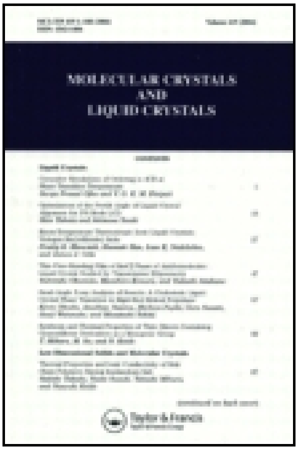

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Photovoltaic Properties of Dye-Sensitized Solar Cells using Metallophthalocyanines with Poly(ethylene glycol) Electrolytes

Jin-Kook Lee [a], Sung-Il Jang [a] [b], Young-Geun Kim [a] [b], Young-Wook Jang [a] [b], Bo-Hwa Jeong [a], Ji-Un Kim [a], Ki-Suck Jung [a] & Mi-Ra Kim [a]

[a] Department of Polymer Science & Engineering, Pusan National University, Busan, Korea

[b] POLYCEN Co., LTD, Busan, Korea

Version of record first published: 22 Sep 2010

To cite this article: Jin-Kook Lee, Sung-Il Jang, Young-Geun Kim, Young-Wook Jang, Bo-Hwa Jeong, Ji-Un Kim, Ki-Suck Jung & Mi-Ra Kim (2008): Photovoltaic Properties of Dye-Sensitized Solar Cells using Metallophthalocyanines with Poly(ethylene glycol) Electrolytes, Molecular Crystals and Liquid Crystals, 491:1, 307-316

To link to this article: http://dx.doi.org/10.1080/15421400802331067

Mol. Cryst. Liq. Cryst., Vol. 491, pp. 307–316, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802331067

Photovoltaic Properties of Dye-Sensitized Solar Cells using Metallophthalocyanines with Poly(ethylene glycol) Electrolytes

Jin-Kook Lee[1], Sung-Il Jang[1,2], Young-Geun Kim[1,2], Young-Wook Jang[1,2], Bo-Hwa Jeong[1], Ji-Un Kim[1], Ki-Suck Jung[1], and Mi-Ra Kim[1]
[1]Department of Polymer Science & Engineering, Pusan National University, Busan, Korea
[2]POLYCEN Co., LTD, Busan, Korea

Dye-sensitized solar cells (DSSCs) were prepared with a poly(ethylene glycol) (PEG) electrolyte using various metallophthalocyanines (MPcs) as an additive. The DSSC device using MPcs has higher power conversion efficiency than that without MPcs, due to decrease of electron transfer distance by the interface adsorption between TiO_2 *film and PEG electrolyte. The best result on power conversion efficiency was 4.18% in DSSC device using InOHPc. The open-circuit voltage* (V_{oc}) *was 0.70 V, the short-circuit current density* (J_{sc}) *was 10.20 mA/cm*^{2}*, and the Fill Factor (FF) was 0.58. The addition of MPcs as an additive is useful to improve the performances of DSSC devices such as* V_{oc}, J_{sc}, *and power conversion efficiency.*

Keywords: dye-sensitized solar cells; meallophthalocyanine; photovoltaic performance; polymer electrolyte

1. INTRODUCTION

The dye-sensitized solar cells (DSSC) comprises a working electrode consisting of a nanoporous TiO_2 films modified with a dye-sensitizer, a platinum counter electrode, and an electrolyte in between two electrodes [1–5]. Enormous efforts have been concentrated on to improve

This research was supported by the Program for the Training of Graduate Students in Regional Innovation which was conducted by the Ministry of Commerce Industry and Energy of the Korean Government.

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

the power conversion efficiency through the optimization of DSSC cell structures and modification of material chemical structures [3,6,7]. For example, the study that follows is divided into three parts. The first describes studies of TiO_2 layer with different thickness [8]. The second study is chemical structure of dye and optical property. In the third part studies on electrolyte have developed by many research groups. Specially, the research on the chemical structure, morphology, optical and electrical properties of the electrolyte are some of the major ones dealing with in the design of high efficiency DSSCs. These approaches include employing a quasi-solid-state type electrolyte to minimize the loss and to obtain relatively high efficiency [9–12]. We proposed the idea of an introduction of various metallophthalocyanines (MPcs) as an additive into the electrolytes to increase the power conversion efficiency in DSSCs. The photovoltaic effects of the DSSC devices on various MPcs or metal-free phthalocyanine as additives into electrolytes were investigated.

