

Electrodeposition of Zn-Mn alloys from recycling battery leach solutions in the presence of amines

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Abstract

The recovery of metal ions by electrodeposition from solutions resulting from the lixiviation of spent Zn-MnO₂ batteries was studied. It was attempted to optimise the electrodeposition process, the selectivity of ion-separation, the morphologic characteristics, and the anticorrosive and galvanic properties of metallic deposits. The simultaneous deposition of zinc and manganese on different ferrous substrates under various experimental conditions was tested. This allowed us to access the efficiency of the electrodeposition, the morphology and composition of the metallic deposits, as well as their performance as galvanic coating layers. The effect of amine additives, namely, of methylamine and ethylenediamine, on the properties of the coatings was also studied. It was shown that the amines with buffering or passivating effects improve the simultaneous deposition of Mn.

Keywords: Zn-Mn electrodeposition, Zn-MnO₂ battery recycling, electrolyte additives.

1 Introduction

The growing quantity of spent Zn-MnO₂ battery disposals is becoming a serious environmental problem. From an environmental point of view, recycling is the best choice to handle these residues. Recycling of metals present in the cells can be done either through hydrometallurgical or pyrometallurgical processes. The hydrometallurgical process involving electrochemical zinc and manganese



recovery by electrodeposition [1–4] is currently being studied in our laboratory [5].

Electrodeposition of zinc has been extensively used to produce protective anticorrosive coatings on iron and its alloys, reducing atmospheric corrosion on these metals. Protective effect is due to the formation of a passivation layer over the zinc surface and, on the other hand, to the galvanic sacrificial effect that zinc shows towards iron and its alloys [5]. Deposition of zinc alloys such as Zn-Ni, Zn-Co and Zn-Mn alloys have also found industrial applications for the improvement of anticorrosive properties of galvanic zinc layers on iron and its alloys [6–13]. Laboratory studies show that Zn-Mn alloys present better corrosion behaviour in saline environment than pure zinc layers [14, 15]. The increase in corrosion resistance was attributed to the formation of a passivating layer and of Mn_2O_3 , which avoids oxygen reduction at the metallic surface. The effectiveness of the anticorrosive behaviour increases with the Mn content of the Zn-Mn superficial alloys, although alloys with 10% Mn are already effective [15].

Various factors interact on the morphology of the produced deposits. Temperature, pH and composition of bath solution, deposition current, and nature of substrate, all have an effect on the deposition mechanism, which explains the formation of deposits with different morphologies, textures, and aesthetic and anti-corrosive properties. For instance, if the deposition is performed at high temperature and at high current density, there is a significant increase in the nucleation density and in the film growth kinetics.

Among the various factors that affect the mechanism of deposition and the morphology of deposited layers, the bath composition has a crucial influence, particularly the content in additives that limit unwanted secondary reactions caused by the presence of metallic cathodic contaminants [16–18]. A large set of additives has been studied to be used in different conditions and to achieve different goals. Surface active additives, such as polyacrylamines, thiourea, benzylideneacetone and coumarin [19–24] have been used to control the shape and size of deposited crystals to achieve smooth and shiny deposit layers. These additives act by adsorption on substrate surface, interfering with the charge transfer process and with the electrostatic interactions between charged species at the surface. This affects the growth process of metallic crystals through the reduction of nucleation rate and, consequently, the type and size of the formed crystalline structures.

Other types of additives have been used to produce pure zinc layers by electrodeposition from sulphuric aqueous solutions that avoid or minimise the effect of co-deposition of metallic contaminants that contribute to the reduction of quality of produced layers and process efficiency itself. These include chemical species that promote the complexation of metallic impurities, therefore increasing the overpotential for their deposition. Glue and Arabic gum [25] have been used in industrial electrodeposition; however other substances have been studied for the same purpose with satisfactory results. Nonylphenol oxyethylene, polyethylene glycol and derivatives, quaternary amines, and EDTA [26–33] may be referred to as examples.



This work presents a study on the effect of additives, namely, methylamine and ethylenediamine, on the simultaneous deposition of zinc and manganese alloy, using leaching solutions from the electrochemical recovery of zinc from spent Zn-MnO₂ batteries. It is intended to optimise the electrodeposition process, selectivity of ion-separation, morphologic characteristics, and anticorrosive and galvanic properties of metallic deposits.

