

以電泳沉積及燒結改善奈米碳管超級電容器效能之研究

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摘要

電容器的優點為充放電快速及可瞬間提供較大之負載電流，但缺點為無法提供較大的能量密度，超級電容器的研發即在克服此問題，但目前超級電容器仍有許多問題待解決，其中之一就是老劣化的問題，而這正是本研究的主題。以前的研究直接以鎳觸媒在石墨電極上成長奈米碳管，本研究利用電泳沉積的方式將奈米碳管沉積到石墨電極的表面上。再將沉積奈米碳管石墨電極放入加熱爐管中，在空氣中直接加熱到500 以上的溫度，希望藉此改善石墨電極超級電容器的老劣化的問題以及增加其電容量。在燒結的試驗中，發現當溫度到達到600 時，可以有較好的電容效果。本研究測試老劣化的主要方法是三極式循環伏安量測法。藉著電泳沉積奈米碳管，可以讓奈米碳管形成交錯縱橫的微小孔洞結構。除了奈米碳管本身提供的高比表面積外，這些微小孔洞也可以讓電荷進入吸附而增加其電容量。本研究用硝酸鎂使奈米碳管帶有電性以利電泳沉積之進行，但卻發現鎂離子會造成奈米碳管會在硫酸電解液中呈片狀剝落，必須要將鎂離子移除後，才克服了這個問題。本研究的結果比直接用鎳觸媒在石墨電極上成長奈米碳管好很多，在老劣化方面確有顯著的改善。

