

Electrochemical recycling of the zinc from spent Zn–MnO₂ batteries

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Received 8 September 2003; accepted 29 September 2003

Abstract

In this work, zinc from the spent Zn–MnO₂ batteries is recycled. Ionic zinc is recovered from acidic or alkaline solutions using a galvanostatic technique. An optimum current density between 10.0 and 25.0 mA cm⁻² was obtained for recovery of ionic zinc from acidic solutions. The optimum current density is equal to 15.0 mA cm⁻² for zinc electrodeposition from alkaline solution. The charge efficiency is 80.0% and decreases with increase of current density. In acidic solutions, hydrogen adsorption catalyse Zn²⁺ electrodeposition. In alkaline solutions, a parallel reaction of the hydrogen evolution inhibits zincate electrodeposition.

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Keywords: Electrochemical recycling; Spent battery; Zinc recovery; Zinc

1. Introduction

Electrochemical recycling of zinc from the exhausted Zn–MnO₂ batteries is of great scientific, technological and environmental interest. Brazil consumes annually about 1 billion batteries. Primary Zn–MnO₂ batteries are used in short applications that need low energy and useful life. This battery type is used by most of the population, an average of six units per person [1]. Secondary alkaline batteries Ni–Cd and Ni–MH are used in applications that require high density of energy, long useful life and high rates of discharge. Ni–MH alkaline batteries are used in cellular telephones and 39 million of these batteries are consumed annually in Brazil. We use the lead-acid batteries, where the weight is not an important factor. The process for recycling of lead from spent lead-acid batteries is well known [2]. Lithium batteries present higher density of energy, but are more expensive.

In Brazil, exhausted Zn–MnO₂ batteries are discarded in domestic garbage and municipal waste [3]. The placement of spent Zn–MnO₂ batteries in domestic garbage has become a serious environmental problem. An alternative would be the incineration. However, that process is not appropriate because of the emissions of toxic gases [4]. Another

alternative is recycling [5–9]. The electrochemical recycling of the zinc from the spent batteries is viable from an environmental point of view. Electrochemical recycling of Zn²⁺ from acidic solutions is atypical behaviour due to the reduction of protons at less cathodic potential. Adsorbed hydrogen catalyses the zinc electrodeposition on steel [10]. This explains the high charge efficiency obtained for Zn²⁺ recovered from acidic solutions. Zinc also is recycled from alkaline solutions. The electrolytic solutions useful for battery recycling does not use cyanide, as in the traditional baths used for zinc electrodeposition in metallurgical industries. In the present work, a method for electrochemical recycling of the zinc from the spent Zn–MnO₂ batteries was developed. The ionic zinc is electrodeposited on steel iron–carbon 1020 and serves as protection towards corrosion.

2. Experimental

2.1. Mechanical process

A mini pilot plant was built in the laboratory for recycling of the spent Zn–MnO₂ batteries (Lechanché or zinc–carbon). The process for the recycling of the batteries requires conditions of selective collection, dismantling, and a sequence of physical and electrochemistry transformations. The spent Zn–MnO₂ primary battery, type AA “mercury free” produced by Panasonic was used in that research. In the

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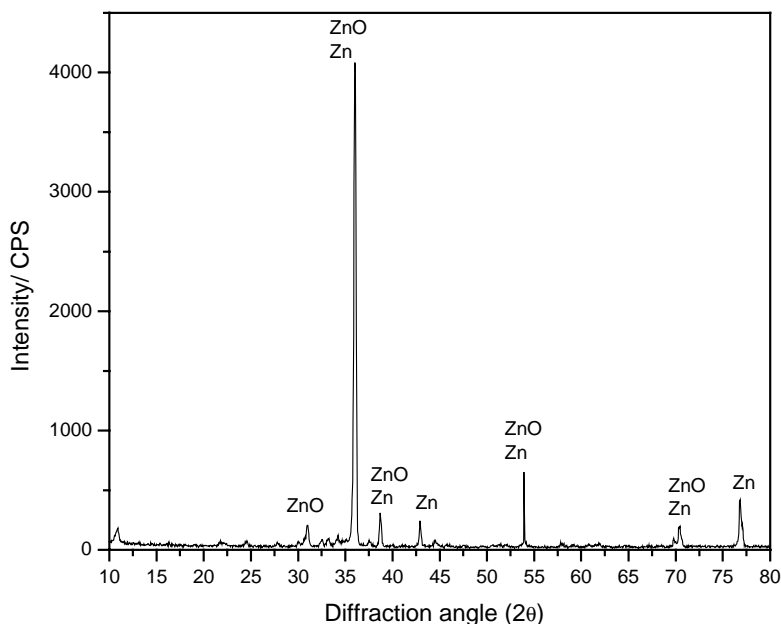


Fig. 1. Typical X-ray diffraction for discharged anode of the spent Zn–MnO₂ batteries.

dismantling, physical separation of the exhausted batteries is performed in different fractions. One part contains the anode, and the other the cathode (MnO₂ and graphite) and the third steel, the separators and current collectors. The anode corresponds to 18.0 and 21% of the total weight of the Zn–MnO₂ batteries.

