

Electrochemical study of the mediators for the Dye-sensitized solar cells

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ABSTRACT

In this study, the important process parameters in fabricating dye-sensitized solar cells(DSSC) such as the sintering temperature of TiO₂ thin film, the additives during the film forming stage such as Triton X-100(surfactant for nano-powders dispersion) as well as polyethylene glycol(PEG, porosity control agent) were extensively studied. Besides, the electrochemical properties of the TiO₂ working electrode were investigated by cyclic voltammetry in comparison with those described in published papers as a basis for further analysis. The results show that the sintering temperature of TiO₂ thin film has prominent effect on the Voc and Isc of the DSSC. The Voc has its maximum value of 417 mV at T=450oC while the Jsc increase as the T was increased. Therefore, Jsc=0.99 mA at T=400 oC and elevated to Jsc=2.7 mA/cm² at 550oC. As the sintering temperature increase, the fill factor (FF) diminished. Consequently, the suitable value for the sintering temperature of TiO₂ thin film is 450~500oC. The surfactant, Triton X-100 has optimal addition amount of 0.05~0.1 ml/3g of P25 in which the DSSC has performance of Voc=518 mV, Jsc=2.1 mA/cm² while the introduction of Triton X-100 has no effect on FF. The porosity control of TiO₂ thin films by the introduction of PEG has been proven. In our study, adding small amount of PEG(0.9g/3g of P25) has improved the Jsc to as high as 3.9 mA/cm², while more PEG has detrimental effects on Jsc owing to the residues of polymer. Besides, the PEG addition has minor effect on Voc of the as-prepared DSSC. Similarly, as PEG exceeded 1.2 g/3g of P25, the FF of DSSC decreased immediately for the similar reason described above. The electrochemical analysis(cyclic voltammetry) shows that the TiO₂ films owns quite good electrochemical reversibility in which there is no evident faradaic current within the operation voltage of the solar cells.

Keywords : dye-sensitized solar cells, TiO₂ , PEG, Triton X-100, cyclic voltammetry

Table of Contents

封面內頁 簽名頁 授權書.....	iii	中文摘要.....	iv	英文摘要.....	v	誌謝.....	vi	目錄.....	vii	圖目錄.....	x	表目錄.....	xiii																						
第一章 緒論		1.1 前言.....	1	1.2 電化學反應系統.....	3	1.3 電化學反應程序.....	5	1.4 色素增感型太陽能電池電化學反應因素.....	8	1.5 色素增感型太陽能電池工作原理.....	9	1.6 研究背景與目的.....	12																						
第二章 文獻回顧與理論說明.....	13	2.1 色素增感型太陽能電池.....	13	2.1.1 有機-無機混合型太陽能電池.....	14	2.1.2 光電化學電池原理.....	17	2.1.3 半導體-電解質界面.....	19	2.1.4 色素增感原理.....	23	2.1.5 DSSC 技術進展.....	25	2.1.6 DSSC未來的研發方向.....	29	2.2 電化學.....	33	2.2.1 電化學反應系統.....	33	2.2.2 影響電化學反應系統的因素.....	36	2.2.3 電解質.....	37	2.2.4 電位測定法.....	42	2.2.5 線性擴散.....	43	2.2.6 循環伏安法(Cyclic Voltammetry,CV).....	44	2.3 溶膠-凝膠法製程簡介.....	53				
第三章 實驗方法.....	56	3.1 實驗器材.....	56	3.2 實驗藥品.....	57	3.3 實驗方式.....	58	3.4 DSSC材料之製備.....	59	3.4.1 二氧化鈦的製備.....	59	3.4.2 工作電極的製備.....	62	3.4.3 染敏色素塗佈.....	63	3.4.4 對電極(counter electrolyte)觸媒塗佈製備.....	68	3.5 DSSC電化學分析實驗.....	68	3.5.1 電化學測試裝置.....	69	3.5.2 電化學分析.....	70	3.5.3 穩定性實驗.....	71	3.5.4 可逆性實驗.....	71	3.5.5 循環伏安法之應用.....	72	3.6 DSSC光電特性(I-V)量測.....	82	3.6.1 DSSC電解液的製備.....	84	3.6.2 DSSC光電轉換效能(IPCE)評估.....	86
第四章 TiO ₂ 工作電極孔隙特性之探討.....	87	4.1 DSSC工作原理.....	87	4.2 TiO ₂ 工作電極燒結溫度之影響分析.....	89	4.3 TiO ₂ 工作電極孔隙度調整-界面活性劑之影響分析.....	92	4.4 TiO ₂ 工作電極孔隙度調整-PEG之影響分析.....	95																										
第五章 DSSC電解質電化學特性探討.....	97	5.1 電解質溫度及掃描速率循環伏安行為的探討.....	97	5.1.1 電解液於不同掃描速率之分析.....	97	5.1.2 電解液於不同溫度之分析.....	99	5.1.3 電解液於高溫度及高掃描速率之分析.....	101	5.2 DSSC對電極之溫度及掃描速率影響分析.....	104																								
第六章 討論與建議.....	109	6.1 綜合討論.....	109	6.2 二氧化鈦薄膜對DSSC太陽能電池影響.....	110	6.3 DSSC電解質對溫度及掃描速率之影響.....	112	6.4 建議.....	113	參考文獻.....	115																								

