

Preparation and characterization of positive electrode of Ni–MH batteries with cobalt additives

M.G. Ortiz ^{a,b,*}, S.G. Real ^{a,b,*}, E.B. Castro ^{a,1}

^a Instituto de Investigaciones Físicoquímicas Teóricas y Aplicadas (INIFTA), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C.C.16, Suc. 4, 1900 La Plata, Argentina

^b Centro de Investigación, Desarrollo en Ciencia y Tecnología de los Materiales (CITEMA), Facultad Regional La Plata, Universidad Tecnológica Nacional, Calle 60 y 124, La Plata, Argentina

ABSTRACT

The present paper shows the preparation and characterization of alkaline batteries cathodes formed by nickel hydroxide with the addition of cobalt. This additive was incorporated by two methods: on the electrode surface, using the electroless technique and by direct incorporation of cobalt powder in the active material. The electrochemical behavior of both nickel hydroxide electrodes was investigated and compared. The results indicate that active materials containing cobalt additive by the electroless technique exhibit an improvement on the electrochemical performance.

Keywords:

Alkaline batteries
Nickel hydroxide electrode
Electroless
Cobalt

1. Introduction

In recent decades much interest has focused on the technologies called clean and consequently has invested in the development of alternative energy sources. Within these devices, alkaline batteries as Ni/H and Ni/MH are included. The positive electrode of them is the nickel hydroxide active material.

Despite the nickel hydroxide material has been widely studied, due to the complex nature of the reactions and structures involved in the redox processes, determining the rest potential, investigations on this subject are still of interest. Furthermore, the nickel hydroxide has a poor conductivity (this is a p-type semiconductor), therefore

additives such as Cd, Zn, Ca, C, Ni, Co [1–6] are commonly used to improve the performance of the material. Among the many chemical compounds that have been studied as additives, the cobalt compounds appear to be the most successful due to different effects: they increase the reversibility of the redox couple Ni(OH)₂/NiOOH and the overpotential of oxygen evolution, decrease the growth of γ-NiOOH species during charging and improve the conductivity [7–9]. During the first loading of the active material, a highly conductive phase (β-COOOH) is generated by the oxidation of the cobalt-based precursor. This material is stable, due to the irreversibility of Co(III)/Co(II) pair [7,8], and is responsible of improving the conductivity of the whole system [9–11].

* Corresponding authors. Instituto de Investigaciones Físicoquímicas Teóricas y Aplicadas (INIFTA), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C.C.16, Suc. 4, 1900 La Plata, Argentina. Tel.: +54 2214257430.

E-mail addresses: mortiz@inifta.unlp.edu.ar (M.G. Ortiz), sreal@inifta.unlp.edu.ar (S.G. Real).

¹ E.B. Castro passed away on February 18th, 2013.

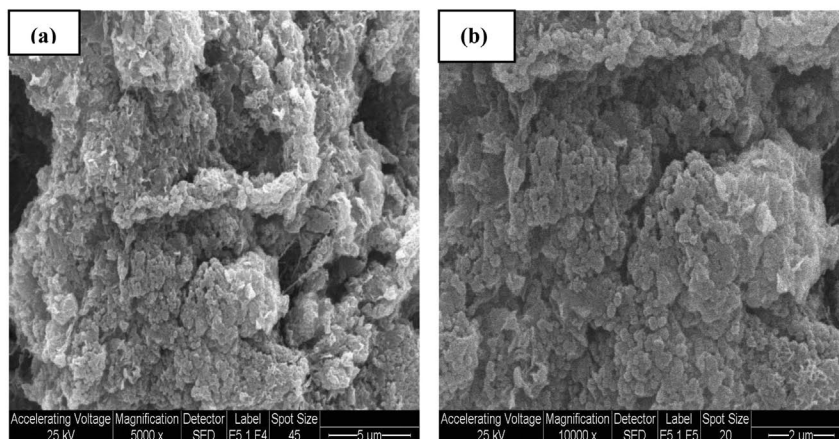


Fig. 1 – SEM micrographs NiCoD: (a) 5000×; (b) 10000×.

