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Electrospinning Synthesis and Electrocatalytic Performance of Cobalt oxide/Carbon Nanofibers Nanocomposite Based PVA for Fuel Cell Applications

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This work concerns carbon nanofibers (CNF) as a material support to prepare nanocomposite electrode, and to use such electrode for fuel cell application. The nanocomposite electrode was produced by electrospinning mixtures of cobalt nitrate with aqueous solutions of polyvinyl alcohol (PVA) followed by high-temperature annealing process. As a result, Cobalt oxide nanoparticles have been formed and incorporated within carbon nanofibers. Conductivity, capacitance and the electrocatalytic activities of the produced nanocomposite have been studied using cyclic voltammetry, and chronoamperometry. Produced materials were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), Energy-dispersive X-ray spectroscopy (EDX) and scanning-electron microscopy (SEM), which revealed that nanofibers in the range of 200–300 nm. The high conducting, and capacitance of the produced nanocomposite are related to the complete transfer of electrospun PVA fiber to active carbon nanofibers, and the presence of well dispersed Cobalt oxide nanoparticle, which lead to the enhancement of connectivity and the electrochemical utilization of pristine CNF during the charge/discharge process. On the other hand, the low electrocatalytic activity of the prepared electrodes towards methanol oxidation reaction can be attributed to the presence of nanostructure Cobalt oxide within the frame structure of carbon nanofibers, in addition to the complete absence of platinum materials. Therefore, based on the above investigations, carbon nanofibers composite electrode can be a potential candidate for a high-performance electrode supporting materials in fuel cells.

Keywords: Polyvinyl alcohol, Carbon nanofibers, Nanocomposite, Methanol Oxidation, Fuel Cells Electrocatalysis

1. INTRODUCTION

The decrease in the size of polymer fibers from micrometers into submicrons and nanometers has many advantages such as increasing the surface area, better mechanical function, and increasing its surface functions in comparison to the original form of the material. The new properties acquired by the shrinkage of the polymer fiber size into nanofibers make it suitable for many significant applications [1-3]. Many techniques have been used to prepare nanofibers such as; self assembly [4, 5], phase separation [6], and electrospinning technique [7, 8].

Electrospinning technique has been used to produce carbon nanofibers (CNF) after high temperature annealing treatment of polymeric nanofibers [9]. The produces carbon nanofibers have many important characteristics such as; simplicity of preparation, electronic conductivity, low cost and high surface area [9]. The superior performance of highly porous nanocarbons and compared them to carbon black in terms of catalyst dispersion and utilization, attracted scientists to use different nanocarbon materials as a catalyst support for fuel cell application. Examples such as carbon nanotubes [10-15], carbon nanocoils [10,16], graphitic nanofibers [10, 17] and carbon nanofibers (CNF), which has been used as a support for different nanomaterials, since it provide a high possibility for a uniform dispersion of loaded catalysts, mechanical support and an electronic continuity, which may affect reaction characteristics of the catalytically active sites [10,18].

The high cost of using platinum (Pt), the best known active and stable metal electrode for methanol oxidation as fuel in direct alcohol fuel cells encourages the researcher to develop new alternatives to reduce the usage of this expensive Pt, yet has high activity for alcohol oxidation kinetics [19]. Many trials have been done to lower the cost of these electrodes by the partial replacement of the amount of platinum used [20]; bimetals such as platinum- Iron [21-22] Platinum-Nickel [23-25] , Platinum-chromium [26], and platinum- cobalt [20].

In this work, we tried to develop a high active supporting material by developing a high surface area conducting carbon nanofibers. Also to study the activity of nonocomposite based on Cobalt oxide loaded on active carbon nanofibers in the absence of of highly expensive Pt catalyst. The carbon nanofibers composites were produced by electrospinning mixtures of the cobalt nitrate with aqueous solutions of polyvinyl alcohol (PVA) followed by high-temperature annealing process. The presence of Cobalt oxide species is expected to enhance and assist the electro-behavior of prepared electrodes.

On the other hand, we would like to mention that, a current study related to using different deposition techniques of Cobalt oxide is under investigation. This study will show the effect of deposition techniques such as microwave and impregnation methods on the electrochemical behavior of prepared naocomposite electrode.

