the introduction of SBA-15.

References

[1] Nazeeruddin M K, Kay A, Rodicio I, Humphry-Baker R, Mueller E, Liska P, Vlachopoulos N and Grätzel M 1993 *J. Am. Chem. Soc.* **115** 6382

[2] Dai S Y, Wang K J 2003 *Chin. Phys. Lett.* **20** 953
Li B, Wang L G, Li J W and Qiu Y 2004 *Chin. Phys. Lett.* **21** 1391

[3] Wang Z S, Li F Y and Huang C H 2001 *J. Phys. Chem.* B **105** 9210
[4] Nakade S, Kambe S, Kitamura T, Wada Y and Yanagida S 2001 *J. Phys. Chem.* B **105** 9150
[5] O'Regan B and Schwartz D T 1998 *Chem. Mater.* **10** 1501
[6] Meng Q B, Takahashi K, Zhang X T, Sutanto I, Rao T N, Sato O and Fujishima A 2003 *Langmuir* **19** 3572
[7] Bach U, Lupo D, Comte P, Moser J E, Weissörtel F, Salbeck J, Spreitzer H and Grätzel M 1998 *Nature* **395** 583
[8] Dupont J, De Souze R F and Suarez P A Z 2002 *Chem. Rev.* **102** 3667
[9] Kubo W, Makimoto Y, Kitamura T, Wada Y and Yanagida S 2002 *Chem. Lett.* bf 31 948
[10] Makimoto Y, Wada Y, Kitamura T, Shigaki K., Inoue T, Ikeda M and Yanagida S 2001 *Bull. Chem. Soc. Jpn.* **74** 387
Stathatos E, Lianos P, Lavrencic-Stangar U and Orel B 2002 *Adv. Mater.* **14** 354
[11] Kubo W, Kitamura T, Hanabusa K, Wada Y and Yanagida S 2002 *Chem. Commun.* 374
Murai S, Mikoshiba S, Sumino H, Kato T and Hayase S 2003 *Chem. Commun.* 1534
[12] Wang P, Zakeeruddin S M, Comte P, Exnar I and Grätzel M 2003 *J. Am. Chem. Soc.* **125** 1166
Xue B F, Wang H X, Hu Y S, Li H, Wang Z X, Meng Q B, Huang X J, Chen L Q, Sato O and Fujishima A 2004 *Chin. Phys. Lett.* **21** 1828
[13] Zhao D Y, Feng J L, Huo Q S, Melosh N, Fredrickson G H, Chmelka B F and Stucky G D 1998 *Science* **279** 548
[14] Quinn B M, Ding Z, Moulton R and Bard A J 2002 *Langmuir* **18** 1734
[15] Kubo W, Murakoshi K, Kitamura T, Yoshida S, Haruki M, Hanabusa K, Shirai H, Wada Y and Yanagida S 2001 *J. Phys. Chem.* B **105** 12809
[16] Papageorgiou N, Athanassov Y, Armand M, Bonhôte P, Pettersson H, Azam A and Grätzel M 1996 *J. Electrochem. Soc.* **143** 3099
[17] Ryuji K and Masayoshi W 2003 *Chem. Commun.* 330