Cobalt species can be incorporated into Ni electrode directly to nickel hydroxide or by cobalt and nickel hydroxide precipitation employing chemical reaction of cobalt–nickel mixed salt alkaline solutions. Furthermore, cobalt can be added on the electrode surface by either microencapsulation, electrochemical deposition using nickel and cobalt nitrates or electroless plating [1,2,12–16]. Since discussions about the way that cobalt additive affects structural and kinetic parameters are still lacking, the present research work compares the electrochemical behavior of cathodes prepared by two ways of adding cobalt to the active material: cobalt incorporated by mixing cobalt additive powder with commercial Ni(OH)₂ and by cobalt depositing on the electrode surface using electroless technique.

2. Experimental

2.1. Preparation of working electrodes

Two working nickel electrodes were prepared by pasting the mixture of Ni(OH)₂ Aldrich containing 23% PTFE onto nickel form substrate. The cobalt additive was added by two

different methods: by directly mixing 5 wt.% of cobalt powder (NiCoD) with the active material Ni(OH)₂ powder [17] and by cobalt electroless (NiCoE) on the active material electrode surface. The electroless deposition of cobalt was carried out by immersing the pasted electrode during 5 min in a solution containing cobalt sulfate, sodium citrate and sodium hypophosphite as described in previous works [15,16,18]. The working electrodes were pressed at 300 kg/cm² for 1 min. The cobalt amount of additive and the electroless deposition time in the working electrode was selected taking into account the best electrochemical behavior obtained in previous investigations [16,17].

2.2. Characterization using optical techniques

The structure and composition of the electrode surface was studied using scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX). The SEM images were obtained employing 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 EDAX Apollo 40 model.

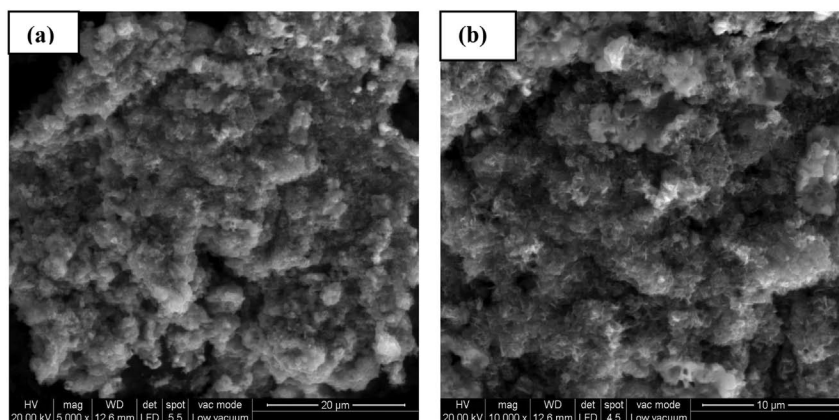


Fig. 2 – SEM micrographs NiCoE: (a) 5000×; (b) 10000×.

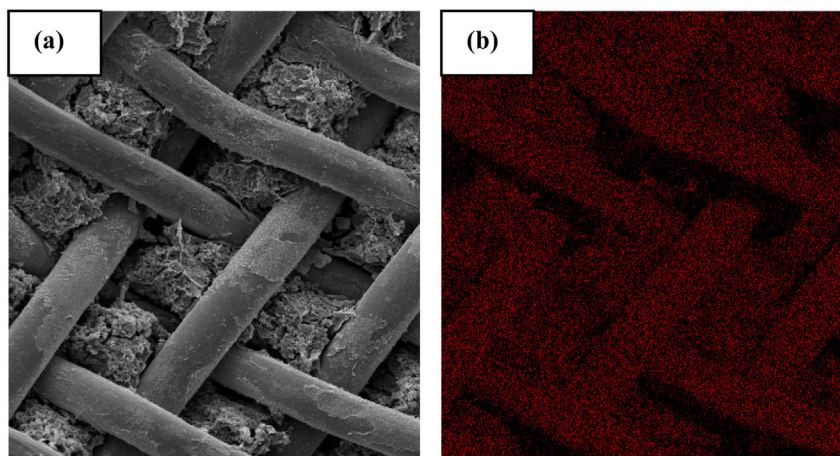


Fig. 3 – NiCoD electrode a) SEM at 500 \times ; b) EDAX Co distribution.

