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METAL OXIDE DOPED GRAPHITIC CARBON NITRIDE AS AN EFFICIENT ELECTRODE MATERIALS FOR SUPERCAPACITORS

Raphael de Souza dos Santos
Thiago Mendes Barbosa
Leandro Marques Samyn
Rajendran Suresh Babu
Ana Lucia Ferreira de Barros
Centro Federal de Educação Tecnológica Celso Suckow da Fonseca
Laboratory of Experimental and Applied Physics (LaFEA), Av. Maracanã 229, Rio de Janeiro – RJ, Brazil
raphaeldesouza89@hotmail.com
thiago.barbosa@aluno.cefet-rj.br
leandro.samyn@cefet-rj.br
suresh.rajendran@aluno.cefet-rj.br
ana.barros@cefet-rj.br

Abstract: *In the present work, two different metal oxides doped graphitic carbon nitride (g-C_3N_4) such as manganese oxide doped g-C_3N_4 and copper oxide doped g-C_3N_4 were synthesized by single-step pyrolysis method and were utilized as efficient electrode materials for supercapacitors. The synthesized materials were mechanically coated on nickel foam as a base electrode. Those two metal oxides were choosing because of their good electrochemical characteristics and redox properties. The pseudocapacitive behaviors of the fabricated electrodes were characterized by cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy. At current density of 0.5 A/g, the manganese oxide electrode presented a specific capacitance of 61 F/g while the copper electrode reached 55 F/g at the same current density in a 3M KOH electrolyte solution. The metal oxide doped with graphitic carbon nitride coating nickel foam electrodes showed good specific capacitances, better power characteristic and cyclic stability.*

Keywords: *supercapacitor, graphitic carbon nitride, copper oxide, manganese oxide, nickel foam*

1. INTRODUCTION

The increasing development of portable and wearable devices and the technological advances as flexibility, high-performance and energy demand increases the attention in more efficient and adaptable energy storage devices (Xu et al, 2018). In addition, reducing dependence on fossil fuels is vital to reduce problems related to it, such as pollution and global warming, motivating studies on supercapacitors increased in part due to low toxicity and high power density (González et al., 2016).

Energy storage devices can be divided into fuel cells, batteries, supercapacitors and electrolytic capacitors that are differentiated by the form of storage, power density and energy density. The supercapacitors have the energy and power density in a range between the usual batteries and capacitors, as in the Figure 1, with a short charge time and good Columbic efficiency (Xiaojuan Zhang et al., 2017); represent an alternative to common electrochemical batteries that are able to quickly accommodate large amounts of energy.

Supercapacitors can be usually divide in double-layers capacitors (EDLCs), that stores charge electrostatically through a thin electron-ion separation layer, pseudocapacitors, that are based on redox reactions in the material storing energy Faradaically, and hybrids, that are composed of EDLC and pseudocapacitive materials combining properties and being able to present better performance.

The supercapacitors, in general, have attracted a lot of attention in part due to their energy density, higher than the capacitors, combined with high power density, fast charging and discharging, high efficiency, long cycle life and superior reversibility. Those characteristics made supercapacitors promising energy-conversion and energy storage devices. Ideal for intermittent power systems, as wind and solar, ignition systems of hybrid vehicles and systems that store the kinetic energy somewhere where the vehicles slow down or stop, furthermore, the preoccupation with the environmental problems and the dependence on fossil fuels with the increase of cost, demand more energy of intermittent power generators, as solar and winder energy (González et al., 2016). And motivate studies on energy stories, as supercapacitors and batteries, to supply the energy necessity.

Figure 1 shows that supercapacitors power and energy densities are between capacitors and batteries. The cycle life of supercapacitors are longer than batteries in continuous charges/discharges (Yu, Davies, and Chen, 2012). It makes supercapacitors more used to several applications as high power energy storages. Supercapacitors and batteries are the biggest future energy storage technologies, according the US Department of Energy (DOE) (Goodenough, 2007).

