Bulgarian Chemical Communications, Volume 48, Special C (pp. 39–42) 2016

Symmetric device performances of carbon based nanostructures for supercapacitors

M. Ates*

Department of Chemistry, Faculty of Arts and Sciences, Namik Kemal University, Degirmenalti Campus, 59030, Tekirdag, Turkey

Received June 26, 2016, Revised September 10, 2016

In this review article, symmetric device performances of carbon based nanostructures were reviewed and presented for supercapacitors. There are many important parameters to affect the supercapacitor device performances. The most important one is the formation of active materials used for electrodes. Nowdays, graphene based nanostructures have been used as an active electrode material due to their storage capability of more charges compared to other carbon materials. Supercapacitors divide two main parts: pseudocapacitors and electrical double layer capacitors (EDLCs). Conducting polymers are also used as important active material components due to their good conductivity. Some techniques were also presented to obtain information about capacitance, such as electrochemical impedance spectroscopy (EIS) etc.

Keywords: Carbon nanostructures, nanomaterials, conducting polymers, supercapacitors, double-layer capacitance, graphene.

INTRODUCTION

Graphene is used in many applications, such as energy storage, environmental protection, chemical conversion, electrocatalysis, nanoelectronics etc. Graphene facile stacking nature caused by the strong π-π interaction and van der Waals forces between graphene layers [1]. 3D porous graphene significantly enhanced the energy storage performance because of increasing surface area and effective pores to transport or store electrons / ions for bulk use in many devices [2, 3]. Zhao et al have studied $Ni(OH)_2$ nanocrystals which have been synthesized via a gas liquid diffusion method at room temperature in the absence of any template or organic surfactant [4]. Supercapacitors have much attention over the past decade due to their extremely high power density, long cycle life and short changing time [5]. Supercapacitors divide into two categories, namely pseudocapacitors [6], and electrical double layer capacitors (EDLCs). EDLC stores electric charges at the interface between the electrode and the electrolytes. Electroactive materials have been made from carbon materials with high surface area, such as graphene, carbon nanotubes and porous carbon [7]. Moden electronic devices, such as electric/hybrid vehicles, mobile communication devices has high-performance energy storage resources [8]. The illustration of supercapacitor device was given in Figure 1.

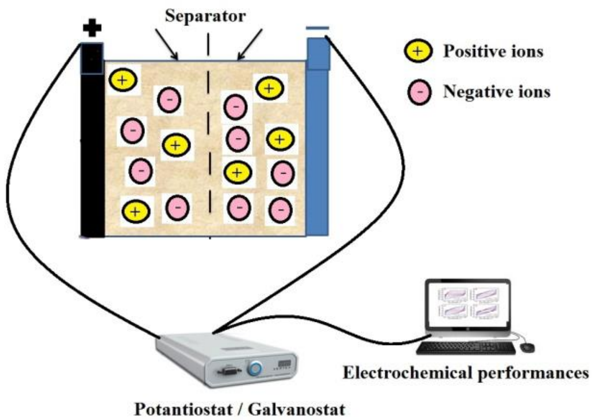

Fig. 1. The illustration of supercapacitor device with all components.

PSEUDOCAPACITORS

Pseudocapacitors have transition metals (Ru, Co, Fe, Mn etc.) oxides higher capacitance and energy density because of the fast and reversible faradaic reactions [9-11]. Among the transition metal oxides, manganese (Mn) compounds have been used due to its multi-oxidation states for charge transfer and reversible adsorption [12]. Mei et al [13] presented that MnO_2-graphene composite has the specific capacitances of C_{sp}= 112 Fg^{-1} in 1 M Na_2SO_4 and C_{sp}= 165 Fg^{-1} in 6 M KOH electrolyte, respectively.In addition, multiwalled carbon nanotubes / α-MnO_2 coaxial nanocable films through electrophrotic deposition process shows a high mass specific capacitance of C_{sp}= 327 Fg^{-1} and good cycle stability [14]. MnO_2 nanorods / graphene composite was synthesized a specific