2.2. Anode characterisation

A typical example of X-ray diffraction for the internal part of the discharged anode of the spent Zn–MnO₂ batteries is

shown in Fig. 1. In comparison with JCPDS cards, it was found that the relative intensities of the diffracted X-ray peaks resemble those tabulated for ZnO and metallic zinc [11,12]. In our work, it has been verified that the composition of the anode depends on the discharge rate and cut-off potential.

2.3. Anode leaching

Dissolution was made in the proportion of 1.0 g of anode material for each 100 ml of the 0.5 mol/l H₂SO₄ solution.

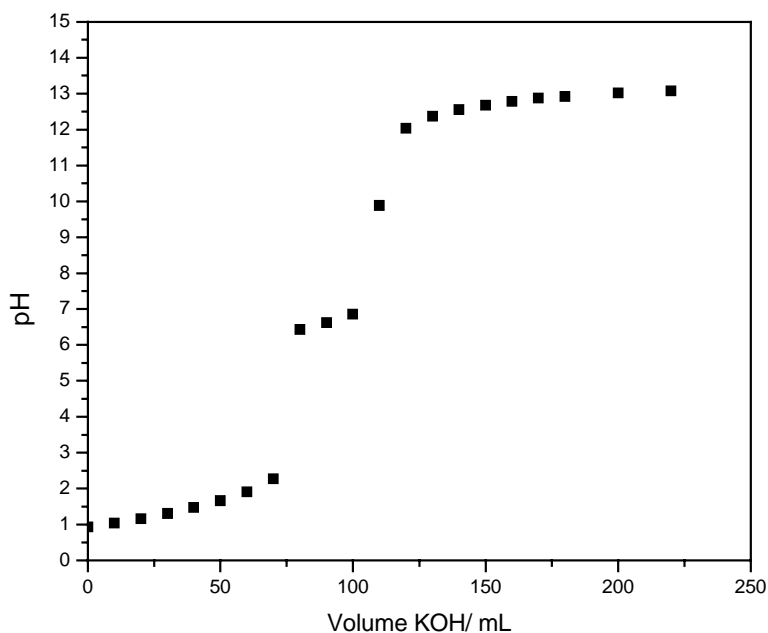


Fig. 2. pH in function of the volume of the 1.0 mol/l KOH, $T = 298\text{ K}$.

The suspension was maintained with constant stirring at 298 K. Under those conditions, the dissolution took 1 week. The suspension was filtered after anode leaching. The pH of the solution before and after the anode dissolution was equal to 0.737 and 0.883, respectively. The difference of the H_2SO_4 amount of substance (mol) before and after the anode dissolution is equivalent to the amount of Zn^{2+} in the leaching solution. The concentration of the ionic zinc in the leaching solution is equal to 0.1413 mol/l. The conductivity of the leaching solution is equal to 90.0 mS cm^{-1} .

The reactions between the anode (surface and bulk) with sulphuric acid solution can be expressed as follows:

Anode surface :