2 Experimental

2.1 Electrodeposition tests

Laboratory electrodeposition tests were performed at constant current using three electrode cells, for 15, 30, 60, and 180 min. A Fluka current source of 100 mA and digital multimeters were used to control and monitor the electrodeposition process. 1 cm² discs made of mild steel normally used in construction reinforcement bars were used as substrate. These discs were mounted in an epoxy resin block to keep the surface area constant and to isolate the copper wire electrical connections. Initially, working electrodes were polished mechanically with P1000 grain size sandpaper and washed with distilled water. Subsequently the electrodes were put in a 40 g/L NaOH solution at 60°C during 2 min, then rinsed with distilled water, dried, and finally etched during 2 min in a 1:1 HCl solution. Prior to immersion in the electrolytic bath, electrodes were rinsed with distilled water and then dried. Following the electrodeposition process, the electrodes were washed with distilled water, dried, and weighted to determine the mass of deposited metal. A 316 L stainless steel mesh with an apparent surface area of 100 cm² was used as the auxiliary electrode. The working electrode potential was measured against a Ag/AgCl, 1M KCl, reference electrode and monitored throughout the electrodeposition process.

Various compositions of electrolytic baths were studied based on results of previous lixiviation tests. Results present in this work refer to tests performed with the plain lixiviation solution, composed of sulphuric acid with 9.3 g/L Zn²⁺, 9.7 g/L Mn²⁺, and 30 mg/L Fe³⁺, at pH = 2.15. Synthetic baths were prepared from pro-analysis sulphates of the respective metals. Tests were performed at 25°C without any agitation of bath solutions. Influence of various additives on electrodeposition process and properties of obtained deposits were studied. Studied additives include 40 ppm methylamine and 40 ppm ethylenediamine. Current densities of 10, 20, and 30 mA/cm² were tested.

Elemental analysis of deposited layers was performed through Energy Dispersive X-Ray Fluorescence Spectroscopy (EDXRF) with a QuanX TN Spectrace device equipped with a rhodium lamp. The aim of these tests was to reach the quantitative and semi-quantitative characterisation of the deposit layers composition and determine the approximate Mn/Zn mass ratio. The obtained quantity and uniformity of the deposits was evaluated visually and an Elcometer® 456 thickness gauge was used to measure the deposit film thickness. The calculated film thickness is an average of 4 different measurements in different regions of the deposit surface.



The process efficiency was determined using the following expression, based on electrode mass variation due to electrodeposition:

$$\eta = \frac{\Delta m_{\text{exp}}}{\Delta m_{\text{Faraday}}} \times 100 \quad (1)$$

where Δm_{exp} is the mass increase due to electrodeposition and $\Delta m_{\text{Faraday}}$ is the mass increase calculated on the basis of Faraday's law.

2.2 Electrochemical tests

Obtained deposits were subjected to anodic polarisation in 3% (w/w) NaCl solutions using a three electrodes cell arrangement. A AEW2 Sycopel Scientific Potentiostat/Galvanostat controlled by a PC was used for the polarisation curves. Potential was scanned from the open circuit potential (OCP) till +1 V vs. Ag/AgCl, with a potential scan rate of 5 mV/s.

Stability of obtained deposits was tested in long term immersion tests in 3% (w/w) NaCl solutions at 25°C. During the immersion period linear polarisation resistance was determined periodically using the same cell arrangement already described and the AEW2 Sycopel Workstation[®]. A polarisation range of ±10 mV and a potential scan rate of 1 mV/s were used.

3 Results and discussion

3.1 Electrodeposition process

Table 1 presents results obtained for the electrodeposition from the plain lixiviation solution (sulphuric acid solutions with 9.3 g/L Zn²⁺, 9.7 g/L Mn²⁺, and 30 mg/L Fe³⁺, at pH = 2.15 and T = 25°C) and the plain solutions with additions of methylamine (40 ppm) and ethylenediamine (40 ppm), at different current densities and deposition times. Figure 1 presents the variation of working electrode potential during electrodeposition testing, at a current density of 20 mA/cm², for the different lixiviation solutions.

Results show that process efficiency tends to decrease as the current density increases. This is due to the fact that for higher current densities there is a simultaneous hydrogen discharge, which could be confirmed visually during the experiments. The increase on hydrogen co-discharge at higher current densities causes an increase in the irregularities observed in the films formed at these current levels. In fact, hydrogen bubbles formation and subsequent detachment from the surface do not allow formation of deposits with high uniformity.