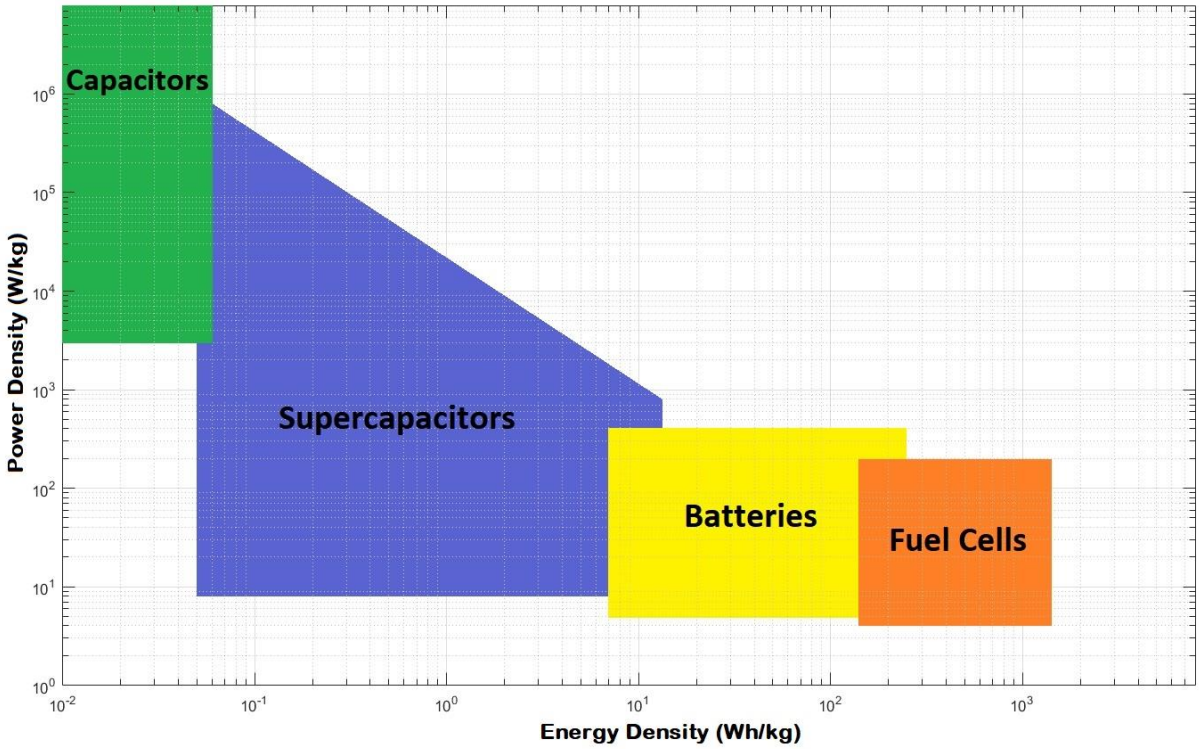

Figure 1. Ragone plot of Energy density vs Power density.

The use of hybrid metal oxides in supercapacitors increased in the past few years. The transition metal oxides, is extensively used in supercapacitors because of their low cost, natural abundance, very good charge storage ability and high theorical capacity (Ensafi et al., 2019). Previous studies revealed an upgraded in the performance using those hybrid metal oxides materials instead of single compounds.

In addition, the carbon nitrides (CN) are an organic component and polymeric semiconductor produced by the union of carbon and nitrogen, and the graphitic carbon nitride (g-C_3N_4) has gained a good attention because it been an excellent chemical stability, with a high surface area and tunable electronic structure. Beyond that, the g-C_3N_4 can be easily obtained by thermal polycondensation of many materials as cyanimide, urea and others. (Ensafi, 2019; Wee-Jun Ong, 2016 and Sridharan, 2014).

In this work, the use of graphitic carbon nitride/copper oxide (g-C_3N_4/CuO) and graphitic carbon nitride/manganese oxide (g-C_3N_4/Mn_2O_4) as promising materials for pseudocapacitors. The materials were evaluated by electrochemical characterizations methods (Babu, 2018; Maier, 2017; Jinlong, 2017; Wu, 2016 and Zheng, 2009).

2. EXPERIMENTAL PROCEDURE

2.1 Material

All chemicals utilized in this work were AnalaR-grade and the nickel foam utilized as base electrode were purchased from Sigma Aldrich.

The nickel foam electrode was cleaned in multiple steps, first the nickel foam was sliced in the desired size (1 cm × 1 cm) and kept in ultrasonic bath in a 3M HCl solution for 30 minutes, after that was also kept in double distilled water, isopropyl alcohol and finally acetone, each step during 30 minutes in ultrasonic bath. Then, it was kept overnight in oven at 70 °C for dry. Besides that all aqueous solutions were prepared with distilled water.

