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# The cobalt content effect on the electrochemical behavior of nickel hydroxide electrodes

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ABSTRACT

In this paper, the study of nickel hydroxide porous electrodes containing different concentrations of cobalt as additive (2–10%), polytetrafluoroethylene (PTFE) as binder material and prepared by chemical impregnation on nickel sintered substrate, are presented. The characterization of the different electrodes is performed using optical techniques such as scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX) and electrochemical techniques as cyclic voltammetry, charge-discharge curves and electrochemical impedance spectroscopy (EIS). The results indicate that the concentration of 5% metallic Co improves the electrochemical behavior of the active material.



## 1. Introduction

In the last years, much interest has been focused on the development of rechargeable alkaline batteries, trying to meet the demands resulting from technological innovations ranging from portable electronics to aeronautical and space applications or electric and hybrid-electric vehicles [1].

In alkaline batteries: Ni–Cd, Ni–Fe, Ni–Zn, Ni–MH and Ni–H, the positive electrode is nickel hydroxide. The electrochemical energy storage in this material is based on the reversible redox reaction, nickel hydroxide/oxhydroxide. The reversibility of this process is an important factor in the performance of nickel hydroxide as active material in the positive electrode. Another feature to consider is the poor electric conductivity of $Ni(OH)_2$ (p-type semiconductor), therefore, additives such as C, Ni, Co, Ca [2–5] are commonly used to improve the active material performance.

In the present work, a study, of the cobalt content effect, on the electrochemical behavior of nickel hydroxide electrodes is presented. The active material consisted of $Ni(OH)_2$ Aldrich and different concentrations of metallic Co (2%, 5% and 10%), 23% PTFE was added as binder material [2]. The mix was pasted onto the nickel foam substrate.

The electrodes were characterized using optical (SEM and EDAX) and electrochemical techniques such as cyclic voltammetry, charge-discharge curves and electrochemical impedance spectroscopy (EIS). The EIS experimental data are analyzed according to a physicochemical model, taking into account the porous nature of the electrode, and the faradaic process coupled to mass transport in the active material. Consequently, structural and kinetic parameters depending on the state of discharge (SOD) of the electrode can be identified, allowing to select the best electrode design.

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## 2. Experimental

### 2.1. *Preparation of the working electrodes*

The working electrodes used for the experiments were prepared on a nickel sintered substrate. The active material consisted of $Ni(OH)_2$ Aldrich containing 23% PTFE and different concentrations of metallic Co, electrode A: 2%, electrode B: 5% and electrode C: 10%. All were pressed with 200 kg/cm$^2$.

### 2.2. *Characterization using optical techniques*

The SEM images were obtained using a scanning electron microscope Philips SEM model 505 with an image digitizer System Soft Imaging ADDA II. The EDAX mapping tests were performed using an ESEM FEI Quanta 200 model microscope. This instrument has an energy dispersive X-ray analysis system, EDAX, Apollo 40 model.

### 2.3. *Electrochemical characterization*

A three-compartment electrochemical cell was employed for the electrochemical experiments. The electrolyte was a 7 M KOH solution at 30 °C. A nickel mesh of large specific area was used as counter-electrode and a Hg/HgO electrode, was used as reference electrode.

The charge-discharge curves at different current densities, the cyclic voltammetry with anodic and cathodic limits to potential default values (0.05 V and 0.7 V respectively) and at scanning rate of 50 mV s$^{-1}$, were performed using a kit Arbin BT2000 model potenciostat.

EIS measurements were carried out potentiostatically at the open circuit potential attained at each SOD, employing a frequency response analyzer Solartron 1250 coupled to a potentiostat EG&G model PAR 273. Measurements were carried out in the 3.15 mHz $\leq f \leq$ 65 KHz frequency range, with a sinusoidal signal perturbation of small amplitude (5 mV), to guarantee a constant state of discharge.

## 3. Results and discussion

### 3.1. *Optical techniques*

#### 3.1.1. *SEM*

SEM technique was used to evaluate the surface morphology of the working electrodes. Fig. 1(a–c) exhibit the surface morphology, at a magnification of 500×, of the electrode A, B and C respectively.

The micrographs show that the electrodes A and C have a compact surface morphology, unlike the electrode B, whose surface morphology appears to be a more porous structure with better defined holes or pores.

#### 3.1.2. *EDAX*

The EDAX mapping analysis carried out by EDAX technique was used to identify the distribution of cobalt in the active material. Fig. 2(b,d,f) shows the EDAX results for the electrodes A, B and C respectively. Fig. 2(a,c,e) shows the corresponding SEM images of the regions analyzed by EDAX, for each electrode, with a magnification of 500×.

Fig. 2 exhibits differences in the distribution of metallic cobalt in the active material depending on Co concentration. Results corresponding to electrodes A and B indicate a more uniform cobalt distribution compared to that exhibited by electrode C. For this electrode areas of higher concentration of cobalt were clearly seen.

### 3.2. *Electrochemical techniques*

#### 3.2.1. *Cyclic voltammetry*

Fig. 3 shows the stabilized voltammograms corresponding to electrodes A, B and C, after 30 cycles at a scan rate of 50 mV s$^{-1}$. Voltammetric peaks associated with the redox reaction $Ni(OH)_2$/NiOOH are observed.

Voltammetric results indicate the better reversibility associated with the redox process, for electrode B, together with a significant decrease in the oxygen evolution reaction overpotential.

#### 3.2.2. *Discharge curves*

Fig. 4 depicts discharge curves, at 1 mA, corresponding to electrodes A, B and C. The electrodes were previously loaded to their maximum capacity. It can be seen in Fig. 4 that electrode B exhibits the best capacity at 1 mA, in comparison to the values presented by electrodes A and C.

#### 3.2.3. *Electrochemical impedance spectroscopy*

3.2.3.1. *Theoretical model*. The impedance response corresponding to nickel hydroxide electrodes was analyzed in terms of a physicochemical model which accounts for the charge/discharge process, taking place at the active material/electrolyte interface of the porous structure of the electrode. The working electrode is described as a porous flooded structure, conformed by spherical NiOOH particles. The faradaic process is related to the charge transfer reaction coupled to the diffusion transport of protons in the active material [6–8].

The impedance function of the porous structure, $Z_p$ may be expressed as [7]:

$$Z_P(j\omega) = \frac{L}{A_{gt}k}\left(\frac{1}{\nu(j\omega)\tanh\nu(j\omega)}\right) \tag{1}$$

Being: $\nu(j\omega) = L(\frac{1}{k})^{1/2} Z_i^{-1/2}(j\omega)$

Where $L$ is the thickness of the electrode, $A_{gt}$ the geometric area, $k$ the effective conductivity of the electrolyte and $Z_i$ the interfacial impedance of the active material/electrolyte interface per unit volume (Ω cm$^3$). $Z_i$, is related to the parallel connection between the impedance of the double layer capacitance ($Z_{dc}$) and the faradaic impedance ($Z_f$).

$$Z_i^{-1} = Z_{dc}^{-1} + Z_F^{-1} \tag{2}$$

$$\text{Being}: \quad Z_{dc} = \frac{1}{j\omega C_{dc} a_e} \quad Z_F = \frac{Z_f}{a_a} \tag{3}$$

$j = \sqrt{-1}$, $C_{dc}$ double layer capacitance per unit interfacial area ($C_{dc} \approx 5 \times 10^{-5}$ F cm$^{-2}$), $a_e$ interfacial area per unit volume