* To whom all correspondence should be sent:
E-mail: mates@nku.edu.tr

capacitance of C_{sp}= 268 Fg^{-1} at a current density of 0.5 Ag^{-1} [15]. The PANI-5% acetylene black (AB) hallowed hybrids show much better electrochemical performance (C_{sp}= 520 Fg^{-1} at 1 Ag^{-1}) than that of pure PANI pseudocapacitors (C_{sp}= 271 Fg^{-1} at 1 Ag^{-1}). In addition, the high power density of P= 1361 Wkg^{-1} and energy density of E= 17.8 $Whkg^{-1}$ at current density of 2 Ag^{-1} even 6.32 $kWkg^{-1}$ and 14.1 $Whkg^{-1}$ at high current density of 10 Ag^{-1} [16]. The fabricated flexible and transport pseudocapacitor of ultrafine Co_3O_4 nanocrystal shows a high capacitance of C_{sp}= 177 Fg^{-1} on a mass basis and C_{sp}= 6.03 $mFcm^{-2}$ based on the area of the active material at a scan rate of 1 mVs^{-1}, as well as a super-long cycling life with 100% retention rate after 20.000 cycles [17]. One of the highest capacitance value was obtained as C_{sp}= 2105 Fg^{-1} for $Ni_{10}Co_5$ LDH NSs/CNs electrode at a current density of 2 Ag^{-1} as well as an excellent cyclic stability as a pseudocapacitive electrode material [18]. Ren et al have reported metallic cobalt pyrite (CoS_2) nanowires (NWs) prepared directly on current collecting electrodes, e.g., carbon cloth or graphite disc, for high-performance supercapacitors [19].

Electrical double layer capacitors

Electrochemical capacitors (ECs) are used for an electrode of a given polarity, opposite charges stored on the electrode surface. Two parallel plates constitude capacitor and the consequent device are called as electrical double layer capacitors (EDLCs) [20]. In literature, Zhou et al have studied highly porous nanostructures with large surface areas, which are typically employed for EDLCs to increase gravimetric energy storage capacity; however, carbon based electrodes with high surface area show in poor volumetric capacitance due to the low packing density of porous materials. They found ultrahigh volumetric capacitance of C_{sp}= 521 Fcm^3 in aqueous electrolytes for non-porous carbon microsphere electrodes codoped with fluorine and nitrogen, which is synthesized by low temperature solvothermal route. The carbon nanostructures including CNTs-based networks, graphene based architectures, hierarchical porous carbon based nanostructures and other even more complex carbon based 3D configurations were studied in literature [21].

Active materials

Active materials were obtained many polymeric and composite materials which include carbon based nanostructures. Composite materials with polymeric matrix consist of a fiber material, which is used as the core and a matrix material [22]. The fiber reinforced materials have more advantages than the other composite materials due to their low weight, resistance against the corrosion, heat sound and electric isolation [23, 24]. Active materials are synthesized by two ways, such as chemical and electrochemical synthesis. The active materials were characterized by FTIR-ATR, ^{1}H-NMR, ^{13}C-NMR, CV, SEM-EDX, and AFM analysis. Symmetric device was fabricated to examine supercapacitor device performances with CV, constant current (CC), and EIS analysis. To understand the more information about energy density, power density and charge transfer resistance (R_{ct}), Warburg impedance etc, Ragone plot and equivalent circuit models were analyzed obtained from electrochemical measurements. The high performance capacitive behaviour depends on the total mass (current collectors, electrolyte type, separator, etc.), thus, the greater percentage of active materials in the electrode material results in more energy storage in the supercapacitor device [25]. Carbons are used to fabricate supercapacitor active electrode materials due to the low cost, easy availability, nontoxic nature, environmental friendless, and stability [26].

Conducting polymers

Conducting polymers were used in many usage areas, such as energy storage (batteries and supercapacitors), electrochromic devices (smart windows, mirrors IR and microwave shutters), antistatic coatings (displays, flat TV screens), semiconductor devices (solar cells), corrosion protection, mechanical actuators, bioapplication (drug delivery systems, artificial muscles, biosensors). A novel synthesis of Cz-EDOT comonomers and their copolymers (EDOTTsCz, EDOTVBCz, and EDOTMetac) were synthesized in our previous studies. The aim of these syntheses is to obtain capacitance performances of the active materials [27]. Three-dimensional (3D) material shows great attention all the time because it exhibits the enhanced capacitive performance comparing with the low dimensional nanoscale building blocks [28].

There are many parameters affecting the conducting polymers, such as current density, used methods, type of solvent and electrolytes, monomer concentration, monomer structure and applied potential etc. The performance of a supercapacitor depends on many factors, such as the active material used as the electrode, the nature of electrolyte, and the interface between electrode and electrolyte [29]. In literature, PANI-based supercapacitor by designed the PANI-acetylene black (PANI-AB) hybrid nanostructures supported by MnO_2 nanotubes have good long-term cycling stability and 86% of the capacitance after 1000 cycles by CV test at a scan rate of 50 mVs^{-1} compared to that of pure PANI based supercapacitors [30]. Li et al have studied PANI/carbon nanotubes with ternary coaxial structures as supercapacitor electrodes via a simple wet chemical method [31].

Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopic analysis (EIS) were examined using Nyquist plots, which show the frequency response of the electrode/electrolyte system, graph the imaginary component (Z′). Nyquist plots show three parts. In the first part, a semicircle in the high to medium frequency region, with the starting cross-point at the Z′ axis, consists of the combined series resistance of electrolyte, electrode and current collectors, such as stainless steel, in the second part; a straight line with a slope of 45^o in the low-frequency range which representative to the semi-infinite Warburg impedance, resulting from the frequency dependence of the ion diffusion / transport in the electrolyte, in the third part; a vertical line at very low frequencies, which is obtained by the accumulation of ions at the bottom of the pores of the electrode [32]. A vertical line proves a good capacitive behaviour without diffusion limitations [33]. A low frequency capacitive value can be calculated from the Nyquist plot according to the following equation 1.

$$C_{sp} = -1 / (2\pi \times f \times Z''), \qquad (1)$$

where f is the frequency and Z″ (f) is the imaginary part of the impedance. The relationship between the specific capacitance and frequency shows the penetration of the alternating current into the bulk pores of the electrode material, which can indicate how many electrolyte ions have reached the pore surfaces at a specific frequency [34]. EIS, CV and CC analysis of different types of polymers and nanocomposites were analyzed in literature [35-37]. Mn_3O_4 samples were prepared in 0.05 M $Mn(NO_3)_2$ solution for 30 min delivered a large gravimetric specific capacitance of C_{sp}= 210 Fg^{-1} at a current density of 0.5 Ag^{-1}, and a good rate capability over other samples [38].

The symmetrical supercapacitors based on the porous silicon carbide spheres (PSiCS) electrode with an aqueous electrolyte (1 M KCl) or an organic electrolyte (1 M tetraethyl ammonium tetrafluoroborate) in acetonitrile were designed in literature [39]. There are many usage areas of supercapacitors from portable electronic devices to electric vehicles. The study written by Niesson et al have mentioned about the steady-state impedance measurements, cross-correlated with cyclic voltammetry, which show discharging of the electrical double layer capacitance [40].

CONCLUDING REMARKS

Supercapacitors have lower energy than batteries but higher power density with fast charge/discharge rates and a much larger cycle life than rechargeable batteries. In this review article, we firstly classified the electrochemical capacitors as pseudocapacitors and EDLCs. Secondly, we investigated the active materials used in supercapacitor devices, conducting polymers, and electrochemical impedance spectroscopy. Symmmetic supercapacitor devices were fabricated by carbon based nanostructures, such as graphene, carbon nanotubes, carbon fibers, etc. Not only the specific capacitance (C_{sp}) performance but also the energy (E) and power density (P) values should be higher for supercapacitors. To obtain the higher C_{sp}, E and P performances, the active electrode materials should be fabricated by higher conductive and higher surface area materials.

Acknowledgments: *Dr. Murat Ates acknowledges to Namik Kemal University for financial support at 2nd AIOC ICNTC 2016 Conference in Zagreb, Croatia.*

REFERENCES

1. J.L. Shi, H.F. Wang, X. Zhu, C.M. Chen, X. Huang, X.D. Zhang, B.Q. Li, C. Tang, Q. Zhang, *Carbon*, **103**, 36 (2016).
2. S. Mao, G.H. Lu, J.H. Chen, *Nanoscale*, **7**, 6924 (2015).
3. J.L. Shi, H.F., Wang, X. Zhu, C.M. Chen, X. Huang, X.D., Zhang, B.Q. Li, C. Tang, Q. Zhang, *Carbon*, **103**, 36 (2016).
4. J. Zhou, Z. Shi, Q. Zhang, *J. Alloys Compounds*, **668**, 176 (2016).
5. B.P. Bastakoti, H.S., Huang, L.C. Chen, K.C.W. Wu, Y. Yamauchi, *Chem. Commun.*, **48**, 9150 (2012).
6. I. Shakir, M. Nadeem, M. Shahid, D.J. Kang, *Electrochim. Acta*, **118**, 138 (2014).
7. M.F. Warsi, I. Shakir, M. Shahid, M. Sarfraz, M. Nadeem, Z.A. Gilahi, *Electrochim. Acta*, **135**, 513 (2014).
8. J. Li, X. Zhang, J. Guo, R. Peng, R. Xie, Y. Huang, Y. Qi, *J. Alloys Comp*., **674**, 44 (2016).
9. W. Li, K. Xu, B. Li, J. Sun, F. Jiang, Z.Yu, R.Zou, Z. Chen, J. Hu, *Chem. Electrochem.* , **1**, 1003 (2014).
10. J. Huang, J. Zhu, K. Qheng, Y. Xu, D. Cao, G. Wang, *Electrochim. Acta*, **75**, 273 (2012).

