

# Fabrication and Electrochemical Study of Novel Photoanodes for Dye-Sensitized Solar Cells

洪健原、姚品全

E-mail: 9806484@mail.dyu.edu.tw

## ABSTRACT

This study divided into two parts, the first part to look at a variety of (LiI, NaI, KI) and Propylene carbonate (PC), 3-Methoxypropionitrile (MPN) and the colloidal gel polymer (polyacrylonitrile, PAN) the composition of the electrolyte system to cyclic voltammetry (cyclic voltammogram, CV) and AC impedance method (AC Impedance), etc. Characteristics of electrochemical; as a dye-sensitized solar cells (Dye-Sensitized Solar Cell, DSSC) electrolyte systems, measurement of its Photoelectric conversion efficiency on a variety of electrolyte systems for the photovoltaic characteristics of the impact of components.

The second part of this study was primarily aimed at the working electrode, in order to spin a good TiO<sub>2</sub> coating solution will be allocated to the ITO coated glass as working electrode after sintering, and with different thickness, to observe the heterogeneous structure of the photoelectric conversion efficiency. Electrolytes are ELM-026 (0.26 M LiI + 0.05 M I<sub>2</sub> + MPN), EKM-034 (0.34 M KI + 0.01 M I<sub>2</sub> + MPN) to observe the performance of its IV.

The results showed that TiO<sub>2</sub> film with the working electrode is directly proportional to the number of spin-coating, and when the working electrode thickness reached at 9.1 μm (six), with the best of the photoelectric conversion efficiency, when it increased again when the electrode thickness, light no further increase in power conversion efficiency, but slightly short-circuit current J<sub>sc</sub>.

Electrochemical analysis shows: MPN solvent system, its J<sub>lim</sub> size NaI > LiI > KI, solvent PC system, the size of its J<sub>lim</sub> for LiI > NaI > KI. Solvent PC / EC = 3:2, the ionic conductivity of up to 8.22 × 10<sup>-2</sup> S / m.

Based on the above conclusions, the best known of these study process parameters: TiO<sub>2</sub> film thickness 9.1 μm, electrolyte is ELM-026, may be the largest photovoltaic conversion efficiency, η = 6.74%. The structure of TCO/P25-TiO<sub>2</sub> (9.1 μm), PV test results are as follows; VOC = 0.740V, JSC = 14.11 mA/cm<sup>2</sup>, FF = 0.56, η = 5.93%; the structure of TCO / Sol-Gel TiO<sub>2</sub> under layer / P25-TiO<sub>2</sub> (9.1 μm), PV test results are as follows; VOC = 0.723V, JSC = 15.01 mA/cm<sup>2</sup>, FF = 0.57, η = 6.14%; the structure of TCO/SnO<sub>2</sub> / Sol-Gel TiO<sub>2</sub> under layer / P25-TiO<sub>2</sub> (9.1 μm), PV test results are as follows; VOC = 0.75V, JSC = 15.22 mA/cm<sup>2</sup>, FF = 0.58, η = 6.74%.

Keywords : Dye-Sensitized Solar Cell、cyclic voltammogram、AC Impedance、Polymer gel electrolyte

