ELECTROCHEMICAL BEHAVIOR OF ELECTRODE MATERIALS BASED ON NICKEL COBALTITE AND COBALT-NICKEL LAYERED DOUBLE HYDROXIDE

Cristiane Garcia Silva[1*], Raylander Rodrigues da Silva [1] and Paulo Roberto Martins[1,2]

[1] Instituto de Química (IQ), Universidade Federal de Goiás (UFG), Goiânia, GO, Brasil
[2]Centro de Excelência em Hidrogênio e Tecnologias Energéticas Sustentáveis (CEHTES), Universidade Federal de Goiás (UFG), Goiânia, GO, Brasil
*Corresponding author. E-mail: cristianegarcia@discente.ufg.br

ABSTRACT

Electrode materials based on $NiCo_2O_4$ associated with CoNi-LDH are interesting in the area of energy storage. In this work, the obtaining of CoNi-LDH from ZIF-67, according to XRD data, was successful. The association of $NiCo_2O_4$ and CoNi-LDH proved to be efficient, where the $NiCo_2O_4$@CoNi-LDH material presented superior electrochemical results when compared to its precursors individually. Furthermore, are observed for $NiCo_2O_4$@CoNi-LDH specific capacitance of 586.96 F g^{-1} and coexistence of charge storage mechanisms controlled by diffusion and capacitive processes, emphasizing the excellent potential of this material in the composition of positive electrodes of energy storage devices.

Keywords: Nickel cobaltite; Metal-organic framework; Cobalt-nickel layered double hydroxide; Electrode materials; Energy storage.

INTRODUCTION

The increase in energy consumption has sparked an intense search for sustainable energy storage technologies. In this sense, the advent of electroactive materials that enable greater electrical conductivity, cycle stability and durability has become part of a list of essential requirements. Thus, the development of electrode materials based on hierarchical core@shell structures, formed by binary metal oxides/layered double hydroxides (LDHs) derived from MOFs (metal-organic frameworks), highlights a viable and interesting alternative [1]. Binary metal oxides exhibit fast diffusion kinetics that favor electron transfers, providing high conductivity [2]. LDHs have layered structures, capable of intercalating chemical species. However, they exhibit slow charge transfer rates and, depending on the method of production, have limited surface area. [3]. Alternatively, MOFs can be used as templates to obtain LDHs. MOFs are highly porous materials, with a large surface area and the possibility of controlling composition and structure. In this context, the electrode materials of this work were based on nickel cobaltite ($NiCo_2O_4$) and cobalt-nickel LDH (CoNi-LDH), anchored in nickel foams (NFs), with the LDH being derived from ZIF-67 (cobalt zeolite imidazole structure belonging to MOFs) [4]. The materials were associated to form hierarchical core@shell structures. Thus, the proposed study meets the emerging needs in obtaining electroactive materials applied in energy storage.

MATERIALS AND METHODS

Binary metal oxides were obtained via hydrothermal and deposited in-situ on NFs (1.0 cm^2). Initially, 1 mmol $Ni(NO_3)_2.6H_2O$; 2 mmols $Co(NO_3)_2.6H_2O$ and 4.67 mmols urea were solubilized in 20 mL deionized water. The reaction mixture and NFs were transferred to a reactor and heated at 120 °C for 10 h. Subsequently, the materials were washed in deionized water and dried at 60 ºC. Finally, the materials were treated at 300 ºC for 2 h, obtaining $NiCo_2O_4$ [2].ZIF-67 was used as a precursor to LDH. For this purpose, 2.5 mmols of $Co(NO_3)_2.6H_2O$ and 10 mmols of 2-methylimidazole were used, solubilized separately in 25 mL of methanol. The 2-methylimidazole solution was added to the $Co(NO_3)_2.6H_2O$ solution and stirred for 12 h. The precursor ZIF-67 was washed in methanol, dried at 60 °C and used in the synthesis of LDH [4]. For this purpose, 0.3 mmols of ZIF-67 and 0.6 mmols of $Ni(NO_3)_2.6H_2O$ were solubilized in 30 mL of ethanol, transferred to a reactor and heated at 80 ºC for 5h. The material obtained (CoNi-LDH) was washed in ethanol and dried at 60 ºC [3]. To obtain CoNi-LDH electrodes, 10 mg of the material was dispersed in glycerin/butanol, and this dispersion was used to modify the NFs. The core@shell hierarchical structures were obtained from NFs already modified with $NiCo_2O_4$, followed by the deposition of 50 μL of the CoNi-LDH dispersion, producing the $NiCo_2O_4$@CoNi-LDH material.

