Effect of Temperature on Characteristic of Carbon Nanotube Nano-composite Electrode Supercapacitor

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In order to evaluate the effect of temperature on the performance of supercapacitor using coconut shell activated carbon (AC)/carbon nanotubes (CNTs) as nano-composite electrodes, the supercapacitor's properties were tested in 4mol L^{-1} KOH solution at 35℃~60℃.The results indicated, when temperature increased from 35℃ to 60℃, the resistance decreased from 0.83Ω to 0.78Ω by 6% and the capacitance increased from 93.32F g^{-1} to 104.36F g^{-1} by 11.8%. It was the contribution of high conductivity and the end open ration of CNTs. These results indicated that CNTs-based nano-composite electrode had good performance at high moderate temperature, and would be a promising material for use in low-cost electrical energy storage device.

Introduction

Since carbon/carbon supercapacitors possess many advantages such as high power density (10 kW kg^{-1}), fast recharge capability (within seconds), long cycle life (>10^5), they have been widely investigated (1-4) and are considered as one of the more promising devices for energy storage (5-8). Currently, commercial electrochemical capacitors (Maxwell, Panasonic, etc.) can be found in hybrid electrical vehicles, industrial power and energy management, and in renewable energy systems (9). However, the commercial supercapacitors' low energy density restricts their application in energy storage systems (10). Usually, two strategies are used to overcome this weakness; one involves adopting nanostructured electrode materials and the other is to increase the operating voltage window. Comparing the two approaches, although using non-aqueous electrolytes can improve a supercapacitor's operating voltage window, the organic electrolytes also suffer from problems such as conductivity, environmental contamination and cost (5, 11, 12). So the development of new nano-electrode materials is a more practical and effective method (6, 13-16).

Carbon nanotubes (CNTs) have attracted a great deal of attention in supercapacitor electrode applications because of superior electric conductivity, unique pore structure and stability (17). By plasma enhanced chemical vapor deposition method, integrated carbon nanotube (CNT) electrodes exhibited a rectangular cyclic voltammogram even at a scan rate of 1000 mV s^{-1}. Meanwhile, capacitance of the CNT electrodes increased from 38.7 to 207.3 F g^{-1} in 6M KOH solution by using ammonia plasma (18). The supercapacitors using multi-walled carbon nanotubes thin film as electrodes exhibited nearly ideal cyclic voltammograms even at a high scan rate of 1000 mV s^{-1}, and had a very high specific power density of about 30 kW kg^{-1} (19). Multiwalled carbon nanotube mixed with $Ni(OH)_2$ (wt.70%) , showed a capacity of 190 mA h g^{-1} at a current density of 0.4 A g^{-1} between 0 and 0.4 V vs. SCE in 6M KOH solution (20). They also exhibited good cycling performance and kept 90% of the initial capacity for over 2000 cycles. When nickel was deposited on the CNT surface, its wettability, electrical conductivity, adhesion strength, and the capacitive behavior was improved in 0.5mol L^{-1} KOH solution (21). Using a carbon nanotube array electrode, a specific capacitance of 365F g^{-1} was achieved with the discharge current density of 210mA g^{-1} in 1mol L^{-1} H_2SO_4 solution. In addition, the carbon nanotube array electrode was found to have low equivalent series resistance (ESR and good cycling stability (22). If the CNTs were treated with carbon dioxide and acid oxidized, its specific capacitance was increased from 21.8 F g^{-1} to 60.4 F g^{-1} in organic electrolyte (23).

Temperature is one of the key factors affecting the performance of a supercapacitor. In order to evaluate the application range of supercapacitor using CNTs (6 wt%)/ AC (96 wt%) as electrode, the effect of temperature on supercapacitor's performance, was tested in 4.0 mol L^{-1} KOH aqueous electrolyte over the temperature range of 35℃~60℃ using a two-electrode symmetrical system by various electrochemical techniques such as cyclic voltammetry, (CV) galvanostatic-cycle (GC) charge and discharge, and potentiostatic charge and galvanostatic discharge, respectively.

Experimental

Activated carbon (AC) was derived from coconut shell carbons activated with CO_2 at 900°C for one hour. After treated, the AC was washed and oven dried at 120℃ for 24h. Multiwall Carbon nanotubes (CNTs) bought from ElectroVac AG Company. These CNTs were rinsed with deionized water, then immersed in a hot (120°C) concentrated nitric acid solution, with the ratio of HNO_3 (volume) to CNTs (weight) being 5:1, for 30 hours and then washed to obtain a neutral solution. The washed CNTs were put into a beaker and placed in an oven at 110℃ for 24h.

