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Short Communication

Development of Composite Material Based on Porous Microfibrous Carbon and Zinc Oxide for Energy Storage Application

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The development of efficient energy storage devices is very important challenge for the progress of the renewable energy. One of the promising energy storage systems is the electrochemical capacitor. In this work, the composite material based on porous microfibrous carbon and zinc oxide by electrodeposition technique for electrochemical capacitor was synthetized and characterized. The formation mechanism of zinc oxide on porous microfibrouse carbon paper was proposed. This mechanism is constituted of three steps (i) production of OH^- ions, (ii) creation of zinc hydroxide $Zn(OH)_2$, (iii) transformation of zinc hydroxide $Zn(OH)_2$ to zinc oxide ZnO. The composite materials based on a porous microfibrouse carbon paper and zinc oxide were studied by cyclic voltammetry and the electrochemical impedance. The synthesized electrodes show a good capacitive behavior. The electrodeposition time of 60 minute allows the formation of excellent electrode for electrochemical capacitor.

Keywords: Energy storage; electochemical capacitor; zinc oxide; porous carbon

1. INTRODUCTION

The environmental effect of fossil energy resources and increasing energy consumption present severe challenges to human well-being, energy security, and environmental protection [1]. An encouraging solution to the global energy problems is the development of the powerful, durable and low-priced renewable energy resources. The ecological impacts of using the renewable energy are clear and known but we must be conscious of the several lacks that slow a massive use of this kind of energy resource. The reliability of supply presents the principal weakness of renewable energy resources. Renewable energy frequently depends on the meteorological conditions for its source of power. When the weather is not favorable, the resources are unavailable or insufficient so the capacity to produce energy decreases dramatically. The development of efficient energy storage devices is imperative for the progress of renewable energy. One of the interesting energy storage devices is the electrochemical capacitors moreover recognized as: supercapacitors or ultarcapacitors [2,3,4,5].

Electrochemical capacitors is a type of energy storage device between the battery and electrostatic capacitor that could be used for several applications mainly in the fields electrical equipment and hybrid electric vehicles and very recently for the storage of renewable energy [6]. Electrochemical capacitors are regrouped into three classes, depending of their active electrode materials: (i) carbons that utilize the double-layer capacitance originate from the separation of charge at the interface among the electrolyte and the [7], (ii) electronically conducting polymers, and (iii) metal oxides [2-9].The two last groups of systems contain pseudofaradic reactions.

Historically, ruthenium oxide was the first used electrode material for electrochemical capacitor [9,10]. (RuO2) based electrodes for supercapacitor display very high capacitive performances and high specific power; however, their applications are limited due to toxicity and high price of this metal oxide [2, 9-10]. In recent years, several researchers aiming on various low-cost metal oxides as substitutes for the replacement of ruthenium oxide in electrochemical capacitor electrodes. Pointing to lower the price of electrochemical capacitors, metal oxides such nickel oxide, manganese oxide, molybdenum oxide and titanium oxide were used as alternative for ruthenium oxide [9-10]. However, zinc oxide (ZnO), is one of promising materials for elecochemical capacitors electrode. This oxide material has been widely applied in optoelectronic and electronic devices, such as light-emitting devices, gas sensors and solar cells,

The composite materials based on carbon and zinc oxide could be efficient electrode materials for electrochemical capacitors. Several techniques have been designated in the previous works [8,11-13] for the production of zinc oxide for example: hydrothermal, laser ablation, sol–gel, chemical vapor deposition, thermal decomposition, combustion, and electrochemical depositions [8,11-13]. The electrodeposition method is known as the efficient technique for the synthesis of nanostructures of ZnO due to its easiness, low temperature procedure, high deposition amount, cheap method and appropriateness for large area substrate [12]. This method used a very low potential or current to produce the ZnO on any conductive palt substrate. In this deposition procedure, the thin layer measurements, structures and electrochemical characteristics could be adapted by the various operating parameters: current intensity, applied voltage, time of deposition and the elecrodeposition bath. Generally, in this deposition process, zinc chloride solutions or zinc nitrate solutions are used as a precursor [8,11-12].