REFERENCES

1. A. J. Bard and L. R. Faulkner, "Electrochemical Methods, Fundamentals and Applications", John Wiley & Sons, Singapore (1980). 2. D. Pletcher, "A First Course in Electrode Processes", The Electrochemical Consultancy, England (1991). 3. D. R. Crow, "Principles and Applications of Electrochemistry", 2nd Ed. Chapman and Hall Ltd. London (1979). 4. 田福助編著, 電化學理論與應用, 先科技P1. 5. 胡啟章編著, 電化學原理與方法, 五南P4. 6. D. Pletcher and F. C. Walsh, "Industrial Electrochemistry", Chapman and Hall Ltd. N.Y. (1990). 7. 張光揮, "循環伏安置備含水鈦鈹氧化物於電化學電容器的應用", 國立中正大學化工研究所碩士論文, 2000. 8. A. M. Couper, D. Pletcher, and F. C. Walsh, Chem. Rev., 90, 837 (1990). 9. Galizzoli D., Tantardini F., Trasatti S., J. Appl. Electrochem., 5, 203 (1975). 10. M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humpbry-Baker, E. Miiller, P. Liska, N. Vlachopoulos, and M. Gratzel (1993) Conversion of Light to Electricity by cis-X2Bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) Charge-Transfer Sensitizers (X = C1-, Br-, I-, CN-, and SCN-) on Nanocrystalline TiO2 Electrodes, J. Am. Chem. Soc., 115, 6382-6390. 11. 劉茂煌, 奈米光電池, http://www.chuang-hua.com/product_catalog_c_001.asp 12. 羅幼旭, TiO2 奈米多孔性薄膜於染料敏化太陽能電池(dye-sensitized solar cell, DSSC)之應用, http://tns.ndhu.edu.tw/~nano/labtext/DSSC_lab.pdf 13. Greg Smestad, "How Dye-Sensitized Solar Cells Work", Solar Ideas in <http://www.solideas.com/solrcell/cellkit.html> 14. Michael Gratzel, Photochemical Cells, Nature, 2001(414) 338-39 15. Michael Gratzel, "Review: Dye-sensitized solar cells", J. of Photochemistry and Photobiology C: Photochemistry Reviews, 2003(4)145-153 16. Greg P. Smestad, Education and Solar Conversion: Demonstrating electron transfer", Solar Eng. Mater. & Solar Cells, 1998(55) 157-178 17. http://www.eifer.uni-karlsruhe.de/seite_162.php 18. 彭懷夫, 中孔性二氧化鈦薄膜於染料敏化太陽能電池之應用, 國立東華大學化學工程學研究所碩士論文, 2004 19. 張芳碩, 染料敏化二氧化鈦光電化學太陽能電池, 國立臺灣大學化學工程學研究所碩士論文, 2004 20. 蔡忠憲, 以二氧化鈦奈米管為前驅物製作染料敏化太陽能電池之陽極電極, 國立成功大學化學工程學研究所碩士論文, 2004 21. 朱奕融, 奈米TiO2粒子應用於染料敏化太陽能電池之研究, 南台科技大學電機工程研究所碩士論文, 2004 22. 郭正鏞, 應用於染料敏化太陽能電池之二氧化鈦薄膜與粉末製程及其特性, 南台科技大學電機工程研究所碩士論文, 2004 23. M Gratzel, "Conversion of sunlight to electric power by nanocrystalline DSSCs" J. Photochem. & Photobio. A: Chem. 2004(164) 3-14 24. M. Gratzel, "Powering the planet", Nature 2000(403) 363 25. C. Anderson and A. J. Bard, "An Improved Photocatalyst of TiO2/SiO2 Prepared by a Sol-Gel Synthesis", J. Phys. Chem., 1995(99) 9882-9885 26. M. Anpo, M. Takeuchi, "The design and development of highly reactive titanium oxide photocatalysts operating under visible light irradiation", Journal of Catalysis, 2003(216) 505-516 27. Poznyak et al., "Structural, Optical, and Photoelectrochemical Properties of Nanocrystalline TiO2-In2O3 Composite Solids and Films Prepared by Sol-Gel Method", J. Phys. Chem. B 2001(105) 4816-23 28. B. O' Regan, M. Gratzel, "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO2 films", Nature 1991(353) 737-40 29. A. Hagfeldt, M. Gratzel, "Light-Induced Redox Reactions in Nanocrystalline Systems" Chem., Rev. 1995(95) 49-68 30. M. Gratzel, "Mesoporous oxide junctions and nanostructured solar cells", Current Opinion in Colloid & Interface Science, 1999(4) 314-21 31. A. Fujishima et al., "Slow interfacial charge recombination in solid-state dye-sensitized solar cell using Al2O3-coated nanoporous TiO2 films", Solar. Energy