2. EXPERIMENTAL

2.1. Nanocomposite based carbon nanofibers preparation

2.1.1. nanofibers preparation

The preparation of the electrospun fibers, which incorporated 10% w/w Cobalt oxide was accomplished by electrospinning aqueous solutions of 10% w/v PVA + cobalt salt ($Co(NO_3)_2.6\ H_2O$) at a potential of 15 kV. The electrospinning apparatus comprised a 20 mL Syringe with a 0.6 mm inner diameter, a graphite electrode, an aluminum collecting drum, and a high voltage supply. A flow rate of 0.3 ml/hour was maintained by connecting a syringe pump to the hypodermic syringe [27].

2.1.2. Cobalt oxide/ Carbon nanofibers preparation

The prepared fibers were collected and dried overnight at room temperature. After that, the dried nanofibers were stabilized at 250 °C in the air for 4 hours to form Cobalt oxide/CNF structure . After that, a carbonization step was achieved by having the sample into a ceramic crucible and transferred into a ceramic tube-furnace. Finally, the Cobalt oxide/CNF were prepared by heat treatment at 800 °C for 5 h (the heating rate of 5 °C min−1) under a high purity nitrogen atmosphere (99.999%) [28].

2.2. Catalyst characterization

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) measurements were carried out using a JEOL-JSM-7100F to show the surface morphology and the metal state of both of produced carbon nanofibers and nanocomposites. Sample measurements were achieved after sputter coating with Gold, the fibers size distribution was measured up to five frames of randomly selected SEM micrograph using software.

On the other hand, Powder X-ray diffraction was recorded on XPERT-PRO-PANalytical diffractometer using CuKα radiation. In addition to that, Thermogravimetric analysis was carried out using a TA Instruments, Q500 TGA, using a platinum cell in nitrogen atmosphere 20 ml/min.

2.3. Electrochemical measurements

Cyclic Voltammetry and chronoamperometry were conducted using μAUTOLAB III/FRA2 Potentiostats/Galvanostats to measure the conductivity, capacitance and electrocatalytic activity of the prepared materials. In this regard, we would like to thank Prof. Abdullah M. Al-Mayouf, chemistry department, King Saud university for his valuable assistant and support to utilize his lab facilities.

The cyclic Voltammetry (CV) curves were collected with a potential window from −0. 6 to +0.6 V (vs. SCE) at a scan rate of 100 mV s^{-1}. In 1M KOH. The electrocatalytic measurements were performed according to the method described in ref. [19] in a solution of 0.5 mol·L^{-1} H_2SO_4 and 0.6 mol·L^{-1} CH_3OH at room temperature. In this case the potential excitation that is applied across the electrode – solution interface in order to obtain a cyclic voltammogram has the following characteristics: (i) positive potential scan from 0 V to +1.2 V vs. Ag/AgCl reference electrode and (ii) a negative scan from +1.2 V to 0 V vs Ag/AgCl. All the measurements have been done in a conventional 25 ml Pyrex glass cell. The reference electrode used in this work is 4 M KCl Ag/AgCl reference electrode. The counter electrode was a Pt wire or 1 mm diameter and 10 cm long.

Although the potential scan was terminated after the 6th cycle, it was continued for some number of cycles. Glassy carbon electrode (GC) (0.03 cm^2) was polished to a by 1.0, and 0.05 μm alumina (CHI Inc., USA), respectively, and then washed in ethanol and ultra-pure water ultrasonically before each experiment and served as substrate for the working electrode. The working electrodes were fabricated by coating catalyst ink onto a glassy carbon electrode. The catalysts ink was prepared by dispersing 1.1 mg Co_3O_4/Carbo nanofibers powder in (0.5 ml isopropyl alcohol + 0.1 ml Nafion solution (10 wt.%)), and sonicated for 30 min. After sonication, a 10 μl of the resulted ink was cast over a glassy carbon electrode of an area of 0.071 cm^2 and dried at the 60 ^{O}C in oven for about 30 minutes. Before inserting the electrode in the electrolytic cell, its surface was flushed with some electrolyte in which measurements will be carried out in order to confirm the surface wet ability.

