Study on structural and enhancement of current in activated carbon by incorporating multiwalled carbon nanotube as binary nanocomposites

Manoranjan Mandal¹, Subhasri Subudhi¹, Sonali Das¹, Kadambinee Sa¹, Injamul Alam¹, BVRS Subramanyam¹, Jagatpati Raiguru² and Pitamber Mahanandia^{1*}

¹ Department of Physics & Astronomy, National Institute of Technology Rourkela,769008, India

² Department of Electrical Engineering, National Institute of Technology Rourkela, 769008, India

Abstract

Supercapacitor (SC) also called ultracapacitor is an electrochemical energy storage device applied to store electrical charges and pulse power supply. It is expected that both energy and power density could be improved by making the SC composite structure using highly conducting materials multiwalled carbon nanotubes (MWCNTs) in activated carbon (AC). Also the performance of SC depends on some major factors of its electrode materials like high electrical conductivity, good mesoporocity, high specific surface area etc., so the structural and electrical study of MWCNTs incorporated in host activated carbon (AC) that forms nanocomposite prepared by a simple, low cost and environment friendly method has been reported. The structural properties of AC, MWCNTs and AC/MWCNTs have been examined by XRD, SEM and Raman spectroscopy. The enhancement of current in AC by adding MWCNTs has been analysed by current(I)-voltage(v) measurements. The observed results suggest that the prepared composite could be used for supercapacitor application.

Keywords: Supercapacitor, pseudocapacitor, activated carbon, carbon nanotube, Raman, SEM and XRD

1. Introduction

To meet the rapidly increasing world-wide energy consumption, advances of renewable energy technology and storage devices are very important. Therefore, developing devices that are cheap, environment-friendly, highly efficient and reproducible energy storage devices are necessary. Supercapacitors (SCs) are among energy storage devices which have gained significant attention owing to their advantages such as long cycle life, high power density, minor environmental impact and rapid charging/discharging process [1,2]. Prominent interest has been concentrated on the application of carbon as electrode materials for SCs such as

activated carbons [3], templated carbons, carbon nanotubes (CNTs) [4-6] and graphene [7-11] due to an easy processability, accessibility and comparatively low cost. They have good stability in different chemical solutions (from acidic to basic) and can perform in a wide range of temperatures. High-surface-area activated carbons (ACs) are major electrode materials for marketable supercapacitors. However, ACs have a low specific capacitance due to their bad electrolyte accessibility, low mesoporosity and low electrical conductivity. Even if they have a high specific surface area (3500 m^2/g) [12]; well-adjusted surface area, conductivity and mesoporosity are thus extremely desirable for carbon electrode materials to be applied in highperformance supercapacitors. CNTs are the favourable nanomaterials for microelectronic and energy storage devices nowadays because of their good electrical conductivity, highly accessible specific surface area, excellent mechanical strength, exceptional nanoscale structures and flexibility [13,14] overcome the limitation of AC. Therefore, by incorporating MWCNTs in AC, it is expected that the life cycle, electrical conductivity, mechanical and thermal stability could be enhanced which results into increasing in both power and energy density of SC. Since the supercapacitor performance depends on the structural and electrical properties of the electrode materials, it is essential to study these properties of MWCNTs incorporated AC electrode material.

Here a simple, cheap and environmental friendly method has been followed to prepare the nanocomposites. The structural properties of AC, MWCNTs and AC/MWCNTs have been examined by XRD, SEM and Raman. Increase in current i.e. increase in conductivity of the MWCNTs mixed AC composites have been observed by current(I)-voltage(V) measurement.

2. Experimental

2.1 Materials

All the chemicals such as benzene (C_6H_6 with > 99.5% purity), nitric acid (HNO₃ with > 98% purity), hydrochloric acid (HCL with > 98% purity), tetrahydrofuran (C_4H_8O with > 99% purity) and ferrocene ($C_{10}H_{10}Fe$ with > 98% purity) were taken from Sigma-Aldrich (India) and has been used without any further purification.

2.2 Preparation of AC/MWCNTs nanocomposite

Commercially available AC has been used. The procured AC has been further activated to increase the mesoporosity by adding proper amount (well dispersed) of nitric acid [15] to activated carbon and kept for 12 hours and then sonicated for two hours. The products are filtered until the pH value comes to neutral (pH=6-7) and then put in an oven at 100° C for 3 hours. Finally, the purified with well-developed mesoporosity activated carbon has been recovered.



Fig.1 Schematic diagram of (a) Single hot zone pyrolysis assisted chemical vapour deposition setup and (b) Calibrated temperature profile across the furnace.

