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HYDROTHERMAL SYNTHESIS OF NICKEL OXIDE FOR SUPERCAPACITORS APPLICATIONS

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Abstract: In this work, hydrothermal synthesis of nickel oxide with surfactant and template was realized in two different temperatures as electrodes for applications in supercapacitors. The synthesized NiO were coated on nickel foam substrates (NiO/NF). The NiO is used because of its low cost and high capacitance, and the NF was chosen as a substrate, due to its high conductivity and porosity that improve the material adherence and the supercapacitor performance. These properties turn the electrodes ideal for supercapacitors applications. The electrodes were analyzed and compared through cyclic voltammetry, charge-discharge test and electrochemical impedance spectroscopy characterizations. At the current density of 1 A/g, the electrode synthesized at 500°C reached 145 F/g specific capacitance, showing better capacity of storing energy in comparison with the NiO synthesized at 300 °C (121.85 F/g) at the same current density, while at current densities higher than 1.5 A/g, the NiO synthesized at 300° showed better specific capacitance results.

Key-words: supercapacitors, nickel foam, hydrothermal method, nickel oxide.

1. INTRODUCTION

With the increase of the energy demand, as well as the current concern with environmental sustainability, the search for alternatives of generation and storage of energy becomes important. In this scenario, the development and study of supercapacitor devices have been gaining ground due to their low environmental damage in comparison with the materials used nowadays in batteries, like lithium, sodium and acid materials (Dubal, 2017 and Qi, 2016).

Supercapacitors are energy storage devices with low toxicity, high power density and low energy density, which are being used in many miniaturized devices such as biosensors, break and ignition systems of hybrid vehicles. They can be classified in electrical double-layer capacitors – that store energy electrostatically –, pseudocapacitors – storing energy through redox reactions, which make the process faster –, and hybrid capacitors, using both ways to store the electrical charge (Rodríguez-Silva, 2016; Zhang, 2017; Chen, 2014; Babu, 2018 and Maier, 2017).

In the pseudocapacitors production, the study of transition metal oxides has increased because of their characteristics of low cost, high capacitance and for being abundant on earth and easy to prepare. The aim of this work is to synthesize nickel oxide by hydrothermal method with two different temperatures for supercapacitors applications. The nickel oxides were synthesized using cetyltrimethyl ammonium bromide surfactant (Wu, 2016 and Jinlong, 2017).

2. EXPERIMENTAL PROCEEDURE

The nickel oxide was prepared with 2 mM of cetyltrimethyl ammonium bromide (CTAB) and 2 mM of nickel nitrate (NiNO₃) by the hydrothermal method. It was prepared two solutions: CTAB mixed with distilled water (DW) and NiNO₃ dissolved with DW. After that, the CTAB solution was slowly added to the NiNO₃ solution and the new mixture was stirred for 20 minutes. Few milligrams of tissue paper were added and the final solution was transferred to the Teflon autoclave. The autoclave was kept for 12 hours at 120 °C, dried at 80 °C overnight and, finally, one sample was sintered at 300 °C (NiO300/NF) and the other at 500 °C (NiO500/NF), both for 2 hours. At the end of the hydrothermal method, the samples were collected, smashed and coated on the nickel foam.

3. RESULTS AND DISCUSSION

The NiO/NF electrodes were analyzed by the electrochemical techniques: cyclic voltammetry, chronopotentiometry and impedance spectroscopy. The electrochemical characterizations were carried out using the IVIUM CompactStat three-electrode system potentiostat, with NiO/NF as working electrode (WE), silver/silver chloride (Ag/AgCl) as reference electrode (RE) and platinum mesh as the counter electrode (CE), as shown in Fig. 1. The three electrodes were submerged in 2M KOH electrolyte solution during the measurements (Metrohm Autolab, 2011).

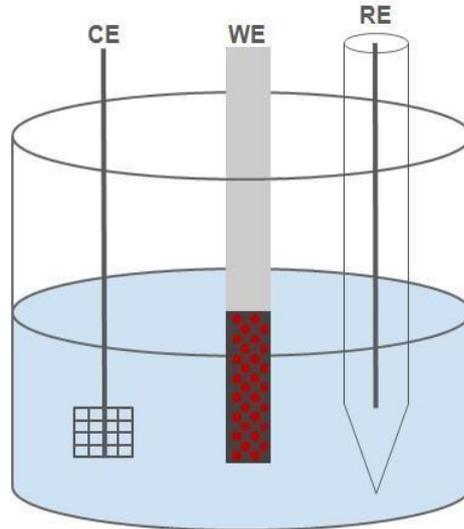


Figure 1. Three-electrode system.

The cyclic voltammetry consists in applying a potential and check the current response. It was applied a potential window from 0 to 0.6 V at different scan rates from 5 to 100 mV/s, and the electrodes behavior are shown in Fig. 2. From the voltammogram, the Faradaic reactions are observed, with the oxidation and reduction peaks. These two peaks reveal a pseudocapacitive property of the electrode, as expected from this kind of redox material. The maximum current reached was 30 mA at a 100 mV/s scan rate in the 300 °C electrode and 25 mA at 100 mV/s scan rate for the 500 °C electrode (Zheng, 2009).