3. RESULTS AND DISCUSSION

3.1. Characterization of the prepared catalyst.

Thermogravimetric analysis (TGA) was used to investigate the thermal stability of PVA nanofibers. It has been reported that, the electrospinning process did not affect the structure of the PVA matrix polymer [30]. The TGA thermogram in a nitrogen atmosphere for electrospun PVA was depicted in figure 1. It reveals that, decomposition of PVA electrospun nanofibers was recorded in three stages. PVA nanofibers sample showed 1.426 and 9.818 % weight loss (first stage) at 30.00 – 200.00 $^{\circ}$C due to the loss of humidity water (dehydration of the PVA polymer), and the water of crystallinity. The most significant loss by about 39.10 % weight loss (second stage) for PVA electrospun nanofibers was recorded at 200 - 347 $^{\circ}$C is due to degradation of the large chain of molecules into smaller fragments. Finally, the weight loss of 21.80 % at the Third stage 400-600 $^{\circ}$C may be due to decomposition to carbon oxide and volatile hydrocarbons.

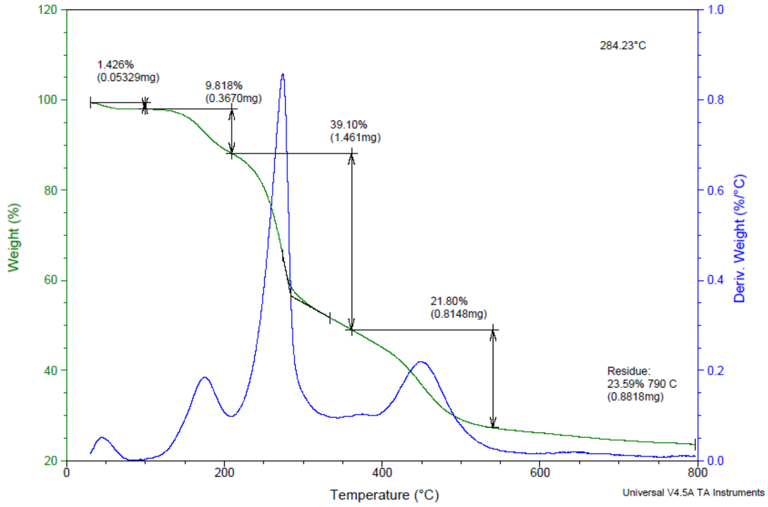

Figure 1. The TGA-thermogram in nitrogen atmosphere for PVA electrospun nanofibers

The morphological characterization of the PVA nanofibers and produced carbon nanofibers electrodes have been investigated and presented by SEM in figure (2a,b and 2c,d) and by EDX in Figure 3 respectively. All polymer compositions before and after fixation and the carbonization step yielded uniform and smooth, beads-free nanofibers. The average diameters of the produced fibers were between 200 and 300 nm. On the other hand, EDX spectra of Cobalt oxide/CNF nanocomposite, as shown in figure 3, confirmed the presence of Cobalt oxide, and the metal weight and atomic ratios are listed in Table 1. Three main components are detected in the prepared nanocomposite, namely: carbon, oxygen, and cobalt with a comparable ratio.