In this work, we present (i) the electrochemical characterization of porous microfibrous carbon paper that will be used as substrate of the zinc oxide electrodeposition, (ii) the electrochemical deposition of zinc oxide on porous microfibrous carbon paper, (iii) the formation mechanism of zinc oxide on porous microfibrous carbon, (iv) the electrochemical characterization of zinc oxide/porous microfibrous carbon composite material by using cyclic voltammetry and electrochemical impedance spectroscopy.

2. EXPERIMENTAL

2.1. Materials preparation.

All chemical substances utilized in this work were obtained from Aldrich. Distilled water of 18 MΩ was used to make the solutions.

Porous microfibrous carbon paper was purchased from Spectracarb (SC 2050). This product was immersed in the bath of concentred sulphuric acid for 4 h at 70 °C, and then was washed recurrently with distilled water. The subsequent sample was dried at 105 ◦C for one night.

The electrodeposition process were completed in a three-electrode cell submerged in a water bath held at 70 °C.

A SP-300 Potentiostat/Galvanostat/FRA Instruments electrochemical workstation was used for the electrodeposition. Pt foil and SCE electrodes were used as secondary and reference electrode respectively. The treated porous microfibrous carbon paper was used as working electrode. The electrodeposition bath was formed from 0.1 M $Zn(NO_3)_2$ and 0,005 M KCl. The electrodeposition experiments were carried out by applying an electric current of 0.5 mA/cm^2 for 15, 30 and 60 minute. The resulting product was washed repeatedly with distilled water and dried at 105 ◦C for one night. At the end, four samples were prepared and denoted hereafter as (C) for porous microfibrous carbon paper, (C-ZnO-15), (C-ZnO-30), (C-ZnO-60) for zinc oxide deposited on porous microfibrous carbon paper time of electrodeposition of 15, 30 and 60 minute respectively.

2.2. Characterization.

Porous microfibrous carbon paper (C) was characterized in the aqueous electrolytes 1 mM K4Fe(CN)6 in 1 M KCl and 1 M H2SO4 by cyclic voltammetry at different scan rate. They were degassed with N_2 prior to electrochemical characterizations and a blanket of the gas was preserved during the experiments.

In addition, Porous microfibrous carbon paper (C) and composite electrode based on Porous microfibrous carbon and zinc oxide (C-ZnO-15), (C-ZnO-30), (C-ZnO-60) were characterized in the electrolyte 0.1 M KOH for all experiments. It was degassed with N_2 prior to electrochemical characterizations and a blanket of the gas was preserved during the experiments as mentioned in [14]. A SP-300 Modular Research Grade Potentiostat/Galvanostat/FRA was used for the cyclic voltammetry and the electrochemical impedance characterizations. The electrochemical impedance characterizations were lead in the constant potential (ac amplitude 10 mV) method by changing the frequencies from 100 kHz to 0.01 Hz series as describe in [15].

3. RESULTS AND DISCUSSION

3.1. Charcterization of Porous microfibrous carbon paper in 1 mM $K_4Fe(CN)_6$ in 1 M KCl by cyclic voltammetry and formation mechanism of zinc oxide on porous microfibrouse carbon paper.

In the goal to assess if this porous microfibrous carbon paper suitable for electrodepostion deposition and electrochemical applications, an electrochemical characterization was performed with the $Fe(CN)_6{}^{3-/4-}$ redox couple.

