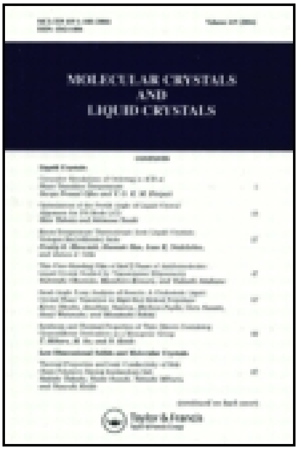

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

# Photovoltaic Properties and Preparations of Dye-Sensitized Solar Cells Using Solid-State Polymer Electrolytes

Mi-Ra Kim [a], Sung-Ho Jin [a], Sung-Hae Park [b], Hyun-Jeong Lee [b], Eun-Hee Kang [b] & Jin-Kook Lee [b]
[a] Center for Plastic Information System, Pusan National University, Busan, Korea
[b] Department of Polymer Science and Engineering, Pusan National University, Busan, Korea

Version of record first published: 20 Aug 2006

To cite this article: Mi-Ra Kim, Sung-Ho Jin, Sung-Hae Park, Hyun-Jeong Lee, Eun-Hee Kang & Jin-Kook Lee (2006): Photovoltaic Properties and Preparations of Dye-Sensitized Solar Cells Using Solid-State Polymer Electrolytes, Molecular Crystals and Liquid Crystals, 444:1, 233-239

To link to this article: http://dx.doi.org/10.1080/15421400500365037

*Mol. Cryst. Liq. Cryst.*, Vol. 444, pp. 233–239, 2006
Copyright © Taylor & Francis LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500365037

# Photovoltaic Properties and Preparations of Dye-Sensitized Solar Cells Using Solid-State Polymer Electrolytes

**Mi-Ra Kim**
**Sung-Ho Jin**
Center for Plastic Information System, Pusan National University, Busan, Korea

**Sung-Hae Park**
**Hyun-Jeong Lee**
**Eun-Hee Kang**
**Jin-Kook Lee**
Department of Polymer Science and Engineering, Pusan National University, Busan, Korea

*Solid-state dye-sensitized solar cells were fabricated using a polymer matrix in polymer electrolyte in the purpose of the improvement of the durability in the dye-sensitized solar cells. In these dye-sensitized solar cells, the polymer electrolyte consisting of* $I_2$*, LiI, ionic liquid, ethylene carbonate/propylene carbonate (EC/PC) and polymer matrix was casted onto* $TiO_2$ *electrode impregnated Ruthenium dye as a photosensitizer. Photovoltaic properties of dye-sensitized solar cells using polymer matrix (PMMA, PEG, or PAN) in solid-state polymer electrolytes were investigated. Comparing photovoltaic effects of cells using hole conducting polymers (BE or 6P) instead of polymer matrix, we have investigated the availability of the solid-state polymer electrolyte in dye-sensitized solar cells.*

**Keywords:** hole conducting polymers; photovoltaic properties; polymer electrolyte; solid-state dye-sensitized solar cell

## INTRODUCTION

Dye-sensitized solar cell (DSSC) constructed using dye molecules, nanocrystalline metal oxides and organic liquid electrolytes have

---

This work was supported by Korea Science and Engineering Foundations (KOSEF) Grant R03-2004-000-10024-0 (2004) and Brain Korea 21.

Address correspondence to Mi-Ra Kim, Center for Plastic Information System, Pusan National University, Busan 609-735, Korea. E-mail: mrkim2@pusan.ac.kr

attractive features of high energy conversion efficiency and low production cost [1,2]. However, presence of traditional organic liquid electrolytes in such cells has some problems such as a less long-term stability and a need for hermetic sealing. Moreover, the electrolyte loss caused by the leakage and volatility of the electrolyte solution has been pointed out to be one of the major problems, which stays the durability of the dye-sensitized solar cell low. Solid-state dye-sensitized solar cell did not need hermetic sealing, but energy conversion efficiency of them decreased in comparison to those of dye-sensitized solar cell with traditional organic liquid electrolytes. Various approaches to these problems have been tried so far. These approaches include employing a gel-type electrolyte to minimize the loss [3–7].