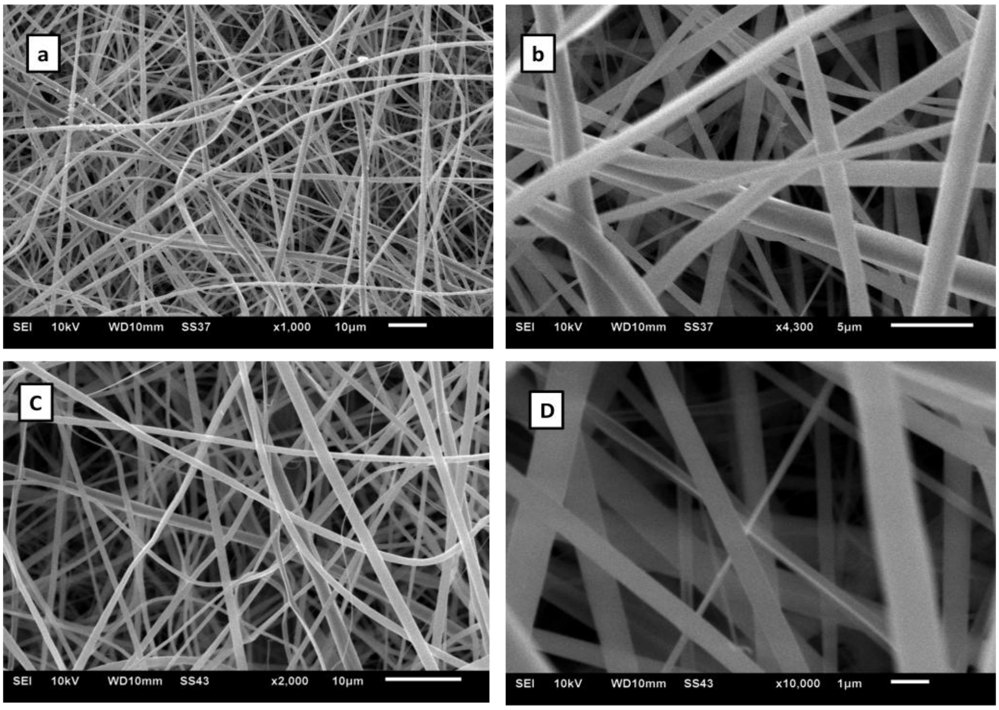

Figure 2. SEM images of PVA nanofibers before carbonization (a,b) and after carbonization(c,d)

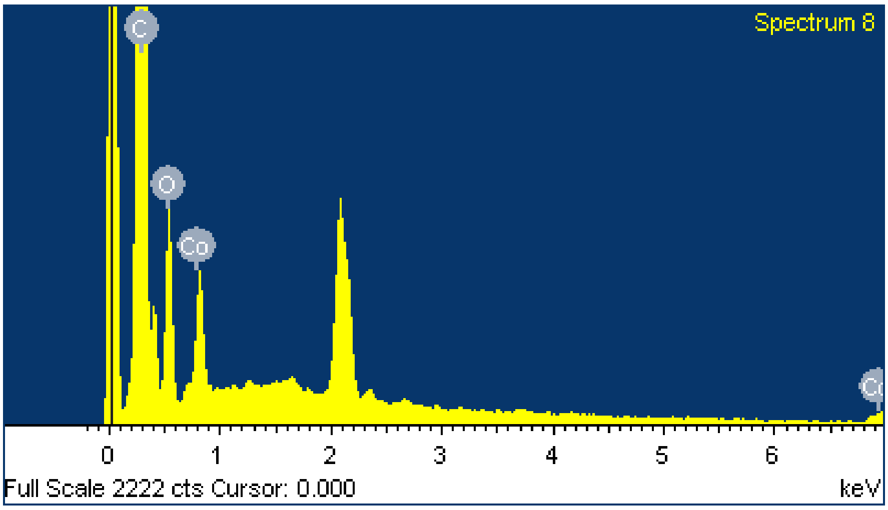

Figure 3. EDX spectra of Cobalt oxide/CNF nanocomposite.

Table 1. The elemental composition of Cobalt oxide/CNF nanocomposite according to EDX analysis.

Element	Weight %	Atomic %
C	74.11	85.84
O	12.71	11.05
Co	13.19	3.11
Totals	100.00	

X-ray diffraction measurements have been achieved to show the successful steps of the synthesis of nanocomposite, figure 4 shows the XRD pattern corresponding to PVA polymer nanofibers containing the cobalt precursor, The appeared peaks correspond to the plains of PVA crystalline. It is considered that this is attributed to longer chain length and higher linearity of PVA chain [29]. On the other hand, the figure shows the XRD pattern of PVA nanofibers after fixation and carbonization process (Carbon nanofibers). XRD patterns reveal the bulk structure of the carbon nanofibers support. It can be seen that peaks of PVA nanofibers have been disappeared and the first peak located at a 2θ value of about 26° is referred to carbon (0 0 2) [9]. On the other hand, XRD measurement has been repeated in the range of Cobalt oxide patterns to show a very small low intensity hump pattern corresponding to Cobalt oxide, which could be attributed to the presence of metal oxide within the framework of carbon nanofibers. The Cobalt oxide reflection intensities at 2θ of 44.8 is corresponding to (4 0 0) plane of the cubic crystal system, which confirmed by standard data card (ref: 01-078-1969).