2.2 Preparation of g-C_3N_4/CuO and g-C_3N_4/Mn_2O_4

The composites of g-C_3N_4/CuO was prepared by a mixture containing 5g of $Cu(NO_3)_2.4H_2O$ and 12g of urea in a porcelain crucible and mixed thoroughly. Then, thermally treated in a furnace at 400ºC for 2h, the material was cooled naturally after which and finally crushed in a dust (Sridharan et al., 2014). The same steps were following to make replacing $Cu(NO_3)_3.9H_2O$ with $Mn(NO_3)_2.4H_2O$ to obtain the g-C_3N_4/Mn_2O_4.

Finally, the working electrodes were prepared by mixture of 80 wt% of the active material (g-C_3N_4/CuO or g-C_3N_4/Mn_2O_4), 10 wt% of activated carbon powder and 10 wt% of PVDF, as a conduction polymer, in NMP, as a binder, and the mixture was spread by uniformly mechanically coated onto a cleaned nickel foam electrodes surface and dried at 100 °C for 24 hours. The mass of the electrodes before and after the deposition of the mixture was measured by electronic weighing balance to know the mass of the active materials in the electrode.

3. ELECTROCHEMICAL CHARACTERIZATION

The cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge-discharge techniques were performed using three-electrode setup with a CompactStat potentiostat from Ivium Technologies in an aqueous 3M KOH solution at room temperature. The coated electrodes were utilized as working electrodes (WE), a silver/silver chloride (Ag/AgCl) as reference electrode (RE) and platinum sheet as counter electrode (CE), as in the Figure 2:

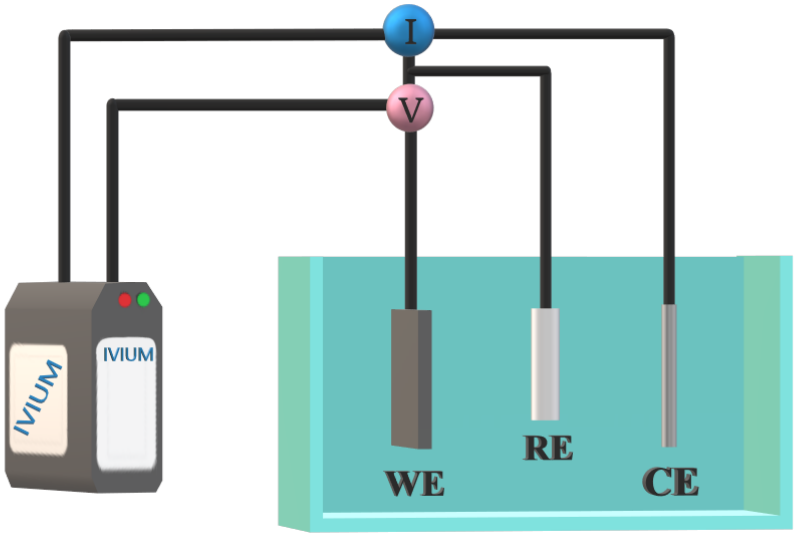

Figure 2. Three-electrode setup for cyclic voltammetry technique.

4. RESULTS AND DISCUSSION

The cyclic voltammogram of the electrodes are exhibit in the Figure 3 and were performed in a potential window from 0 to 0.5 V. It reveals the Faradaic properties of the material by the redox peaks associated to the reactions that occurs when voltage is applied. The CV was performed at different scan rates from 5 to 200 mV/s. The oxidation and reduction peaks reveal a pseudocapacitive property of the materials and the reversibility of the process, furthermore, the curve show a characteristic of cathodic electrode for both and a charge higher in the g-C_3N_4/CuO/NF than in g-C_3N_4/Mn_2O_4/NF. With a maximum current of approximately 52,8 mA on 0.41V and 38,8 mA on 0,36V at 200 mV/s that was obtained for the g-C_3N_4/CuO/NF and the g-C_3N_4/Mn_2O_4/NF, respectively.