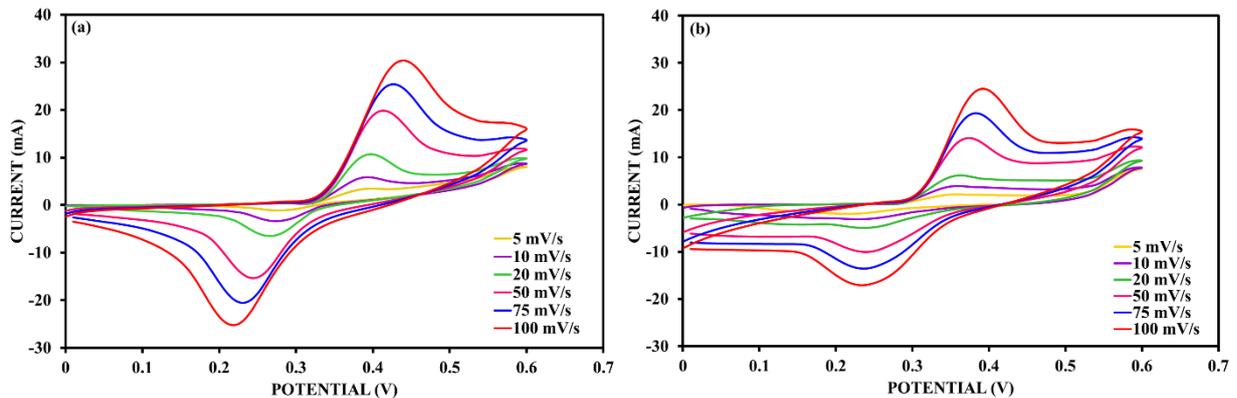


Figure 2. Cyclic voltammogram of (a) NiO300/NF and (b) NiO500/NF.

In the chronopotentiometry test the electrodes were charged and discharged at current densities of 1 A/g, 1.5 A/g, 2 A/g, 3 A/g and 5 A/g. It is notable from the Fig. 3 that the current density is inversely proportional to the charge/discharge time of the supercapacitor. The expected for an ideal device is to obtain the same time to charge and discharge. However, in practice the graphical curves exhibit a more exponential form than linear, due to the resistances associated during the processes, like the resistance of the substrate surface and the electrolyte solution. As can be seen in Fig. 3 there is no symmetry in charge and discharge times of both NiO300/NF and NiO500/NF. The NiO500/NF obtained a faster charge/discharge cycle with a smaller difference between the time to charge and the time to discharge, as can be confirmed from Fig. 4.

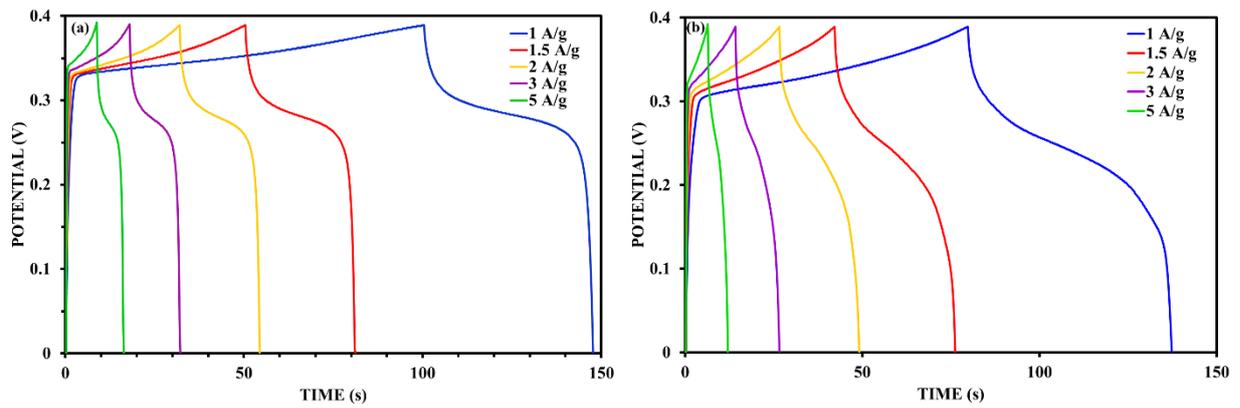


Figure 3. Chronopotentiometry test of (a) NiO300/NF and (b) NiO500/NF.

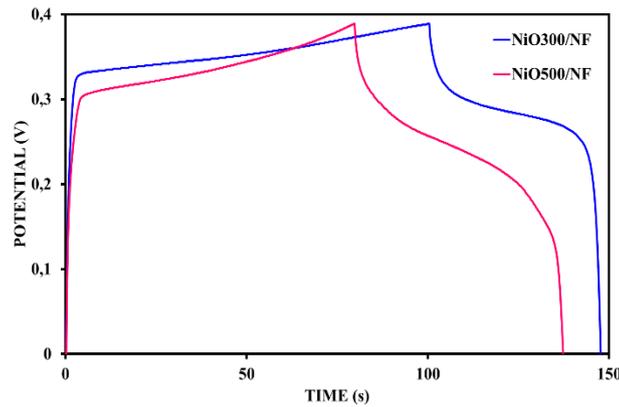


Figure 4. Chronopotentiometry test at 1 A/g current density.