Phthalocyanines (Pcs) are of enormous technological importance for the manufacture of blue and green pigments and as catalysts for removal of sulfur from crude oil [13–15]. Other areas of interest in a variety of high technology fields [16] – such as for use in semiconductor devices, photovoltaic and other types of solar cell, electrophotography, rectifying devices, molecular electronics, electrochromic display devices, photosensitizers and deodorants – have stimulated research into Pcs, particularly over the last decade. Several results concerning DSSCs using Pcs have been reported. But they were studies of DSSCs using Pc as a photosensitizer. These studies have shown that the power conversion efficiency of that DSSC at AM 1.5 illumination stayed at 0.47% [10] through the optical properties of Pcs such as the photostability, the intensive absorption in far-red/near-IR regine, and low probability of desorption from the semiconductor surface once adsorbed, etc [11]. However, the efficiency of these DSSCs was unsatisfactory compared to that using traditional ruthenium bipyridine complex dye due to low solubility of Pcs in most organic solvents.

In this study, we prepared the electrolytes by using various MPcs such as hydroxyindium (InOHPc), chloroindium (InClPc), hydroxygallium (GaOHPc), chlorogallium (GaClPc), copper (CuPc), or metal-free phthalocyanine (H_2Pc) with polymer matrix such as poly(ethylene glycol) (PEG), and their photovoltaic properties were investigated by solar simulator at AM 1.5. The purpose of this paper is two-fold: (1) we expect the increase of short circuit current density (J_{sc}) of the DSSC device by the introduction of the MPcs in the electrolyte, and (2) obtain the effects of the metals of Pcs on the property of the electrolyte with polymer matrix.

2. EXPERIMENTAL

2.1. Materials

Polyethylene glycol (PEG, $M_w = 20{,}000$), tetrabutylammonium iodide (TBAI), iodine (I_2), 1-propyl-3-methylimidazolium iodide (PMII), propylene carbonate (PC) and ethylene carbonate (EC) were purchased from Sigma Aldrich company and used as supplied without the purification. Fluorine-doped SnO_2-layered (FTO) glass (15ohm/sq), Pt-Catalyst T/SP, cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II)bis-tetrabutylammonium dye (N719 dye) and Ti-Nanoxide HT were purchased from Solaronix SA and used as supplied. Pcs such as InOHPc, InClPc, GaOHPc, GaClPc, CuPc, and H_2Pc were supplied from Phthalos Co.

2.2. Fabrications of DSSC devices

DSSC has been established, as described in the multilayer structure. The functional components are sandwiched between two FTO electrodes. A nanoporous TiO_2 film is deposited on the negative electrode. A dye-sensitizer is adsorbed and covalently bound on TiO_2 nanoparticles. The counter electrode consists of FTO with thermally deposited Pt. Finally, the space between the TiO_2/dye surface and counter electrode is filled with a polymer electrolyte that typically contains the I_3^-/I^- redox couple, which makes a convenient combination with TiO_2 and dye.

The working electrode was prepared as follows. The TiO_2 paste with 9 nm particle size was placed on an FTO glass by doctor blade method, followed by sintering at 120°C for about 40 min and at 450°C for about 60 min in air to give a TiO_2 electrode with an effective area of $0.49\,cm^2$, and a TiO_2 film thickness of 10 μm. The nanoporous TiO_2 electrode was dipped in dye solution that dye was dissolved in a concentration of 10 mg of N719 dye per 50 ml of absolute ethanol solution at room temperature over night. The dye adsorbed TiO_2 electrode was dipped in electrolyte solution at room temperature for 24 hours. The electrolyte are containing I_2, TBAI, PMII as an ionic liquid, EC/PC (4:1 as v/v), a polymer matrix such as PEG and MPc (PEG:MPc = 1:1 as w/w) as an additive in an organic solvent such as acetonitrile. Figure 1 shows the chemical structures of various MPcs used and the structure of DSSC device. After that, the electrolyte was casted onto electrolyte immersed dye adsorbed TiO_2 electrode and was dried at about 60°C for 2 hours to evaporate wholly the organic solvent.

