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Effect of cobalt electroless deposition on nickel hydroxide electrodes

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ABSTRACT

The effects of cobalt additive on the positive electrode surface of nickel alkaline batteries are investigated. Electrode surface modifications by electroless cobalt deposits were made at different immersion times. The performance of nickel hydroxide electrodes was studied by optical techniques, such as scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX) and electrochemical methods as cyclic voltammetry, charge–discharge curves and electrochemical impedance spectroscopy (EIS). According to these results, electroless cobalt deposits obtained with 5 min of immersion time in the electroless-bath exhibit a better electrode performance.

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Introduction

In batteries development, the current technology requires systems with higher specific energies [1–3], in which battery chemistry plays a crucial role, due to the increasing demand of portable electronic devices and electric vehicle applications. Particularly, the development and commercialization of nickel/metal hydride (Ni–MH) technology provide the possibility of producing batteries with high specific energy. The positive nickel electrode strongly influences the operation of this and others alkaline batteries. The electrochemical energy storage in the nickel hydroxide electrodes is related to the reversible insertion of H⁺ into the

nickel hydroxide/oxyhydroxide. Besides, reversibility of this process is an important requirement for batteries electrode materials.

It is known that low-cost pasted nickel electrode can be built on nickel foam. Nevertheless, nickel hydroxide is a p-type semiconductor and has a low conductivity; consequently an additional resistance is generated among the active material particles, the nickel substrate and the electrolyte that yields to a relatively low utilization of the active material [4,5]. To overcome this problem, battery manufacturers typically add a few percent of cobalt powder as a conductor in the lattice of nickel hydroxide. After initial oxidation, cobalt is oxidized into a highly conductive β-CoOOH [6] that ensures an efficient conductive network and leads to a higher utilization

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of the nickel hydroxide. In addition, due to the irreversibility of the couple Co(III)/Co(II), β -CoOOH remains in the active material and improves their utilization and electron conductivity [7,8]. Furthermore, the incorporation of cobalt as additive in relatively large amount could result in a substantial decrease in discharge potential plateau and increase in cost [9,10]. In addition, distribution of cobalt powder on the nickel hydroxide surface can be non-uniform; hence the additive cannot effectively increase the utilization of the active material.

The electroless cobalt coating method has been previously employed as a technique for improving nickel hydroxide electrode performance [11,12]. Nevertheless, discussions about the way that electroless cobalt film affects structural and kinetic parameters are still lacking. Accordingly, in this paper we discuss the electrochemical performance of pasted nickel hydroxide electrodes after surface modifications by electroless cobalt deposits.

Experimental

Preparation of nickel hydroxide electrodes

The nickel hydroxide electrodes were prepared by mixing active material ($\text{Ni}(\text{OH})_2$ Aldrich) and 23 wt.% PTFE, as binder material. The mixture was pasted on the nickel form substrate. The electroless surface deposition of cobalt on pasted nickel hydroxide electrodes was carried out according to experimental routines, previously described in the literature [13]: palladium (sensitization–activation process) and cobalt plating solutions. Cobalt sulfate (99.0% Mallinckrodt; 25 g l^{-1}) was used as the source of cobalt and sodium hypophosphite (99.0% Biopack; 25 g l^{-1}) as the reducing agent. The bath was stirred vigorously at 55°C .

Three working electrodes were prepared by immersing the pasted nickel hydroxide material into the electroless cobalt plating bath at different times: 5, 15 and 30 min. They are referred in the text as electrodes:

- NiCoEL5: 5 min,
- NiCoEL15: 15 min,
- NiCoEL30: 30 min.

The corresponding geometric area and thickness are exhibited in Table 1.

Measurement procedures

The electron microscopic studies were carried out by 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.

Electrochemical experiments were performed in a conventional three compartment glass cell. with 7 M KOH as electrolyte at 30°C . A large specific area nickel mesh was employed as counter-electrode and $\text{Hg}/\text{HgO}_{\text{ss}}$ was used as reference electrode.

The Arbin BT2000 model potentiostat was employed to perform the charge–discharge curves at different current densities and the cyclic voltammetric experiments. Full charges of the studied electrodes were obtained at $I = 0.001 \text{ A}$ and discharge curves, at different currents ($0.00015 \text{ A}–0.001 \text{ A}$), were registered for a cut off voltage of 0.2 V. Voltammograms were carried out at 0.005 V s^{-1} scan rate between cathodic 0.05 V and anodic 0.55 V limits respectively.

Prior to cyclic voltammetric and EIS experiments, the electrodes were activated by charge–discharge cycling until the capacity was stabilized.

EIS measurements were performed using a PAR potentiostat and a Schlumberger 1250 frequency response analyzer ($19.9 \text{ mHz} \leq f \leq 65 \text{ kHz}$) and a small amplitude (0.005 V) signal perturbation to assure a constant state of discharge (SOD). EIS experiments were carried out potentiostatically at a constant SOD.

Results and discussion

Electrode surface characterization

SEM

Fig. 1(a)–(c) exhibit the SEM micrographs, at a magnification of 8000X, of NiCoEL5, NiCoEL15, NiCoEL30 respectively. The pictures show that the surface morphologies for the NiCoEL5 and NiCoEL15 electrodes are very similar with defined holes or pores in the porous structure. However, it can be distinguished, that NiCoEL30 samples exhibit more compact morphology and closed porous structure when compared with electrodes NiCoEL5 and NiCoEL15.

EDAX

The compositional EDAX studies of the electrodes revealed the presence of Pd from the electroless solutions. This element content shows no changes, as expected, for the three studied samples since immersion time was the same (15 min) in the palladium solution. The semi quantitative EDAX elements analysis for Co, Ni and O (weight–weight percentage, wt.%) are indicated in Table 2.

These results show that Co content (wt.%) increases with immersion time in the electroless cobalt plating bath.

The cobalt distribution in the studied electrodes was analyzed by EDAX cobalt signal mapping (Figs. 2–4(b)) for the SEM areas shown in Figs. 2–4(a). These pictures indicate that cobalt signal appears to be homogenous in all the cases but its intensity increases with immersion time in the cobalt plating bath, in good agreement with Table 2 results.

Table 1 – Geometric characteristics of working electrodes.

Electrode	Area [cm^2]	Thickness [cm]
NiCoEL5	0.38	0.12
NiCoEL15	0.40	0.11
NiCoEL30	0.40	0.11

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