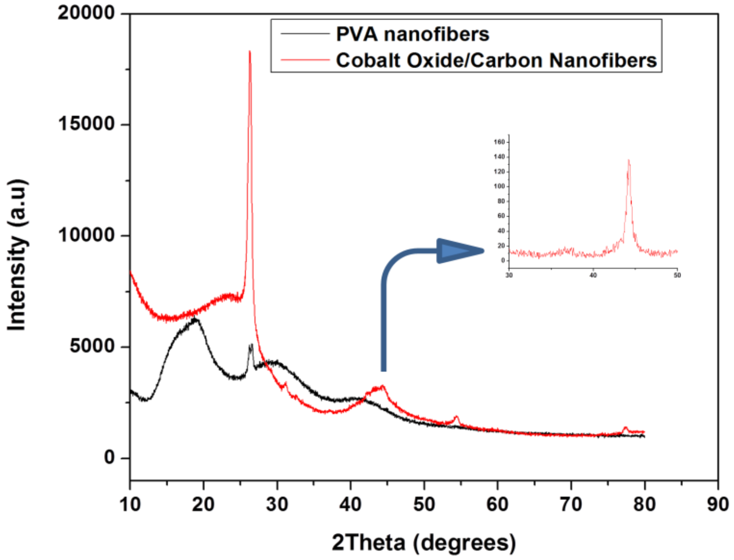

Figure 4. XRD pattern of PVA nanofibers and Cobalt Oxide/CNF nanocomposite .

3.2. Electrocatalytic measurements

The electrochemical performances of the prepared materials were analyzed using cyclic Voltammetry (CV). Figure 5 shows the CV curves of unloaded carbon nanofibers (CNF) and carbon nanofibers loaded with Cobalt oxide electrodes at a scan rate of 100 mV s−1 between −0.6 and +0.6 V (vs. SCE) in 1 M KOH aqueous electrolyte. A typical rectangular shape has been observed at CV curves. On the other hand, carbon nanofibers loaded with Cobalt oxide exhibit a larger CV area than that of unloaded carbon nanofibers, indicating a higher specific capacitance compared with the unloaded Carbon nanofibers. This is could be attributed to the presence of well dispersed Cobalt oxide nanoparticles, which lead to enhancement of connectivity and the electrochemical utilization of pristine CNF during the charge/discharge process [28]. The stability of the Cobalt oxide/CNF catalyst was depicted in figure 6, the CV was repeated for higher number of cycles. Figure 6 shows repeated CVs of Cobalt oxide/CNF in a solution of 1 M KOH at a scan rate of 50 mV s^{-1}. It indicates that the Cobalt oxide/CNF nanocomposite catalyst is stable after repeating the scanning for 6 cycles.

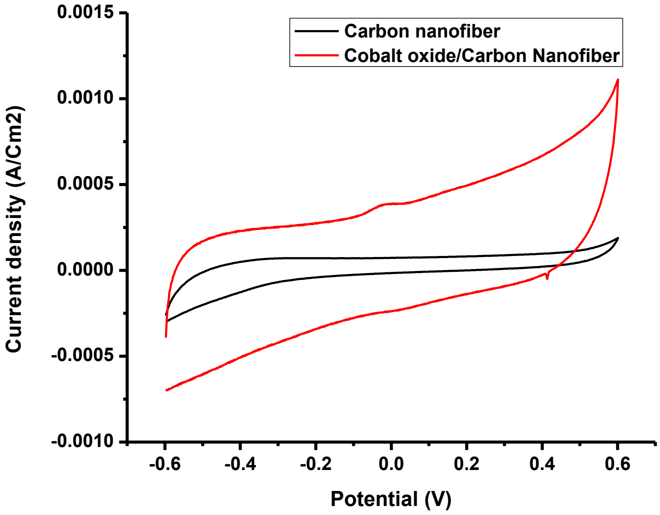

Figure 5. CV curves of (a) pure carbon nanofibers and Cobalt oxide/CNF electrodes at sweep rate of 50 mV s^{-1}