The counter electrode was also prepared by similar method that TiO_2 film was coated. Pt paste was placed on an FTO glass by doctor

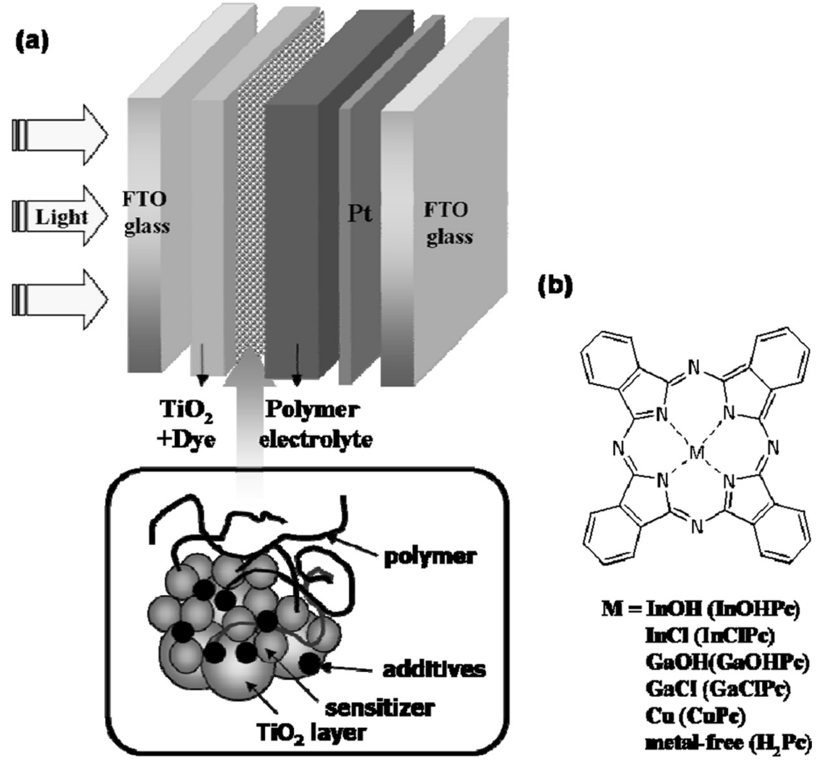

FIGURE 1 The structure of DSSC device (a) and the chemical structures of various metallophthalocyanines (b).

blade method, followed by sintering to at 100°C for about 10 min prior firing at 450°C for about 50 min in air. In assembling of DSSC devices, the working electrode and the counting electrode were clamped together.

2.3. Measurements

The thickness of TiO_2 layer and polymer electrolyte films were measured by using a scanning electron microscope (SEM) and Alpha-step IQ. The photovoltaic characteristics of DSSC devices were measured using a Solar Simulator (150 W simulator, PEC-L11, PEC-CELL) under a simulated solar light with an ARC Lamp power supply (AM 1.5, 100 mW/cm^2). The solar simulator was calibrated to Si reference cell verified. The active area of DSSC device measured by using a black mask was $0.49\,cm^2$.

The charge transfer resistances of the DSSCs were measured by alternating current (AC) impedance test using electrochemical impedance analyzer (Reference 600, GAMRY instruments). The EIS data were measured at 1–10^6 Hz of frequency range and room temperature, and fitted by Z-MAN software (WONATECH) and Echem analyst (GAMRY). The applied bias voltage and ac amplitude were set the open circuit voltage of cells and 50 mV, respectively.