Variations of the working electrode potential (vs. Ag/AgCl reference electrode) during the electrodeposition process (Figure 1) show that the electrode potential increases during electrodeposition as a consequence of the decrease on the overvoltage associated to the cathodic process, caused by a gradual increase in the deposition area. Indeed, if the electrodeposition area increases, current density diminishes and, consequently, it is expected that the cathodic overpotential decreases.



Table 1: Summary of results of the electrodeposition tests performed.

Current density (mA/cm ²)	Time (min)	Efficiency (%)	Deposit thickness (μ m)	Mn/Zn ratio	Deposit aspect
plain lixiviation bath					
10	15	72	11.0	0.61	Uniform
	30	50	11.5	0.22	Uniform
	60	69	30.7	0.20	Uniform
20	15	59	25.6	0.17	Uniform, but non adherent at edges
	30	62	25.2	0.15	Uniform, but non adherent at edges
30	15	55	44.7	0.11	Uniform, but non adherent at edges
40 ppm methylamine					
10	15	87	18.5	4.56	Uniform
	30	78	26.2	2.99	Uniform
	60	84	39.3	1.74	Uniform, but with some irregularities
20	15	80	35.2	0.07	Uniform, but non adherent at edges
	30	90	64.0	0.17	Uniform, but non adherent at edges
30	15	54	39.1	0.13	Uniform, but non adherent at edges
40 ppm ethylenediamine					
10	15	84	17.7	3.30	Uniform
	30	80	24.6	2.70	Uniform
	60	85	43.5	0.27	Uniform, but with some irregularities
20	15	30	27.2	0.20	Uniform, but non adherent at edges
	30	75	43.8	0.24	Uniform, but non adherent at edges
30	15	50	25.3	0.17	Uniform, but non adherent at edges

Since the electrode potential varies during electrodeposition it causes a variation on the ratio of the electrodeposited amounts of Zn and Mn. The standard potential of the Mn^{2+}/Mn couple is -1.402 V vs. $Ag/AgCl$, i.e., more negative than that of the Zn/Zn^{2+} couple, which is -0.982 V vs. $Ag/AgCl$. Therefore, electrodeposition at a lower polarisation (less negative potential) favours the formation of alloys with higher zinc content. This is confirmed by the observed Mn/Zn ratio in the deposits, as determined by EDXRF analysis (Table 1). These results show that, as the electrodeposition time increases, the Mn/Zn mass ratio decreases, i.e., the mass of deposited manganese decreases in relation to that of deposited zinc. On the other hand, results are consistent with a mechanism that assumes more tendency for Mn to deposit over Fe substrates than Zn does. That explains the relatively higher deposition of Mn at the initial stages of the process.

The analysis of the variation of the Mn/Zn mass ratio with the applied current density shows that, as the current increases, there is a small decrease in the

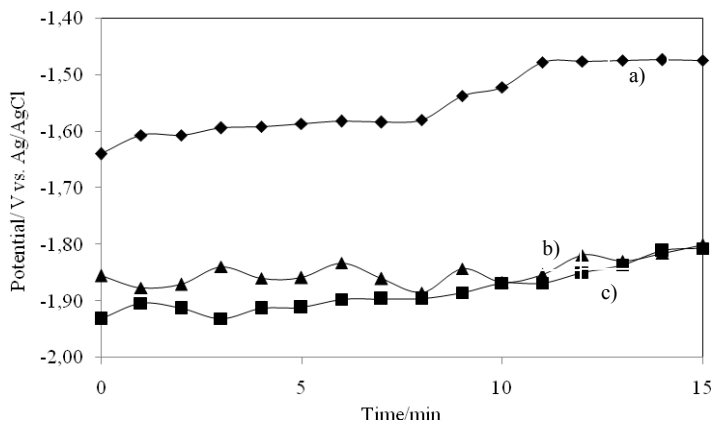


Figure 1: Variation of the working electrode potential during electrodeposition of Zn-Mn alloys at 20 mA/cm²: a) Plain lixiviation bath; b) 40 ppm methylamine; c) 40 ppm ethylenediamine.

Mn/Zn mass ratio. This limitation on the Mn deposition at higher currents could be related with a certain inhibitor effect caused by hydrogen liberation, as referred by some authors [27].

Another aspect to consider in the analysis of these results is the fact that Zn-Mn alloys formed by electrodeposition show necessarily a gradient of Mn/Zn mass ratio between the substrate and the external surface. This makes the alloys more rich in manganese at the interface with the iron substrate, and more rich in zinc at the external surface. This fact may have a negative influence on the anticorrosive behaviour of the alloys when used as corrosion resistant coating, since in case of a scratching failure, conditions for galvanic corrosion between the layers may be created.