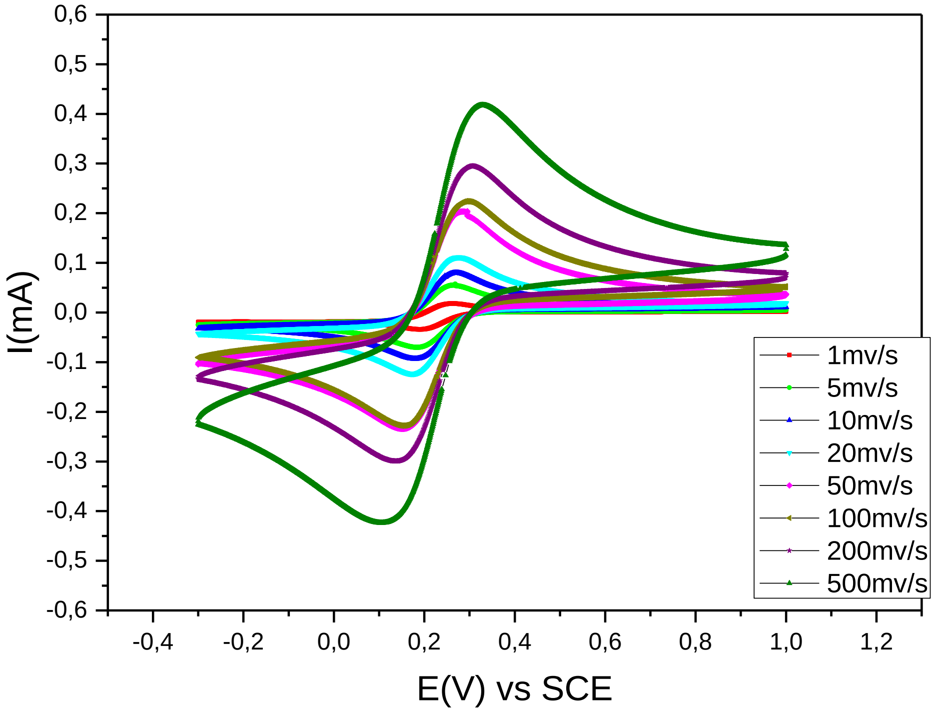

Figure 1. The cyclic voltammogram (CV) of porous microfibrouse carbon paper electrode (C) in a 1 mM $K_4Fe(CN)_6$ + 1 M KCl solution. The scan rates were from 1 to 500 mV s^{-1}.

Figure 1 shows cyclic voltammograms for porous microfibrous carbon paper (C) electrode recorded in 1 mM $K_4Fe(CN)_6$/1 M KCl at a different scan rate from 1 to 500 mV/s. The cyclic voltammograms of electrode at a different scan rate are well-defined with a separation between the anodic and cathodic peak potentials of 0.12 and 0.32 V and an apparent redox potential (taken as the average between the cathodic and anodic peak potential) of 0.20 for the C electrode. It is necessary to note that even at very high scan rate the anodic and cathodic peak potentials are well defined.

The electroactive area of the C electrode was calculated by utilizing the Randles-Sevcik equation:

$$Ip = (2,65 \times 10^5)\, n^{3/2} A C D^{1/2} \nu^{1/2}$$

where Ip is the peak current after deduction of the double layer current (A), n is the number of electrons contributing in the redox reactions, A is the working electrode surface (cm^2), D is the diffusion coefficient (7.64×10^{-6} cm^2 s^{-1} at 25 °C), C is the concentration of the investigation molecule (1×10^{-6} $mol \cdot cm^{-3}$) and ν is the scan rate ($V \cdot s^{-1}$). Based on the previous equation, the electroactive area of the porous microfibrous carbon paper electrode is 4.2 cm^2. It is necessary to mention that the geometric surface area is 1 cm^2. This is an indication of the porous structure of this carbon electrode. For this electrode, the ratio of the electroactive area to geometric area is estimated to 4.20 which very near to the value for carbon material electrode (3.71) in the work of Brett and coworker [16]. The high electroactive area of the electrode used in our work could do to (i) the porous nature of the microfibrous carbon paper itself, (ii) the fictionalization that occurs in the preparation process of carbon paper which consist on the immersion in the bath of concentered sulfuric acid for 4 h at 70 °C, followed by washing with distilled water and drying at 105 ◦C for one night. Brett et *al.* have mentioned that the functionalization increases the electactive area of carbon materials [16].