3. RESULTS AND DISCUSSION

In general, the power conversion efficiency of DSSC is mainly dependent on the ionic conductivity of the polymer matrix. It was also demonstrated that the ionic conductivity of polymer electrolytes can be increased as the state and additives in electrolytes. It has been found that the ionic conductivity of the polymer electrolytes can be increased by incorporating appropriate species and amounts of suitable plasticizers or additives into them [17,18].

We have made of a DSSC device using PEG electrolyte without the MPcs in order to compare to the results with that using the MPcs with PEG electrolyte. The thicknesses of the cells were measured about 10 μm of TiO_2 deposited layer and 3 μm of PEG electrolyte film layer by SEM and Alpha-step IQ, respectively. The photocurrent-voltage curves of DSSC devices using PEG electrolyte with/without the MPcs are shown in Figure 2 and their photovoltaic characteristics are summarized in Table 1. In the DSSC devices without the MPcs, the open-circuit voltage (V_{oc}) is 0.75 V, and the short-circuit current density (J_{sc}) is 6.77 mA/cm^2. The fill factor is 0.54, and overall power conversion efficiency is 2.72% under 100 mA/cm^2 of light density.

When MPcs were added into the electrolytes, the distinctive results were obtained by the investigation of photovoltaic performances of various devices. Among DSSCs using various MPcs, the DSSC device using an InOHPc as an additive with PEG electrolyte showed the highest conversion efficiency. The efficiency was shown remarkably a high value when InOHPc was including in the PEG electrolyte to compared to the value of that without MPcs in the PEG electrolyte. Figure 3 displayed the comparison of characteristics with the important four parameters on DSSC devices employing polymer matrixes with and without Pcs (H_2Pc or InOHPc). Current-voltage characteristics showed a significant improvement in the photovoltaic performance upon the addition of InOHPc into PEG electrolytes, which has the highest value of 4.18% of power conversion efficiency. The power conversion efficiency increased about two times in comparison with the value of that without InOHPc, and three times when using H_2Pc

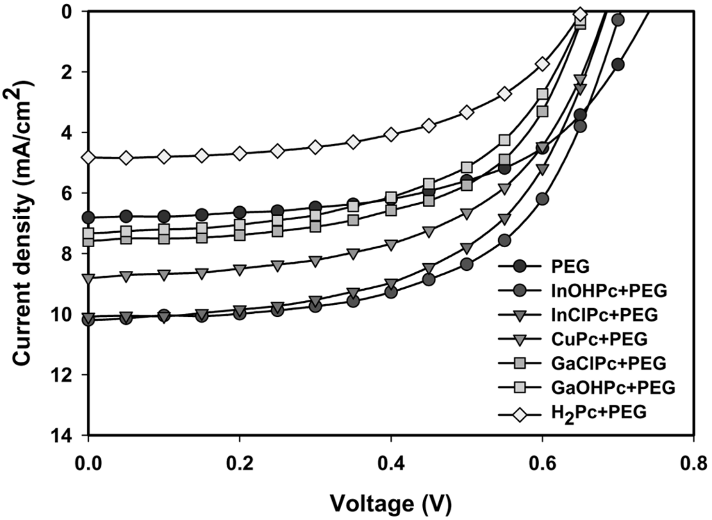

FIGURE 2 Photocurrent-voltage characteristic of the DSSC device compared with various metallophthalocyanines as additives using PEG as polymer matrix under AM 1.5; light density: 100 mA/cm^2; active area: 0.49 cm^2.

instead of InOHPc. The main reason for these results seemed to be caused by the delocalization of electrons among hydroxyl groups of InOHPc, ether groups of PEG and the surface of the TiO_2 layer. The introduction of the InOHPc as an additive helps the interface adsorption between the TiO_2 surface and the PEG electrolyte. It can attribute to bringing PEG matrixes closer to dye molecules oxidized by light. This conjugated structure can improve the electron transfer from polymer matrixes toward dyes adsorbed onto nanoporous TiO_2 layers.

