X CONGRESSO NACIONAL DE ENGENHARIA MECÂNICA 2018
20 A 24 DE MAIO DE 2018 SALVADOR – BA – BRASIL

$CuCo_2O_4$ NANOPARTICLES COATED ON NICKEL FOAM ELECTRODE FOR HIGH-PERFORMANCE SUPERCAPACITORS

Mariana de Almeida Maier, mariana.3almeida@gmail.com
Rajendran Suresh Babu, ryesbabu@gmail.com
Gabriela Corbetta Sánchez, gabicorsan@yahoo.com.br
Leandro Marques Samyn, Leandro.samyn@cefet-rj.br
Daniel da Motta Sampaio, mottasampaio@gmail.com
Ana Lucia Ferreira de Barros, ana.barros@cefet-rj.br

Centro Federal de Educação Tecnológica Celso Suckow da Fonseca, Laboratory of Experimental and Applied Physics – LaFEA, Maracanã Avenue 229, Rio de Janeiro - RJ, Brazil

Abstract: *In this work will be presented a promissor material, the ternary oxide $CuCo_2O_4$ coated on nickel foam electrode in the construction of a high-performance supercapacitor. The $CuCo_2O_4$ was synthesized by hydrothermal method for 12 hours at 450ºC. The performance analysis was carried out through the physical and electrochemical characterizations, such as cyclic voltammetry, charge-discharge test and field emission scanning electron microscopy. The electrode showed the specific capacitance of 203.56 F/g at 0.5 A/g current density, obtained in a 2 M KOH electrolytic solution. The $CuCo_2O_4$ presented satisfactory results, since it combines the advantages of all components: good conductivity, good electrochemical performance, low toxicity and pseudocapacitive properties. Also, the FESEM image confirmed the material in nanosized sheet-like structure with some porosity and high surface area, allowing the ions movement between the electrode and the electrolyte and turning the reactions faster.*

Key-words: *supercapacitor, pseudocapacitor, metal oxide, copper, cobalt.*

1. INTRODUCTION

The global development and the necessity of a full time connection through electronic devices enhance the energy demand. Therefore, it is crucial the process of generation and distribution of energy as well as its storage stage. The most common electrical charge storage devices used are batteries, which do it electrochemically. Besides them, it can be used fuel cells, capacitors and supercapacitors, the focus of this work.

Fuel cells convert chemical energy into electrical energy through hydrogen by reactions that unite the hydrogen atoms with oxygen forming water molecule, or another fuel. Conventional capacitors are formed by two conducting plates (electrodes) and an isolator material (dielectric) between them. The supercapacitors, or electrochemical capacitors, have an electrolytic solution (electrolyte) separating the electrodes, which facilitates and allows the charge transport at the electrolyte/electrode surface (Campanari, 2009; Winter, 2004 and An, 2017).

The Ragone plot (Fig. 1) shows a comparison of these devices. Supercapacitors are intermediate devices between batteries and conventional capacitors, once they store more energy than capacitors and are capable to release it faster than batteries. Because of these characteristics, they have been studied for many applications, such as hybrid vehicles and biosensors (Yu, 2013; Carignano, 2017 and Rodriguez-Silva, 2016).

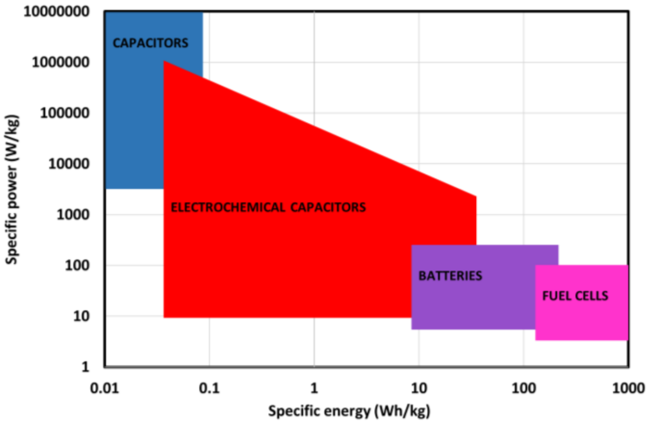

Figure 1. Ragone plot.