Mater. Solar Cells, 2004(81) 197-203 32. Cahen et al., "Nature of Photovoltaic Action in Dye-Sensitized Solar Cells", J. Phys. Chem. B, 2000(104) 2053-59 33. L. L. Kazmerski, "Photovoltaics: A review of cell and module technologies", Renewable Sustainable Energy Rev. 1997(1) 71-170 34. J. Ferber et al., "An electrical model of the dye-sensitized solar cell", Sol. Energy Mater. Sol. Cells 1998(53) 29-54 35. Park et al., "Dye-sensitized TiO2 solar cells: structural and photoelectrochemical characterization of nanocrystalline electrodes formed from the hydrolysis of TiCl4", J. Phys. Chem. B 1999(103) 3308-14 36. J. Y. Ying, C. P. Mehnert, and M. S. Wong, "Synthesis and Application of Supramolecular Templated Mesoporous Materials", Angew. Chem. Int. Ed. Engl., 1999(38)56. 37. Q. Huo, D. I. Margolese, U. Ciesla, P. Feng, T. E. Gier, P. Sieger, R. Leon, P. M. Petroff, F. Schuth, G. D. Stucky, "Generalized Synthesis of Periodic Surfactant/Inorganic Composite Materials", Nature, 1994(368) 317. 38. C. T. Kresge, M. J. Roth, J. C. Vartuli, and J. S. Beck, "Ordered Mesoporous Molecular Sieves Synthesized by a Liquid-Crystal Template Mechanism", Nature, 1992(359) 22. 39. 21] C. Y. Chen, H. X. Li, M. E. Davis, "Studies on Mesoporous Materials. Synthesis and Characterization of MCM-41" Microporous Mater., 1993(2)17. 40. F. Chen, M. Liu, "Preparation of mesoporous Tin Oxide for Electrochemical Applications", Chem. Commun., 1999, pp1829. 41. D. M. Antonelli, J. Y. Ying, "Synthesis and Characterization of Hexagonally Packed Mesoporous Tantalum Oxide Molecular Sieves", Chem. Mater., 1996(8) 874. 42. D. M. Antonelli, J. Y. Ying, "Synthesis of Hexagonally Packed Mesoporous TiO2 by a Modified Sol-Gel Method", Angew. Chem. Int. Ed. Engl., 1995(34) 2014. 43. 林正豐, 奈米二氧化鈦之製備及活性測定, 國立臺灣大學化學工程學研究所碩士論文, 2001 44. 董建岳, 中孔奈米晶型二氧化錫之製備, 國立臺灣大學化學工程學研究所碩士論文, 2004 45. Martin A. Green, Solar Cells, Operating Principles, Technology and System Applications, Prentice-Hall, 1982 46. Tomas Markvart(Editor), Solar Electricity, John Wiley & Sons, 1994 47. http://www.asiaa.sinica.edu.tw/~whwang/articles/wide_field_astrophoto/reciprocity_chemistry.html 48. M. Gratzel, Photoelectrochemical Cells, Nature, 2001(414) 338 49. H. A. Agrell, Interactions in Dye-sensitized Solar Cells, Uppsala Dissertations, 2003 50. M. Gratzel, Ultrafast electron injection, J. Phys. Chem. B 1997(101) 9342 51. Judy Hart, Csiro sustainability network update-no.35E, 2003 52. I Roel van de Krol, Electrical and optical properties of TiO2 in accumulation and of lithium titanate, Li0.5TiO2, J. Appl. Phys., 2001(90) 2235 53. M. Gratzel, Dye sensitized and organic solar cells, Solar Eng. Mater. & Solar Cells, 2003(76) 1-2 54. M. Gratzel, Low cost photovoltaic modules based on dye sensitized nanocrystalline titanium oxide and carbon powder, Solar Eng. Mater. & Solar Cells, 1996(44) 99-117 55. 賴俊吉, 「新型高效率染料敏化奈米TiO2 太陽能電池(DSSCs)之研究」 NSC91-2216-E-027-001, 國立台北科技大學 有機高分子研究所 56. 蔡裕榮「以溶膠凝膠法製備透明導電氧化物薄膜的探討」國立中正大學化學系碩士論文 2002 57. J. Herrero, C. Guillen, Transparent films on polymers for photovoltaic applications, Vacuum, 2002(67) 611-616 58. H. Kim, et al., Indium tin oxide thin films grown on flexible plastic substrates by pulsed-laser deposition for organic light-emitting diodes, Appl. Phys. Lett., 2001(79) 284 59. P. M. Sommeling, et al., Flexible Dye-Sensitized