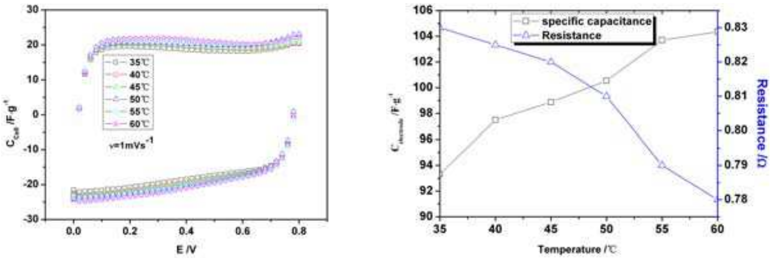
The electrode was manufactured according to the following process: Different compositions of the active materials, which were "x" wt% activated carbon, "y" wt% CNT, 4 wt% PTFE (polytetrafluoroethylene from Dupont), where x+y = 96 and y = 0, 2, 4, 6, 10, 16 and 20%, were put in a small beaker and ultrasonicated for 5min, and moved to hot water (80°C) for 10min. Finally, they were rolled into a single piece and then cut into small round pieces (15mm diameter). Finally, it was dried for more than 2 days at room temperature.

Using nickel mesh as a current collector, the cell was assembled by inserting one layer of porous polymeric separator between the two symmetrical electrodes. In order to maintain the cell under pressure, two PMMA plates were used to clamp the nickel mesh. The cell was immersed in 4mol L^{-1} KOH solution for 2 days at room temperature before testing.

The electrochemical measurements were conducted in 4.0 mol L^{-1} KOH aqueous electrolyte at room temperature using a two-electrode symmetrical system on a CHI660 electrochemical station. Interrupt current method was used to test the change of supercapacitor's resistance. That is, the cell was charged at 1mA, and then the current was interrupted suddenly when the potential reached 0.8V. The equivalent series resistance (ESR) was calculated according the potential drop near 0.8V. CV was measured between 0 and 0.8V at 1mV s^{-1}. GC curves were measured in the potential range 0 to 0.8V at 1mA. Galvanostatic discharge was carried immediately at -0.1A after potentiostatic charging (@0.8V) for 20min.

Results and disscusion

Figure 1 illustrated the curves of cyclic voltammogram, specific capacitance and resistance of CNTs/AC supercapacitor in 4 mol L^{-1} KOH solution at different temperatures. From Fig.1, the CV curves were all close to an ideal rectangular shape, and enlarged slightly with temperature increasing. In addition, the calculated resistance decreased while the electrode's specific capacitance improved. For example, as the temperature increased from 35℃ to 60℃, the cell's resistance decreased from 0.83Ω to 0.78Ω (decreasing 6%) and the capacitance increased from 93.32F g^{-1} to 104.36F g^{-1} (increasing 11.8%).

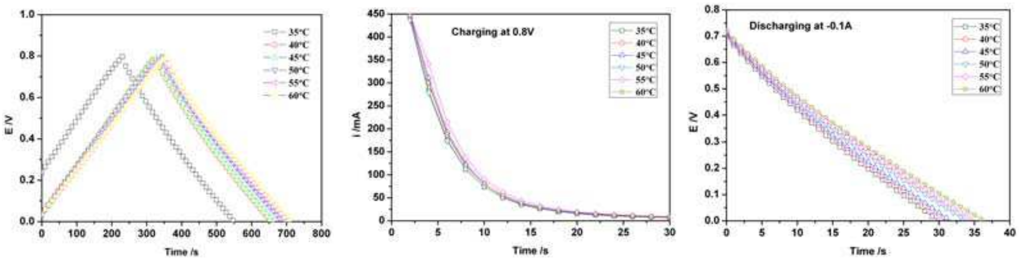


(a) (b)

Fig.1 The effect of temperature on the curves of the specific capacitance and the resistance (a) CV curves (b) the specific capacitance and the resistance

The effect of temperature on the charging/discharging kinetics was shown in figure 2. The capacitor had an ideal triangle-like charge/discharge curve, which were similar to an ideal polarized electrode during galvanostatic cycling. That is, a linear relation was obtain between the potentials and the charge/discharge time under a constant current (24). At the same time, the charging/discharging curves shifted to the right gradually with temperature increasing. So, the area under the curve increased, which was consistent with the aforementioned results of the CV curves. Meanwhile, all the curves were symmetrical and linear, which suggested the nano-composite electrodes had excellent reversibility and better charging/discharging properties.

When the capacitors were charged at 0.8V, the time to charge was almost the same for all of the temperatures. Discharging at -0.1A (from 0.8V to 0V) revealed a movement toward to right side, Although charging at 0.8V showed that under a constant voltage driving force the capacitor charged at an almost constant rate over the temperature range studied, discharge of the capacitor under a constant flux (0.1A) showed that more energy had been stored at higher temperatures. That meant the higher the temperature was the more energy the supercapacitor stored.



(a) (b) (c)

Fig.2 The effect of temperature on GC, potentiostatic charging and galvanostatic discharging curves

(a) GC curves (b) potentiostatic charging curves (c) galvanostatic discharging curves

The observed effect of temperature on the behavior of the supercapacitor could be explained by analysis of the role of the CNT's in the nano-composite electrode electrode. First, the electrical conductivity of CNTs is higher than that of AC and using HNO_3 to treat CNTs could improve their conductivity (25). Second, after being boiled in concentrated HNO_3 solution, most ends of the CNTs were opened (Fig.3) and their surface chemistry were changed, which increased surface area and introduced more carbonyl and carboxy functional groups onto the walls of the CNTs. This would allow to adsorb more ions and keep good interconnection with AC (25). The good conductivity and connectivity to the high surface area of AC would improve the accessibility of charge to the structure. Finally, the higher temperatures would be expected to decrease the cell resistance through effects on electrolyte density, viscosity, and ion mobility. So, the higher the temperature was the more the cell stored energy. The results indicated that carbon nanotube addition to an activated carbon would be a promising nano-composite material for use in supercapacitors.