Multi walled carbon nanotube (MWCNTs) have been produced by simple pyrolysis method [16] as shown in Fig.1. Initially 2 ml of benzene was taken in a measurement tube and then 25 mg of ferrocene was added to it. Then the mixture was put into the quartz tube whose one end was closed and the other was attached to a rubber bladder to accumulate the remaining by products. The quartz tube was put into an air oven at 850°C for four hours. Around 78mg of carbon nanotube was obtained. MWCNTs are ultra-sonicated in an isopropyl alcohol (IPA) for

30 minutes to acquire the homogeneous diffusion and then heated at 550° C to take away the amorphous carbon. The purification of MWCNTs have been followed as per the standard procedure [17] and recovered 48 mg of purified MWCNTs.

The purified AC and MWCNTs (5 wt.%) were sonicated for 2 hours individually after grinding. The nanocomposite was prepared by mixing together and put into the magnetic stirring for 5 hours. Finally the material has been recovered after drying in air for 2 hours at 80°C to get the AC/MWCNTs binary nanocomposites.

3. Results and discussion

The surface morphology of as synthesized nanocomposite has been carried out by Scanning electron microscope (SEM) are shown in Fig.2. The surface morphology of AC showing the large number of pores responsible to access the electrolyte ions results into increase the specific capacitance shown in Fig.2(a). MWCNTs shows uniform and aligned nature which responsible for fast ions transportation results into increase power density. The average diameter was 155 nm as shown in Fig.2(b). Figure 2(c) represents the surface morphology of the composite and distribution of MWCNTs in AC are well observed in the SEM images.



Fig. 2 SEM images of (a) AC, (b) MWCNTs and (c) AC/MWCNTs nanocomposite.

The crystal quality and phase purity of prepared nanocomposite were analysed by powder XRD. Fig.3 (a) shows the XRD analysis of AC, MWCNTs and AC/MWCNTs nanocomposite. The peaks at $2\theta = 23.91^{\circ}$ and 43.43° are the typical peaks with the diffraction plane (002) and (101) observed for AC [18] confirm the presence of graphite crystalite with less broadening i.e more crystality. MWCNTs shows a strong peak at 26.08° with the diffraction plane (002), reveals that nanotubes are cylindrical and multiwall in nature [19].



Fig. 3 (a) XRD and **(b)** Raman spectra of AC, MWCNTs and AC/MWCNTs nanocomposite. The crystal structure with the diffraction plane (002) and (101) observed for AC/MWCNTs nanocomposites as shown in Fig.3(a) and shows the increase in broadening i.e decrease in crystality reveals presence of more defects might be due to the presence of MWCNTs.

Raman spectra of AC, MWCNTs and AC/MWCNTs nanocomposite has been shown in Fig.3 (b). The characteristic bands of AC i.e. D and G bands at ~ 1338 cm^{-1} and ~ 1598 cm^{-1} [20] and similarly for MWCNTs, D band at ~ 1347 cm^{-1} and G band at ~ 1573 cm^{-1} [21]. The characteristics bands of the composite, D band at ~ 1347 cm^{-1} and G band at ~ 1581 cm^{-1} . The intensity ratio of D and G bands (I_D/I_G) gives the amount of structural defects and (I_D/I_G) value for AC and MWCNTs are 1.09 and 0.98, where as for their nanocomposite this value decreases to 0.93. This decrease in (I_D/I_G) value reveals that the structural defects decreases and G peak intensity increases in AC/MWCNTs nanocomposite may be due to the presence of MWCNTs.



Fig. 4 Current (I) –Voltage (V) curve of (a) AC, (b) MWCNTs and (c) AC/MWCNTs nanocomposite.

The electrical properties of binary nanocomposite as well as the individuals are analysed by I-V measurement as shown in Fig.4. AC is showing non ohmic due to the presence of impurities as well as defects and the calculated sheet resistance and maximum current were 97.18K Ω and 0.11mA at 10V. MWCNTs gives the linearity behaviour of current with voltage implieses ohmic nature and the sheet resistance and maximum current were 0.64K Ω and 10.07mA at 5.28V. By incorporating MWCNTs over host AC,the sheet resistance and current have been found 0.93K Ω and 10.10mA at 9.31V. However, the current increase in nanocomposite comparatively larger than AC. The improve in current i.e. increase in conductivity in AC/MWCNTs nanocomposite may be due to the presence MWCNTs. This result reveals that comnbination of porosity with better conductivity in this composite could be used as a electrode material for supercapacitor.

4. Conclusion

We have successfully prepared AC/MWCNTs binary nanocomposite by a simple processing method. The structural properties of the prepared nanocomposite have been investigated. The electrical study was analysed by current(I)-voltage(V) measurement of the nanocomposite which confirmed the ohmic behaviour and increase in current i.e increase in conductivity is due to the presence of MWCNTs. The finding suggests that the nanocomposite could be used for supercapacitor.