RESULTS AND DISCUSSION

Thermogravimetric analysis (TGA) **Fig. 1 (A)**, showed lower thermal stability for CoNi-LDH in relation to ZIF-67. Thus, the first mass loss event of CoNi-LDH occurs in the region of 25 to 225 °C (-13.69%) and is attributed to the elimination of H_2O and the release of organic compounds from the synthesis. The mass loss from 225 to 286 °C (-20.40%) comes from the decomposition of residual 2- methylimidazole, originating from ZIF-67, and from the dehydration/dihydroxylation of the material, related to the formation of cobalt and nickel oxides. From 286 °C onwards the loss can be attributed to the degradation of the lamellar structure of the material (-9.80%).

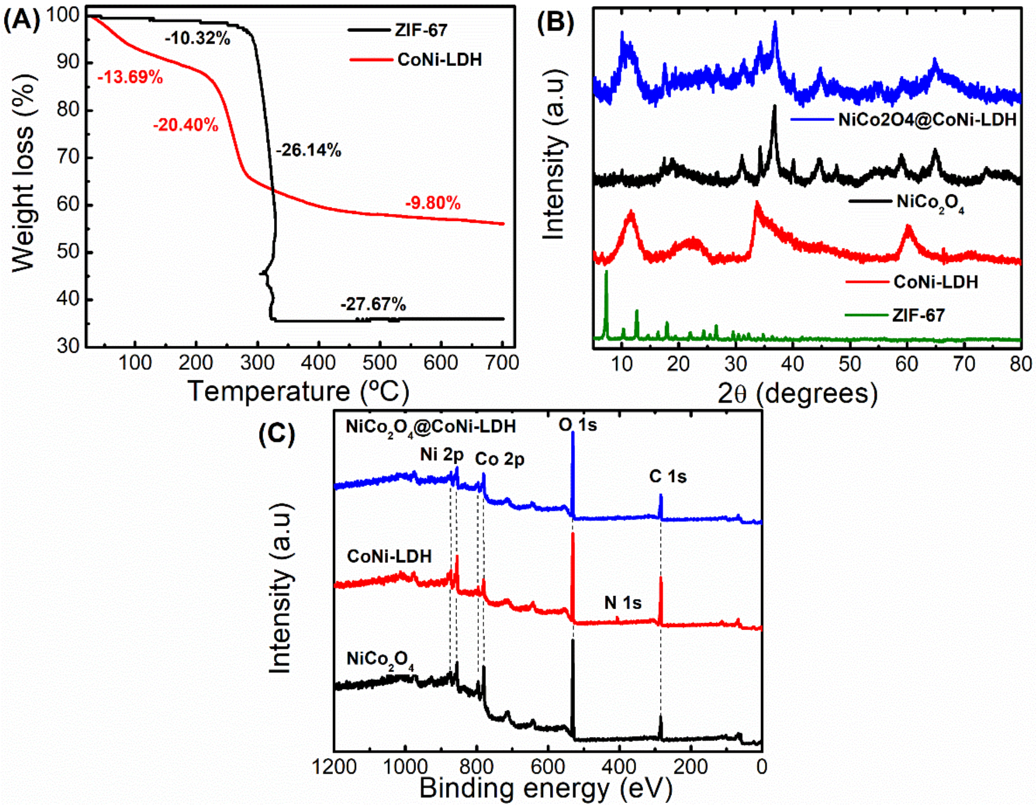

Figure 1: TGAs of ZIF-67 and CoNi-LDH **(A)**. In **(B)** Diffraction patterns of ZIF-67, CoNi-LDH and $NiCo_2O_4$ (powder) and $NiCo_2O_4$@CoNi-LDH (film). In **(C)** XPS survey spectra of CoNi-LDH, $NiCo_2O_4$ (powder) and $NiCo_2O_4$@CoNi-LDH (film).

The X-Ray diffractograms (**Fig. 1 (B)**) demonstrate that the synthesis of CoNi-LDH, using ZIF-67, was successful, since reflection peaks (003), (006), (009) and (110) were verified, respectively in the 2θ regions at 11.52°, 22.54°, 33.72° and 60.06°. Furthermore, the diffractograms show that the $NiCo_2O_4$@CoNi-LDH material presented peaks originating from both $NiCo_2O_4$ and CoNi-LDH. The XPS survey spectra (**Fig.1 (C)**) confirm the existence of Ni, Co, O and C. Furthermore, it highlights the presence of N in the 406 eV region in CoNi-LDH, originating from the nitrate used in the synthesis.

Fig. 2 (A–C) shows the voltametric profiles of $NiCo_2O_4$, CoNi-LDH and $NiCo_2O_4$@CoNi-LDH in the potential window from -0.10 to +0.60 V at 20 mV s^{-1}. Analyzing the 50th cycle ΔE, i_{pa} and specific capacitance (F g^{-1}), are respectively 160 mV; 13.97 mA and 392.72 F g^{-1} ($NiCo_2O_4$); 150 mV; 15.69 mA and 483.00 F g^{-1} (CoNi-LDH) and 160 mV; 21.57 mA and 586.96 F g^{-1} ($NiCo_2O_4$@CoNi-LDH).