Usually the supercapacitors can be classified as an electrical double layer capacitor (EDLC), pseudocapacitor or hybrid supercapacitor. The difference consists in the energy storage form between electrode and electrolyte. The charge storage form of the EDLCs is electrostatically, through the ions attraction and charges separation. In the electrochemical storage of pseudocapacitors, the reduction and oxidation (redox or Faradaic) reactions occur at the electrode/electrolyte interface, turning the charging and discharging processes faster. The hybrid supercapacitors unite both storage types, combining materials with electrostatic (carbon-based materials – carbon nanotubes, graphite, graphene, etc.) and electrochemical (transition metals, metal oxides, conducting polymers, etc.) properties in their composition (Babu, 2018 and Maier, 2017).

Among the components used on the pseucapacitors fabrication, conducting polymers, hexacyanoferrates and metal oxides, like RuO_2 and MnO_2 are highlighted. In oxide-based pseudocapacitors, the studies of different metal junctions in the composition have been revealed better performance than the obtained with single components. Therefore, in this work, the $CuCo_2O_4$ was synthesized by hydrothermal method and coated on nickel foam (NF) as a promisor material for pseudocapacitors electrodes composition (Babu, 2018; Maier, 2017; Wang, 2016; Subramanian, 2004 and Huang, 2015).

2. EXPERIMENTAL PROCEDURE

All the chemical components and the nickel foam electrode were purchased from Synth and Sigma Aldrich. The ethanol, acetone and isopropyl alcohol were purchased from Dinâmica Ltda and the distilled water was obtained by Cristófoli WS-303 distiller in the laboratory.

The ternary oxide was prepared by hydrothermal method using a solution containing 0.001 M $Cu(NO_3)_2 \bullet 3H_2O$, 0.002 M $Co(NO_3) \bullet 6H_2O$, 0.012 M C_6H_9NO, 300 mg of polyvinylpyrrolidone (PVP), 18 ml of distilled water and 18 ml of ethanol mixed together and kept at 140ºC for 24 hours in Teflon lined autoclave in muffle furnace.

The aqueous oxide solution passed through the centrifugation process. It was washed several times with distilled water and isopropyl alcohol to remove all the impurities, and then it was dried at room temperature. The final precipitate was dried at 60ºC and finally calcined at 450ºC for 3 hours.

The nickel foam electrode was pre-cleaned with 3 M HCl solution for 30 min in a sonication process. After the synthesis and cleaning processes, a homogeneous mixture of $CuCo_2O_4$, PVDF binder and activated carbon powder in the ratio of (8:1:1) was coated on the nickel foam surface uniformly and dried at 100ºC for 24 hours.

3. RESULTS AND DISCUSSION

The physical characterization was carried out using field emission scan electron microscopy (FESEM) to study the morphology and the size of the material. From the image obtained by FESEM technique (Fig. 2) it can be noted that the formed material shows a sheet-like shape with numerous pores. The size of the nanoparticles is less than 50 nm, being easily attached on the high-porosity NF surface and the layer's gap facilitates the ions absorption and desorption during the loading and releasing charge in the electrochemical process.

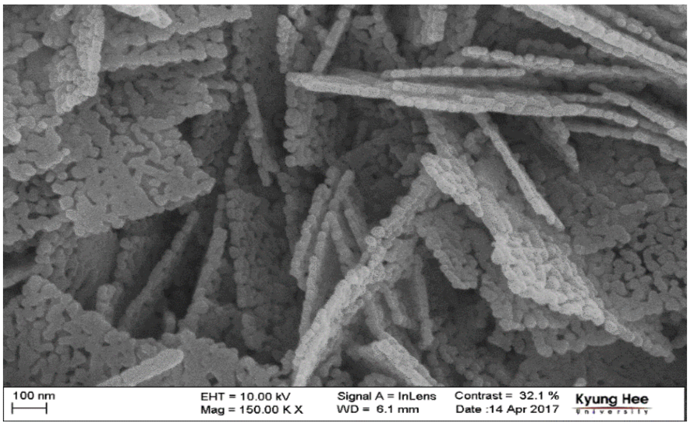

Figure 2. FESEM image of $CuCo_2O_4$.

