Characterization of a zinc-nickel alloy coating obtained from an electrolytic bath produced with spent batteries as raw materials

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Abstract.
Alkaline and Ni-MH spent batteries contain heavy metals such as zinc and nickel that may affect the environment. Such materials can be used for the manufacturing of Zn-Ni anticorrosive coatings, which have better behavior against corrosion than the traditional galvanized steel. In this work, spent alkaline and Ni-MH batteries were disassembled, to extract the metals of interest. The electrode powders extracted from these batteries were leached, by separate, in ammonia plus citric acid solutions. Once the pregnant solutions were chemically analyzed to determine the concentration of zinc and nickel, an alkaline electrolytic bath was prepared with a mass proportion of 2:1 Zn-Ni. A potentiostatic deposition over low carbon steel was made using this bath. Then, the morphology and composition of the obtained coating was analyzed by scanning electron microscopy (SEM-EDS) and finally the electrochemical stability 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). SEM results show a homogeneous, compact and adherent coating on steel and the electrochemical tests indicated that the properties of the galvanized coating were improved by the addition of 8.92 wt % of nickel.

1. Introduction
The current consumption of electronic devices represents a large concern around the world since the untreated derived electronic wastes (e-waste) entail environmental problems [1]. Furthermore, e-wastes are composed of toxic heavy metals that are contributing to the pollution in the world, impacting the water reserves and soils. Hence, a myriad of studies has been done in recent years to recover those metals contained in e-waste, some of them employing pyrometallurgy and others a combination of hydro and electrometallurgy. According to some authors [2], pyrometallurgy is not the best choice, because a great number of metal fumes that may affect the human health are emitted. On the other hand, implementing hydrometallurgical and electrometallurgical techniques can be considered less harmful [3] and prone to generate more value-added specialty materials. Alkaline batteries contain Zn and Ni-MH batteries contain Ni in their formulation. By combining Zn and Ni in a solution obtained from the hydrometallurgical recycling of alkaline and Ni-MH batteries, Zn-Ni alloy coatings could be obtained. Zinc-nickel coatings are known for providing a good surface
finishing and better mechanical properties and corrosion resistance than traditional galvanized steel [4]. It is worth noting that the electrochemical synthesis of zinc-nickel coatings is an anomalous deposition, in which the reduction potential of the zinc is shifted to more positive values, promoting in such a way the alloy synthesis [5]. Whence usually alkaline baths with ammonium are employed to obtain that alloy since in high pH media, hydrogen evolution takes places at more electronegative values according to the equilibrium equation of water decomposition represent in the Pourbaix diagram [6]. Ammonium acts as a complexing agent, keeping metals ions in solution in the form of \((\text{Zn(NH}_3)_4^{2+}\) and \((\text{Ni(NH}_3)_6^{2+}\)) [6] and with the addition of another complexing agent, such as citric acid, the reduction potential of zinc and nickel can be shifted to more electropositive values [6]. The latter means that implementing an alkaline bath with high pH adding ammonium and citrate, zinc-nickel alloy electrodeposition process could take place at more electropositive potentials avoiding, in such a way, the evolution of hydrogen gas and its incorporation into the coating. With all these ideas in context, the aim of the present work is to innovate in the recycling of spent batteries (alkaline and Ni-MH) by taking advantage of their chemical composition. By using leaching procedures, an electrolytic bath containing Zn and Ni can be formulated, using complexing agents such as ammonia and citric acid, in order to be used for the synthesis of a Zn-Ni alloy coating on a carbon steel surface.