## Table of Contents

封面內頁

簽名頁

授權書.....iii

中文摘要.....iv

英文摘要.....vi

誌謝.....viii

目錄.....ix

圖目錄.....xii

表目錄.....xvi

第一章 緒論.....1

1.1 前言.....1

1.2 研究動機.....2

1.3 本文架構.....4

第二章 文獻回顧與理論原理.....5

2.1 太陽電池簡介.....5

2.1.1 有機太陽電池.....5

2.2 染料敏化太陽電池之工作原理.....7

2.3 染料敏化太陽電池組成簡介.....10

2.3.1 TiO<sub>2</sub>工作電極.....10

|   |     |
|---|-----|
| 2.3.2 染料.....                                 | 12  |
| 2.3.3 電解質.....                                | 13  |
| 2.3.4 對電極.....                                | 15  |
| 2.4 DSSC之交流阻抗等效電路.....                        | 16  |
| 2.5電化學測試元件(electrochemical cell).....         | 18  |
| 2.6循環伏安(cyclic voltammogram , CV)[29~30]..... | 21  |
| 2.7交流阻抗( AC Impedance) [32].....              | 23  |
| 2.7.1 基本元件：電阻、電容和電感.....                      | 27  |
| 2.7.2 複合元件與簡單電路.....                          | 29  |
| 第三章 實驗製備方法與儀器.....                            | 41  |
| 3.1實驗設備.....                                  | 41  |
| 3.2藥品耗材.....                                  | 42  |
| 3.3 實驗方法.....                                 | 43  |
| 3.3.1實驗流程.....                                | 43  |
| 3.3.2 ITO玻璃基板之清洗.....                         | 46  |
| 3.3.3電解液配置.....                               | 46  |
| 3.3.4染料配製.....                                | 49  |
| 3.3.5 P25-TiO <sub>2</sub> 漿料配製.....          | 52  |
| 3.3.6 TiO <sub>2</sub> 薄膜光電極製備.....           | 53  |
| 3.3.7 新穎光電極製備.....                            | 55  |
| 3.3.8 Pt對電極製備.....                            | 57  |
| 3.3.9元件組裝.....                                | 57  |
| 3.4 儀器量測分析.....                               | 58  |
| 3.4.1 電化學量測.....                              | 58  |
| 3.4.2 SEM分析.....                              | 60  |
| 3.4.3 紫外光-可?光光譜儀(UV-VIS)分析.....               | 61  |
| 3.4.4 DSSC光電量測.....                           | 61  |
| 第四章 結果與討論.....                                | 64  |
| 4.1電解質系統分析.....                               | 64  |
| 4.1.1電化學測試分析(一).....                          | 64  |
| 4.1.2電化學測試分析(二).....                          | 69  |
| 4.1.3 電化學測試分析(三).....                         | 83  |
| 4.2 工作電極製備分析.....                             | 87  |
| 4.2.1 SEM分析.....                              | 87  |
| 4.3 UV-VIS分析.....                             | 92  |
| 4.3.1 D719染料於D.I Water溶劑分析[51].....           | 92  |
| 4.3.2 D719染料於乙醇溶劑分析.....                      | 95  |
| 4.4 光電量測部份.....                               | 97  |
| 4.4.1 TCP(花青素)染料系統.....                       | 97  |
| 4.4.2 D719染料系統.....                           | 105 |
| 4.4.3 探討Work electrode部份.....                 | 113 |
| 第五章 結論與建議.....                                | 121 |
| 5.1 結論.....                                   | 121 |
| 5.2 建議.....                                   | 124 |
| 參考文獻.....                                     | 125 |
| 口試委員提問問題與解答.....                              | 132 |

## REFERENCES

- [1] [http://cdnet.stpi.org.tw/techroom/market/energy/2009/energy\\_09\\_003.htm](http://cdnet.stpi.org.tw/techroom/market/energy/2009/energy_09_003.htm).
- [2] 張正華、李陵嵐、葉楚平、楊平華編, “有機與塑膠太陽能電池”, 五南圖書出版公司.
- [3] V. Y. Merritt, and H. J. Hovel, “Organic solar cell of hydroxy squarylium”, Appl. phys. Lett, vol. 29, p. 414, 1976.
- [4] C. W. Tang, “Two-layer organic photovoltaic cell”, Appl. phys. Lett, vol. 48, pp. 183 – 185, 1986.