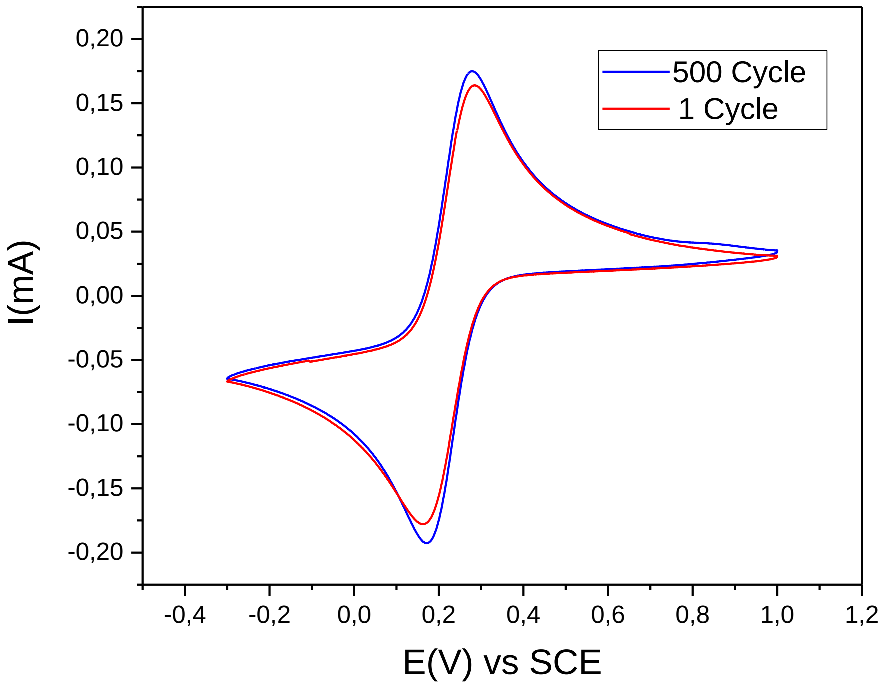

Figure 2. The first nd 500th cycle of cyclic voltammogram (CV) of porous microfibrouse carbon paper electrode (C) in a 1 mM $K_4Fe(CN)_6$ + 1 M KCl solution. The scan rates was 20 mV s^{-1}.

Figure 2 displays the cyclic voltammograms of the porous microfibrous carbon paper electrode at scan rate 20 mV/s, the first and the 500th cycles were recorded, these two votmogramm show a quasi-perfect similarity, which is an indication of the excellent stability of the carbon electrode over long cycling.

The porous microfibrous carbon paper electrode is suitable for electrodeposition as substrate and for electrochemical applications. This electrode will be used as substrate for zinc oxide electrochemical deposition.

Figure 3 is an illustration of the formation mechanism of zinc oxide on porous microfibrouse carbon paper. The proposed mechanism is constituted in three steps (i) production of OH^- ions, (ii) creation of zinc hydroxide $Zn(OH)_2$, (iii) transformation of of zinc hydroxide $Zn(OH)_2$ into zinc oxide ZnO.

(i) Production of OH^- ions: the porous microfibrouse carbon paper is immerged in the electrodeposition bath which constitute of $Zn(NO_3)_2$,$6H_2O$ + KCl. The application of electric current allows the variation in the electrode potential and the formation of OH^- ions that will be preferentially located in the pores and near to the electrode surface. The formation reaction of OH^- ions are due to:

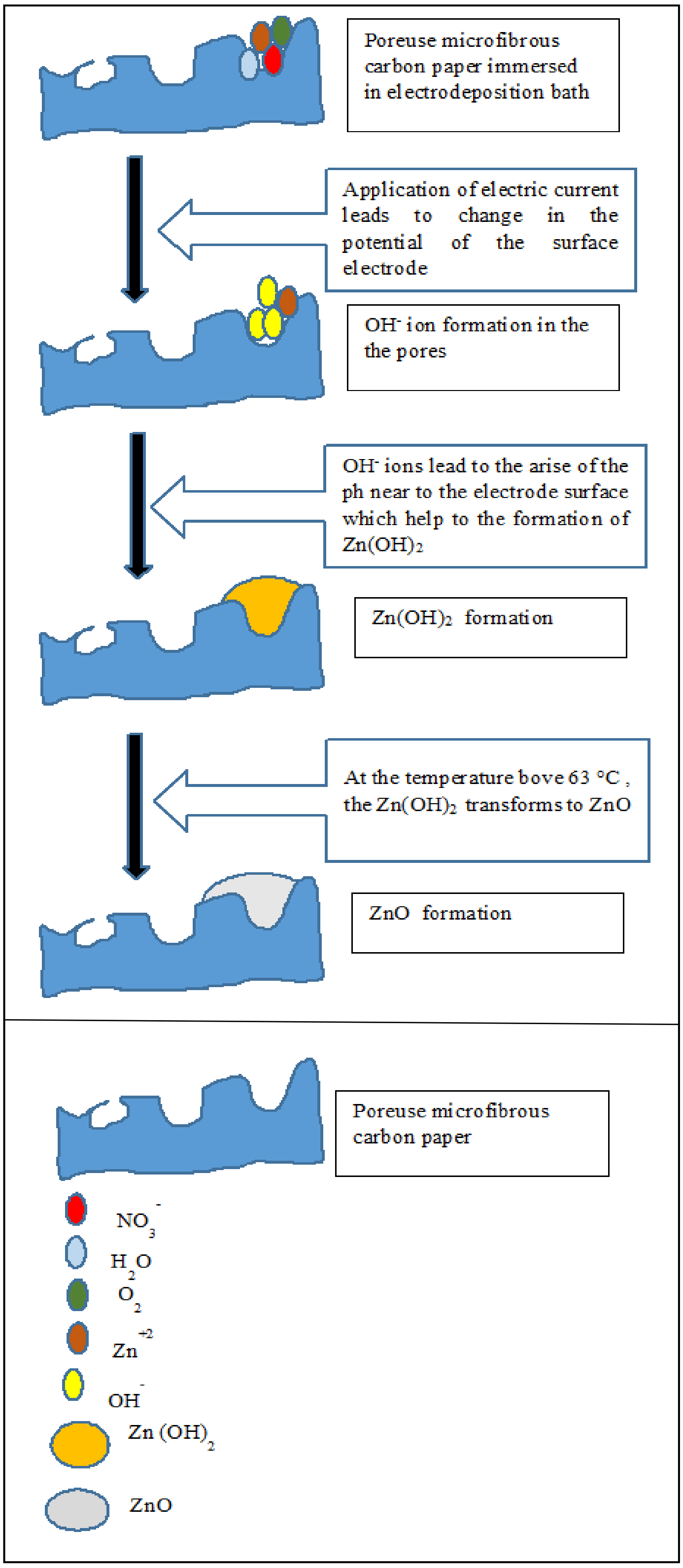

Figure 3. Formation mechanism of zinc oxide on porous microfibrouse carbon paper

Reduction of nitrate ions

$NO_3^- + 2e^- + \mathrm{H2O} \longrightarrow 2\,OH^- + NO_2^- \qquad E=+0.01\ V_{/ENH} \qquad (1)$

Reduction of oxygen

$\frac{1}{2}$ O2 + 2 e- + H2O $\longrightarrow$ 2OH- E=+0.40 V/$_{\mathrm{ENH}}$ (2)

OH^- ions leads to arise pH in the interface electrode electrolyte particularly in the pores. It is necessary to mention the importance of porous structure that allows the trap of OH^- ions near to the carbon electrode.

(ii) Creation of zinc hydroxide $Zn(OH)_2$

In this step, there is a reaction between OH^- and Zn^{+2} ions that exist at the interface electrode electrolyte following the reaction:

$Zn^{2+} + OH^- \longrightarrow Zn(OH)_2$ (3)

The porous nature of microfibrouse carbon paper and the existence of OH^- ions in the pores allow the formation of zinc hydroxide at the electrode surface and not in the electrolyte bulk like in the case of non-porous electrode.

(iii) Transformation of zinc hydroxide $Zn(OH)_2$ into zinc oxide ZnO.

