

色素增感型太陽電池電解質系統之電化學研究

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摘要

本研究針對工作電極的重要製程參數對DSSC光電轉換效率之影響，作較為詳細探討與解釋。主要參數包括控制TiO₂薄膜孔隙度的添加劑(polyethylene glycol, PEG)、影響奈米TiO₂晶粒分散情形，以利於成膜的界面活性劑(Triton X-100)以及TiO₂薄膜的燒結溫度。此外對於工作電極的電化學特性略加探討，以與文獻中發表結果對照，作為爾後研究之參考依據。結果顯示TiO₂薄膜的燒結溫度與開路電壓與短路電流之影響甚為明顯，燒結溫度為450oC時，有最大之開路電壓，Voc=417 mV，短路電流隨燒結溫度增加而增加，由400oC時Jsc=0.99 mA/cm²，增為550oC時，Jsc=2.7 mA/cm²，填充因子FF超過500oC時開始明顯下降，?合以上數據，推論450~500oC為適當之燒結溫度。Triton X-100的添加量，在0.05~0.1 ml/3g of P25內均為適宜。此時Voc=518 mV，Jsc=2.1 mA/cm²，填充因子FF與Triton X-100的添加量關聯性很低。PEG(polyethylene glycol, MW=6000)的添加，可以調整TiO₂薄膜的孔隙特性，經過多次的樣品製備與量測所得結果顯示：PEG的添加有助於短路電流之提昇，最大值出現於PEG=0.9g/3g of P25，此時Jsc=3.9 mA/cm²，反之PEG的添加與否，對DSSC的Voc影響很小，不過PEG添加超過0.15g/3g of P25時，填充因子FF因為TiO₂薄膜內含有機雜質成份漸增，因而導致FF下降。電化學分析(循環伏安法)得知：在工作電壓範圍內，無明顯氧化-還原峰，顯示本研究製備之TiO₂薄膜工作電極具有良好的電化學特性。

關鍵詞：奈米TiO₂粉體，色素增感型太陽電池，染料，電解質

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參考文獻

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. 張光輝, " 循環伏安置備含水釤鉻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. Humphry-Baker, E. Müller, 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 = Cl-, 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, 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. Graztel, Photoelectrochemical Cells, Nature, 2001(414) 338 49. H. A. Agrell, Interactions in Dye-sensitized Solar Cells, Uppsala Dissertations, 2003 50. M. Graztel, Ultrfast 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, Li_{0.5}TiO₂, J. Appl. Phys., 2001(90) 2235 53. M. Graztel, Dye sensitized and organic solar cells, Solar Eng. Mater. & Solar Cells, 2003(76) 1-2 54. M. Graztel, 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/PETfilms 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. Takurou 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 polymersubstrates-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 considerarions 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 cellulosederivatives, 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 unheatedpolymer 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 transparencyprepared by DC magnetron sputtering., Thin Solid Films, 1995(270) 37-42 77. Dong-Sing Wuu, 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「銦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 form 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. 陳瑋駿、胡啟章:溶膠-凝膠法製備氧化釤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:電子槍蒸鍍氧化銦錫薄膜在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