The galvanostatic charge-discharge (GCD) tests of the electrodes were performed at various current densities of 0.5 to 5 A/g with the maximum potential of 0.4 V that is the potential window that occur the redox reaction of the electrode. Figure 4 shows that the behavior of charge/discharge had less time when current density increased. The electrodes showed a characteristic hybrid behavior combining the EDLC and pseudocapacitor properties of metal oxides and g-C_3N_4. The quickly drop at the beginning of the discharge cycle is associated to resistances from the substrate surface and the electrolyte solution. The electrodes are partially symmetric in charge and discharge time of both electrodes, trending to a triangular shape typical for ideal capacitor, but with a slop, common for pseudocapacitors, which results by the electrochemical redox reactions. In Figure 5 is possible to observe that the g-C_3N_4/CuO/NF presents a faster discharge cycle compared with the g-C_3N_4/Mn_2O_4/NF electrode.

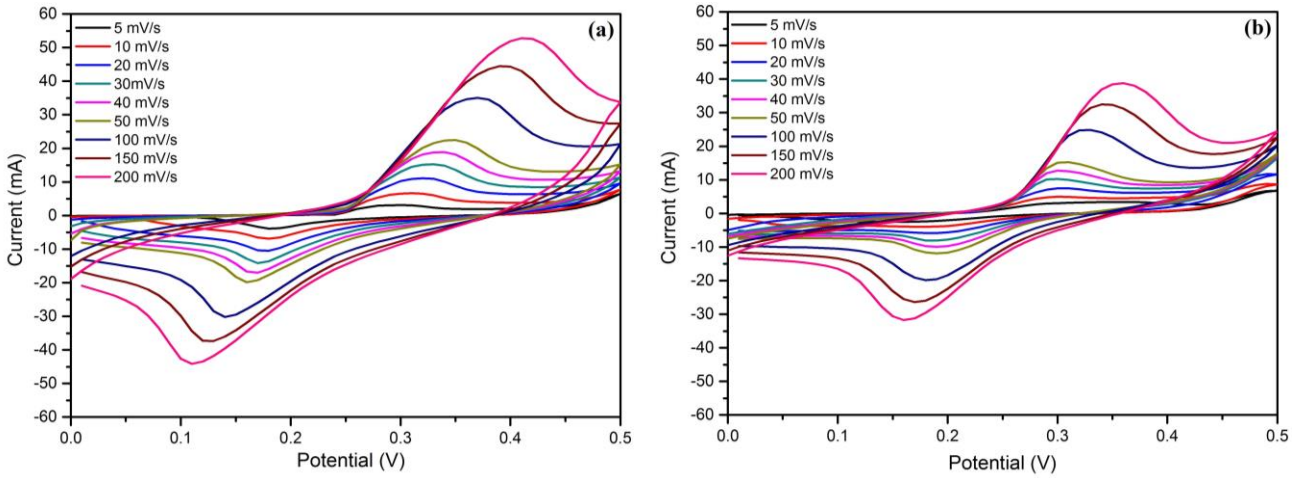

Figure 3. Cyclic voltammogram of (a) g-C_3N_4/CuO/NF and (b) g-C_3N_4/Mn_2O_4/NF at various scan rates.