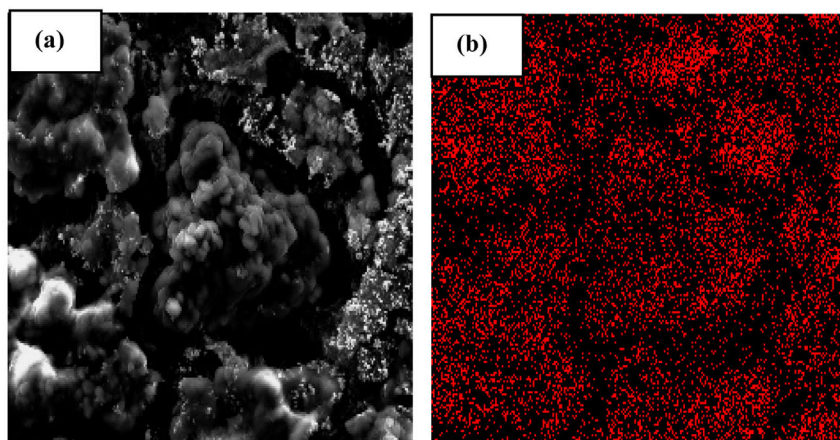


Fig. 4 – NiCoE electrode a) SEM at 5000 \times ; b) EDAX Co distribution.

2.3. Electrochemical characterization

Electrochemical measurements were performed in a conventional three-compartment glass cell at 30 °C and KOH solution 7 M was used as electrolyte. A nickel mesh of large

specific area was used as a counter electrode and Hg/HgO_{ss} was employed as the reference electrode.

The charge–discharge curves at different current densities, the cyclic voltammetry (at scanning rate of 5 mV s⁻¹, with anodic and cathodic limits to potential default

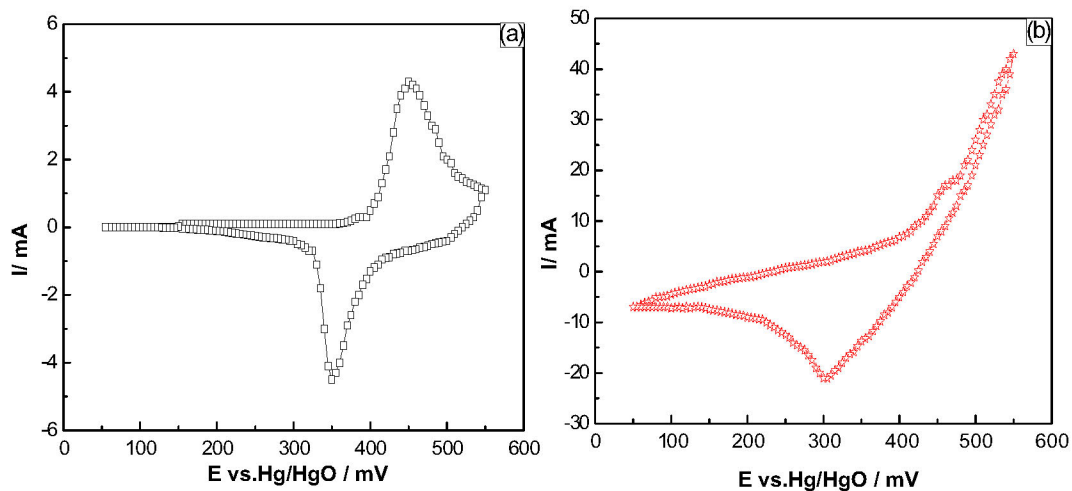


Fig. 5 – Cyclic voltammograms for electrodes NiCoD and NiCoE.