Electrodeposits of Zn-Mn alloys produced in baths with additions of amines, methylamine and ethylenediamine, generally display a behaviour similar to that described for electrodeposits obtained from plain sulphuric lixiviating baths. This is true, namely, in terms of the visual aspect, the fact that deposits produced at lower current densities show higher uniformity and homogeneity, the fact that the electrodeposition potential increases during the deposition process, and finally the fact that this potential decreases as the current density increases. However, there is a significant decrease of the electrodeposition potential when amines are present in the bath, as compared to the same parameter in the absence of amines. That means that there is a clear additive effect in the overpotential associated with the metallic reduction process when amines are present. This fact can be explained if it is assumed that amines produce a certain surface inhibition, which excludes part of the surface from the ionic discharge process. Since amines have an adsorption capacity, it is probable that the inhibiting effect results from some passivation of the substrate and the consequent formation of deposits over it. On the other hand, it was also observed that amines increased

the current efficiency of the deposition process (see Table 1). Thus, the results are consistent with an adsorption of amines at the electrode surface reducing the hydrogen discharge, so that the cathodic polarisation of hydrogen shifts more negative, therefore catalysing the deposition of zinc and manganese.

Another aspect that deserves reference in the analysis of these results is concerned with the fact that the addition of amines seems to promote a significant increase in deposition of Mn relatively to the deposition of Zn. This increase in the deposition of Mn becomes more important as the electrodeposition process goes slower, that is, as current density decreases. This observation is in agreement with the proposed mechanism, since as the electrodeposition overpotential increases (lower electrode potentials), it also increases the tendency for the Mn deposition. This behaviour is probably due to the formation of a more stable complex compound between the amines and Zn^{2+} than with Mn^{2+} . These results also confirm that amines improve the production of thicker deposit coatings, implying an increase in the efficiency of the electrodeposition process (see Table 1).

3.2 Corrosion behaviour

Table 2 presents values of corrosion potentials (E_{corr}) and corrosion currents (i_{corr}) of steel samples coated with Zn-Mn deposit layers and steel samples without any coating immersed in a 3% NaCl solution at 25°C. The corrosion current was determined by the Stern-Geary equation assuming a value of 0.026 V for the parameter B:

$$\frac{\Delta E}{\Delta I_{app}} = \frac{\beta_a \beta_c}{2.3 \times i_{corr} (\beta_a + \beta_c)} = \frac{B}{i_{corr}} \quad (2)$$

As it can be seen, corrosion potentials of mild steel coated with Zn-Mn alloy by electrodeposition are all of the order of -1 V vs. Ag/AgCl, except that of the steel sample coated with the alloy with the highest Mn content (electrodeposition at 10 mA/cm² for 15 min) that shows a more negative value closer to the Mn^{2+}/Mn standard potential. The lower the corrosion potential, the higher the galvanic and protection effect of the coating.

Figure 2 shows anodic polarisation curves, including the backward scanning, of the steel surfaces, coated with Zn-Mn alloy layers obtained from the plain lixiviation bath and the plain solutions with additions of methylamine (40 ppm) and ethylenediamine (40 ppm), immersed in a 3% NaCl solutions at 25°C. All curves display a similar behaviour showing a spike with a current intensity that is proportional to the thickness of the deposit layer. The reduction of current following the peak could be explained by the attempt of passivation by the iron substrate. This hypothesis is corroborated by the fact that no peak appears during the backward scanning.

These results show that, when compared with deposits produced without any additive, deposits formed in baths with amines display higher polarisation of the anodic dissolution process in test salt solutions, which is positive in terms of their anticorrosive behaviour. On the other hand, it can be seen that the polarisation resistance of the coatings with higher Mn content is also higher.



Table 2: Corrosion characteristics of samples immersed in 3% NaCl solutions.

