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

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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.

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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 $\text{Ni}(\text{OH})_2/\text{NiOOH}$ and the overpotential of oxygen evolution, decrease the growth of $\gamma\text{-NiOOH}$ species during charging and improve the conductivity [7–9]. During the first loading of the active material, a highly conductive phase ($\beta\text{-COOOH}$) is generated by the oxidation of the cobalt-based precursor. This material is stable, due to the irreversibility of $\text{Co}(\text{III})/\text{Co}(\text{II})$ pair [7,8], and is responsible of improving the conductivity of the whole system [9–11].

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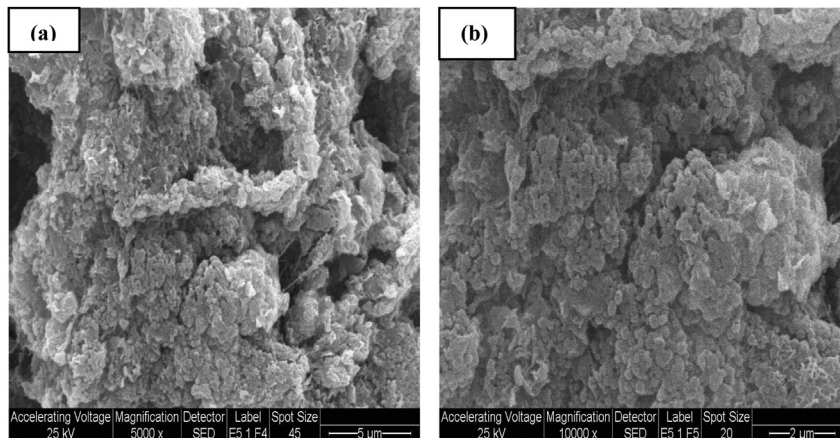


Fig. 1 – SEM micrographs NiCoD: (a) 5000×; (b) 10000×.

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/cm^2 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.

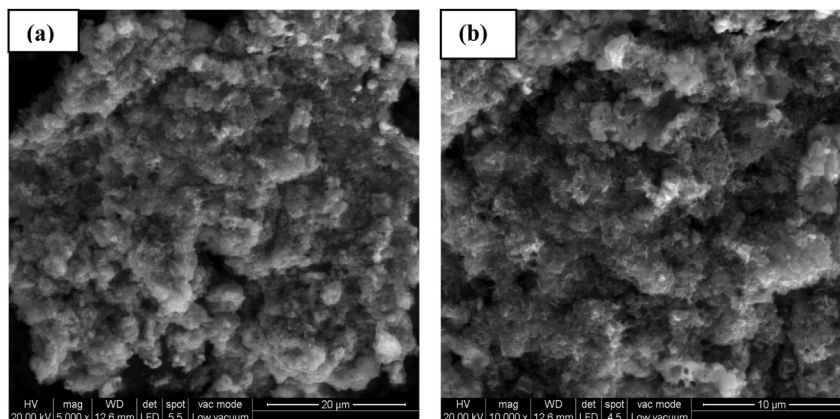


Fig. 2 – SEM micrographs NiCoE: (a) 5000×; (b) 10000×.

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