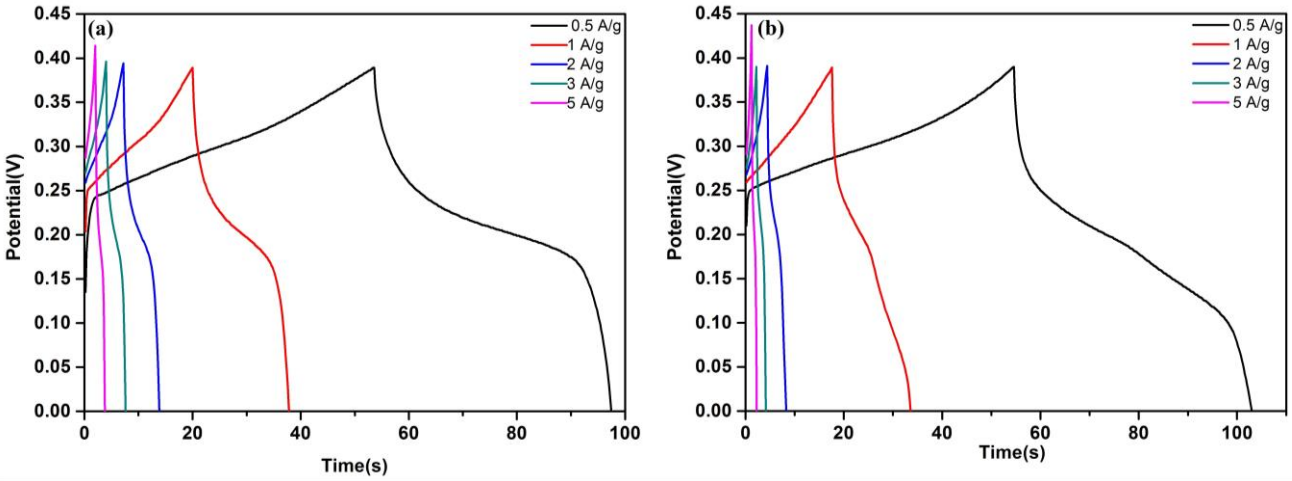

Figure 4. Galvanostatic charge and discharge behavior of (a) g-C_3N_4/CuO/NF and (b) g-C_3N_4/Mn_2O_4/NF at various current densities.

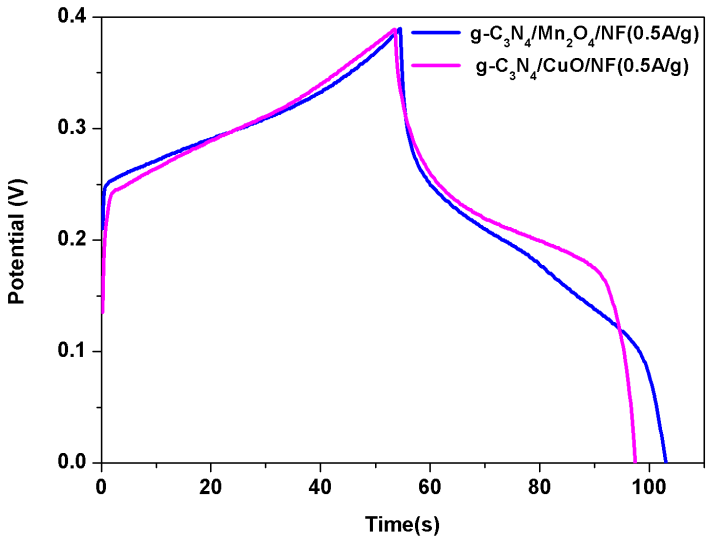

Figure 5. Comparison of charge and discharge behavior at current density of 0.5 A/g for g-C_3N_4/CuO/NF (pink line) and g-C_3N_4/Mn_2O_4/NF (blue line).

Regardless the total time of charge and discharge of the electrode the value of the specific capacitance (S_C), depends on other factors as particle size, redox reactions and other variables such as optimization of electrolytes and its concentration. From the charge/discharge graphics (Fig. 4) is possible to determine the S_C of the electrodes from the Eq. (1) where I is the current, ΔV is the potential, m is the mass of deposited material and Δt is the discharge time. In Figure 6 is possible to see the results and a comparison between the two electrodes.

$$Sc = \frac{I * \Delta t}{m * \Delta V} \tag{1}$$

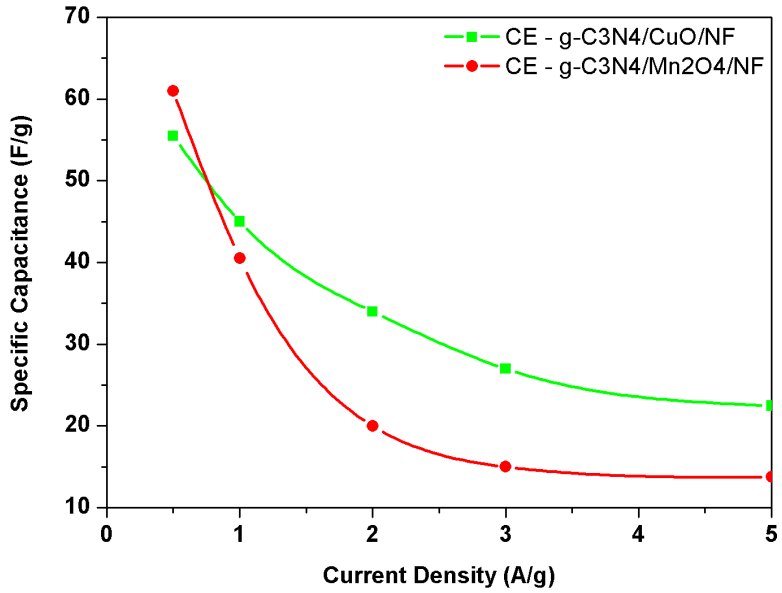

Figure 6. Specific capacitance of g-C_3N_4/CuO/NF and g-C_3N_4/Mn_2O_4/NF at different current densities.