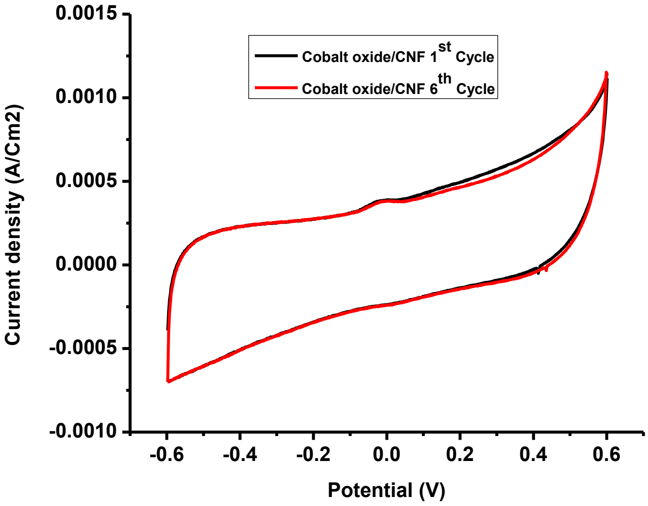

Figure 6. Repeated CVs of Cobalt oxide/CNF in a solution of 1M KOH at a scan rate of 100 mV s^{-1}.

The electrocatalytic activity of prepared nanocomposite catalysts was depicted in figure 7. The figure shows the cyclic voltammetry response of Unloaded CNF and CNF loaded with Cobalt oxide in 0.5 M H_2SO_4 containing methanol. It has been reported that, CNF supports provide an electronic continuity, a mechanical support, and a uniform dispersion as well as a high catalytic activity of catalysts used for methanol oxidation in DMFC [10]. Different electrochemical activities have been observed by methanol system. The performance is strongly influenced by the presence of Cobalt oxide in the composite structure. It is apparent from figure 7 that, the peak current density for Cobalt oxide/CNF nanocomposite is higher than those of unloaded CNF, suggesting that the presence of Cobalt oxide can improve its activity. This could be attributed to two factors; The first is the synergistic effect between the loaded Cobalt oxide and the support CNF materials lead to the formation of active edges and corners, and the second is the enhancement of electronic continuity, which may affect reaction characteristics of the material active sites [10,18]. On the other hand, the low electrocatalytic activity of prepared catalysts towards methanol oxidation reaction compared to previous studies [10,19,20] could be attributed to the presence of nanostructure Cobalt oxide within the frame structure of carbon nanofibers, in addition to the complete absence of platinum materials.

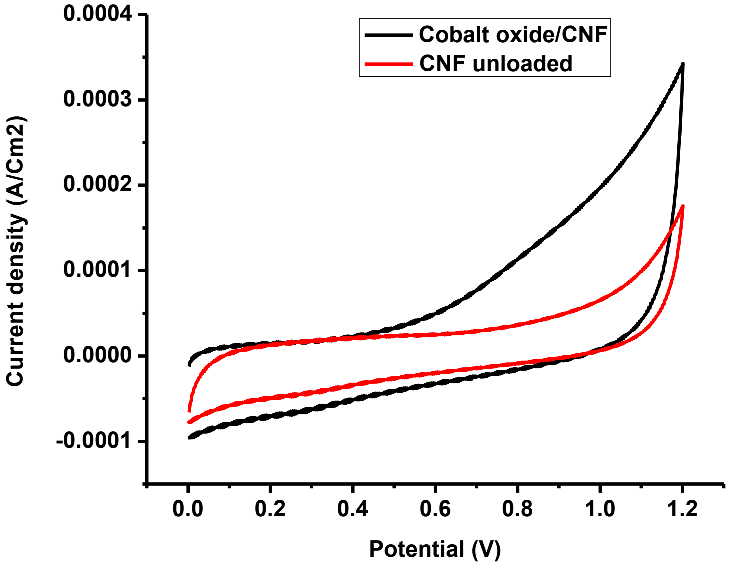

Figure 7. Cyclic voltammograms of Cobalt oxide/CNF and uloaded CNF electrocatalysts prepared by in (0.6 M MeOH + 0.5 M H_2SO_4) solution The potential range is from 0 to +1.2 V at 100 mV s^{-1}.