Although the total time of charge and discharge was greater for NiO300/NF electrode, the specific capacitance (SC) depends on other variables. From the graphs (Fig. 3) of time versus potential, the SC were calculated following the Eq. (1), where ΔI is the current, ΔV is the potential, m is the mass of deposited material and Δt is the discharge time. The results were plotted and shown in Fig. 5.

$$SC = \frac{\Delta i \cdot \Delta V}{m \cdot \Delta t} \tag{1}$$

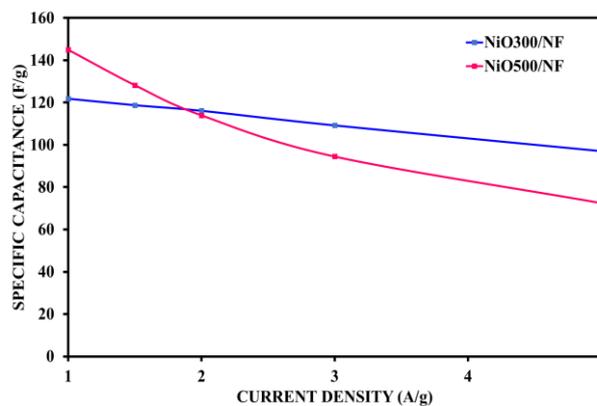


Figure 5. Specific capacitance of NiO300/NF and NiO500/NF at different current densities.

The NiO300/NF electrode reached 121.85 F/g at 1 A/g while the NiO500/NF electrode reached 145 F/g at the same current density. Although the NiO500/NF had achieved higher specific capacitance at 1 A/g, the NiO300/NF had better results at current densities higher than 1.5 A/g and decreased the specific capacitance in a smaller rate. It proves that probably the electrode synthesized at 300°C has better stability.

The electrochemical impedance spectroscopy aims to reveal the behavior of the reactions occurring between the electrode and electrolyte interface and between the substrate and material interface. From this method, the resistance and

the capacitance relative to the reactions can be analyzed by the graph that relates the real and imaginary impedances involved. When the results are displayed in the Nyquist Plot, two different regions are obtained: a semicircular part and a linear one. The first part indicates the resistance of the material at high frequencies, while the linear form means the diffusion of the material in low frequencies. From Fig. 6, it is observable that the semicircles showed with small radius and the diffusion of both electrodes was high. These results showed the expect behavior for supercapacitors devices (Barsi, 2013).

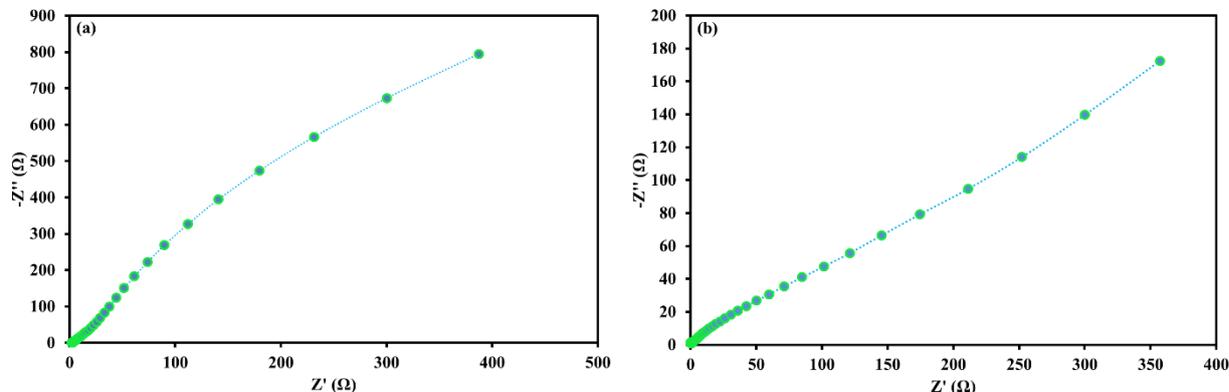


Figure 6. Impedance spectroscopy of (a) NiO300/NF and (b) NiO500/NF.

4. CONCLUSION

In this work we have successfully synthesized NiO by hydrothermal method with aid of surfactant and template. The nickel oxide was coated on nickel foam substrates at two different temperatures. The electrodes performances were analyzed through electrochemical characterizations that revealed not only the pseudocapacitive property of both material, but also the good conductivity and diffusion in KOH electrolyte solution. The better performance was showed for the material produced at 500°C, which reached 145 F/g at 1 A/g, with a more symmetric charge and discharge time and better diffusion, compared with the electrode synthesized at 300°C. Because of these good results, the nickel oxide is an alternative promisor material for pseudocapacitors composition.

5. ACKNOWLEDGEMENTS

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7. RESPONSIBILITY NOTICE

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