In this work, the electrodeposition is effectuated at 70 °C. At temperature above of 63 °C the zinc hydroxide Zn $(OH)_2$ is not stable and transform to zinc oxide following the reaction:

$Zn(OH)_2 \longrightarrow ZnO + H_2O$ (4)

Several works have proposed nearly similar formation mechanism of zinc oxide on different kind of substrates. Lee et *al.* Have studied the electrodeposition of zinc oxide on indium tin oxide (ITO) substrates. They explain that the formation of ZnO could occur in three steps: (i) surface pH enhancement due to the adsorption of hydroxide ion; (ii) the formation of intermediate species (i.e., zinc hydroxide (Zn $(OH)^{+\,+}$); (iii) ZnO deposition with the production of water [17]. Aziz and coworkers have prepared ZnO by electrodeposition technique from aqueous zinc nitrate solution at 65 °C onto fluorine doped tin oxide (FTO) coated glass substrates [18], the proposed formation mechanism is approximately similar to that one proposed in our work. Yoshida and co-authors have proposed mechanism of cathodic electrodeposition of zinc oxide thin films from aqueous zinc nitrate baths [19], this mechanism confirms our claims. The main novelty in our proposed mechanism in comparison to the aforementioned propositions is that the porous structure of the substrate could be an important parameter to facilitate the electodepostion of zinc oxide.

3.2. Cyclic voltammetry (CV) for porous microfibrouse carbon paper and zinc oxide deposited on porous microfibrous carbon paper in 0.1 M KOH electrolyte

The studied electrodes are : (C) porous microfibrouse carbon paper, (C-ZnO-15), (C-ZnO-30), (C-ZnO-60) for zinc oxide deposited on porous microfibrous carbon paper using time of electrodeposition of 15, 30 and 60 minute respectively. In Figure 4, we present the cyclic voltammogram (CV) of studied electrodes in a 0.1 M KOH electrolyte at a scan rate 20 mV/s over the potential windows of 1000 mV. The Figure 4a presents the cyclic voltammogram of porous microfibrouse carbon paper which also the substrate. No reox pics were observed over the studied potential windows, in addition the current density of the response is very low. These allows to this material to be an excellent substrate for elector deposition. The cyclic voltammogram (CV) of zinc oxide deposited on porous microfibrous carbon paper using time of electrodeposition of 15 (C-ZnO-15) is presented in Figure 4.b. We can observe a redox pic at 0.2 and 0.4 V / SCE and the density of current is higher than the response of the porous microfibrouse carbon paper (substrate), this could be an indication of the formation of the electrodeposition film. For the electrode C-ZnO-30, we note that the current density is higher than the response of C and C-ZnO-15 electrodes. In addition, the cyclic voltammogram like box shape (Figure 4.c), which means that material, could be a suitable electrode for energy storage devices. The cyclic voltammogram (CV) of zinc oxide deposited on porous microfibrous carbon paper using time of electrodeposition of 60 minute (C-ZnO-60) is presented in Figure 4.d.

