

Influence of Na^+ , K^+ , Mn^{2+} , Fe^{2+} and Zn^{2+} ions on the electrodeposition of Ni-Co alloys: Implications for the recycling of Ni-MH batteries

S Blanco¹, R Orta-Rodriguez² and P Delvasto¹

¹ Universidad Industrial de Santander, Bucaramanga, Colombia

² Universidad Simón Bolívar, Caracas, Venezuela

E-mail: delvasto@uis.edu.co

Abstract. A hydrometallurgical recycling procedure for the recovery of a mixed rare earths sulfate and an electrodeposited Ni-Co alloy has been described. The latter step was found to be complex, due to the presence of several ions in the battery electrode materials. Electrochemical evaluation of the influence of the ions on the Ni-Co alloy deposition was carried out by cyclic voltammetry test. It was found that ions such as K^+ , Fe^{2+} and Mn^{2+} improved the current efficiency for the Ni-Co deposition process on a copper surface. On the other hand, Na^+ and Zn^{2+} ions exhibited a deleterious behaviour, minimizing the values of the reduction current. The results were used to suggest the inclusion of additional steps in the process flow diagram of the recycling operation, in order to eliminate deleterious ions from the electroplating solution.

1. Introduction

Ni-MH batteries are mainly composed of nickel (in oxidized and metallic form), cobalt, alkaline electrolyte substances and rare earths metal alloys [1-5]. Although it is difficult to get exact numbers for the usage of Ni-MH batteries in Latin America, it has been reported that this kind of batteries account for 2.7% (by weight) of the total household spent batteries, as collected in communal recycling procedures in Venezuela [6]. This number can be regarded as representative, for most countries within the region. New legislation changes issued in the Latin American countries have encouraged the application of valorisation strategies, not only to prevent environmental damage, but also to recover metal values from this kind of electronic wastes. A feasible solution for this local problem could be the adoption of small-scale hydrometallurgical facilities, in order to process these wastes without the need of exporting them to other countries, most of which are usually located in Europe and East Asia [7]. Nickel, cobalt and rare earths are strategic materials, which are worth to be recovered from depleted Ni-MH batteries; nevertheless, the hydrometallurgical recycling of Ni-MH batteries is a challenging issue, due to its internal chemical complexity [1-8]. In a previous paper [7], a small-scale hydrometallurgical processing route was devised, comprising a chemical stage and an electrochemical stage. During the chemical stage, the active electrode materials of the Ni-MH batteries were leached using aqueous H_2SO_4 . The obtained pregnant solution was then submitted to pH adjustment in a settling reactor, in which the rare earths were recovered as an insoluble complex sulphate. The remnant solution, containing nickel, cobalt and some other ions is then electrolyzed, in order to recover a Ni-Co alloy [7]. This latter stage is not yet well understood, because of the interaction of the several ions present in the solution.

Based on the above described situation, the present paper deals with the application of electrochemical techniques to study the co-deposition of nickel and cobalt from solutions containing several ions, as those obtained after leaching the internal components of Ni-MH batteries with H₂SO₄. In particular, cyclic voltammetry was performed over Ni and Co sulphate synthetic solutions, so that the effect of ions such as Na¹⁺, K¹⁺, Mn²⁺, Fe²⁺ and Zn²⁺ was individually evaluated. The objective is to draw useful conclusions, which will be used for the design of small scale recycling procedures, intended for the local processing of spent Ni-MH batteries in the Latin American countries.

2. Experimental

The synthetic electrolytes were formulated in concordance with the composition of the solutions obtained by the processing of spent Ni-MH batteries [7]. In order to evaluate the influence of each ion independently, 6 solutions were prepared (Table 1). Nickel, cobalt, iron, manganese and zinc ions were obtained by the addition of the respective sulphate, (NiSO₄, CoSO₄, FeSO₄, MnSO₄, ZnSO₄). In order to reproduce the solution management conditions given during the recycling of Ni-MH spent batteries [7], the synthetic solutions studied in this work were acidified to pH 1 using H₂SO₄ before being adjusted to pH 4 with NaOH or KOH, as source of Na⁺ or K⁺, respectively. Electrochemical evaluation of the influence of the ions on the Ni-Co alloy deposition was carried out by cyclic voltammetry test. A three-electrode electrochemical cell was used, with a Pt wire as auxiliary electrode, a 1mm diameter copper disk as working electrode and an Ag/AgCl electrode as reference. All experiments were performed using a potentiostat AUTOLAB PGSTAT 302N.

Table 1. Chemical composition (mole/liter) of the evaluated Ni-Co solutions.