Current density (mA/cm ²)	Time (min)	Plain lixiviation bath		40 ppm methylamine		40 ppm ethylenediamine	
		<i>E_{corr}</i> (V vs. Ag/AgCl)	<i>i_{corr}</i> (mA/cm ²)	<i>E_{corr}</i> (V vs. Ag/AgCl)	<i>i_{corr}</i> (mA/cm ²)	<i>E_{corr}</i> (V vs. Ag/AgCl)	<i>i_{corr}</i> (mA/cm ²)
Plain steel	-	-0.54	-	-	-	-	-
	15	-1.13	0.68	-1.10	0.35	-1.15	0.45
10	30	-0.99	0.70	-1.05	0.50	-1.08	0.62
	60	-0.98	0.93	-1.98	0.61	-0.93	1.37
20	15	-1.00	0.58	-0.93	1.63	-0.95	1.81
	30	-0.99	1.50	-0.89	3.47	-0.92	1.66
30	15	-1.01	2.20	-0.91	2.10	-0.91	4.91

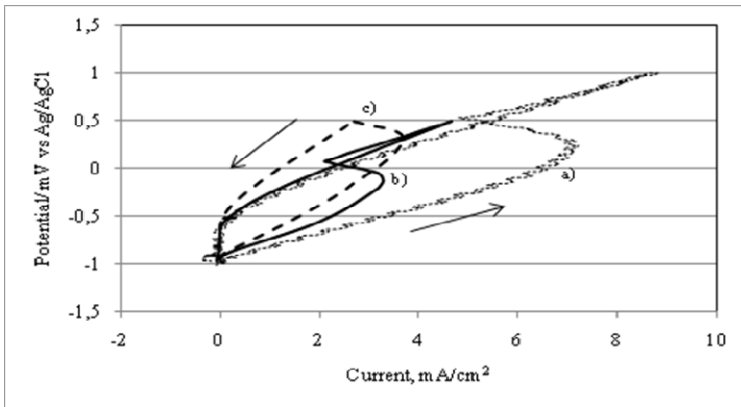


Figure 2: Polarisation curves of steel samples coated with Zn-Mn alloy electrodeposited from sulphuric baths, immersed in 3% NaCl solutions, at 25°C, and at 20 mA/cm²: a) Plain lixiviation bath; b) 40 ppm methylamine; c) 40 ppm ethylenediamine.

Since the electrodeposition with amines increases the Mn content of the coatings, the explanation of the increased of corrosion resistance is associated to the formation of a rich manganese surface alloy. It was reported that a Zn-Mn alloy with a manganese content of approximately 30% shows the highest corrosion resistance [12]. This highest corrosion resistance has been associated with the formation of a monophasic structure of the coating. Boshkov [15] studied the influence of bath composition on the corrosion behaviour of Zn-Mn coatings and reported that alloys with manganese contents around 11% had a higher corrosion resistance due to a formation of monophasic structure.

Manganese atoms are randomly distributed in this monophasic structure and dissolve first under corrosion attack as Mn^{2+} ions, causing evolution of hydrogen and, consequently, a slight increase of the pH value. At these conditions, zinc hydroxide chloride monohydrate (ZHC) forms as a compact layer covering almost the whole surface.

A clear conclusion is that the presence of Mn in Zn electrodeposits contributes to better anticorrosive and protective performance of mild steels in saline environments.

In summary, the produced alloys display higher anodic dissolution overpotentials (see figure 2) and higher polarisation potentials, with a clear positive influence on anticorrosive properties of these coatings. This effect can be explained by the fact that there is a relative increase in the Mn content of the produced alloy in this case, when compared with the coatings produced by electrodeposition without any additive.

The amines facilitate manganese incorporation, limit hydrogen evolution reaction, and prevent the dendrite growth that leads to porous deposits. Thus, the additive improves the visual appearance of the coatings and leads to the formation of adherent and compact layers with high percentage of manganese.

4 Conclusion

The obtained results allow the following conclusions:

- Lixiviation solutions resulting from the hydrometallurgical treatment of spent domestic batteries, mainly, Zn-MnO₂-batteries, can increase their value directly as electrodeposition baths of zinc alloys;
- Quality of deposits produced from this lixiviation solutions depends strongly on the magnitude of the electrodeposition current: homogeneous and uniform deposit layers with good anticorrosive properties are obtained, preferentially, at low current densities;
- Mn/Zn mass ratios in the produced deposit layers suffer an influence of electrodeposition current densities, electrodeposition duration, and of the presence of additives in the electrodeposition baths. Lower electrodeposition currents and shorter electrodeposition durations benefit the deposition of Mn in relation to Zn;
- Buffering and passivating additives having adsorption effect, such as methylamine and ethylenediamine, also benefit the deposition of Mn;
- Addition of methylamine and ethylenediamine to the electrodeposition baths contributes to the production of deposit coatings with better anticorrosive performances;
- Methylamine reveals a better corrosion performance than ethylenediamine;
- The increase in Mn contents of the electrodeposited coating layer reveals beneficial anticorrosive effects to mild steel in saline environments.



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