關鍵詞：奈米碳管;電泳沉積法;超級電容器;老劣化

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參考文獻

- [1] 馬振基, “奈米材料科技原理與運用”, 全華科技圖書股份有限公司, 92年。
- [2] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, “buckminsterfullerene.” *Nature*, 318 (1985) 162-163.
- [3] S. Iijima, “Helical microtubules of graphitic carbon,” *Nature*, 354 (1991) 56 [4] D. S. Bethune, C. H. Kiang, M. S. de Vries, G. Gorman, R. Saroy, J. Vazquez, and R. Beyers. “Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls,” *Nature*, 363 (1993) 605.
- [5] E. Thostenson, Z. Ren, T. W. Chou, “Advances in the Science and Technology of Carbon Nanotubes and their Composites: A review,” *Composites Science and technology*, 61 (2001) 1899-1912 [6] Kotz, R., Carlen M. “Principle and applications of electrochemical capacitors.” *Electrochimica Acta*, 45 (2000) 2483-2498 [7] Burke A. “Ultracapacitors: why, how, and where is the technology.” *Journal of Power Sources*, 91 (2000) 37-50 [8] C. Niv, E. K. Sichel, R. Hoch, D. Moy, H. Tennent, “High power electrochemical capacitors based on carbon nanotube electrodes,” *Appl. Phys. Lett.*, 70 (1997) 1480-1482 [9] M. S. Dresselhaus, G. Eklund, P. C. Eklund, “Fullerenes and carbon nanotubes,” Academic Press, San Diego, (1996) 224 [10] M. M. J. Treacy, T. W. Ebbesen, J. M. Gibson, “Exceptionally high Young's modulus observed for individual carbon nanotubes,” *Nature* 381 (1996) 678-680 [11] MR Falvo, GJ Clary, RM II Taylor, V Chi, FP Brooks, “S Washburn, R Superfine,” *Nature*, 389 (1997) 582 [12] N. Krishnakutty, C. Park, N. M. Rodriguez, R. T. K. Baker, “Mechanical and thermal properties of carbon nanotubes,” *Carbon*, 27 (1995) 925-930 [13] J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, “Nanotube molecular wires as chemical sensors,” *H. Dai, Science*, 287 (2000) 622 [14] J. H. Hafner, C. L. Cheung, C. M. Lieber, “Direct Growth of Single-Walled Carbon Nanotube Scanning Probe Microscopy Tips,” *Journal America Chemical Society*, 121 (1999) 9750 [15] B. Vigolo, A. Penicaud, C. Coulon, C. Sauder, R. Paillet, C. “Macroscopic Fibers and Ribbons of Oriented Carbon Nanotubes,” *Journet, P. Bernier, and P. Poulin, Science*, 290 (2000) 1331 [16] I. Corni, M. P. Pyan, A. P. Boccaccini, “Electrophoretic deposition: from traditional ceramics to nanotechnology,” *journal of the European ceramic society*, 28 (2008) 1353-1367.
- [17] A. T. Kuhn, “Industrial Electrochemical Processes,” Elsevier, Amsterdam, The Netherlands, (1971) 128 [18] A. Formetro, L. Montanaro, M. V. Swain, “Micromechanical characterization of electrophoretic-deposited green films,” *J. Am. Ceram. Soc.*, 82 (1999) 3521 – 3549 [19] J. A. Lewis, “Colloidal processing of ceramics,” *J. Am. Ceram. Soc.* 82 (2000) 2341-59 [20] R. Z. Ma, J. Liang, B. Q. Wei, B. Zhang, C. L. Xu, D. H. Wu, J. “Study of electrochemical capacitors utilizing carbon nanotube electrodes,” *Power Sources* 84 (1999) 126 – 129.
- [21] J. A. Siracuse, J. B. Talbot, E. Sluzky, and K. R. Hesse, “The adhesive agent in cataphoretically coated phosphor screens,” *J. Electrochem. Soc.* 137 (1990) 346-348.
- [22] B. E. Russ, and J. B. Talbot, “An analysis of the binder formation in electrophoretic deposition,” *J. Electrochem. Soc.* 145 (1998) 1253-1256.
- [23] B. Gao, G. Z. Yue, Q. Qiu, Y. Cheng, H. Shimoda, L. Fleming, and O. Zhou, “Fabrication and Electron Field Emission Properties of Carbon Nanotube Films by Electrophoretic Deposition,” 23 (2001) 1770-1773 [24] A. J. Bard and L. R. Faulkner, “Electrochemical Methods, Fundamentals and Applications”, John Wiley & Sons, Singapore (1980).
- [25] D. Pletcher, “A First Course in Electrode Processes”, The Electrochemical Consultancy, England (1991).
- [26] D. R. Crow, “Principles and Applications of Electrochemistry”, 2nd Ed. Chapman and Hall Ltd. London (1979) [27] 胡啟章, “電化學原理與方法”, 五南圖書出版公司, 2002年 [28] 陳奕勳, “陽極沈積錳系水合氧化物於電化學超級電容器之應用”, 國立中正大學化學工程研究所碩士論文, 2003.
- [29] 薛皓之, “以無電鍍鍍觸媒成長奈米碳管應用於電化學超級電容器之研究”, 大葉大學電信工程學系碩士論文, 2006.
- [30] A. J. Bard, and L. R. Faulkner, “Electrochemical Principles, Methods, and Applications,” Oxford University, Britain, (1996).
- [31] Bard, A. J.; Faulkner, L. R., “Electrochemical Methods Fundamental and Application,” John Wiley & Sons, Canada, 1980.
- [32] J. S. Mattson, and Jr. H. B. Mark, “Activated Carbon: Surface Chemistry and Adsorption from Solution,” Wiley-Vch: New York, (1998)
- [33] J. P. Zheng and T. R. Jow, “A New Charge Storage Mechanism for Electrochemical Capacitors,” *J. Electrochem. Soc.*, 142, (1995) L6-L8
- [34] H. Zhao, H. Song, Z. Li, G. Yuan, Y. Jin, “Electrophoretic deposition and field emission properties of patterned carbon nanotubes,” *Appl. Surf. Sci.* (2005) 242 [35] C. Du and N. Pan, “High power density supercapacitor electrodes of carbon nanotube films by electrophoretic deposition,” *Nanotechnology* 17 (2006) 5314 – 5318 [36] T. Ito, L. Sun, R. M. Crooks, “Electrochemical Etching of Individual Multiwall Carbon Nanotubes,” *Electrochem. Solid State Lett.* 2003, 6, C4-C7.
- [37] Y. S. Park, Y. C. Choi, K. S. Kim, D. C. Chung, “High yield purification of multiwalled carbon nanotubes by selective oxidation during thermal annealing,” *Carbon* 39 (5) (2001) 655 – 661.
- [38] A. R. Boccaccini, J. Cho, J. A. Roether, Boris J. C. Thomas, E. J. Minay, Milo S. P. Shaffer, “Electrophoretic deposition of carbon nanotubes,” *Carbon* 44 (2006) 3149 – 3160 [39] C. Lia, D. Wang, T. Liang, X. Wang, J. Wu, X. Hu, J. Liang, “Oxidation of multiwalled carbon nanotubes by air: benefits for electric double layer capacitors,” *Powder Technology* 142 (2004) 175 – 179 [40] C. Du and N. Pan, “Supercapacitors using carbon nanotubes films by electrophoretic deposition,” *Journal of Power Sources* 160 (2006) 1487 – 1494 [41] S. R. C. Vivekchand, A. Govindaraj, Md. Motin Seikh and C. N. R. Rao, “A new method of purification of carbon nanotubes based on hydrogen treatment”, *J. Phys. Chem. B* 108 (2004) 6935-6937.
- [42] A. Dekanski, J. Stevanovic, R. Stevanovic, B. Z. Nikolic, V. M. Jovanovic, “Glassy carbon electrodes I. Characterization and electrochemical activation,” *Carbon* 39 (2001) 1195 – 1205