Chronoamperometric experiments were carried out at a given potential to confirm the activities and stabilities of Cobalt oxide/CNF nanocomposite in 0.5 M H_2SO_4 containing methanol. The chronoamperometry profiles at a potential of 0.30 V vs. SCE are shown in figure 8. It can be seen from figure 8 that, A gradual decay of the current density during the chosen time was observed. This can be attributed to the the poisoning of Cobalt oxide/CNF nanocomposite surface by few produced intermediate species of methanol oxidation such as CO_{ads}, CH_3OH_{ads}, and CHO_{ads}, which formed during the methanol oxidation reaction and adsorbed on the active surface sites [20,31].

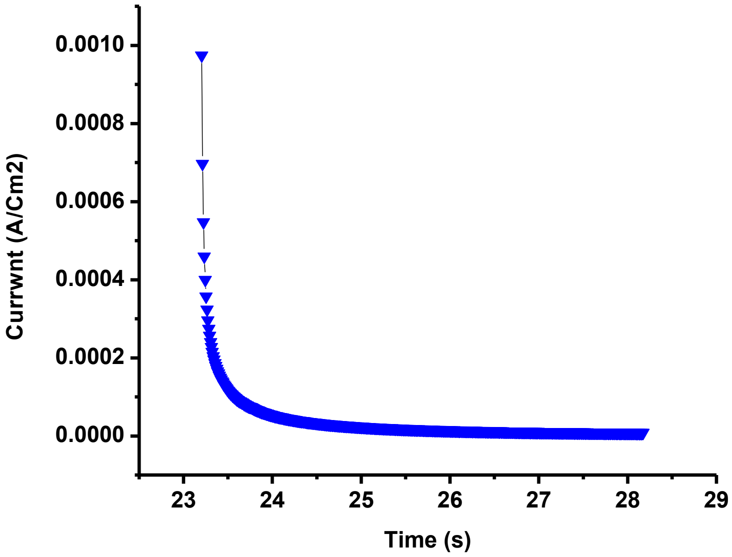

Figure 8. Chronoamperograms of Cobalt oxide/CNF at potential values of 0.3 V in (0.6 M MeOH + 0.5 M H_2SO_4) solution.

4. CONCLUSION

In summary, we have reported a successful way to prepare highly active, and high surface area carbon nanofibers as a supporting material with diameter range of 200-300 nm. The prepared carbon nanofibers were used to host Cobalt oxide to prepare nanocomposite electrocatalyst electrode. The conductivity, the capacitance and the electrocatalytic behavior of this nanocomposite was tested using cyclic Voltammetry, and chronoamperometry, It has been shown that, the electrochemical activity of the Co oxide/CNF catalyst is higher than that of the unloaded CNF. The low electrocatalytic activity of prepared catalysts towards methanol oxidation reaction can be attributed to the presence of nanostructure Cobalt oxide within the frame structure of carbon nanofibers, in addition to the complete absence of platinum materials. Further study is under investigations, which aims to improve the electrochemical activity by means of using the different deposition technique and using different metal oxide loading such as Ni oxide.

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References

1. F. Lin, L. Shuhong, L. Huanjun, Z. Jin, S. Yanlin, J. Lei, Z. Daoben, *Angewandte Chemie International Edition*, 41(2002) 1221.
2. C.R. Martin, *Chemistry of Materials*, 8(1996)1739.

