Synthesis and characterization of Zn/Ni-Co bilayer coatings using the metals recovered from spent household batteries as raw materials

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Abstract.
Spent household batteries are a secondary resource that can provide different metals for several industrial processes. This work aims the valorization of these metals using a combination of hydrometallurgical and electrochemical techniques, in order to obtain a bilayer coating of Zn/Ni-Co over low-carbon steel. The procedure starts with the collection and disassembling of the spent alkaline batteries (65.48 wt % of Zn) and discarded Ni-MH rechargeable batteries (72.49 wt % of Ni and 7.42 wt % of Co) prior to obtaining their electrode materials. These materials were leached in two separated alkaline solutions of NaOH and ammonia (NH₄OH) with complexing agents added. Later on, both solutions were used as deposition baths. Once the reduction potential of the metal ions was determined, the coatings were obtained by potentiostatic electrodeposition. The morphology and composition of the coating was studied by scanning electron microscopy (SEM-EDS). Finally, the corrosion resistance of the coating in 3.5 wt % of NaCl solution was evaluated by the following techniques: open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV). The results show that the second Ni-Co layer displaces the corrosion potential to more electropositive values and reduces the exchange current density forty times as compared to the Zn layer.

1. Introduction
According to the environment ministry bureau, in Colombia between 2002 and 2008, more than 14,000 tons of zinc and 100 tons of nickel were released into the environment from the inadequate disposal of spent alkaline and Ni-MH rechargeable batteries [1]. Such a problem is a consequence of the fact that the country does not have appropriate environmental technologies to process electronic waste materials (e-waste). Since these heavy metals represent a great risk to human health and the environment, several studies aiming to provide local solutions on a small scale have been done [2]. The recycling of these materials is part of the so-called urban mining process, in which the metals extracted from the batteries are considered as a secondary mineral resource. This process brings ecological benefits, preventing the influx of heavy metals into the environment and promoting, in the same time, economic benefits, since the recovered metals can be used as raw material for other industrial processes. In this sense, the present investigation proposes the recovery and valorization of the metals contained in the batteries to use them for the synthesis of an anticorrosive bilayer coating Zn / Ni-Co over low carbon steel. The first layer consists of an electrochemical galvanization, a technique widely used to coat the steel with zinc, which forms a stable oxide layer and protects the steel from corrosion. It is worth noting that the synthesis of this coating is carried out in acidic baths with and without cyanide, as well as in basic baths without cyanide[3]. The latter stand out for being less polluting and with the addition of a complexing agent, the
hydrogen reduction potential can be shifted to more electronegative values, reducing its incorporation in the coating [3]. Although zinc as a sacrificial coating provides an acceptable degree of protection against corrosion, in recent years several attempts have been done to improve its properties [4]. The use of a second layer of nickel-cobalt alloy provides a barrier effect and isolates the galvanized steel from the medium avoiding premature mechanical damages since these coatings exhibit excellent properties such as hardness and wear resistance [5].

2. Experimental procedure

2.1. Extraction of electrode materials from the spent batteries
The spent batteries (alkaline and Ni-MH) were obtained from the e-waste collection stations of the Industrial University of Santander, Colombia. The plastic cover (labels) of the batteries were removed and their metal cases opened with manual tools, in order to liberate the active electrode materials [6]. In the case of alkaline batteries, the anodic material, which contains 65.48 wt % of Zn, was removed and separated from the cathodic powder (rich in manganese compounds). For the Ni-MH rechargeable batteries, both anodic and cathodic powders were extracted together, as a mixture[7]. Such a mixed powder contained (wt %): 72.49 % Ni, 7.42 % Co and 4.84 % La. Finally, these electrode powders were dried at 100 °C for 24 hours and grinded in a mortar.