In this study, the photovoltaic effects and the preparations of the solid-state dye-sensitized solar cells based on polymer matrix as polymer electrolytes are investigated. The energy conversion efficiency ($\eta$) of the solar cell device was calculated by the values of open-circuit voltage ($V_{oc}$) and short-circuit current ($J_{sc}$), and fill factor (FF) was calculated by the values of $V_{oc}$, $J_{sc}$, and $\eta$. In additional, we have compared the photovoltaic effects as redox reaction in the polymer electrolytes using various polymer matrices and hole conducting copolymers.

## EXPERIMENTAL

Polyacrylonitrile (PAN, $M_w = 22{,}600$), polymethylmethacrylate (PMMA, $M_w = 15{,}000$), lithium iodide (LiI), iodine ($I_2$), 1-ethyl-3-methylimidazolium chloride, propylene carbonate (PC) and ethylene carbonate (EC) were purchased from Sigma Aldrich company and used as supplied without the purification. Polyethylene glycol (PEG, $M_w = 7{,}500$) and acetonitrile was purchased from Junsei chemical Co., Ltd. Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(N,N′-(4-butylphenyl-1,1′-biphenylene-4,4′-diamine))] (BE, $M_w = 20{,}000$) and poly[(9,9-dihexyl fluorenyl-2,7-diyl)-co-(bithiophene)] (6P, $M_w = 15{,}000$) were purchased from American Dye Source, Inc. *Cis*-di(thiocyanato)- N,N-bis(2,2′- bypyridil-4,4′-dicarboxylic acid) ruthenium (II) complex (Ru-dye), Fluorine-doped $SnO_2$-layered (FTO) glass (15 ohm/sq), Pt-Catalyst T/SP, and Ti-Nanoxide HT were purchased from Solaronix SA and used as supplied.

We have prepared the dye-sensitized solar cell devices, using Ruthenium dye (Ru-dye) as a photosensitizer, sandwiched with $TiO_2$ deposited and Pt-coated electrode as two electrodes. The structure of the dye-sensitized solar cell device was shown in Figure 1. The dye-sensitized solar cell was fabricated as following process; a volume of ca. 10 μl/cm$^2$ of the transparent pastes (Ti-Nanoxide HT) was

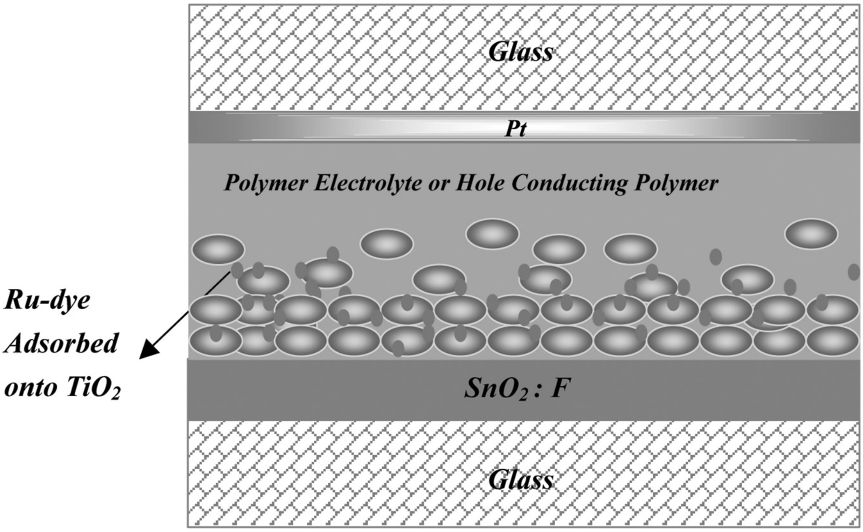

**FIGURE 1** The structure of the dye-sensitized solar cell device.

spreaded on FTO glass by the doctor blade method. After heating up the FTO glass spreaded $TiO_2$ nanoparticle to ca. 100°C for about half an hour, the sintering process was completed and the $TiO_2$ deposited- electrode was cooled down from 100°C to ca. 60°C as the controlled cooling rate (3°C/min) to avoid cracking of the glass. The sensitizer *cis*-di(thiocyanato)-N,N-bis(2,2′-bypyridil-4,4′-dicarboxylic acid) ruthenium (II) complex (Ru-dye) was dissolved in pure ethanol in a concentration of 20 mg of dye per 100 ml of solution. $TiO_2$ electrode deposited by the doctor blade method and sintering process was dipped in this solution for 24 hours. The electrolyte solution was casted onto $TiO_2$ electrode impregnated dye-sensitizer and then was dried at 60°C for 2 hours. In Table 1, the compositions of the contents in electrolyte