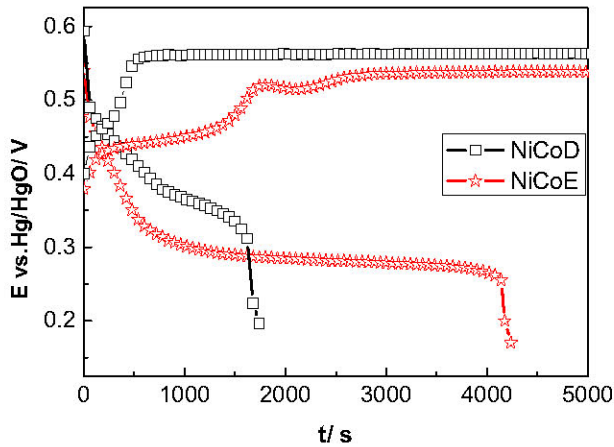


Fig. 6 – Charge–discharge curve for electrodes NiCoD and NiCoE.

values of 0.05 V and 0.7 V respectively), and electrochemical impedance spectroscopy (EIS) measurements were performed under potentiostatic control using a frequency response analyzer Solartron 1250 coupled to a potentiostat EG&G model PAR 273. EIS measurements were carried out in the $19.9 \text{ mHz} \leq f \leq 65 \text{ KHz}$ frequency range, employing a sinusoidal signal perturbation of small amplitude (5 mV), to assure a constant state of discharge.

3. Results and discussion

3.1. Surface characterization

3.1.1. SEM

Figs. 1 and 2 show SEM images of electrodes NiCoD and NiCoE respectively. Figs. 1a and 2a exhibit the SEM micrographs at a magnification of $5000\times$. The surface morphologies, for both electrodes, present similar porous structure. The same appearance can be observed a higher magnification in the Figs. 1b and 2b. Consequently, it is apparent that surface

topography becomes independent of the cobalt incorporation method.

3.1.2. EDAX

The information about the way that cobalt is distributed in the electrode surface can be obtained by analyzing the EDAX maps where, after selecting the topographical image of the surface as a reference, the distribution of the cobalt is represented as colored dots. Figs. 3b and 4b show the cobalt distribution in the NiCoD and NiCoE electrode surfaces for the SEM areas exhibited in Figs. 3a–4a. These pictures indicate that cobalt distribution is uniform on the surface of both electrodes.

3.2. Electrochemical characterization

3.2.1. Cyclic voltammetry

Fig. 5a–b shows the stabilized voltammograms corresponding to working electrodes, after 20 cycles. Voltammetric peaks associated with the redox reaction $\text{Ni(OH)}_2/\text{NiOOH}$ are observed. In addition, the oxidation reaction at both electrodes appears to be separated from the oxygen evolution reaction. Voltammetric results indicate similar reversibility related to the redox process, along with a significant increase in current for electrode NiCoE, associated with the $\text{Ni(OH)}_2/\text{NiOOH}$ pair.

3.2.2. Galvanostatic charge–discharge

Fig. 6 shows typical charge–discharge curves of the Ni(OH)_2 electrodes carried out at 1 mA and -1 mA , respectively. It can be seen that, for Ni(OH)_2 electrodes containing cobalt on their surface, the charge and discharge plateau voltage values are lower and capacity values are higher than that corresponding to NiCoD. These results indicate that in the case of NiCoE electrodes, the active material utilization is improved.

3.2.3. Electrochemical impedance spectroscopy

Fig. 7a–b shows Nyquist EIS plots, at 20% of state of discharge (SOD) of NiCoD and NiCoE respectively. The plots exhibit in the high frequencies range a linear behavior with a slope of