2.2. Hydrometallurgical treatment
Leaching process of zinc from alkaline batteries was carried out in an alkaline bath with 43.48 g/L of Zn-rich anodic powder, 240 g/L of NaOH and 11.3 g/L of EDTA at a temperature of 80 °C, under stirring at 700 rpm for two hours [3]. The obtained solution was filtered to separate insoluble matter. The electrode mixed powder from Ni-MH spent batteries was leached in HCl 4 M at room temperature and a solids concentration of 50 g/L, under stirring at 270 rpm for 2 hours [8]. The obtained solution was then filtered and conditioned, by incrementing its pH up to a value of 8, using ammonia and citric acid [9]. During conditioning, all sediments formed were filtered out.

2.3. Synthesis and evaluation of the coatings
Depositions of the coatings were made in a three-electrode cell, using a graphite rod as a counter electrode, Ag/AgCl as reference electrode and AISI SAE 1020 steel as working electrode. The reduction of the species was studied by cyclic voltammetry. For the Zn galvanized coating on low carbon steel it was established a reduction potential of -1.58 V vs Ag/AgCl for 1800 seconds and for the nickel-cobalt alloy deposition over the previously galvanized steel a potential of -1.45 V vs Ag/AgCl for 5000 seconds was employed. The depositions were all made at room temperature. The coatings were evaluated by the measurement of open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV), in 3.5 wt % of NaCl solution. All electrochemical tests were made using a GAMRY 750 potentiostat/galvanostat. The morphology and composition evaluation of the coatings were determined using a Scanning Electron Microscopy (SEM) Quanta 650 FEG (Field Emission Gun), coupled with semiquantitative microchemical analysis (EDS).

3. Results

3.1. Synthesis of the coatings
The chronoamperometric response of the reduction of the ions under potentiostatic control for each bath is shown in figure 1. In both cases, the reduction current tends to increase over time, since the continued stirring assures that the electrode surface always has available metal ions. The difference between both current responses are related to the surface process and the available area. Therefore, the surface area for the nickel-cobalt synthesis is greater than the geometrical area of the electrode, due to the morphology of the previous zinc coating. Hence, the nickel reduction current is higher than the zinc reduction current and it requires more time to obtain a full coverage of the electrode (figure 1(b)).
Figure 1. Chronoamperometry of: (a) Deposition of Zinc at -1.58 V vs Ag/AgCl on low carbon steel and (b) deposition of Nickel-Cobalt at -1.45 V vs Ag/AgCl on galvanized steel (25°C).

3.2. Electrochemical evaluation

The open circuit potential value for each system can be seen in the table 1. Its values represent the equilibrium potential of the main elements for every layer of the system (iron of the base steel, zinc and nickel-cobalt from the successive coatings). The Nyquist plot in figure 2(a) shows the response of the bare and coated steel in the electrochemical impedance spectroscopy evaluation. The response of bare steel (red dots) shows its typical behavior with one semicircle and a projected charge transfer resistance of \(780 \Omega \cdot \text{cm}^{-2}\), related to the iron oxidation. Galvanized steel suffered a drastic reduction of the total resistance (green dots) where the projected total resistance is close to \(22 \Omega \cdot \text{cm}^{-2}\). This change can be appreciated in the insert of the figure 2(a). The reduction in the resistance means that the charge transference on the surface of the electrodeposited zinc is faster than the charges transference of the bare steel, which indicates that, as expected, Zn is acting as a sacrificial material. The impedance spectra of the galvanized steel are characterized by two depressed capacitive semicircles expanding towards lower frequencies that is a common behavior for sacrificial materials coatings [10]. The response of the bilayer coated sample (blue dots) showed two overlapped semicircles with a total resistance larger than the bare and galvanized steel (990 \(\Omega \cdot \text{cm}^{-2}\) approximately). Such a response confirms the full coverage of the galvanized steel surface with the nickel-cobalt layer and supports the idea that it increases the resistance of the zinc layer, by acting as a protective barrier. In the figure 2(b), it can be seen the polarization curves of the two evaluated coatings and of the bare steel. The cathodic branch of the bare steel (red line) has the typical response of the oxygen reduction under mixed control, where its Tafel slope cannot be related to the transferred electrons under kinetic control. The anodic branch describes the oxidation of the metallic iron to produce \(\text{Fe}^{2+}\) ions, with an anodic Tafel slope of 76 mV.dec\(^{-1}\), confirming the transference of two electrons according to the Butler-Volmer equation [11]. Green line represents the response of the galvanized steel. The more significant change in this curve is the variation of the corrosion potential from -0.58 V to -1.1 V vs Ag/AgCl approximately, this change confirms the full coverage of the steel with the zinc coating. The anodic branch corresponds to the oxidation of zinc. In this case, the experimental value of the Tafel slope is larger than the expected theoretically using the Butler-Volmer equation (59 mV.dec\(^{-1}\)). This difference means that the charge transfer resistance in the surface is increasing, which is consistent with the formation of stable corrosion products on the surface of the electrode. Then, the evaluation of the bilayer coating is represented by the blue line. Its behavior is similar to the bare steel but, in this case, the oxidation is related to the anodic reaction of nickel. This similarity comes from the fact that both anodic reactions involve 2 electrons and the increment in the Tafel slope is related to the passivation of the nickel layer. The characteristic values for all these processes are summarized in table 1.
Figure 2. (a) Nyquist and (b) potentiodynamic polarization plots for the bare steel, the galvanized steel and the bilayer coating (Zn/Ni-Co) on galvanized steel.