**TABLE 1** Compositions of Contents of Polymer Electrolyte Solutions in Dye-Sensitized Solar Cells

| Polymers[1] | LiI | $I_2$ | PC/EC[2] | Ionic Liquid[3] |
|---|---|---|---|---|
| 40 mg | 12 mg | 12 mg | 0.16 ml/0.04 ml | 40 mg |

[1] PEG, PMMA, PAN, BE, or 6P.

[2] PC: propylene carbonate; EC: ethylene carbonate.

[3] 1-ethyl-3-methylimidazolium chloride.

Solvent: 1 ml of acetonitrile/1ml of chlorobenzene.

solutions were listed. LiI, $I_2$ and polymers were dissolved in acetonitle and chlorobenezene solution, and then EC and PC as a plasticizer were added into this solution. Polymer electrolytes were usually consisted of 0.5 M of LiI, 0.25 M of $I_2$, and 1.5 M of ionic liquid in acetonitrile solution. Typically in dye-sensitized solar cells, an iodide/tri-iodide ($I^-/I_3^-$) redox couple dissolved in organic solvents has been used. However, use of the volatile organic solvents caused deterioration of the cell by evaporation of the solvent over the prolonged use. Ionic liquids were collected due to be the most appropriate solvents to solve such problems.

The dye-sensitized solar cells were assembled by fixing a $TiO_2$ electrode casted with polymer electrolyte and a Pt counter electrode.

The thickness of the $TiO_2$ layer and polymer electrolyte layer were examined with a scanning electron microscope (SEM) and Alpha-step IQ. UV-visible absorption spectra were recorded on UVIKON 860 spectrophotometer. Photo-electrochemical measurements were performed using an AM 1.5 solar simulator furnished with ARC Lamp power supply, and the photointensity was 100 mW/cm$^2$. The measurements were made on open cell, and the electrode size was 100 mm$^2$. The measurements were carried out four times and the mean was used as the results.

## RESULTS AND DISCUSSION

The UV-visible absorption spectra of $TiO_2$ deposited on FTO glass, $TiO_2$ impregnated Ru-dye sensitizers on FTO glass and Ru-dye in ethanol solution were shown in Figure 2. The absorption spectrum of $TiO_2$ impregnated Ru-dye sensitizers on FTO glass was appeared broadly the maximum at 375 and 527 nm. The absorption spectrum of Ru-dye in ethanol solution was also appeared broadly the maximum at 380 and 530 nm. This solution was prepared by adding 1 mg of Ru-dye into 5 ml of pure ethanol solution. After Ru-dye absorbing onto $TiO_2$ deposited glass, the absorbance peaks and intensity of UV-visible absorption spectra had not been mostly changed. Moreover, only $TiO_2$ deposited on FTO glass did not absorb the light in the region of the visible light.

The I-V curves of dye-sensitized solar cells compared with different polymer electrolytes in the illumination were shown in Figure 3, and theirs characteristics were summarized in Table 2. The thickness of the cell were measured about 6–9 µm of $TiO_2$ deposited layer and 3 µm of polymer electrolyte layer by SEM and Alpha-step IQ, respectively. The photovoltaic effect of the solar cell device was measured by solar simulator under 100 mW/cm$^2$ AM 1.5. The photovoltaic