TABLE 1 The Photovoltaic Characteristics of the DSSC Devices Compared with Various Phthalocyanines using PEG Electrolyte Under AM 1.5 Illumination

	Voc (V)	Jsc (mA/cm^2)	FF	Efficiency (%)
PEG	0.75	6.77	0.54	2.72
InOHPc + PEG	0.70	10.2	0.58	4.18
InClPc + PEG	0.69	10.1	0.56	3.89
GaOHPc + PEG	0.65	7.33	0.54	2.58
GaClPc + PEG	0.66	7.59	0.58	2.87
CuPc + PEG	0.69	8.81	0.55	3.33
H_2Pc + PEG	0.65	4.83	0.54	1.70

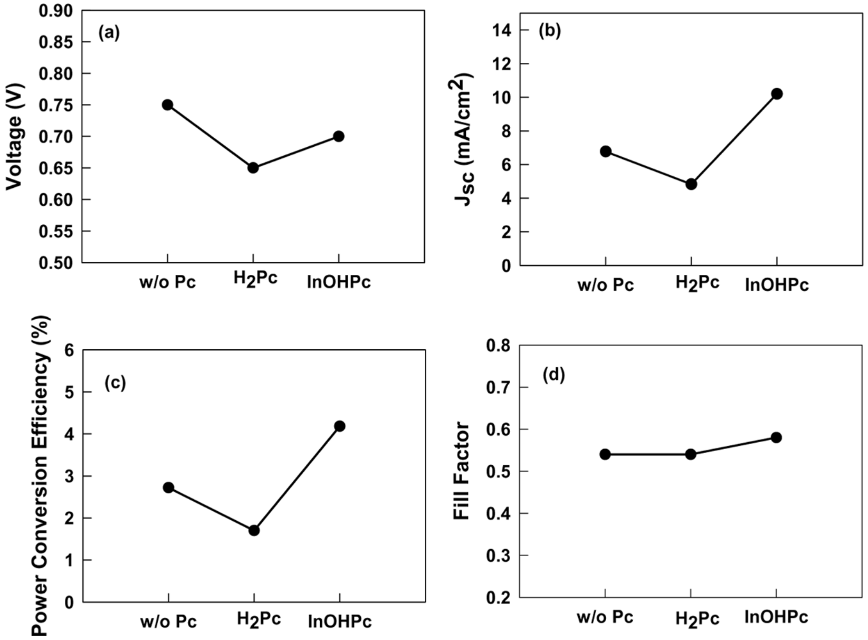

FIGURE 3 Comparison of photovoltaic properties of DSSC devices with the addition of InOHPc or H_2Pc as an additive into PEG electrolytes. DSSC devices were measured by solar simulator under AM 1.5; light intensity: $100\,mA/cm^2$; active area: $0.49\,cm^2$.

Consequently, the availability of electron transfer on the interface increased due to the decreasing of the electron transfer distance between TiO_2 layers and PEG electrolytes by the additives.

TABLE 2 The Series Resistances (R_S), the Charge Transfer Resistance of the Pt/electrolyte ($R1_{CT}$) and TiO_2/electrolyte ($R2_{CT}$) in the DSSC Devices Under AM 1.5 by the EIS Measurement

	R_S (Ω)	$R1_{CT}$ (Ω)	$R2_{CT}$ (Ω)
PEG	32.23	10.88	7.45
InOHPc + PEG	20.68	10.06	5.87
InClPc + PEG	20.15	10.09	6.45
GaOHPc + PEG	22.59	8.15	7.54
GaClPc + PEG	23.35	8.70	8.56
CuPc + PEG	20.22	10.54	6.89
H_2Pc + PEG	34.26	11.84	14.86

When using H_2Pc, on the contrary, the photocurrent of DSSC devices decreased with the addition of H_2Pc. The chemical nature of Pcs, such as well-stacked and intramolecular aggregation, resulted in low solubility in organic solvents and low miscibility with polymer matrixes. H_2Pc makes interrupts the contact or the interface adsorption between PEG electrolyte and dyes, or TiO_2 surfaces, on each other. The difficulty of interface adsorption resulted in the low electron transfer from the PEG electrolyte to oxidized dye molecules. This result shows the importance of the metal of the Pc as well as the Pc itself as an additive on DSSC characteristics.