Code	Ni	Co	Na	K	Fe	Mn	Zn
Ni-Co	0.4	0.04					
Ni-Co+0.015M Na	0.4	0.04	0.015				
Ni-Co+0.02M K	0.4	0.04		0.02			
Ni-Co+0.001M Fe	0.4	0.04			0.001		
Ni-Co+0.012M Mn	0.4	0.04				0.012	
Ni-Co+0.005M Zn	0.4	0.04					0.005

3. Results and discussion

Figure 1(a) shows cyclic voltammograms of a 1mm radius polycrystalline copper disk electrode in 0.4M Ni²⁺-0.04M Co²⁺ solution. The observed behaviour is similar to results reported in the literature [9-13], showing the typical reduction and oxidation zones. The reduction zone starts at -0.45V vs Ag/AgCl with a maximum at -0.66V vs Ag/AgCl characteristic of the co-deposition of nickel and cobalt according to the following reactions:



The increment in the cathodic current at more negative potentials (-0.69V vs Ag/AgCl) correspond to the hydrogen evolution reaction,



These reactions is catalysed by the nickel compound, and represent the principal limitation for the electrodeposition process, the hydrogen evolution decreases the current efficiency and it is expected to affect negatively the mechanical properties of the obtained coating, due to hydrogen entrapment. The inclusion of potassium, iron and manganese ions in the solution clearly modified the electrodeposition

process and the hydrogen evolution reaction. With the addition of potassium, the reduction reaction starts at the same potential than that of the solution without extra ions, and the reduction maximum is maintained near -0.66V vs Ag/AgCl . The main variation is shown by the reduction current, which changed from $-8.9 \times 10^{-5}\text{A}$ in the Ni-Co solution to $-27.4 \times 10^{-5}\text{A}$ in the Ni-Co-K solution. It is well known that the reduction potential of potassium is more negative, so the potassium co-electrodeposition can be dismissed, then, the variation in the reduction current could be related to a change in the ions mobility in the solution, and its effect over the migration current. The inclusion of manganese in the solution produced a similar effect, in which the reduction potential was maintained and the reduction current changed to $-33.8 \times 10^{-6}\text{A}$. The influence of the iron ions in the solution is different, in this case the reduction current shows an increment but the curve does not show a well-defined reduction peak. The reduction potential of iron ions is in the evaluated range, and the co-deposition with nickel and cobalt is possible, a chemical analysis of the obtained deposit is needed to confirm this hypothesis and evaluate the formation of alloys or the segregation of the components in different areas of the electrode. The reduction of the hydrogen evolution current could be related to a change in the deposit composition. The catalytic effect of the nickel could be reduced by the co-deposition of iron or by an increment of the concentration of cobalt.