- [5] P. Peumans, V. Bulovic, and S. R. Forrest, "Efficient photon harvesting at high optical intensities in ultrathin organic double-heterostructure photovoltaic diodes", *Appl. Phys. Lett.*, vol. 76, pp. 2650–2652, 2000.
- [6] P. Peumans, and S. R. Forrest, "Very-high-efficiency double-heterostructure copper phthalocyanine/C60 photovoltaic cells", *Appl. Phys. Lett.*, vol. 79, pp. 126–128, 2001.
- [7] J. Xue, S. Uchida, B. P. Rand, and S. R. Forrest, "4.2% efficient organic photovoltaic cells with low series resistances", *Appl. Phys. Lett.*, vol. 84, p. 3013, 2004.
- [8] F. Padinger, R. S. Rittberger, and N. S. Sariciftci, *Adv. Funct. Mater.*, vol. 13, p. 85, 2003.
- [9] K. Kalyanasundaram, M. Gratzel, "Applications of functionalized transition metal complexes in photonic and optoelectronic devices", *Coordination Chemistry Reviews*, vol. 77, pp. 347–414, 1998.
- [10] D. Matthews, P. Infelta, M. Gratzel, "Calculation of the photocurrent-potential characteristic for regenerative, sensitized semiconductor electrodes", *Sol. Energy Mater. Sol. Cells*, vol. 44, pp. 119–155, 1996.
- [11] M. Gratzel, "Photoelectrochemical cells", *Nature*, vol. 414, pp. 338–344, Nov 15, 2001.
- [12] 郭春億, "電解質水溶液之性質", 靜宜大學應用化學系研究所.
- [13] 劉茂煌, 奈米光電池, 工業材料雜誌203期, P93.
- [14] K. Kalyanasundaram and M. Gratzel, "Applications of functionalized transition metal complexes in photonic and optoelectronic devices," *Coordination Chem. Rev.*, vol. 77, pp. 347–414, 1998.
- [15] K. Hara, Y. Tachibana, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara, H. Arakawa, "Dye-sensitized nanocrystalline TiO<sub>2</sub> solar cells based on novel coumarin dyes," *Sol. Energy Mater. Sol. Cells*, vol. 77, p. 89, 2003.
- [16] T. Horiuchi, H. Miura, S. Uchida, "Highly-efficient metal-free organic dyes for dye-sensitized solar cells", *Chem. Commun.*, p. 3036, 2003.
- [17] 童永樑, 鈦金屬染料在染料敏化太陽電池的演進, 工業材料雜誌255期, P110.
- [18] 蔡松雨, 染料敏化太陽電池技術介紹, 工業材料雜誌241期, 96年1月, P107.
- [19] G. Schlichthorl, S. Y. Huang, J. Sprague, and A. J. Frank, "Band edge movement and recombination kinetics in dye-sensitized nanocrystalline TiO<sub>2</sub> solar cells: a study by intensity modulated photovoltage spectroscopy," *J. Phys. Chem B*, vol. 101, 8141–8155, 1997.
- [20] Liu, Y., Hagfeldt, A., Xiao, X., Lindquist, S. *Sol. Energy Mater. Sol. Cells*, vol. 55, pp. 267–281, 1998.
- [21] Hara, K. et al. *Sol. Energy Mater. Sol. Cells*, 70, 151–161(2001).
- [22] Y. Liu, A. Hagfeldt, X. R. Xiao, and S. E. Lindquist, "Investigation of influence of redox species on the interfacial energetics of a dye-sensitized nanoporous TiO<sub>2</sub> solar cell," *Sol. Energy Mater. Sol. Cells*, vol. 55, p. 267, 1998.
- [23] A. Kay, M. Gratzel, "Low cost photovoltaic modules based on dye sensitized nanocrystalline titanium dioxide and carbon powder," *Sol. Energy Mater. Sol. Cells*, vol. 44, pp. 99–117, 1996.
- [24] Tsuyoshi Asano, Soichi Uchida, Takaya Kubo, and Yoshinori Nishikitani "Dye-Sensitized Solar Cells Fabricated with Novel Polymeric Solid Electrolyte Films" 3rd World Conference on Photovoltaic Energy Conversion, pp. 11-18, May 2003.
- [25] Tsuyoshi Asano, Takaya Kubo, Yoshinori Nishikitani "Electro-chemical properties of dye-sensitized solar cells fabricated with PVDF-type polymeric solid electrolytes," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 164, pp. 111–115, 2004.
- [26] Liyuan Han, Naoki Koide, Yasuo Chiba, Ashrafal Islam, Takehito Mitate "Modeling of an equivalent circuit for dye-sensitized solar cells: improvement of efficiency of dye-sensitized solar cells by reducing internal resistance" *C. R. Chimie*, vol. 9, pp. 645–651, 2006.
- [27] Anneke Hauch, Andreas Georg b "Diffusion in the electrolyte and charge-transfer reaction at the platinum electrode in dye-sensitized solar cells" *Electrochimica Acta*, vol. 46, pp. 3457–3466, 2001.
- [28] M. Berginc, U. Opara Krasovec, M. Jankovec, M. Topic "The effect of temperature on the performance of dye-sensitized solar cells based on a propyl-methyl-imidazolium iodide electrolyte," *Solar Energy Materials & Solar Cells*, vol. 91, pp. 821–828, 2007.
- [29] 胡啟章, 電化學原理與方法, 第六章, 五南圖書出版公司.
- [30] Bard, Allen J. Faulkner, Larry R., "Electrochemical Methods Fundamental and Application," John Wiley & Sons, Canada, 1980.
- [31] Wayne M. Campbell, Anthony K. Burrell, David L. Officer, Kenneth W. Jolley "Porphyrins as light harvesters in the dye-sensitized TiO<sub>2</sub> solar cell," *Coordination Chemistry Reviews*, vol. 248, pp. 1363–1379, 2004.
- [32] 史美倫, 交流阻抗譜原理及應用, 國防工業出版社, 第一章, 中國.
- [33] O.A. Ilperuma, M.A.K.L. Dissanayake, S. Somasunderam, L.R.A.K. Bandara, "Photoelectrochemical solar cells with polyacrylonitrile-based and polyethyleneoxide-based polymer electrolytes," *Solar Energy Materials & Solar Cells*, vol. 84, pp. 117–124, 2004.
- [34] Kalyanasundaram, K., Vlachopoulos, N., Krishnan, V., Monnier, A., Gratzel, M., *J. Phys. Chem.*, vol. 91, pp. 2342–2347, 1987.
- [35] Vlachopoulos, N., Liska, P., McEvoy, A. J., Gratzel, M., *Surf. Sci.*, 189/190, pp. 823–831, 1987.
- [36] Dabestani, R., Bard, A. J., Campion, A., Fox, M. A., Mallouk, T. E., Webber, S. E., White, J. M., *J. Phys. Chem.*, 92, pp. 1872–1878, 1988.
- [37] Boschloo, G. K.; Goossens, A. *J. Phys. Chem.*, vol. 100, pp. 19489–19494, 1996.
- [38] Andrew Stanley, Dennis Matthews, "The Dark Current at the TiO<sub>2</sub> Electrode of a Dye-Sensitized TiO<sub>2</sub> Photovoltaic Cell," *Aust. J. Chem.*, vol. 48, pp. 1293–1300, 1995.
- [39] Jin-Kook Lee, Bo-Hwa Jeong, Sung-II Jang, Yun-Seon Yeo, Sung-Hae Park, Ji-Un Kim, Young-Guen Kim, Yong-Wook Jang, Mi-Ra Kim,