Nanocrystalline TiO₂ Solar Cells, EPVSEC-16, Glasgow, 1-5 May, 2000 60. 馮名正, ITO包覆SiO₂顆粒及其膜之製備與物性研究, 台北科技大學碩士論文, 2004 61. Y. Shigesato, et al., Early stages of ITO deposition on glass or polymer substrates, *Vacuum*, 2000(59) 614-621 62. A. Bessiere, et al., Sol-gel deposition of electrochromic WO₃ thin film on flexible ITO/PET substrate, *Electrochimica Acta*, 2001(46) 2251-2256 63. C. Nunes de Carvalho, et al., Properties of ITO films deposited by plasma enhanced RTE on unheated polymer sheets-dependence on RF electrode distance from substrates, *J. Non-Crystal. Solids*, 2004(338-340) 630-633 64. T. Ohishi., Preparation and properties of anti-reflection/anti-static thin films formed on organic film by photo-assisted sol-gel method, *J. Non-Crystal. Solids*, 2003(332) 87-92 65. Daeil Kim, Influence of negative metal ion bombardment on the properties of ITO/PET films deposited by dc magnetron sputtering, *J. Non-Crystal. Solids*, 2003(331) 41-47 66. T. Ohishi., Gas barrier characteristics of a polysilazane film formed on an ITO-coated PET substrate, *J. Non-Crystal. Solids*, 2003(331) 41-47 67. Takuro N. Murakami, et al., Low temperature preparation of mesoporous TiO₂ films for efficient dye-sensitized photoelectrode by chemical vapor deposition combined with UV light irradiation. 68. C. Nunes de Carvalho, et al., ITO films deposited by rf-PERTE on unheated polymer substrates-properties dependence on In-Sn alloy composition, *Materials Sci. & Eng. B*, 2004(109) 245-248 69. Frederik C. Krebs, et al., Production of large-area polymer solar cells by industrial silkscreen printing, lifetime considerations and lamination with polyethyleneterephthalate, *Solar Eng. Mater. & Solar Cells*, 2004(83) 293-300 70. Marcello Antinucci, et al., Development and characterization of electrochromic devices on polymeric substrates, *Solar Eng. Mater. & Solar Cells*, 1995(39) 271-287 71. Young-Soon Kim, et al., Influence of O₂ admixture and sputtering pressure on the properties of ITO thin films deposited on PET substrate using RF reactive magnetron sputtering, *Surface and Coating Technology*, 2003(173) 299-308 72. J. W. Bae et al., Tin-doped indium oxide thin film deposited on organic substrate using oxygen ion beam assisted