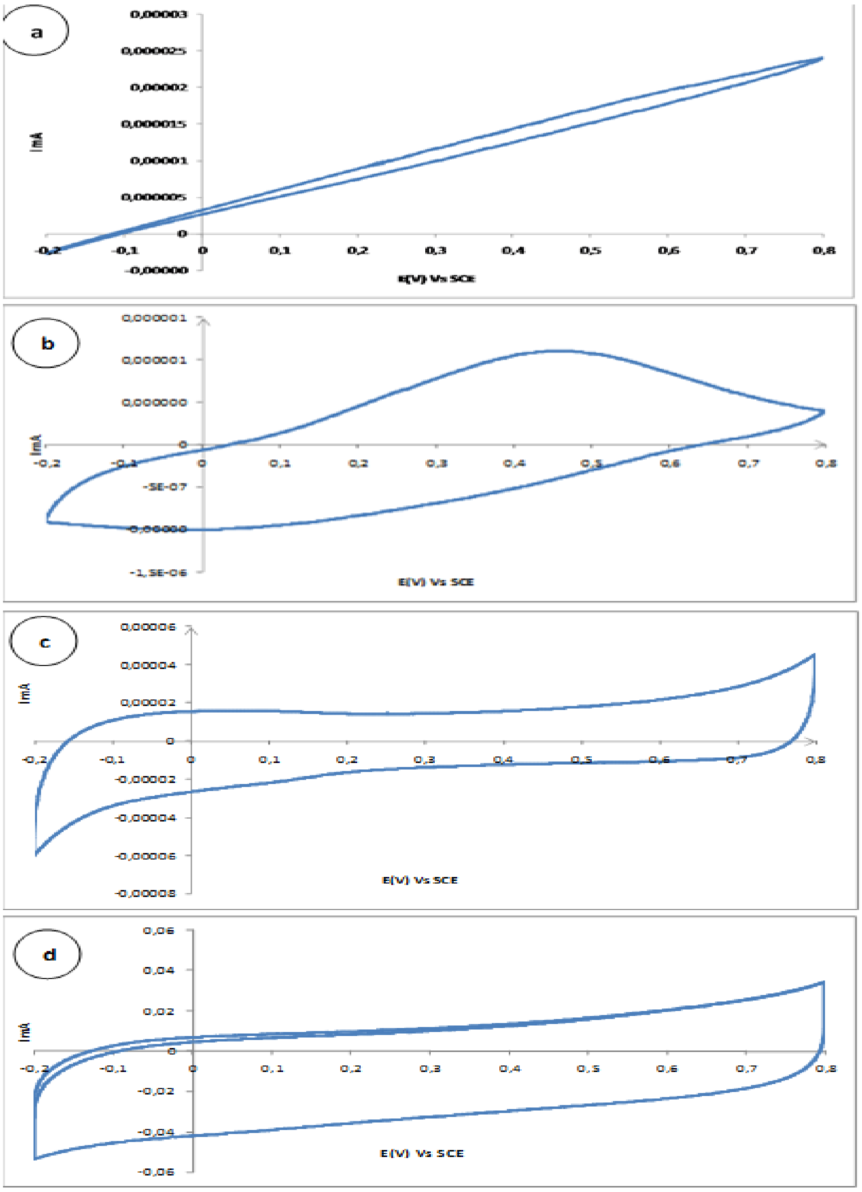

Figure 4. The cyclic voltammogram (CV) of electrodes : a- C; b- C-ZnO-15; c- C-ZnO-30; d- C-ZnO-60 aqueuse electrolyte 0.1 M KOH at potential scan rate 20 mV/s.

This electrode show very higher current response in comparison to that of all other studied electrode in this work and the shape of CV is rectangular [1,11]. This electrode is an excellent electrode for electrochemical electrode.

At this point, it is interesting to discuss the mechanism for the charge storage of zinc oxide in KOH electrolyte. Two mechanisms were suggested to clarify the ZnO charge storage comportment. The first mechanism suggests the intercalation of alkali metal cations (K^+) or protons (H^+) in the electrode substance in reduction phase tracked by deintercalation in oxidation pahse [20].

$ZnO + H^+ + e^- \rightarrow ZnOH$

or

$ZnO + K^+ + e^- \rightarrow ZnOK$

The second mechanism is founded adhesion of electrolyte cations (K^+) on the surface of ZnO structure

$(ZnO)_{surface} + K^+ + e^- \rightarrow (ZnO^-C+K^+)_{surface}$

We believe that for the ZnO layer coated on porous microfibrouse carbon paper, a combination of these two mechanisms is effective. This charge storage mechanism is similar to other metals oxides [3,9-21].

3.3. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy measurements for C and C-ZnO-60 electrodes were achieved at 0 V vs SCE and subsequent Nyquist plots are demonstrated in Figure 5.