The electrochemical measurements were carried out with three-electrode system multi-potentiostat, using Ag/AgCl as the reference electrode, platinum mesh as the counter electrode and $CuCo_2O_4$/NF as the working electrode, submersed in 2 M KOH electrolyte solution. The cyclic voltammogram behavior, showed in Fig. 3, reveals the Faradaic property of the electrode, in which the peaks associated to the redox reactions occur in the potential window from 0 to 0.6 V. For this potential window it was applied a scan rates from 5 to 150 mV/s, reaching around 100 mA. Along the scan rate increasing, the anodic peak shifted to positive potential while the cathodic peak reduction moved to lower potentials, confirming the quasi-reversible characteristics of the electrode.

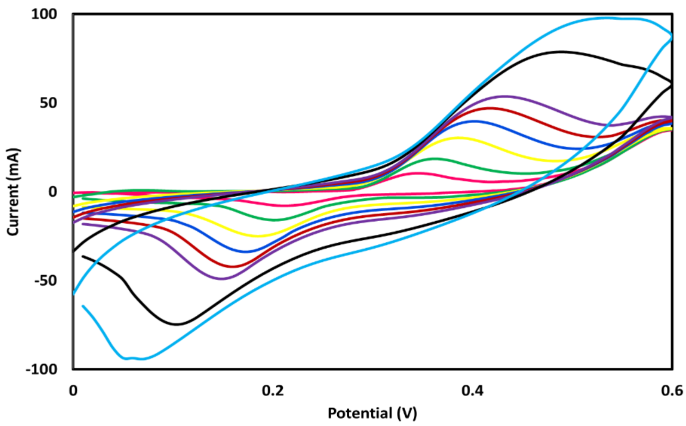

Figure 3. Voltammogram of $CuCo_2O_4$ at different scan rates from 5 to 150 mV/s.

After the cyclic voltammetry study, the galvanostatic charge-discharge (CD) test was carried out, in which the electrode was submitted to many CD cycles using different current densities from 0.5 to 5 A/g. From the Fig. 4 it can be observed that when the current density increases, the time of charge and discharge decreases. It occurs due to the fast ions transfer between the electrode and electrolyte surface. The charge and discharge times are almost the same, giving a symmetric behavior expected for an ideal supercapacitor CD graph.

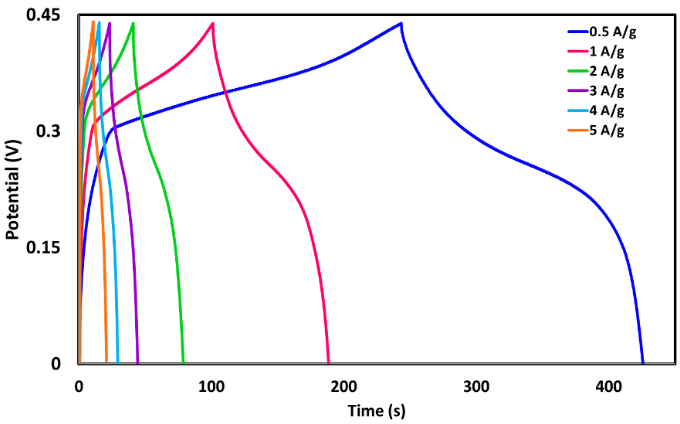

Figure 4. Charge-discharge behavior of $CuCo_2O_4$/NF electrode.

From the CD test it was calculated the specific capacitance (S_c) using the Eq. (1) bellow, where *i* is the discharge current, *V* is the potential window, *m* is the mass of the material coated on the NF substrate, and *t* is the discharge time.

$$c = \frac{i * V}{m * t} \tag{1}$$

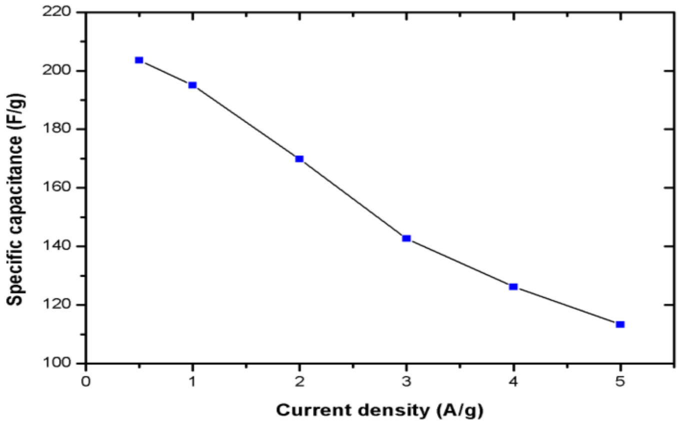

Figure 5. Specific capacitances at different current densities of $CuCo_2O_4$/NF.