The g-C_3N_4/Mn_2O_4/NF electrode presented a specific capacitance of 61 F/g while the g-C_3N_4/CuO/NF electrode had achieved 55 F/g at the same current density (0.5 A/g). Despite of the g-C_3N_4/Mn_2O_4/NF electrode had achieved higher specific capacitance, the value decreased inversely proportional with the increase of the current density reaching a specific capacitance value lowest than the g-C_3N_4/CuO/NF electrode at higher current density of 1 A/g. The results show that the g-C_3N_4/CuO/NF electrode presents a better stability than the g-C_3N_4/Mn_2O_4/NF electrode.

In addition, the supercapacitive properties of an electrode material also depend on energy density and power density, as in the Figure 1, and this properties have been essential to characterization for supercapacitors. The energy and power density can be calculated by the Eq. 2 and Eq. 3, where C is the specific capacitance, V is the operating potential and t is the discharge time (Babu, 2018):

$$Energy\ density\ (E) = \frac{1}{2} * \frac{CV^2}{3.6} \tag{2}$$

$$Power\ density\ (P) = \frac{E}{t} * 3600 \tag{3}$$

Analyzing the energy density and power density for both electrodes, calculated at different currents densities, the maximum energy density of 1.36 Wh/kg occur on g-C_3N_4/Mn_2O_4/NF at 0.5 A/g current density, followed by g-C_3N_4/CuO/NF at 0.5 A/g with 1.22 Wh/kg. The highest power energy of 1000 kW/kg was obtained for the g-C_3N_4/Mn_2O_4/NF and g-C_3N_4/CuO/NF at 5 A/g current density. The figure 7 shows the plot of energy density vs power density (Ragone plot).

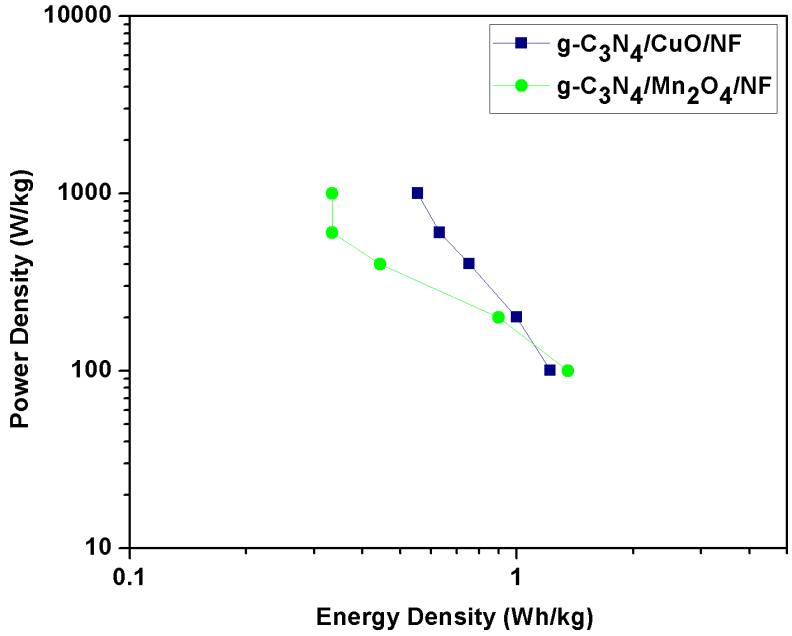

Figure 7. Ragone plot of g-C_3N_4/CuO/NF and g-C_3N_4/Mn_2O_4/NF electrodes.

The electrochemical behavior of the utilized materials frequently depends on chemical reactions that may occur between the electrode surface and the electrolyte. The electrochemical impedance spectroscopy (EIS) allows identifying the chemical process that may occur during charge and discharge of the supercapacitors. From EIS is possible to relate the chemical reactions with electrical parameters allowing determining the equivalent electrical circuit. This way is possible to calculate the electrolyte resistance, equivalent series resistance and others important parameters. From the Nyquist plot (Fig. 8 and Fig. 9) is possible to identifying two regions: one semi-circular and other linear. Figures 8 and 9 show the resistances of the electrolyte solution were the graphic cuts the horizontal axis at the beginning of the semicircle. The linear part indicates the diffusion process in low frequencies. As can be seen the g-C_3N_4/Mn_2O_4/NF electrode (Fig 9) present a diffusion indicating more influence of the equivalent capacitance different from the g-C_3N_4/CuO/NF electrode (Fig. 8) that showed a diffusion in which indicates a higher influence from the equivalent resistance of the material.