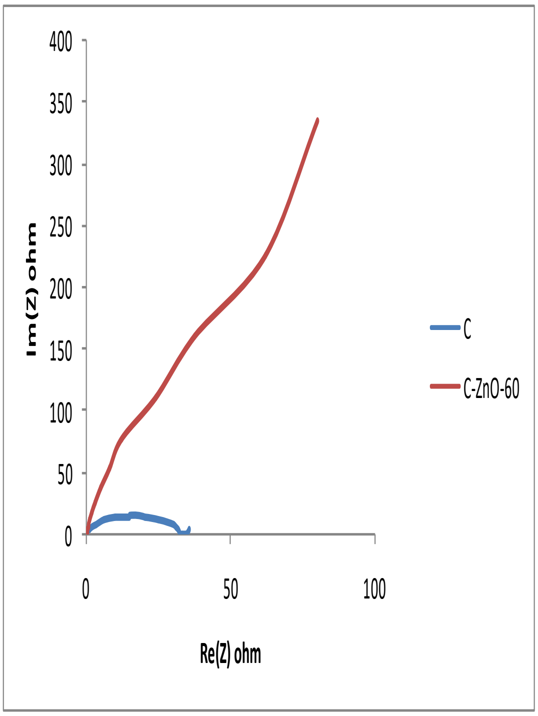

Figure 5: Impedance spectra of C and C-ZnO-60 electrode aqueuse electrolyte 0.1 M KOH, applied voltage 0 vs SCE, frequency: from 100 KhZ to 10 mHz.

The Nyquist diagrams of C electrode consist of semi-circle with high diameter. The Nyquist plot of C-ZnO-60 electrode is constituted of (i) a semi-cercle in the high and medium frequencies domain [22], (ii) at the low frequencies domain, a 45° slope line that matches to Warburg impedance, this could be due to the ions diffusion through thick layer of the porous electrode [15,22]; (iii) in low-frequency domain, a vertical line that could be attributed to the ions agglomeration at the deep lowest region of the electrode pores. The nearly vertical line reveals an excellent capacitive character without diffusion limitation. The Nyquist diagram indicate that the incorporation of ZnO on carbon substrate minimizes the contact resistance at the interface electrolyte/electrode, and these allows an enhancement of the charge transfer performance for the electrode [23].

These findings confirm the cyclic voltammetry outcomes. In other words, the C-ZnO-60 could be an excellent electrode for electrochemical capacitors and might be employed for energy storage devices.

Several relevant and recent works confirm the claims presented in the present paper. Lim and coworkers [24] have studied the effect of ZnO electrodeposited on carbon film and subsequently used this material as part of composite for solar hydrogen production. Seong et *al*. have synthetized nanostructure of zinc oxide by electrodeposition on single-walled carbon nanotubes electrodes [25]. Liu and coauthors have deposited electrochemically a ZnO on three-dimensional, interconnected, and porous carbon nanofiber Buckypaper substrates [26], the resulting materials have used in for photovoltaic applications. Yu and collaborator have interested to the elecrodeposition zinc oxide on carbon fibers and their feasibility for environmental applications [27]. Antunes et *al.* have electrochemically deposited ZnO on exfoliated Tips of carbon nanotube films [28].Based on the results of the present work and the recent open literature, the electrodeposition of zinc oxide on carbon material could open new insights in the development of material and electrochemical applications. For better performances of electrodeposited ZnO on carbon materials in several applications such as: energy storage devices, photovoltaic, hydrogen production, sensors, it is necessary to improve the following points: (i) the suable choice of carbonic substrate, (iii) the comprehension of formation mechanism of ZnO on that carbonic substrate, (iii) a the control of the ZnO morphology by adjusting the synthesis conditions. The present study is a contribution to clarify the aforementioned issues.

4. CONCLUSION

To conclude, simple composites electrodes synthetized by electrodepostion technique of the zinc oxide on a porous microfibrouse carbon paper substrate. These electrodes were considered for supercapacitors applications. The composite material based on a porous microfibrouse carbon paper and zinc oxide were studied by cyclic voltammetry, and the electrochemical impedance. The porous microfibrouse carbon paper is an efficient substrate for zinc oxide electrodeposition. The formation mechanism of zinc oxide on porous microfibrouse carbon paper was proposed. This mechanism is constituted in three steps (i) production of OH^- ions, (ii) creation of zinc hydroxide $Zn(OH)_2$, (iii) transformation of zinc hydroxide $Zn(OH)_2$ to zinc oxide ZnO. An electrodeposition time of 60 minute allows a formation of the excellent electrode for electrochemical capacitor.

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