3. Z.-M. Huang, Y. Z. Zhang, M. Kotaki, S. Ramakrishna, *Composites Science and Technology*, 63(2003) 2223.
4. G. Liu, J. Ding, L. Qiao, A. Guo, B.P. Dymov, J.T. Gleeson, T. Hashimoto, K. Saijo, *Chemistry – A European Journal*, 5(1999) 2740.
5. G.M. Whitesides, and B. Grzybowski, *Science*, 295(2002) 2418.
6. Z.R. Ma PX, *J. Biomed Mat Res*., 46(1999) 60.
7. J.M. Deitzel, G.D. Kleinmeyer, J.K. Hirvonen, N.C. Beck Tan, *Polymer*, 42(2001) 8163.
8. D.R. Salem, ed. Structure formation in polymeric fibers. ed. R.D. Fong H. 2001, Hanser: Munich.
9. T. Maiyalagan, K. Scott, *J. Power Sources* 195 (2010) 5246.
10. Y.I. Kim, D. Soundararajan, C.W. Park, S.H. Kim, J.H. Park, J.M. Ko. *Int. J. Electrochem. Sci*., 4 (2009) 1548.
11. Y.Y. Tong, C. Rice, A. Wieckowski, E. Oldfield, *J. Am. Chem. Soc*. 122 (2000) 1123.
12. W. Li, C. Liang, J. Qiu, W. Zhou, H. Han, Z. Wei, G. Sun, Q. Xin. *Carbon*. 40, (2002) 791.
13. L. WZ, W. X, C. ZW, W. M, Y. YS, *J Phys Chem* B. 110, (2006) 15353.
14. S. Ramaprabhu, M.M. Shaijumon, N. Rajalakshmi, *Appl Phys Lett*. 88 (2006) 253105.
15. K.T. Jeng, C.-C. Chien, N.-Y. Hsu, S.-C. Yen, S.D. Chiou, S. Hsine, Y.M. Liang, H.M. Zhang, B.L. Yi, Z.H. Zhang, Z.C. Tan, *Carbon* 43 (2005) 3144.
16. K.W. Park, Y.E. Sung, S. Han, Y. Yun, T. Hyeon, *J Phys Chem* B. 108 (2004) 939.
17. S. Kim, Y. Jung, S.J. Park, *Colloids and Surfaces A:Physiochem. Eng. Aspects*. 313, (2008) 220.
18. I.S. Park, K.W. Park, J.H. Choi, C.R. Park, Y.E. Sung, *Carbon*. 45, (2007) 28.
19. A. A. Elzatahry, A. M. Abdullah, T. A. Salah El-Din, A. M. Al-Enizi, A. A. Maarouf, A. Galal, H. K. Hassan, E. H. El-Ads, S. S. Al-Theyab, A. A. Al-Ghamdi, *Int. J. Electrochem. Sci*., 7 (2012) 3115 .
20. R.S. Amin, A.A. Elzatahry, K.M. El-Khatib, M. E. Youssef, *Int. J. Electrochem. Sci*., 6 (2011) 4572.
21. W. Li, Q. Xin, Y. Yan, *Int. J. Hydrogen Energy*, 35(2010)2530.
22. W. Li, W. Zhou, Z. Zhou, H. Li, Z. Zhou, B. Zhou , et al.,*Electrochim Acta* ;49(2004)1045.
23. L. Xiong, A. Kannan, A. Manthiram, *Electrochem Commun* ;4(2002)898.
24. H. Yang, C. Coutanceau, J.M. Leger, N. Alonso-Vante, C. Larmy, *J Electroanal Chem*, 205(2005)305.
25. F. Bensebaa, A. A. Farah, D. Wang, C. Bock, X. Du, J. Kung, Y. Le, *J. Phys. Chem*. B , 109(2005)15339.
26. P. Pharkya, A. Alfantazi, Z. Farhat, *J Fuel Cell Sci Technol*, 2(2005)171.
27. A.A. Elzatahry, A.M. Al-Enizi, E.A. Elsayed, R.R. Butorac, S.S. Al-Deyab, M.A.M. Wadaan, A. H. Cowley, *International Journal of Nanomedicine* 7(2012) 2829.
28. Z. Taiab, X. Yana, J. Langa, Q. Xue, *J. Power Sources* 199 (2012) 373.
29. S. Ramakrishna, K. Fujihara, W. E. Teo, T.C. Lim, Z. MaAN, INTRODUCTION TO ELECTROSPINNING AND NANOFIBERS S. ed.,2005, World Scientific Publishing Co. Pte. Ltd.
30. M. S. Peresin, Y. Habibi, J. O. Zoppe, J. J. Pawlak, O. J. Rojas, *Biomacromolecules*, 11(2010), 674.
31. F. Ye, X. Cao, L. Yu, S. Chen, W. Lin, *Int. J. Electrochem. Sci*., 7 (2012) 1251.