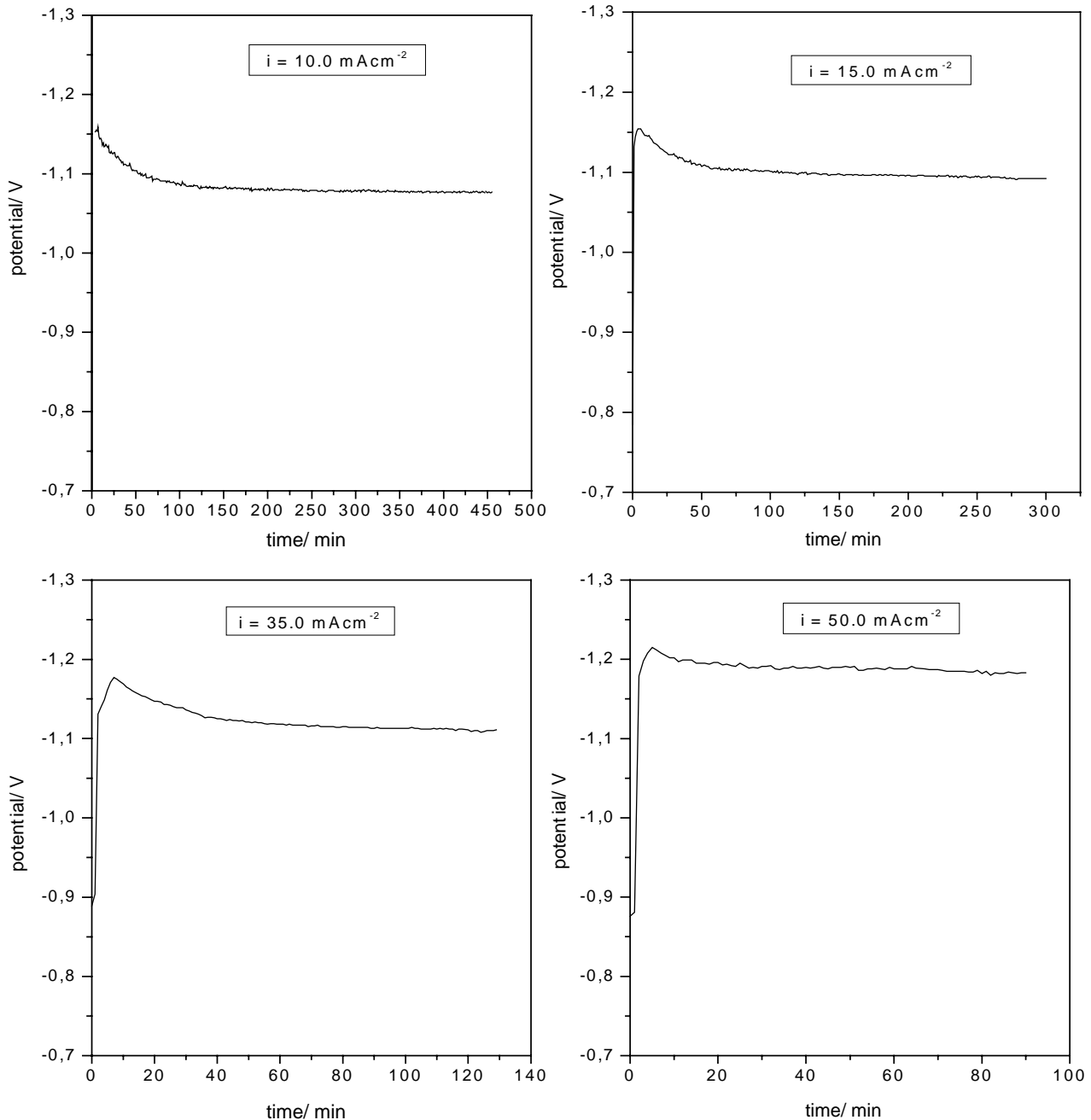
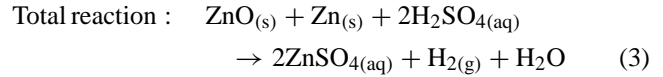
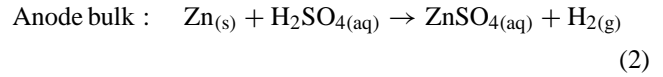


Fig. 3. Typical chronopotentiogram for zinc electrodeposition in acidic solutions, 0.5 mol/l H_2SO_4 , 298 K, without stirring, $q_{\text{applied}} = 271.3 \text{ C cm}^{-2}$.

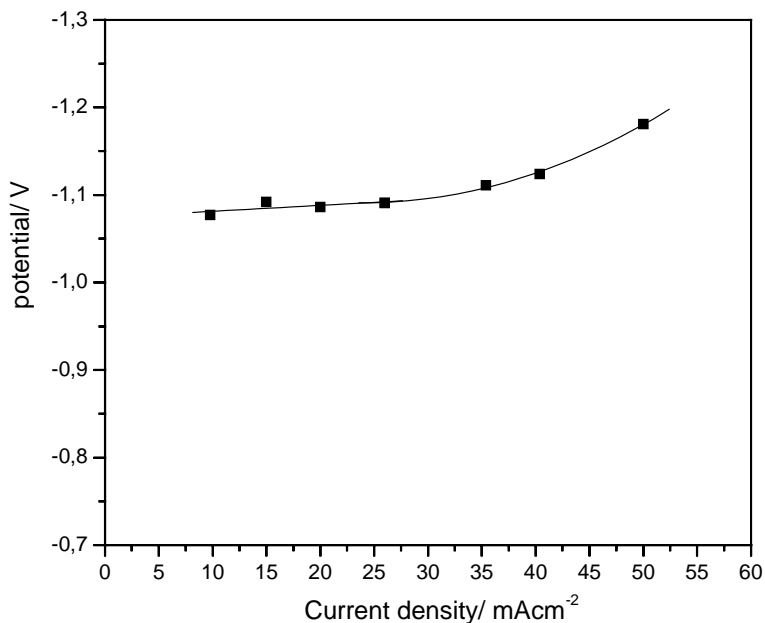
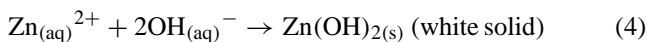


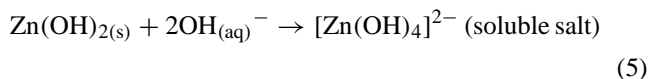
Fig. 4. Potential vs current density for zinc electrodeposition, acidic solutions, 0.5 mol/l H₂SO₄, 298 K, without stirring, $q_{\text{applied}} = 271.3 \text{ C cm}^{-2}$.