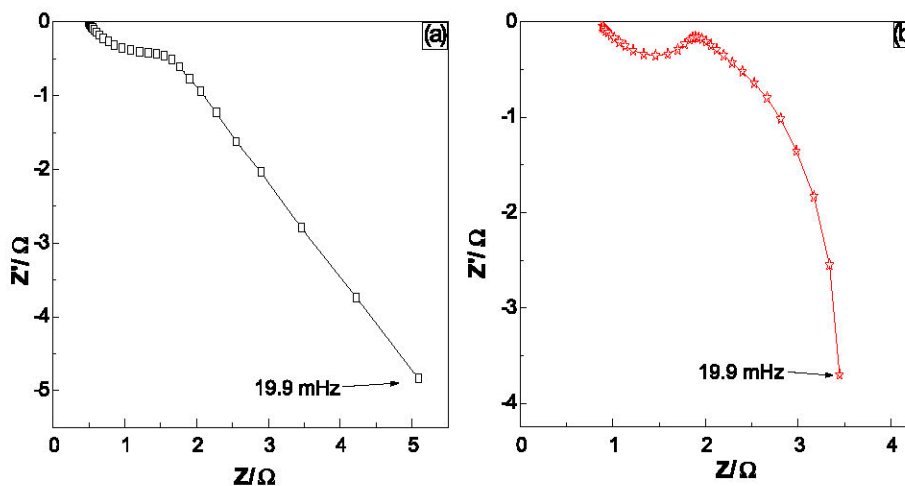


Fig. 7 – Nyquist plots (at SOD of 20%) for electrodes: a) NiCoD and b) NiCoE.

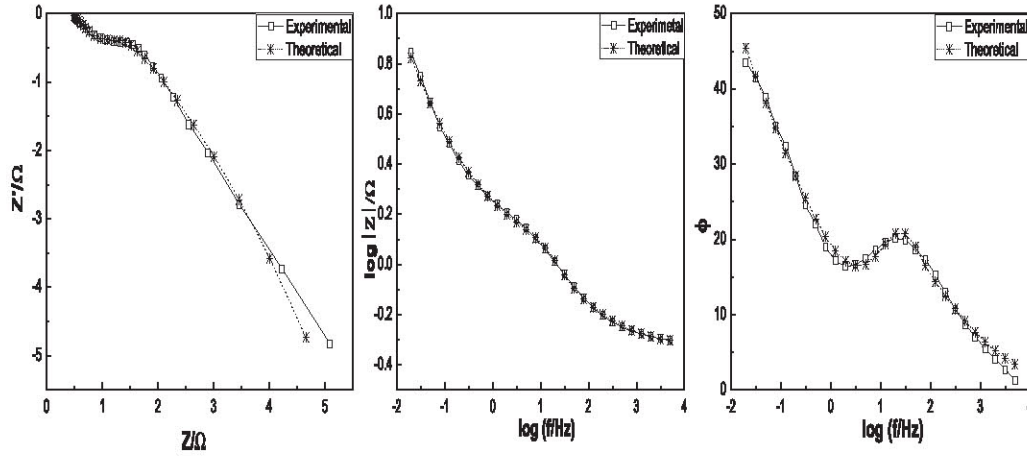


Fig. 8 – Theoretical and experimental impedance diagrams for electrode NiCoD.

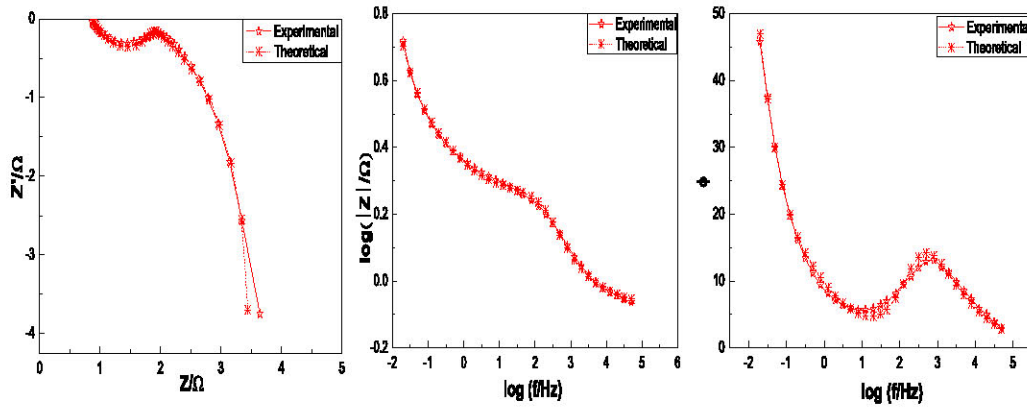


Fig. 9 – Theoretical and experimental impedance diagrams for electrode NiCoE.

approximately 45° , a typical response associated with a porous structure; at intermediate frequencies a semicircle that corresponds to the charge transfer resistance can be seen and at low frequency interval a line related to proton diffusion impedance is shown.