To prove these results, the interfacial charge transfer resistances were investigated by the EIS measurement. The charge transfer resistances of the FTO/TiO_2/electrolyte/Pt/FTO cells are summarized in Table 2. Nyquist plots of the cells and the equivalent circuit are shown in Figure 4. The R_S, $R1_{CT}$ and $R2_{CT}$ are series resistance, the charge transfer resistance of Pt/electrolyte interface, and the charge transfer

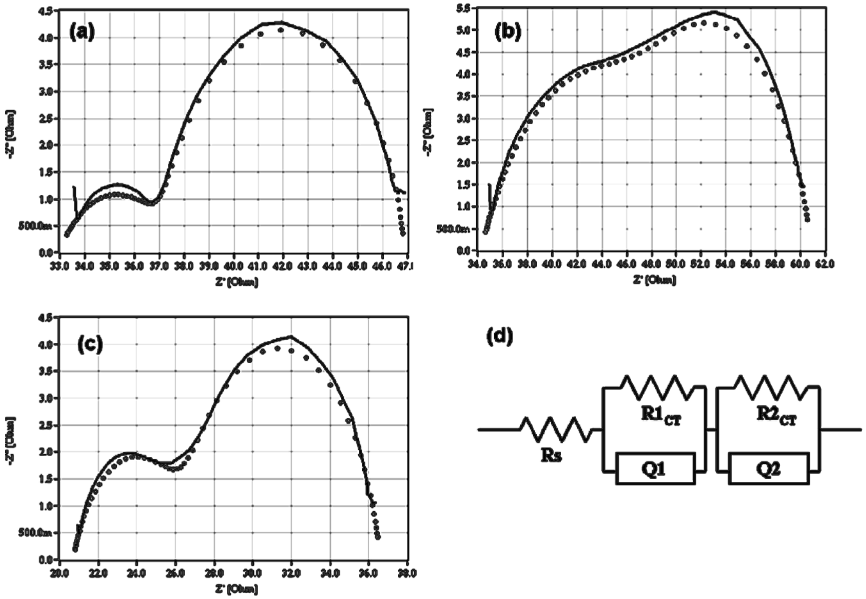

FIGURE 4 Nyquist plots of the FTO/TiO_2/electrolyte/Pt/FTO device using PEG electrolyte without Pcs (a), PEG electrolyte with H_2Pc (b), PEG electrolyte with InOHPc (c) (solid line: real data; dotted line: fitted data). The equivalent circuit of the device (d) (R_S: Series resistance, $R1_{CT}$: charge transfer resistance of Pt/electrolyte, $R2_{CT}$: charge transfer resistance of TiO_2/electrolyte, Q1 and Q2: constant phase element).

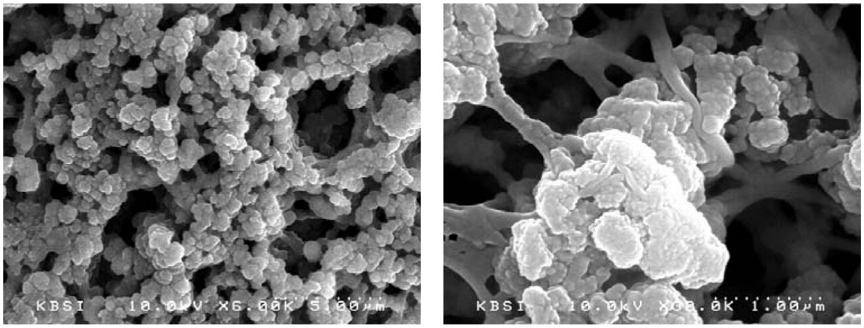

FIGURE 5 The SEM surface images of the working electrode; (left) electrolyte film using PEG and InOHPc onto TiO_2 electrode; (right) the extended image.

resistance of TiO_2/electrolyte interface, respectively. Low interfacial charge transfer resistance ($R2_{CT}$) resulting from small semi-circle was observed for the DSSC containing PEG with InOHPc, and the $R2_{CT}$ increased respectably by the introduction of H_2Pc instead of InOHPc. The $R2_{CT}$ of the DSSC using PEG without MPcs was also higher than that of the DSSC using PEG with InOHPc. These results showed that the charge transfer resistances between TiO_2 surface and PEG electrolyte decreased by the introduction of InOHPc, and the good electron transport resulting from the low resistance affected to the high value of the J_{sc}.