Table 1. Electrochemical parameters and corrosion resistance of the bare steel, galvanized steel and Zn/Ni coating.

| Sample           | OCP (V) | $i_{\text{corr}}$ ($\mu$A cm$^{-2}$) | $E_{\text{corr}}$ (V) | $\beta a$ (mV dec$^{-1}$) | $R_{\text{tot}}$ (Ω cm$^2$) |
|------------------|---------|----------------------------------|----------------------|--------------------------|----------------------------|
| Bare steel       | -0.55   | 26.11                            | -0.58                | 76                       | 780                        |
| Galvanized       | -1.00   | 889                              | -1.11                | 193                      | 22                         |
| Bilayer coating  | -0.53   | 21.36                            | -0.52                | 112                      | 990                        |

3.3. Morphology and composition evaluation
Figure 3(a) and (b) shows a homogeneous and compact coverage of the steel with zinc, that also can be confirmed by the EDS spectra result (99.23 wt % of Zn) shown in the figure 3(c). The microstructure of the zinc coating is characterized by an array of euhedral zinc crystals that cover evenly the steel surface. The change on morphology observed on figure 3.c and d, when compared to the galvanized steel alone, evidences the deposition of the nickel-cobalt alloy over the Zn crystals. The EDS results showed that the layer had 81.4 wt % of Ni and 6.5 wt % of Co. Furthermore, it can be observed a full coverage of the galvanized with the nickel-cobalt alloy, since the euhedral structure of the preceding Zn coating cannot be recognizable anymore.

4. Discussion
The figure 4 summarizes the proposed protection mechanism for the steel surface by the bilayer coating obtained in this work. Nickel-cobalt layer acts as a first protection layer that prevent the zinc coating from premature damages, and if such a layer breaks down or peels off, the zinc layer starts to oxidize and to form stable oxides, acting as a sacrificial material to protect the steel surface. The applied electrodeposition processes developed compact and homogenous coatings with the expected composition. As seen in table 1, the electrochemical evaluation showed that the second nickel-cobalt layer displaces the corrosion potential to a more electropositive value, reduces the exchange current density forty times and increases the charge transfer resistance when compared to the galvanized steel alone. This confirms the barrier effect of nickel-cobalt, which isolates galvanizing from the medium and protects it from premature mechanical and chemical damages [5].
5. Concluding remarks
This work shows that spent alkaline and Ni-MH batteries can be used as precursor materials in complex electroplating processes. This could be a promising way to grant the valorization of this type of wastes. By recovering the metals contained in these batteries, we were able to produce an anticorrosive Zn/Ni-Co bilayer coating, which provided effective barrier and sacrificial protection to steel surfaces under harsh environments. The bilayer coating developed was compact and homogenous and its electrochemical evaluation showed that it provided forty times more corrosion protection than galvanized steel alone.

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![Figure 4. Bilayer coating protection mechanism.](image)

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