The experimental data are interpreted by 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. This model was described in previous publications [17,19,20]. The experimental spectra are compared with the theoretical results obtained according to the mentioned physicochemical model. A good agreement between experimental and theoretical results is exhibited in Figs. 8 and 9.

Table 1 exhibits the parameters related to the properties of the active materials obtained by fitting experimental data according to the theoretical model.

The electrodes were compared for a constant state of discharge (SOD = 20%) and, according to SEM results, considering similar porosity that is contained in the effective conductivity of liquid k values [20]. From the fitting procedure, similar values of the diffusion coefficient (D) and exchange current density (i_0) for both electrodes were obtained (Table 1). Table 1 shows that effective conductivity of solid phase σ and real active area per unit volume values (A) are higher for NiCoE samples.

It should be noted here that estimated D and σ values are in accordance with those reported in the literature [9,21,22].

According to all results, the better voltammetry and charge–discharge responses obtained with electrode NiCoE indicate that adding cobalt by electroless method allows improving the active material utilization. Furthermore, considering the impedance data and the estimated characteristic parameters, according to the physicochemical model,

Table 1 – Estimated parameters derived from experimental data fitting procedure.

Electrode	SOD	C_i [$F\text{ cm}^{-3}$]	κ [$\Omega^{-1}\text{ cm}^{-2}$]	σ [$\Omega^{-1}\text{ cm}^{-1}$]	A (cm^{-2})	D [cm^2/s]	i_0 [$A\text{ cm}^{-2}$]
NiCoD	20	0.11	0.045	0.48	2411	4.3×10^{-13}	1.0×10^{-3}
NiCoE		0.15		1.25	3200	5.0×10^{-13}	1.2×10^{-3}

the improvement in the active material utilization exhibited by NiCoE electrodes is probably due to their higher σ and A values (Table 1). It is apparent that, electrode surfaces modified by electroless coatings allow diminishing the distance between the nickel hydroxide and the current collector, increasing the conducting network and consequently the discharge depth of active materials [9,23].

4. Conclusions

Nickel hydroxide electrodes with cobalt electroless or post-added cobalt powder were prepared and their electrochemical behaviors were studied.

Results indicate that different methods of incorporating cobalt additives modify the electrochemical properties of the nickel hydroxide electrode. When comparing the two methods, it was observed that the incorporation of cobalt by electroless (NiCoE) improves the electrochemical performance of nickel hydroxide electrodes.

For cobalt coated samples a better voltammetry and charge–discharge responses were obtained. These results along with the impedance data indicate that improvements of the active material utilization can be related to their higher σ and A values.

Acknowledgments

We acknowledge the financial support from the Argentina organizations: Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and Universidad Tecnológica Nacional (UTN).