Figure 5 shows the SEM surface images of PEG electrolyte film using PEG with InOHPc. The PEG electrolyte film was fabricated by the casting method onto the nanocrystalline TiO_2 electrode adsorbed the N719 dyes, after 3 hours in the dry oven. We can confirm the nanopore-filled PEG electrolyte into TiO_2 layer and the morphology of the PEG in the electrolyte from the extended image.

4. CONCLUSION

The DSSC devices using various MPcs with PEG electrolyte were successfully fabricated and their photovoltaic properties were investigated. The introduction of MPc into PEG electrolytes makes it remarkably to improve the power conversion efficiency with the increase of the J_{sc}. The best result of DSSC devices was 4.18% of power conversion efficiency in DSSC device using the InOHPc, and 0.70 V of V_{oc}, 10.20 mA/cm^2 of J_{sc}, and 0.58 of FF. The results indicate that the MPcs are promising materials as additives of the electrolytes rather than the sensitizer for DSSC application. Therefore, these findings will open up a new approach for MPcs in applications of DSSCs.

REFERENCES

[1] Gratzel, M. (2003). *Nature*, *421*, 586.

[2] O'regen, B. & Gratzel, M. (1991). *Nature*, *353*, 737.

[3] Nazeeruddin, M. K., Kay, A., Rodicio, I., Humphry-Baker, R., Muller, E., Liska, P., Valchopoulos, N., & Gratzel, M. (1993). *J. Am. Chem. Soc.*, *115*, 6382.

[4] Tennakone, K., Fermando, C. A. N., & Dewasurendra, M. J. (1997). *J. Photochem. B*, *38*, 75.

[5] Komiya, R., Han, L., Yamanaka, R., Islam, A., & Mitate, T. (2004). *J. Photochem. and Photobiol. A: Chem.*, *164*, 123.

[6] Brabe, C. J., Arendse, F., Comte, P., Jirousek, M., Lenzmann, F., Shklover, V., & Gratzel, M. (1997). *J. Am. Chem. Soc.*, *80*, 3157.

[7] Sayama, K., Sugihara, H., & Arakawa, H. (1998). *Chem. Mater.*, *10*, 3825.

[8] Otaka, H., Kira, M., Yano, K., Ito, S., Mitekura, H., Kawata, T., & Matsui, F. (2004). *J. Photochem. and Photobiol. A: Chem.*, *164*, 67.

[9] Kusama, H. & Arakawa, H. (2004). *J. Photochem. and Photobiol. A: Chem.*, *164*, 103.

[10] Usui, H., Matsui, H., Tanabe, N., & Yanagida, S. (2004). *J. Photochem. and Photobiol. A: Chem.*, *164*, 97.

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

[12] Wang, P., Zakeeruddin, S. M., Exnar, I., & Grätzel, M. (2002). *Chem. Commun.*, *24*, 2972.

[13] Leznoff, C. C. & Lever, A. B. P. (1989). *Phthalocyanines-Properties and Applications*, VCH: New York, 1–4.

[14] Moser, F. H. & Thomas, A. H. (1983). *The Phthalocyanines*, *1–2*.

[15] Shirai, H., Kobayashi, N., & Kobayashi, N. (1997). *Phthalocyanies-chemistry and Functions*, IPC: Tokyo.

[16] Kobayashi, N., Mack, J., Ishii, K., & Stillman, M. J. (2002). *Inorg. Chem.*, *41*, 5350.

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

[18] Tennaknoe, K., Senaderra, G. K. R., Pereva, V. P. S., Kottegoda, I. R. M., & De Silva, L. A. A. (1999). *Chem. Mater.*, *11*, 2474.