11. R.B. Rakhi, W. Chen, M.N. Hedhili, D. Cha, H.N. Alshareef, *ACS Appl. Mater. Interfaces*, **6**, 4196 (2014).
12. S. He, W. Chen, *J.Power Sources*, **294**, 150 (2015).
13. J. Mei, L. Zhang, *J. Solid State Chem*., **221**, 178 (2015).
14. H. Fang, S. Zhang, X. Wu, W. Liu, B. Wen, Z. Du, T. Jiang, *J. Power Sources*, **235**, 95 (2013).
15. Y. Cao, Y. Xiao, Y. Gong, C. Wang, F. Li, *Electrochim. Acta*, **127**, 200 (2014).
16. Y. Xi, G. Wei, X. Liu, M. Pang, L. Liu, Y. Yang, Y. Ji, V.Y. Izotov, N.I. Klyui, W. Han, *Chem. Eng. J*., **290**, 361 (2016).
17. X. Liu, Y.Q. Gao, G.W., Yang, *Nanoscale*, **8**, 4227 (2016).
18. G. Nagaraju, G.S.R. Raju, Y.H. Ko, J.S. Yu, *Nanoscale*, **8**, 812 (2016).
19. R. Ren, M.S. Faber, R. Dziedzic, Z.H. Wen, S. Jin, S. Mao, J.H. Chen, *Nanotechnology*, **26**, Article number: 494001 (2015).
20. P.R. Bandaru, H. Yamada, R. Narayanan, M. Hoefer, *Materials Science and Engineering R*, **98**, 1 (2015).
21. H. Jiang, P.S. Lee, C.Z. Li, *Energy & Environmental Science*, **6**, 41 (2013).
22. C. Misirli, N. Becenen, M. Sahin, *Applied Mechanics and Materials*, **555**, 406 (2014).
23. N. Becenen, *Tekstili Obleklo*, **57**, 8 (2009).
24. N. Becenen, B. Eker, M. Sahin, *J. Reinforced Plastics and Composites*, **29**, 3637 (2010).
25. S.H. Kazemi, M.A. Kiani, M. Ghaemmaghami, H. Kazemi, *Electrochim. Acta*, **197**, 107 (2016).
26. P.V. Adhyapak, T. Maddanimath, S. Pethkar, A.J. Chandwadkar, Y.S. Negi, K. Vijayamohanon, *J. Power Sources*, **109**, 105 (2002).
27. M. Ates, N. Uludag, T. Karazehir, F. Arican, *Ovidius University Annals of Chemistry*, **23**, 63 (2012).
28. Y. Zhang, Z. Hu, Y. An, B. Guo, N. An, Y. Liang, H.Wu, *J.Power Sources*, **311**, 121 (2016).
29. A.G. Pandolfo, A.F. Hollenkamp, *J. Power Sources*, **157**, 11 (2006).
30. Y. Xi, G. Wei, X. Liu, M. Pang, L. Liu, Y. Yang, Y. Ji, V.Y. Izotov, N.I. Klıyui, W. Han, C*hemical. Eng. J*., **290**, 361 (2016).
31. Q. Li, J. Liu, J. Zou, A. Chunder, Y. Chen, L. Zhai, *J. Power Sources*, **196**, 565 (2011).
32. M.J. Kim, J.H. Kim, *Phys. Chem. Chem. Phys*., **16**, 11323 (2014).
33. M.J. Kim, J.H. Kim, *ACS Appl. Mater. Interfaces*, **6**, 9036 (2014).
34. W. Xing, S.Z. Qiao, R.G. Ding, F. Li, G.Q., Lu, Z.F. Yan, H.M. Cheng, *Carbon*, **44**, 216 (2006).
35. A.S. Sarac, S. Sezgin, M. Ates, C.M. Turhan, *Adv. Polym. Technol.*, **28**, 120 (2009).
36. M. Ates, A.S. Sarac, *Prog. Org. Coat*., **65**, 28 (2009).
37. M. Ates, J. Castillo, A.S. Sarac, W. Schuhmann, *Microchim. Acta*, **160**, 247 (2008).
38. Z. Qi, A. Younis, D. Chu, S. Li, *Nano-Micro Letters*, **8**, 165 (2016).
39. K. Myeongjin, O. Ilgeun, K. Jooheon, *Phys. Chem. Chem. Phys*., **17,** 16367 (2015).
40. A.H. Niessen, J. De Jonge, P.H.L. Notten, J. *Electrochem. Soc*., **153**, A1484 (2006).