REFERENCES

- [1] Cheng Shao-an, Wenhua Leng, Zhang Jianqing, Cao Chunan. Electrochemical properties of the pasted nickel electrode using surface modified Ni(OH)₂ powder as active material. *J Power Sources* 2001;101:248–52.
- [2] Wang Xianyou, Luo Hean, Yang Hongping, Sebastian PJ, Gamboa SA. Oxygen catalytic evolution reaction on nickel hydroxide electrode modified by electroless cobalt coating. *Int J Hydrogen Energy* 2004;29:967–72.
- [3] Nathira Begum S, Muralidharan VS, Ahmed Basha C. The influences of some additives on electrochemical behavior of nickel electrodes. *Int J Hydrogen Energy* 2009;34:1548–55.
- [4] Zhu Wen-Hua, Ke Jia-Jun, Yu Hong-Mei, Zhang Deng-Jun. A study of the electrochemistry of nickel hydroxide electrodes with various additives. *J Power Sources* 1995;56:75–9.
- [5] Provazi K, Giz MJ, Dall'Antonia LH, Córdoba de Torresi SI. The effect of Cd, Co, and Zn as additives on nickel hydroxide opto electrochemical behavior. *J Power Sources* 2001;102:224–32.
- [6] Yuan Anbao, Cheng Shaoan, Zhang Jianqing, Cao Chunan. The influence of calcium compounds on the behaviour of the nickel. *Electrode J Power Sources* 1998;76:36–40.
- [7] Benson P, Briggs GWD, Wynne Jones WFK. The cobalt hydroxide electrode—I. Structure and phase transitions of the hydroxides. *Electrochim Acta* 1964;9:275–80.
- [8] Benson P, Briggs GWD, Wynne Jones WFK. The cobalt hydroxide electrode—II. Electrochemical behavior. *Electrochim Acta* 1964;9:281–8.
- [9] Oshitani M, Yufu H, Takashima K, Tsuji S, Massumaru Y. Development of a pasted nickel electrode with high active material utilization. *J Electrochem Soc* 1989;136:1590.
- [10] Pralong V, Chabre Y, Delahaye-Vidal A, Tarascon JM. Study of the contribution of cobalt additive to the behavior of the nickel oxy-hydroxide electrode by potentiodynamic techniques. *Solid State Ionics* 2002;147:73–84.
- [11] Xia Yang, Yang Yifu, Shao Huixia. Differences in the effects of Co and CoO on the performance of Ni(OH)₂ electrode in Ni/MH power battery. *J Power Sources* 2011;196:495–503.
- [12] Chang Zhaorong, Zhao Yujuan, Ding Yunchang. Effects of different methods of cobalt addition on the performance of nickel electrodes. *J Power Sources* 1999;77:69–73.
- [13] Constantin Delia Maria, Rus Eleonora Maria, Oniciu L, Gherari Lucretia. The influence of some additives on the electrochemical behavior of sintered nickel electrodes in alkaline electrolyte. *J Power Sources* 1998;74:188–97.
- [14] Audemer A, Delahaye A, Farhi R, Sac-Epée N, Tarascon JM. Electrochemical and Raman studies of Beta-Type nickel hydroxides Ni_{1-x}Co_x(OH)₂ electrode materials. *J Electrochem Soc* 1997;144(8):2614–20.
- [15] Wang Xianyou, Yan Jie, Yuan Huatang, Zhou Zhen, Song Deying, Zhang Yunshi, et al. Surface modification and electrochemical studies of spherical nickel hydroxide. *J Power Sources* 1998;72:221–5.
- [16] Ortiz MG, Castro EB, Real SG. Effect of cobalt electroless deposition on nickel hydroxide electrodes. *Int J Hydrogen Energy* 2014;39(11):6006–12.
- [17] Ortiz MG, Castro EB, Real SG. The cobalt content effect on the electrochemical behavior of nickel hydroxide electrodes. *Int J Hydrogen Energy* 2012;37:10365–70.
- [18] Huang XH, Yuan YF, Wang Z, Zhang SY, Zhou F. Electrochemical properties of NiO/Co-P nanocomposite as anode materials for lithium ion batteries. *J Alloy Compd* 2011;509:3425–9.
- [19] Castro EB, Cuscueta DJ, Milocco RH, Ghilarducci AA, Salva HR. An EIS based study of a NiMH battery prototype. Modeling and identification analysis. *Int J Hydrogen Energy* 2010;35:5991.
- [20] Real SG, Ortiz MG, Castro EB, Visintin A, Becker D, Garaventa G. Dynamic monitoring of structural changes in nickel hydroxide electrodes during discharge in batteries. *Electrochim Acta* 2011;56(23):7946–54.
- [21] Zhang Chaojiong, Park Su-Moon. The anodic oxidation of nickel in alkaline media studied by spectroelectrochemical techniques. *J Electrochem Soc* 1987;134(12):2966–70.
- [22] Mao Z, De Vidts P, White RE, Newman J. Theoretical analysis of the discharge performance of a NiOOH/H₂ cell. *J Electrochem Soc* 1994;141:54–64.
- [23] Barnard R, Randell CF, Tye FL. Studies concerning charged nickel hydroxide electrodes I. Measurement of reversible potentials. *J Appl Electrochem* 1980;10:109–25.