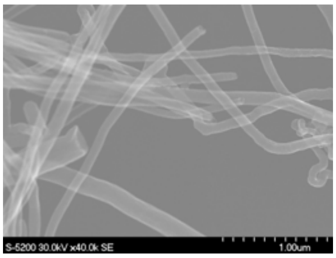


Fig.3 SEM of CNTs boiled in concentrated acid solution

Conclusions

Therefore, for the capacitor using AC/CNTs as electrode, its capacitance was increased and equivalent series resistance was reduced when increasing operating temperature of the aqueous electrolyte. As a result, its energy and power output were improved. The above mentioned results indicated the CNTs-based nano-composite electrode had good performance at high moderate temperature, and would be a promising material for use in electrical energy storage device.

Acknowledgments

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References

1. Y.W. Cheng, S.T. Lu, H.B. Zhang, C.V. Varanasi, J. Liu. *Nano Lett.*, **12, 4206** (2012).
2. X.F. Wang, D.Z. Wang, J. Liang. *J Inorg Mater.*, **17, 1167** (2002).
3. A.Celzard, F. Collas, J.F. Mareche, G. Furdin, I. Rey. *J Power Sources*, **108, 153** (2002).
4. J. Gamby, P.L. Taberna, P. Simon, J.F. Fauvarque, M. Chesneau. *J Power Sources*, **101, 109** (2001).
5. W. Zhang, C. Ma, J. Fang, J. Cheng, X. Zhang, S. Dong, et al. *Rsc Adv.*, **3, 2483** (2013).
6. Q.Q Li, F. Liu, L. Zhang, B.J. Nelson, S.H. Zhang, C. Ma, et al. *J Power Sources*, 2**07, 199** (2012).
7. Y.P. Zhai, Y.Q. Dou, D.Y. Zhao, P.F. Fulvio, R.T. Mayes, S. Dai. *Adv Mater.*, **23, 4828** (2011).
8. K. Naoi. *Fuel Cells*, **10, 825** (2010).
9. C. Portet, P.L. Taberna, P. Simon, E. Flahaut, C. Laberty-Robert. *Electrochim Acta.*, **50, 4174** (2005).
10. T. Sato, Y. Suda, H. Uruno, H. Takikawa, H. Tanoue, H. Ue, et al. *J Phys Conf Ser.*, **40, 352** (2012).
11. K. Tonurist, T. Thomberg, A. Janes, I. Kink, E. Lust. *Electrochem Commun.*, **22, 77** (2012).
12. S. Yamazaki, T. Ito, M. Yamagata, M. Ishikawa. *Electrochim Acta.*, **86, 294** (2012).
13. T.Z. Ren, L. Liu, Y.Y. Zhang, Z.Y. Yuan. *J Solid State Electr.*, **17, 927** (2013).
14. Q. Liu, O. Nayfeh, M.H. Nayfeh, S.T. Yau. *Nano Energy*, **2, 133** (2013).
15. E. Montibon, M. Lestelius, L. Jarnstrom. *J Appl Polym Sci.*, **125, E34** (2012).
16. H. Tian, Y. Yang, D. Xie, T.L. Ren, Y. Shu, C.J. Zhou, et al. *Nanoscale,* **5, 890** (2013).
17. M. Noked, S. Okashy, T. Zimrin, D. Aurbach. *Carbon*, **58, 134** (2013).
18. B.J.Yoon, S.H. Jeong, K.H. Lee, H.S. Kim, C.G. Park, J.H. Han. *Chem Phys Lett.*, **388, 170** (2004).
19. C.S. Du, J. Yeh, N. Pan. *Nanotechnology*, **16, 350** (2005).
20. Y.G. Wang, L.Yu, Y.Y. Xia. *J Electrochem Soc.*, **153, A743** (2006).
21. M.S. Wu, C.Y. Huang, K.H. Lin. *Electrochem Solid St.*, **12, A129** (2009).
22. Q.L. Chen, K.H. Xue, W. Shen, F.F. Tao, S.Y. Yin, W. Xu. Electrochim Acta, 49, 4157 (2004).
23. C.S. Li, Y.J. Qiao, J.J Wu, D.Z. Wang, D.B. Yuan. *Sci China Technol Sc.*, **53, 1234** (2010).
24. J.M. Shen, A.D. Liu, Y. Tu, G.S. Foo, C.B. Yeo, M.B. Chan-Park, et al. *Energ Environ Sci.*, **4, 4220** (2011).
25. J.A. Starkovich, E.M. Silverman and H.-H. Peng, **US20130183439A1**, 2012.

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