The graph in Fig. 5 shows the specific capacitance found at different current densities. The higher capacitance value of 203.56 F/g is associated to the lower current density of 0.5 A/g. The high current density of 5 A/g makes the charge and discharge processes faster (Fig. 4), decreasing the specific capacitance to 113.33 F/g. Despite this, it still maintaining the redox reactions on the electrode surface and thus showing the good ability of the $CuCo_2O_4$/NF nanoparticles electrode to store energy.

4. CONCLUSIONS

This work presented a new promising material to be used in supercapacitors applications. The ternary metal oxide $CuCo_2O_4$ showed a high-performance, because it combines the advantages of good conductivity, low toxicity and pseudocapacitive properties of the single components. The voltammogram confirmed the reversible property of the material, even at high scan rates. The FESEM image also confirmed that the material nanoscale structure presents high surface area and porosity, which allows the movement of ions between the electrode and the electrolyte solution, accelerating the redox reactions. This facile charge transport provides a high specific capacitance of 203.56 F/g, including this ternary oxide in the list of materials applied in the energy storage field.

5. ACKOWLEDGMENTS

We would like to thank the financial supports by the Brazilian agencies such as CAPES (BEX 5383/15-3), (PNPD-PhD scholarships), CNPq (304051/2014-4) and FAPERJ (E-26/110.087/2014, /213.577/2015 and /216.730/2015).

6. REFERENCES

An, L. and Jung, C.Y., 2017, “Transport Phenomena in Direct Borohydride Fuel Cells”, Applied Energy, Vol. 205, pp. 1270-1282.

Babu, R.S. et al., 2018, “Novel Polyaniline/Manganese Hexacyanoferrate Nanoparticles on Carbon Fiber as Binder-Free Electrode for Flexible Supercapacitors”, Composites Part B: Engineering, Vol. 143, pp.141-147.

Campanari, S., Manzolini, G. and De La Iglesia, F.G., 2009, “Energy Analysis of Electric Vehicles Using Batteries or Fuel Cells Through Well-to-Wheel Driving Cycle Simulations”, Journal of Power Sources, Vol. 186, pp. 464-477.

Carignano, M.G. et al., 2017, “A novel Energy Management Strategy for Fuel-Cells/Supercapacitor Hybrid Vehicles”, IFAC-PapersOnLine, Vol. 50, pp. 10052-10057.

Huang, M. et al., 2015, “MnO_2-Based Nanostructures for High-Performance Supercapacitors”, Journal of Materials Chemistry A, Vol. 3, pp. 21380-21423.

Maier, M.A. et al., 2017, “Binder-Free Polyaniline Interconnected Metal Hexacyanoferrates Nanocomposites (Metal = Ni, Co) on Carbon Fibers for Flexible Supercapacitors”, Journal of Materials Science: Materials in Electronics, Vol. 28, pp. 17405-17413.

Rodriguez-Silva, A.A. et al., 2016, “Supercapacitor-Based Biosensor for Low Density Lipoprotein Detection”, Journal of The Electrochemical Society, Vol. 163, pp. B256-B263.

Subramanian, V. et al., 2004, "Mesoporous Anhydrous RuO_2 as a Supercapacitor Electrode Material", Solid State Ionics, Vol. 175, pp. 511-515.

Wang, H., Lin, J. and Shen, Z.X., 2016, "Polyaniline (PANi) Based Electrode Material for Energy Storage and Conversion", Journal of Science: Advanced Materials and Devices, Vol. 1, pp. 225-255.

Winter, M. and Brodd, R.J., 2004, "What Are Batteries, Fuel Cells, and Supercapacitors?", Chemical Reviews, Vol. 104, pp.4245-4269.

Yu, G. et al., 2013, "Hybrid Nanostructured Materials for High-Performance Electrochemical Capacitors", Nano Energy, Vol. 2, pp. 213-234.

7. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.