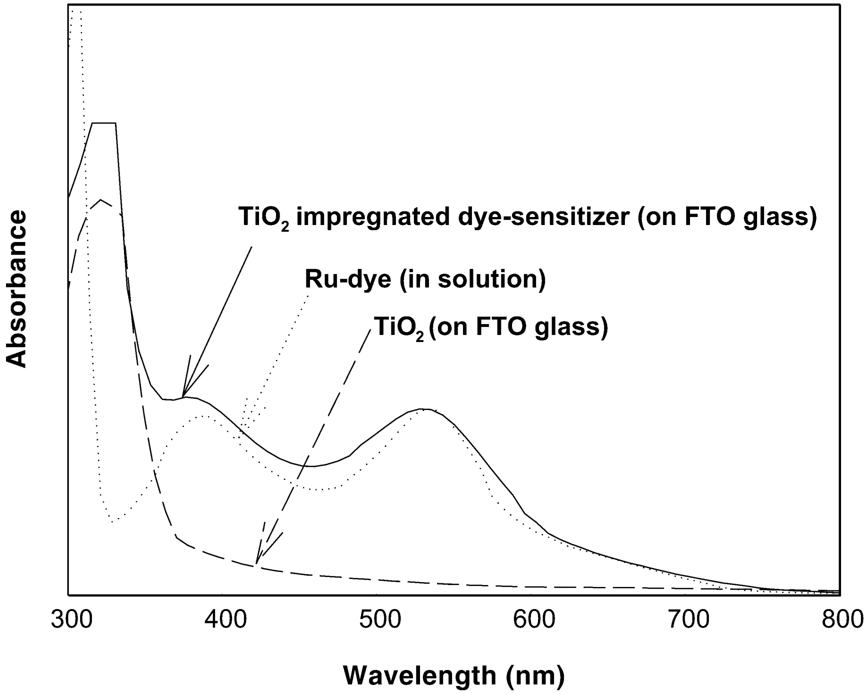

**FIGURE 2** UV-vis spectra of $TiO_2$ impregnated dye-sensitizers on FTO glass (solid line), Ru dye in ethanol solution (dotted line), $TiO_2$ on FTO glass (dashed line).

parameters of the cells such as open circuit voltage ($V_{oc}$), short circuit current ($J_{sc}$), fill factor (FF) and conversion efficiency ($\eta$) were calculated from the analysis of I-V characteristics. In case of using hole conducting polymers (6P and BE), the open-circuit voltage ($V_{oc}$) is 0.48 and 0.53 V. The short-circuit current ($J_{sc}$) is 0.40 and 0.37 mA/cm$^2$ and the fill factor (FF) is about 0.42 and 0.40, respectively. In using polymer matrix (PMMA, PEG and PAN), the open-circuit voltage ($V_{oc}$) is 0.58–0.72 V. The short-circuit current ($J_{sc}$) is 0.51–0.70 mA/cm$^2$ and the fill factor (FF) is about 0.39–0.49, respectively. This result was due to availability of electron transfer by the contact surface between polymer electrolytes and $TiO_2$ electrode, or polymer electrolytes and Pt counter electrode. The conversion efficiency ($\eta$) of cells using polymer matrix (ca. 0. 2%) were shown over two times of value at its of cells using hole conducting polymers (ca. 0.08%). In hole conducting polymers, a large amount of holes can be transferred within polymer electrolyte, however, due to incomplete $I^-/I_3^-$ redox