2. Experimental procedure

2.1. Extraction of the electrode materials from the spent batteries and metals leaching procedure
The spent batteries (alkaline and Ni-MH) were obtained from the e-waste collection stations of the Industrial University of Santander, Colombia. In order to obtain the active electrode materials rich in zinc and nickel from the batteries, their plastic cover (labels) and metal cases were removed with manual tools [7]. The anodic material extracted from alkaline batteries (65.48 wt % Zn), was removed and separated from the cathodic powder (rich in manganese compounds). In the case of Ni-MH rechargeable batteries, anodic and cathodic powders were extracted together, as a mixture [8]. 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 ground using a mortar. The leaching process of zinc from alkaline batteries was carried out in an alkaline bath with 43.48 g/L of Zn-rich anodic powder, 1.8 g/L of citric acid and adding ammonia as needed, until reaching pH 10, at a temperature of 70 °C, under stirring at 700 rpm for five hours [6]. 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 [3]. The obtained solution was then filtered and conditioned, by incrementing its pH in a two steps process using ammonia. In the first step, until pH 4, the solution was heated at 70 °C to precipitate rare earth elements (Nd, La, Pr, Ce) and, finally, in the second step the pH was shifted to a value of 10 adding citric acid (1.8 g/L) and ammonia. During conditioning, all sediments formed were filtered out. By using atomic absorption spectroscopy (AAS), it was determined that the Zn-rich solution contained 3.3 g/L of Zn and the Ni-rich solution contained 8.8 g/L of Ni. Finally, the electrolytic bath for the obtention of the Zn-Ni alloy was made by mixing both solutions, to obtain a Zn:Ni mass proportion of 2:1.

2.2. Synthesis and evaluation of the coatings
The electrochemical behavior of the species in three solutions (Zn-rich, Ni-rich, and Zn-Ni alloy) was studied by cyclic voltammetry. The deposition of Zn and Zn-Ni alloy over plain carbon steel was made at -1.35 and -1.32 V vs Ag/AgCl, respectively, for 3600 s in continuous stirring (700 rpm). In both cases, a three-electrode cell was used with a graphite rod as a counter electrode, an Ag/AgCl electrode as a reference and AISI SAE1020 steel as the working electrode. The morphology and chemical composition of the coatings were studied by scanning electron microscopy (SEM-EDS). The anticorrosive properties of the coatings were evaluated by the measurement of open circuit
potential (OCP), electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV), in a 3.5 wt% of NaCl solution using a potentiostat/galvanostat Gamry 750.

3. Results

3.1. Synthesis of the coatings and their morphological characterization

Figure 1 a. show the cyclic voltammetry for the electrochemical behavior of Zn-rich, Ni-rich, and Zn-Ni alloy solutions, on the working electrode surface (steel), in which the evaluated range for potential in each system was limited by the stability of the substrate.

![Figure 1](image_url)

**Figure 1.** (a) Cyclic voltammetry of Zn-rich, Ni-rich, and Zn-Ni alloy solutions and (b) deposition of zinc coating at -1.35 V vs Ag/AgCl and Zinc-Nickel alloy coating at -1.32 V vs Ag/AgCl on a steel surface.

The blue line represents the Zn-rich solution response with the variation of the potential. It can be detected a drastic increase (absolute values) of the reduction current at potentials lower than -1.1 V, which is related to the reduction and deposition of zinc-bearing ionic species, reaching a maximum at -1.25 V vs Ag/AgCl and, subsequently, there is a decrease in the current due to the transport of the zinc ions from the solution to the electrode surface. The following increases of the current values for potentials lower than -1.4 V vs Ag/AgCl correspond to the hydrogen evolution that comprises the creation of the bubbles in the substrate surface. The reduction reaction of zinc was found to be reversible, it means that the electrodeposited zinc showed a total dissolution at the anodic currents. Nickel reduction (red line), started at -0.7 V vs Ag/AgCl. Subsequently, a notable increase of the current at -0.95 V vs Ag/AgCl can be observed, showing a maximum at -1.14 V vs Ag/AgCl, followed by the hydrogen evolution reaction. In this case, there is not a complete reversibility of the reduction reaction of the ions in the solution, since the oxidation reaction was displaced towards more electropositive potential values, starting at -0.5 V vs Ag/AgCl. Such a behavior could be related to the stability of the deposited material over the electrode surface. Finally, the voltammetry for the solution rich on zinc and nickel ions, represented by the green line, reduction process starts approximately at -0.6 V vs Ag/AgCl where the main maximum of current is appreciated, between the zinc and nickel maximum reduction current. At the anodic zone from the curve, the total oxidation is lower than the reduction, which means that the zinc-nickel coating is more stable than zinc deposit. The addition of nickel to the solution displaced the reduction potential of zinc towards more electropositive values, which is referred to as anomalous deposition, i.e. there was an underpotential deposition below the thermodynamic reported potential, such a variation promotes the alloy formation [5]. The displacing of the potential and the stability of the deposited material promotes the electrodeposition of an alloy. That is the reason why voltammetry curve (figure 1(a)) does not show different maximum peaks at the anodic zone, instead, it shows a non-sharp maximum. For the zinc-
nickel alloy, the hydrogen reaction starts at more electropositive values of potential than zinc, because nickel is catalytic for H$_2$ evolution. Furthermore, there are no adherent products on the electrode surface at potential values higher than -1.2 V vs Ag/AgCl. Figure 1(b) shows the chronoamperometry response of the potentiostatic deposition using zinc and zinc-nickel solutions, in both processes the obtained current is stable through the studied time, with a mild increase of 1 mA approximately. Such an increase could be related to the tridimensional growth of the coating that entails the augmentation of the available area for the electrodeposition over time. The similarity of both curves is due that the deposition is controlled by transport phenomena since the systems have the same stirring and ions concentration as well. As a result, the control is convective i.e. all reactions depend on the stirring speed.