Acknowledgement

This work was financially supported by Ministry of Human Resource Development (MHRD), government of india through National Institute of Technology Rourkela (NITR).

References

[1] Liu C, Li F, Ma LP, Cheng HM. Advanced materials for energy storage. Adv. Mater 2010;22: 28-62.

[2] Simon P, Gogotsi Y. Materials for electrochemical capacitors. Nat. Mater 2008; 7: 845-857.

[3] Frackowiak E, Beguin F. Carbon materials for the electrochemical storage of energy in capacitors. Carbon 2001; 39: 937–950.

[4] Taberna PL , Chevalier G, Simon P , Plée D , Aubert T . Activated carbon–carbon nanotube composite porous film for supercapacitor applications. Mater Res Bull 2006; 41: 478-484.

[5] Futaba DN, Hata K, Yamada T, Hiraoka T, Hayamizu Y, Kakudate Y, Tanaike O, Hatori H, Yumura M, Iijima S. Shape-engineerable and highly densely packed single-walled carbon nanotubes and their application as super-capacitor electrodes. Nat. Mater. 2006; 5: 987–994.

[6] Izadi-Najafabadi A, Yasuda S, Kobashi K, Yamada T, Futaba D. N, Hatori H, Yumura M, Iijima S, Hata K. Extracting the full potential of single-walled carbon nanotubes as durable supercapacitor electrodes operable at 4V with high power and energy density. Adv. Mater. 2010; 22: 235-241.

[7] Huang J, Wang J, Wang C, Zhang H, Lu C, Wang J. Hierarchical Porous Graphene Carbon-Based Supercapacitors. Chem. Mater. 2015; 27: 2107–2113. [8] Wang Y, Shi ZQ, Huang Y, Ma YF, Wang CY, Chen MM, Chen YS. Electrochemical synthesis of highly corrugated graphene sheets for high performance supercapacitors. J. Phys. Chem. C 2009; 113: 13103–13107.

[9] Stoller MD, Park SJ, Zhu YW, An JH, Ruoff RS. Graphene-Based Ultracapacitors. Nano Lett. 2008; 8: 3498–3502.

[10] Wang DW, Li F, Zhao JP, Ren WC, Chen ZG, Tan J, Wu ZS, Gentle I, Lu GQ, Cheng H M. Fabrication of Graphene/Polyaniline Composite Paper via in Situ Anodic Electropolymerization for High-Performance Flexible Electrode. ACS Nano. 2009; 3: 1745– 1752.

[11] Sun YQ, Wu QO, Shi GQ. Graphene based new energy materials. Energy Environ. Sci. 2011; 4:1113–1132.

[12] Li Li Zhang, Zhao X S. Carbon-based materials as supercapacitor electrodes. Chem. Soc. Rev. 2009; 38: 2520-2531

[13] Guldi DM, Rahman GMA, Zerbetto F, Prato M. Carbon Nanotubes in Electron Donor–Acceptor Nanocomposites. Acc. Chem. Res. 2005; 38: 871–878.

[14] Bandaru PR. Electrical properties and applications of carbon nanotube structures. Nanotechnol. 2007; 7:1239–67.

[15] Satapathy D, Natarajan GS. Surface modification of granular activated carbon by nitric acid for the enhancement of copper adsorption. Indian J Chem; 2006, 45: pp 2011-2016.

[16] Mahanandia P, Vishwakarma PN, Nanda KK, Prasad V, Subramanyam SV, Dev SK, Satyam PV. Multiwall carbon nanotubes from pyrolysis of tetrahydrofuran. Mater Res Bull 2006; 41:2311–2317.

[17 Mahanandia P, Vishwakarma PN, Nanda KK, Prasad V, Barai K, Mondal AK, Sarangi S. Synthesis of multi-wall carbon nanotubes by simple pyrolysis. Solid State Commun.2008; 145: 143–148.

[18] Xie Z, Guan W, Ji F, Song Z, Zhao Y. Facile chemical synthesis, electromagnetic response and enhanced microwave absorption of cobalt powders with controllable morphologies. J Chem 2014; 2014:1-9.

[19] Sankal S, Kaynak C. Using various techniques to characterize oxidative functionalized and aminosilanized carbon nanotubes for polyamide matrix. J Reinf Plast Comp. 2012; 32:75–86.

[20] Shu J, Cheng S, Xia H, Zhang L, Peng J, Zhang CLS. Facile synthesis of MOF-derived ultrafine Co nanocrystals embedded in a nitrogen-doped carbon matrix for the hydrogen evolution reaction. RSC Adv. 2017; 7: 14395.

[21] Zhang L, Yang J, Wang X, Zhao B, Zheng G. Temperature-dependent gas transport performance of vertically aligned carbon nanotube/parylene composite membranes. Nanoscale Res Lett 2014; 9:448.