- “ Multi-layered TiO<sub>2</sub> nanostructured films for dye-sensitized solar cells, ” J Mater Sci: Mater Electron, pp. 608-739, South Korea, 2009.
- [40] Zhaoyue Liu, Kai Pan, Min Liu, Meijia Wang, Qiang L?u, Jinghong Li, Yubai Bai, Tiejun Li, “ Al<sub>2</sub>O<sub>3</sub>-coated SnO<sub>2</sub>/TiO<sub>2</sub> composite electrode for the dye-sensitized solar cell, ” Electrochimica Acta, vol. 50, pp. 2583 – 2589, 2005.
- [41] Liu. Y, Hagfeldt. A, Xiao. X, Lindquist. S, Sol. Energy Mater. Sol. Cells, vol. 55, pp.267 – 281, 1998.
- [42] Hara, K. et al, Sol. Energy Mater. Sol. Cells, vol 70, pp. 151 – 161, 2001.
- [43] Anneke Hauch , Andreas Georg b “ Diffusion in the electrolyte and charge-transfer reaction at the platinum electrode in dye-sensitized solar cells ” Electrochimica Acta,vol. 46, pp. 3457-3466, 2001.
- [44] 林明獻, “ 太陽電池技術入門 ” , P1-7.
- [45] O.A. Ilperuma, M.A.K.L. Dissanayake, S.Somasundaram, “ Dye-sensitised photoelectrochemical solar cells with polyacrylonitrile based solid polymer electrolytes, ” Electrochimica Acta,vol. 47, pp. 2801-2807, 2002.
- [46] M. Kajiwara and H. Saito, Polymer, 17, 1013(1976).
- [47] Y. W. Chen-Yang, J. J. Hwang, J. Y. Kau, “ Polybisaminophosphazene-silver nitrate complexes: Coordination and properties, ” J. Polym. Sci. A: Polym.Chem, vol. 35, pp. 1023-1031, 1997.
- [48] M.A.K.L. Dissanayake , L,RA,K, Bandara ,R.S.P. Bokalawala , P.A.R.D Jayathilaka ,O.A. Ilperuma , S. Somasundaram , “ A novel gel polymer electrolyte based on polyacrylonitrile (PAN) and its application in a solar cell ” Materials Research Bulletin , vol. 37, pp. 867-874, 2002.
- [49] Lasse Bay, Keld West, Bjorn Winther-Jensen, Torben Jacobsen , “ Electrochemical reaction rates in a dye-sensitised solar cell-the iodide/tri-iodide redox system, ” Solar Energy Materials & Solar Cells,vol. 90, pp. 341 – 351, 2006.
- [50] Y. W. Chen-Yang, J. J. Hwang, and A. Y. Huang Macromolecules, “ Polyphosphazene Electrolytes 2 : Synthesis and Properties of Poly((amino)(2-methoxyethoxy)ethoxy)-phosphazene, ” Macromolecules, vol. 33, pp 1237 – 1244, 2000.
- [51] A Stanley and D Matthews, “ The Dark Current at the TiO<sub>2</sub> Electrode of a Dye-Sensitized TiO<sub>2</sub> Photovoltaic Cell, ” Aust.J.Chem, vol. 48, pp. 1293-1300, 1995.
- [52] 林明獻, “ 太陽電池技術入門 ” ,全華書局.
- [53] 蔡忠憲, “ 以二氧化鈦奈米管為前驅物製作染料敏化太陽電池之陽極電極 ” ,成功大學 化學工程學系.
- [54] Martin A.Green, “ Operating Principles Technology and System Applications,National Library of Australia Cataloguing-in-Publication entry, ” SOLAR CELLS , 1982.