The SEM images (backscattered electron) of the coatings showed in figure 2(a) and figure 2(b) show a total, homogeneous and compact coverage of the zinc coating over steel, with a composition of 96.60 wt % of Zn as indicated by the EDS results (figure 2(c)) of the entire area figure 2(a).

![Zn coating over steel](image1.png)
![Zn-Ni alloy coating over steel](image2.png)

**Figure 2.** Zn coating over steel originally at (a) 500x, (b) 5000x, and (c) EDS spectrum of (a) area. Zn-Ni alloy coating over steel originally at (d) 500x, (e) 5000x, and (f) EDS spectrum of (d) area.
The morphology of the zinc coating exhibited feathery-dendritic crystals of HCP zinc \( \eta \) phase (HCP) [9]. Figure 2(d) shows that zinc-nickel alloy also presents a regular grain size and full surface coverage. The addition of nickel produces a variation on the morphology of the deposit, changing plates structure to a structure of granular agglomerates (figure 2(e)). Zn-Ni alloy contains 8.92 wt % of Ni and is considered out of equilibrium since its structure is formed by distorted \( \eta_d \) and \( \gamma_d \) phases, and not by \( \delta \) phase alone, as indicated by the thermodynamic equilibrium diagram [9]. The substitution of zinc atoms in HCP structure by nickel atoms, promote the formation of distortionate \( \eta_d \) phase up to 7.4 wt % of Ni, that is considered the critical percent of nickel that can replace zinc atoms on that phase [9]. Once this percent is reached, the formation of unsaturated Zn-Ni cubic phase (BCC) would start.

3.2. Electrochemical evaluation

The open circuit potential value for each system can be seen in table 1. These values represent the equilibrium potential of the main elements in the coatings. Figure 3(a) shows a Nyquist plot of the electrochemical impedance spectroscopy evaluation of bare steel, Zn coating (galvanized) on steel and Zn-Ni coating on steel. The red dots describe bare steel behavior, characteristic by one semicircle and a total charge transfer resistance of 780 \( \Omega \cdot \text{cm}^{-2} \).

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

| Sample            | OCP (V) | \( i_{\text{corr}} \) (\( \mu \text{A cm}^{-2} \)) | \( E_{\text{corr}} \) (V) | \( \beta a \) (mV dec\(^{-1} \)) | \( R_{\text{tot}} \) (\( \Omega \cdot \text{cm}^{-2} \)) |
|-------------------|---------|-----------------------------------------------|---------------------------|-------------------------------|--------------------------|
| Bare steel        | -0.55   | 17.9                                         | -0.59                     | 76                            | 720                      |
| Zn coating        | -0.98   | 376                                          | -1.06                     | 108                           | 33                       |
| Zn-Ni coating     | -0.93   | 192                                          | -0.93                     | 87                            | 94                       |

Figure 3. (a) Nyquist and (b) potentiodynamic polarization plots for the bare steel, Zn coating and Zn-Ni coating on steel.