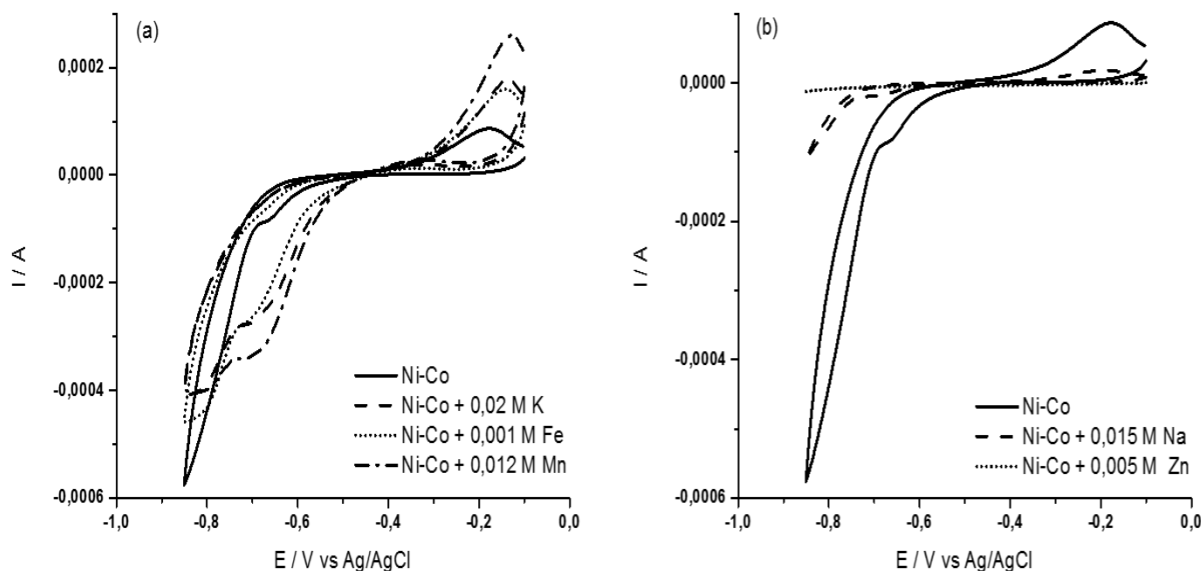


Figure 1. (a) Cyclic voltammetry of copper in 0.4M Ni^{2+} , 0.04M Co^{2+} solutions including the influence of the presence of K^+ , Fe^{2+} and Mn^{2+} ions, pH:4.0, $T:25^\circ\text{C}$, $v:50\text{mV.s}^{-1}$. (b) Cyclic voltammetry of copper in 0.4M Ni^{2+} , 0.04M Co^{2+} solutions including the influence of the presence of Na^+ and Zn^{2+} ions, pH:4.0, $T:25^\circ\text{C}$, $v:50\text{mV.s}^{-1}$.

Figure 1(b) shows the influence of the presence of sodium and zinc ions in the electrolyte on the electrochemical response. With the addition of these elements to the solution, the reduction and oxidation peaks show a significant decrease. In the case of the addition of zinc, the decrease in the current could be related to the precipitation of non-conductive zinc compounds on the electrode surface. The stability of the zinc ions could be affected by the presence of sulphate ions, promoting the formation of zinc sulphate complex on the electrode surface. These less conductive sulphates could act as a physical barrier [14]. In addition, despite the explanation for the deleterious effect of Na ions is not straightforward, it has been previously reported that Na ions decrease the current efficiency in the electrodeposition of Co powders [15] and this was attributed to a non-uniform layer of deposited metal on the surface of the electrode, that seems to facilitate hydrogen evolution. A similar phenomenon could be happening in the experiment showed in Figure 1(b).

4. Implications of these findings for the electrochemical recycling of spent Ni-MH batteries

The chemical complexity of the leachates obtained from the hydrometallurgical processing of spent Ni-MH implies important challenges that need to be addressed. Briefly, in our previous work, we suggested a route comprising: the leaching in sulfuric acid of the internal component of the batteries, a precipitation stage to generate an insoluble sulphate containing the rare earths and a final electroplating stage to recover Ni and Co in the form of an alloy coating or deposit. The results showed herein indicate that once the rare earths are segregated from leachate, further conditioning of the solution must be done, in order to get rid of deleterious ions present such as Na and Zn. Since most Na present may arise from the use of NaOH as precipitating agent, other Na-free bases should be explored if a technology based in this process is to be implemented. In addition, an intermediate process needs to be included, aiming to scavenge the Zn and to withdraw it from the solution, in order to prevent its build up on the surface of the deposition electrode and to improve the current efficiency in the recovery process of the Ni-Co alloy. A scheme of the process flow diagram for such operation sequence is shown in Figure 2.