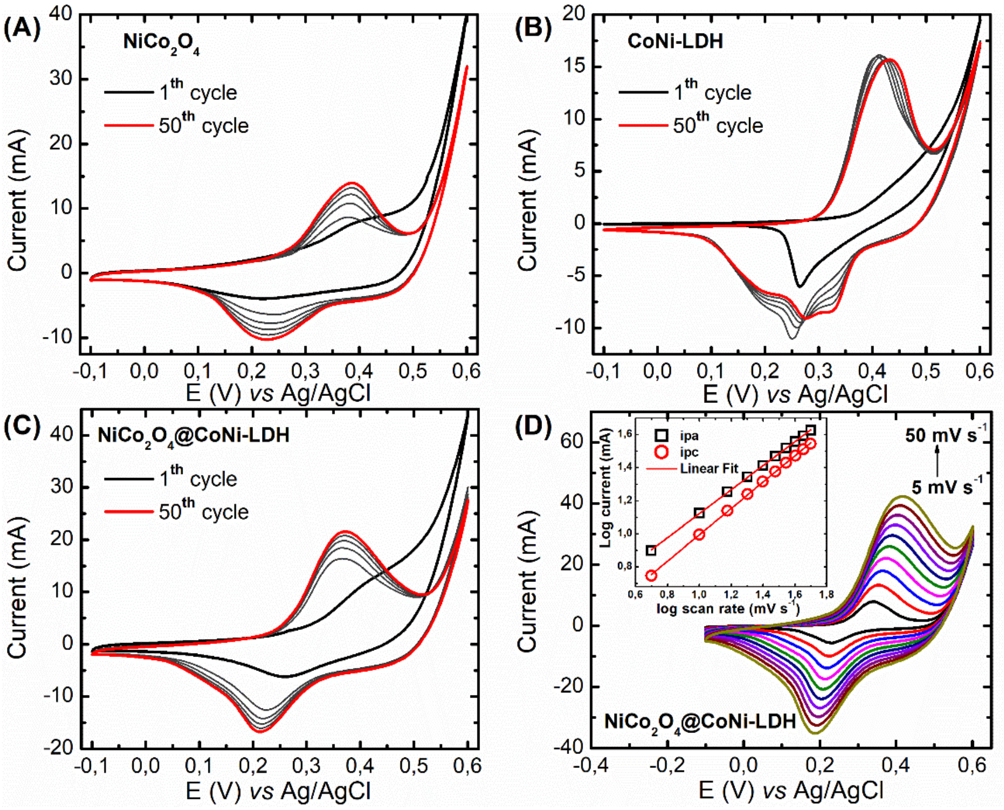

Figure 2: Cyclic voltammograms of $NiCo_2O_4$ **(A)**, CoNi-LDH **(B)** and $NiCo_2O_4$@CoNi-LDH **(C)** at 20 mV s^{-1} in 1 mol L^{-1} KOH solution. In **(D)** voltammograms of $NiCo_2O_4$@CoNi-LDH at different scan rates (5 - 50 mV s^{-1}), the inset in Logarithm relationship between anodic and cathodic current *vs* scan rate.

In **Fig. 2 (D)** the voltammograms of $NiCo_2O_4$@CoNi-LDH show a potential shift as a function of the increase in scan rates, caused by the limitation in the electron transfer kinetics. Furthermore, there was na increase in i_{pa} and i_{pc} with the progressive increase in velocities, caused by the rapid kinetics of ion transport. The parameter b of the logarithmic relationship of i_{pa} e i_{pc} *vs* scan rates was 0.73 (i_{pa}) and

0.80 (i_{pc}), indicating the coexistence of mechanisms controlled by diffusion and capacitive processes.

CONCLUSION

In this work, $NiCo_2O_4$ anchored on NFs were synthesized by in-situ deposition. Furthermore, CoNi-LDH derived from ZIF-67 was successfully prepared, as reflected by reflection peaks in the X-ray diffractograms. The XPS survey spectrum analysis showed peaks analogous to the binding energies of Ni and Co metals. The association of materials in the form of hierarchical structures containing $NiCo_2O_4$@CoNi-LDH proved to be efficient, with its electrochemical performance being superior to that reported for its precursors. Thus, a larger integrated area was evidenced in the voltammogram of $NiCo_2O_4$@CoNi-LDH, in addition to anodic peak current and specific capacitance, respectively, of 21.57 mA and 586.96 F g^{-1}.

ACKNOWLEDGMENT

This work is supported by Fundação de Amparo à Pesquisa do Estado de Goiás (FAPEG 202310267000212). Besides, the authors are grateful to the Conselho Nacional de Desenvolvimento Científico e Tecnológico by the fellowships granted to C.G.S (CNPq 140928/2022-7) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior to R.R.S (CAPES 88887.971852/2024-00).

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