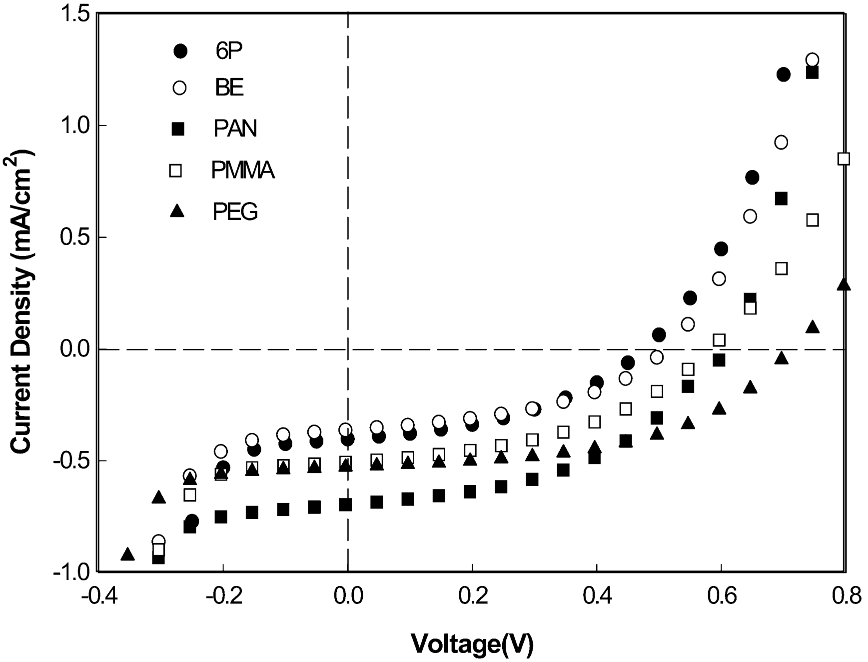

**FIGURE 3** I-V curves of dye-sensitized solar cells using solid-state polymer electrolyte in illumination at 100 mW/cm$^2$.

reaction by the electron exchange between $I_2$ and $Li^+I^-$ in solid-state polymer electrolyte, the conversion efficiency of its using hole conducting polymer had lower value than that in polymer matrix. The role of polymer matrix in dye-sensitized solar cells is very important in order to increase power conversion efficiency of cells in solid-state polymer electrolyte. Polymer matrix is helpful for the electron movement in solid-state polymer electrolyte by supporting an iodide/tri-iodide

**TABLE 2** $V_{oc}$, $J_{sc}$, FF, $\eta$ Data of Dye-Sensitized Solar Cells Using various Polymer Electrolytes

| | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF | $\eta$ (%) |
|---|---|---|---|---|
| 6P | 0.48 | 0.40 | 0.42 | 0.082 |
| BE | 0.53 | 0.37 | 0.40 | 0.085 |
| PMMA | 0.58 | 0.51 | 0.44 | 0.132 |
| PEG | 0.72 | 0.53 | 0.49 | 0.195 |
| PAN | 0.61 | 0.70 | 0.39 | 0.196 |

($I^-/I_3^-$) redox couple, therefore, the redox reaction was well occurred in solid-state polymer electrolyte of the solar cell.

## CONCLUSIONS

Solid-state dye-sensitized solar cells were successfully prepared by using polymer matrix or hole conducting polymers. In case of using hole conducting polymers as polymer electrolyte, $V_{oc}$, $J_{sc}$, FF, and $\eta$ measured by Solar simulator were shown mostly lower value than those in polymer matrix, due to incomplete $I^-/I_3^-$ redox reaction of the hole conducting polymers in solid-state polymer electrolyte. The polymer electrolyte containing polymer matrix was more available than that containing only hole conducting polymer in solid-state dye-sensitized solar cells.

## REFERENCES

[1] O'Regan, B. & Grätzel, M. (1991). *Nature*, *353*, 737.

[2] Nazeeruddin, M. K., Kay, A., Rodico, I., Humphry-Baker, R., Muller, E., Liska, P., Valachopoulos, N., & Grätzel, M. (1993). *J. Am. Chem. Soc.*, *115*, 6382.

[3] Cao, F., Oskam, G., & Searson, C. (1995). *J. Phys. Chem.*, *99*, 17071.

[4] Kubo, W., Murakoshi, K., Kitamura, T., Wada, Y., Hanabusa, K., Shirai, H., & Yanagida, S. (1998). *Chem. Lett.*, 1241.

[5] Matsumoto, M., Miyazaki, H., Matsuhiro, K., Kumashiro, Y., & Takaoka, Y. (1996). *Solid State Ionics*, *89*, 263.

[6] Mikoshiba, S., Sumino, H., Yonetsu, M., & Hayase, S. (2000). Preprint of 16th European Photovoltaic Solar Energy Conference and Exhibition, Glasgow.

[7] Tennakone, K., Kumara, G. R. R. A., Kumarasinghe, A. R., Wijayantha, K. G. U., & Sirimanne, P. M. (1995). *Semicond. Sci. Technol.*, *10*, 1689.