

고분자 전해질을 이용한 염료감응형 태양전지의 제작과 광기전 특성

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

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

Abstract : Solid-state dye-sensitized solar cells were fabricated using a polymer matrix in 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 I₂, LiI, ionic liquid, ethylene carbonate/propylene carbonate and polymer matrix was casted onto TiO₂ electrode impregnated Ruthenium complex dye as a photosensitizer. Photovoltaic properties of solid-state dye-sensitized solar cells using polymer matrix (PMMA, PEG, or PAN) were investigated. Comparing photovoltaic effects of cells using hole conducting polymers (BE or 6P) instead of polymer matrix, we investigated the availability of the solid-state polymer electrolyte in dye-sensitized solar cells.

1. Introduction

Dye-sensitized solar cells constructed using dye molecules, nanocrystalline metal oxides and organic liquid electrolytes have 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 power 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 ⁽³⁻⁵⁾.

In this study, the preparations and the photovoltaic effects of the dye-sensitized solar cells based on polymer matrix as solid-state polymer electrolytes are investigated. We have compared the photovoltaic effects as redox reaction in the polymer electrolytes using various polymer matrices and hole conducting copolymers.

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2. Experimental

2.1 Materials

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'-bipyridil-4,4'-dicarboxylic acid) ruthenium (II) complex (N3 dye), Fluorine-doped SnO_2 -layered (FTO) glass (15ohm/sq), Pt-Catalyst T/SP, and Ti-Nanoxide HT were purchased from Solaronix SA and used as supplied.

2.2 Fabrications of Dye-Sensitized Solar Cell Devices

We have prepared the dye-sensitized solar cell devices, using Ruthenium dye (N3 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 is shown in Figure 1. The dye-sensitized solar cell was fabricated as following process; a volume of ca. $10\mu l/cm^2$ of the transparent pastes (Ti-Nanoxide HT) was spreaded on FTO glass by the doctor blade method. After heating up the FTO glass spreaded TiO_2 nanoparticle to ca. $100\text{ }^\circ C$ for about half an hour, the sintering process was completed and the TiO_2 deposited- electrode was cooled down from $100\text{ }^\circ C$ to ca. $60\text{ }^\circ C$ as the controlled cooling rate ($3\text{ }^\circ C/min$) to avoid cracking of the glass. The N3 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 $60\text{ }^\circ C$ for 2 hours. Polymer electrolytes were usually consisted of LiI, I_2 , and a 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.

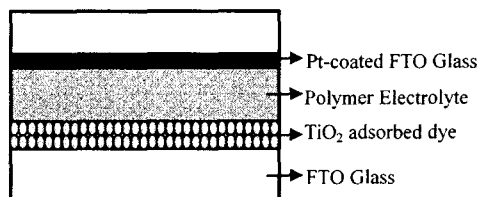


Figure 1. The structure of the dye-sensitized solar cell device.

2.3 Measurements

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. Photoelectrochemical measurements were performed using an AM 1.5 solar simulator furnished with ARC Lamp power supply, and the photointensity was 100 mW/cm^2 .

3. Results and Discussion

The UV-visible absorption spectra of TiO_2 deposited on FTO glass, TiO_2 impregnated N3 dye sensitizers on FTO glass and N3 dye in ethanol solution are shown in Figure 2. The absorption spectrum of TiO_2 impregnated N3 dye sensitizers on FTO glass was appeared broadly the maximum at 375 and 527 nm. The absorption spectrum of N3 dye in ethanol solution was also appeared broadly the maximum at 380 and 530 nm. This solution was prepared by adding 1mg of N3 dye into 5 ml of pure ethanol solution. After N3 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.

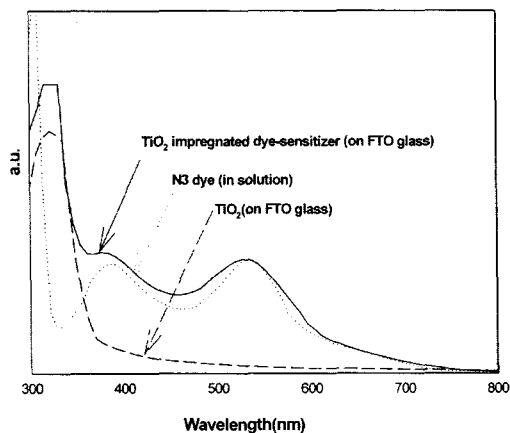


Figure 2. UV-vis spectra of TiO₂ impregnated dye-sensitizer on FTO glass, N3 dye in ethanol solution, TiO₂ on FTO glass.

The I-V curves of dye-sensitized solar cells compared with different polymer electrolytes in the illumination are shown in Figure 3, and their characteristics are summarized in Table 1. The thickness of the cell were measured about 6-9 μm of TiO₂ deposited layer and 3 μm of polymer electrolyte layer by SEM and Alpha-step IQ, respectively. The photovoltaic effect of the dye-sensitized solar cell device was measured by solar simulator under 100 mW/cm^2 at AM 1.5. The photovoltaic parameters of the cells such as open circuit voltage (Voc), short circuit current (Jsc), fill factor (FF) and power conversion efficiency were calculated from the analysis of I-V characteristics. In case of using hole conducting polymers (6P and BE), the open-circuit voltage (Voc) is 0.48 and 0.53 V. The short-circuit current (Jsc) 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 (Voc) is 0.58 - 0.72 V. The short-circuit current (Jsc) 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 TiO₂ electrode, or polymer electrolytes and Pt counter electrode. The power conversion efficiency 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 reaction by the electron exchange between I_2 and Li^+T^- 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 (I/I_3^-) redox couple, therefore, the redox reaction was well occurred in solid-state polymer electrolyte of the solar cell.

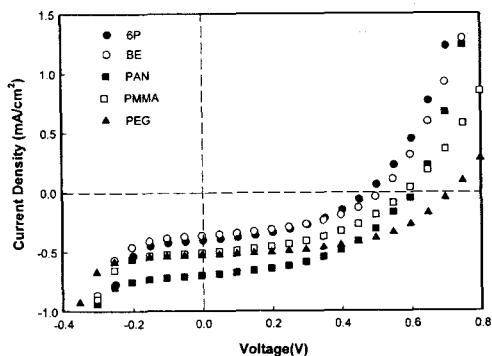


Figure 3. I-V curves of dye-sensitized solar cell devices using various polymer matrix or hole conducting polymers in illumination at 100 mW/cm^2 .

Table 1. Photovoltaic performances of dye-sensitized solar cell devices using various polymer electrolytes

	Voc (V)	Jsc (mA/cm^2)	FF	Eff. (%)
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

4. Conclusion

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, Voc, Jsc, FF, and power conversion efficiency 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.

Acknowledgement

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) R03-2004-000-10024-0 (2004) and the Ministry of Information & Communications, Korea, under the Information Technology Research Center (ITRC) Support Program.

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