Because zinc acts as a sacrificial material, its total resistance (33 \( \Omega \cdot \text{cm}^{-2} \)) is lower than bare steel, as can be observed by the blue dots. It also means that the charge transfer on zinc coating is faster than the charge transfer on bare steel. Furthermore, the sacrificial behavior zinc coating behavior can be evidenced by two depressed capacitive semicircles, on the impedance spectra, expanding to lower frequencies. For the zinc-nickel coating (green dots), is quite to note that also exposes the typical behavior of sacrificial coatings and its total charge transfer resistance (94 \( \Omega \cdot \text{cm}^{-2} \)) is approximate 3 times better than zinc coating. That result confirms full coverage of the steel with the Zn-Ni alloy and such alloy coating has a better behavior against corrosion than the Zn deposit alone. Figure 3(b) shows the polarization curves of the two evaluated coatings and bare steel, in all cases, the cathodic Tafel slope exposes higher values than the estimated by the Butler-Volmer equation [10], which means that
the oxygen evolution is under mixed control. Comparing the Zn and Zn-Ni curves, it can be appreciated that Zn (blue line) shows a continuous dissolution up to -0.61 V vs Ag/AgCl, where there is a drop of the current due to the total dissolution of the coating and the subsequent oxygen evolution reaction over the surface of the bare steel. Then, at values higher than -0.45 V vs Ag/AgCl the shape of the curve corresponds to the iron dissolution, that was confirmed by visual inspection after the test finished. Conversely, the zinc-nickel coating (green line) presents an anodic dissolution followed by a stability zone between -0.53 to -0.19 V vs Ag/AgCl, where the current does not show a significant variation. Such a behavior is promoted by the nickel effect, which seems to be stabilizing the passive layer. Additionally, at higher potentials, a dissolution of the coating can be observed but unlike Zn coating alone, the Zn-Ni coating did not dissolve. The stability potential of the Zn-Ni coating is more electropositive than the Zn alone, i.e. the nickel is fulfilling the objective of making the coating less active. The characteristic values for all these processes are summarized in table 1.

4. Concluding remarks
A Zn-Ni alloy coating over steel was successfully synthesized implementing zinc and nickel pregnant solutions obtained from the hydrometallurgical treatment of spent alkaline and Ni-MH batteries. This process this kind of e-wastes, generating innovative alternatives to reduce world pollution produced by those toxic heavy metals. Furthermore, zinc-nickel alloy coating over steel obtained promoted effective sacrificial protection with a better resistance than traditional galvanized steel.

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References
[1] Widmer R, Oswald-Krapf H, Sinha-Khetriwal D, Schnellmann M and Böni H 2005 *Environ. Impact Assess. Rev.* **25** 436–458
[2] Soare V, Burada M, Dumitrescu D, Constantin I, Soare V, Popescu J and Carcea I 2016 *IOP Conf. Ser.: Mater. Sci. Eng.* **145** 022039-022048
[3] Delvasto P, Rodríguez R O and Blanco S 2016 *J. Phys. Conf. Ser.* **687**, 012107-012110.
[4] Baldwin K and Robinson M 1993 *Corros. Sci.* **35** 1267–1272
[5] Rodriguez I, Valentin G and Lapicque F 1999 *J. Appl. Electrochem.* **92** 1035–1044
[6] Barceló G, García J, Sarret M, Müller C and Pregonas J 1994 *J. Appl. Electrochem.* **24** 1249–1255
[7] Kuo Y M, Lin C, Wang J W, Huang K L, Tsai C H and Wang C T 2016 *Environ. Technol.* **37** 1490–1500
[8] Lin S, Huang K, Wang I, Chou I, Kuo Y, Hung C and Lin C, 2016 *J. Air Waste Manag. Assoc.* **66** 296–306
[9] Bonino J P and Rousset A 1999 *Structure*. **4** 881–886
[10] Bard A J and Faulkner L R 2001 *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, New York. 98-100