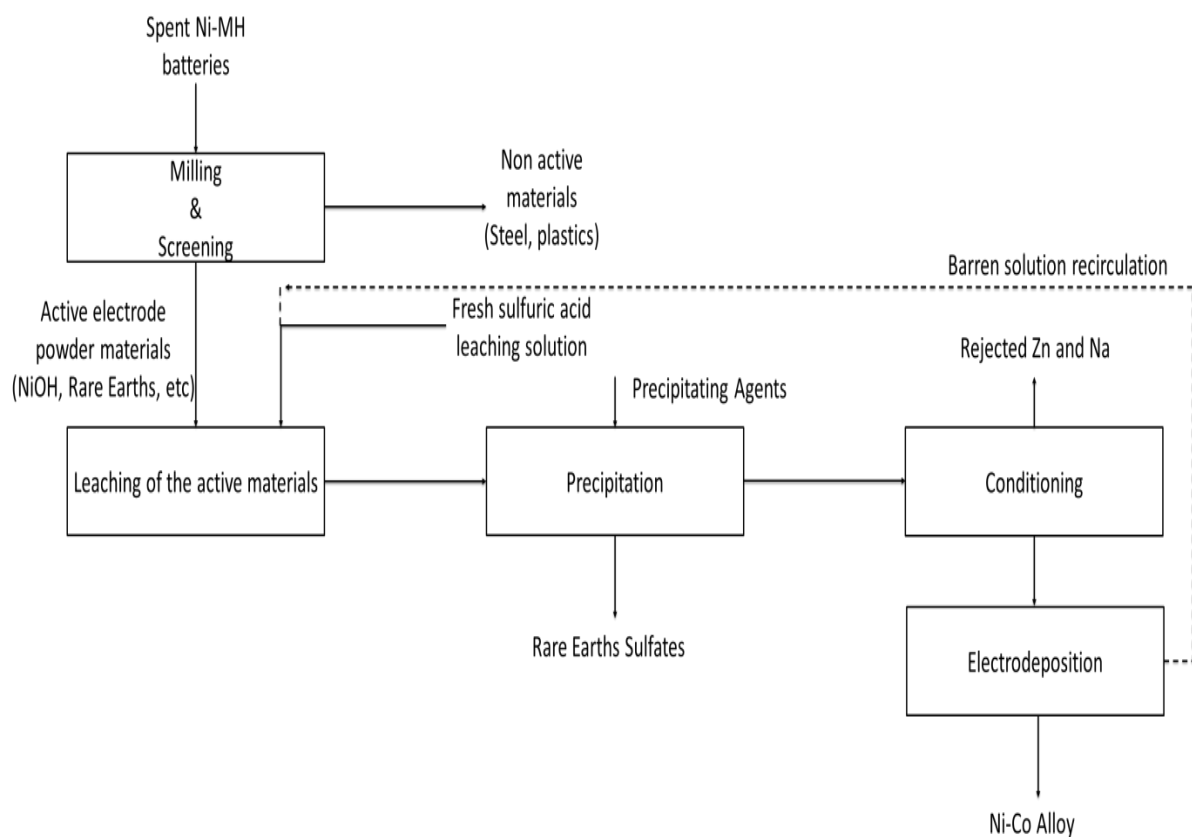


Figure 2. Process flow diagram of the proposed recycling operation for spent Ni-MH batteries.

5. Concluding remarks

The deposition of Ni-Co coatings from multi-metallic sulphate solution is a complex process. It was found that ions such as K^+ , Fe^{2+} and Mn^{2+} improve the current efficiency for the Ni-Co deposition process on a copper surface. On the other hand, Na^+ and Zn^{2+} ions exhibited a deleterious behaviour, minimizing the values of the reduction current. The latter implies that a hydrometallurgical recycling procedure to recover a Ni-Co alloy from spent Ni-MH batteries needs to include additional stages for the conditioning of the solution, in order to eliminate those deleterious ions, which are present in the electroplating solution.

References

- [1] Zambrano A, Romero C, Moccia A, Orta-Rodríguez R, López J and Delvasto P 2015 *Producción+Limpia* **10**(1) 51
- [2] Santos V E O, Celante V G, Lelis M F F and Freitas M B J G 2012 *J. Power Sources* **218** 435
- [3] Rozario A, Silva e Silva R K and Freitas M B J G 2006 *J. Power Sources* **158** 754
- [4] Ito M, Kashiwaya K, Sumiya N, Furuya H, Hiroyoshi N and Tsunekawa M 2010 *Int. J. Miner. Process.* **97** 92
- [5] Ni-MH Linyan Li L, Xu S, Ju Z and Wu F 2009 *Hydrometallurgy* **100** 41
- [6] Moccia A, Romero C, Orta-Rodríguez R and Delvasto P 2015 *Av. Quím.* **10** 11
- [7] Delvasto P, Orta-Rodríguez R and Blanco S 2016 *J. Phys.: Conf. Series* **687** 012107
- [8] Yang X, Zhang J and Fang X 2014 *J. Hazard. Mater.* **279** 384
- [9] Zamani M, Amadeh A and Lari Baghal S 2016 *Trans. Nonferrous Met. Soc. China* **26** 484
- [10] Rahman I Z, Khaddem-Mousavi M V, Gandhi A A, Lynch T F and Rahman M A 2007 *J. Phys.: Conf. Series* **61** 523
- [11] Vazquez-Arenas J, Altamirano-Garcia L, Treeratanaphitak T, Pritzker M, Luna-Sánchez R and Cabrera-Sierra R 2012 *Electrochim. Acta* **65** 234
- [12] Vazquez-Arenas J, Treeratanaphitak T and Pritzker M 2012 *Electrochim. Acta* **62** 63
- [13] Schweckandt D S and Aguirre M C 2015 *Procedia Mater. Sci.* **8** 91
- [14] Granados Neri M, Mendoza Huizar L and Rios-Reyes C 2011 *Quim. Nova* **34** 439
- [15] Zhelibo E and Andrushchenko V 1986 *Sov. Powder Metall+* **25** 531