deposition., *Surface and Coating Technology*, 2000(131) 196-200 73. P. L. Almeida, et al., Composite systems for flexible display applications from cellulose derivatives, *Synthetic Metals*, 2002(127) 111-114 74. F. L. Wong, et al., Flexible organic light-emitting device based on magnetron sputtered indium-tin-oxide on plastic substrate, *Thin Solid Films*, 2004(466) 225-230 75. C. Nunes de Carvalho, et al., Properties of ITO films deposited by rf-PERTE on unheated polymer substrates-dependence on oxygen partial pressure., *Thin Solid Films*, 2003(427) 215-218 76. T. Minami, et al., Physics of very thin ITO conducting films with high transparency prepared by DC magnetron sputtering., *Thin Solid Films*, 1995(270) 37-42 77. Dong-Sing Wu, et al., Improvement of ITO Films on PET substrates by Hot-Wire Surface treatment 78. 游騰昇「有機太陽能電池元件之成長與光電特性之研究」, 大葉大學電機系碩士論文, 2004年 79. 黃菁樺「錒錫氧化物透明導電薄膜之成長與光電特性之研究—應用於發光二極體」, 大葉大學電機系碩士論文, 2003年 80. Radhouane Bel Hadj Tahar, Takayuki Ban, Yutaka Ohya, and Yasutaka Takahashi, " Electronic transport in tin-doped indium oxide thin films prepared by sol-gel technique ", *J. Appl. Phys.* 83 (4), 15 February (1998) 2139-2141 81. Yuzo Shigesato, Satoru Takaki, and Takeshi Haranoh, " Electrical and structural properties of low resistivity tin-doped indium oxide films ", *J. Appl. Phys.* 71 (7), 1 April (1992) 3356-3364 82. A.K. Kulkarni, Kirk H. Schulz, T.S. Lim, and M. Khan, " Dependence of the sheet resistance of indium-tin-oxide thin films on grain size and grain orientation determined from X-ray diffraction techniques ", *Thin Solid Films* 1999(345) 273-277 83. 鄭淵升「塑膠基板上沈積ITO薄膜之光電及機械性質研究」, 國立清華大學材料工程系碩士論文, 2001年 84. 黃崇傑, " 塑膠基板沈積ITO薄膜技術 " *電子與材料*第10期, p.115. 85. 許登貴「ITO薄膜的製備與表面分析」, 國立台北科技大學有機高分子研究所碩士論文, 2002年 86. Morrison, *Electrochemistry at Semiconductor and Oxidized Metal Electrodes*, Plenum Press, 1984 87. 胡啟章: *電化學原理與方法*, 五南出版社 88. 陳璋駿、胡啟章:溶膠-凝膠法製備氧化鈦奈米微粒於超高電容器之應用; 中正大學化工系碩士論文, 2002年 89. 郭彥廷、吳春桂:導電高分子與二氧化鈦之奈米複合材料的合成與性質探討, 中央大學光電研究所碩士論文, 2002年 90. 陳靜怡、洪敏雄:氧化鋅中介層對ITO透明導電膜性質之影響, 成功大學材料系, 2004年 91. 劉建成、廖深茂:電子槍蒸鍍氧化錒錫薄膜在AlGaInP發光二極體應用之研究, 中原大學電子工程系碩士論文, 2003年 92. 吳嘉城、武東星, 姚品全:「藍寶石晶片薄化技術與應用」, 大葉大學電機系碩士論文, 2003年 93. Karin Westermark, " Dye/Semiconductor Interface ", Ph.D Dissertation, Uppsala 2001