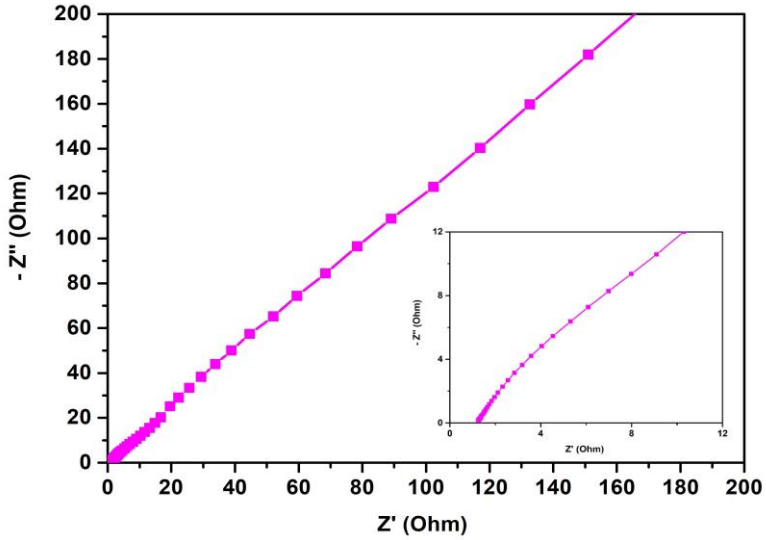

Figure 8. Nyquist plots of the g-C_3N_4/CuO/NF (Inset: Magnified the high frequency region).

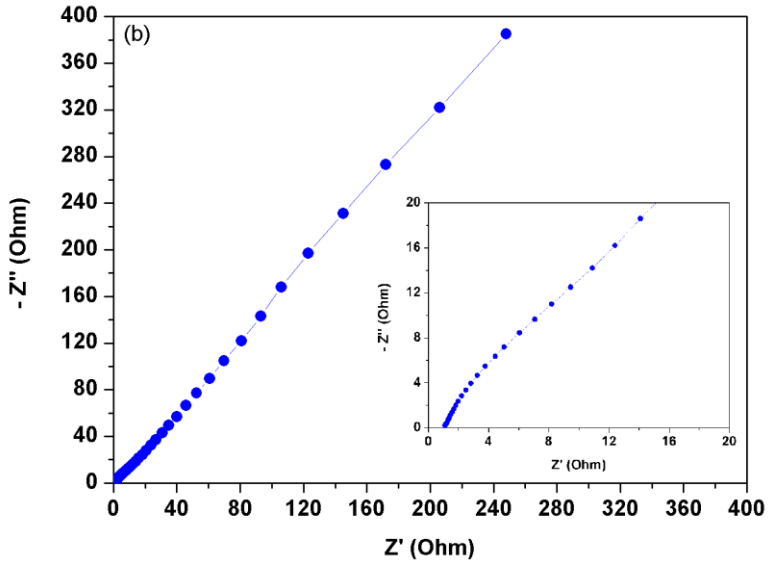

Figure 9. Nyquist plots of the g-C_3N_4/Mn_2O_4/NF electrodes. (Inset: Magnified the high frequency region).

5. CONCLUSION

In this work were successfully synthesized two different metal oxides doped g-C_3N_4 in single-step pyrolysis method and utilized as electrode materials for supercapacitors. The Mn_2O_4/g-C_3N_4 reached 61 F/g, was highest capacitance value than CuO/g-C_3N_4 (55.5 F/g). The electrode with copper base coating showed to be more stable with the increase of the current density despite present a lower specific capacitance. The electrochemical characterization shows that both electrode material presented pseudocapacitive properties and also good conductivity in 3M KOH electrolyte solution. The good results confirmed that g-C_3N4 sheets are promising materials for substrates used in supercapacitors.

6. ACKNOWLEDGEMENTS

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