2.4. Alkaline bath

For preparation of the alkaline bath, a solution of 1.0 mol/l KOH was added by dripping until pH equalled 13.0. After pH 13.0 one solution of the 6.0 mol/l KOH was added in the leaching solution. The variation of the pH as a function of 1.0 mol/l volume KOH is shown in Fig. 2. In the interval 6.0 and 7.5 occurs the precipitation of the zinc hydroxide. The reaction can be written as follows:



The zinc precipitated is dissolved at a pH 13:



The conductivity of the alkaline solution is equal to 180.0 mS cm⁻¹.

2.5. Electrochemical cell

The working electrode was made with steel 1020. These electrodes were prepared from a rectangular sheet with a

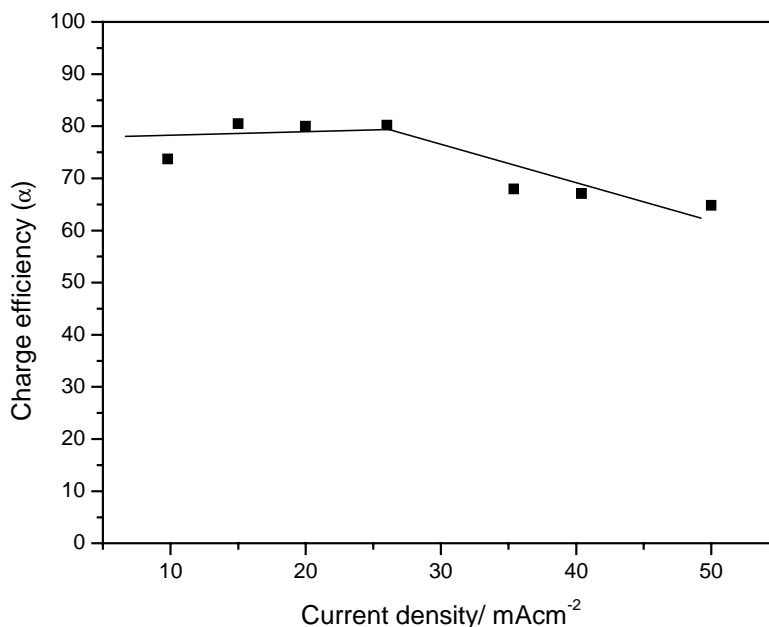


Fig. 5. Charge efficiency vs current density for zinc electrodeposition, acidic solutions, 0.5 mol/l H₂SO₄, 298 K, without stirring, $q_{\text{applied}} = 271.3 \text{ C cm}^{-2}$.

geometric area of 0.20 cm^2 . The auxiliary electrode was made with a platinum sheet with geometric area of 3.75 cm^2 . The reference electrode was Ag/AgCl/NaCl saturated. Before each electrochemical experiment the work electrode were sanded with 600 grit sandpaper and then rinsed with distilled water. The galvanostatic experiments were performed with a regulated power supply built in the laboratory. The work and the auxiliary electrodes were connected to the voltage meter and linked to the microcomputer by an RS232 interface. The electrolyte solutions were prepared with pure water. The solutions were changed after each experiment. All electrochemical experiments were performed at 298 K. X-ray diffraction was carried out by using the Rotaflex-Rigaku model 200B diffractometer, copper radiation, and nickel filter.

3. Results and discussion

3.1. Recycling of zinc from acidic solutions

In the initial electrodeposition process we observed a peak potential (Fig. 3). This potential is associated with the hydrogen evolution and the formation of active zinc sites by nucleation, as initially found by Cachet and Wiart [10]. The reaction potential (measured for constant charge density) is independent of the current density in the interval between 10.0 and 27.0 mA cm^{-2} , as can be seen in Fig. 4. The peak potential became more cathodic for current density larger than 27.0 mA cm^{-2} . This demonstrates that for current density between 10.0 and 27.0 mA cm^{-2} the polarisation resistance $(d\eta/di)_q$ is very low. $(d\eta/di)_q$ increases with increase of the current density. Due to the reaction

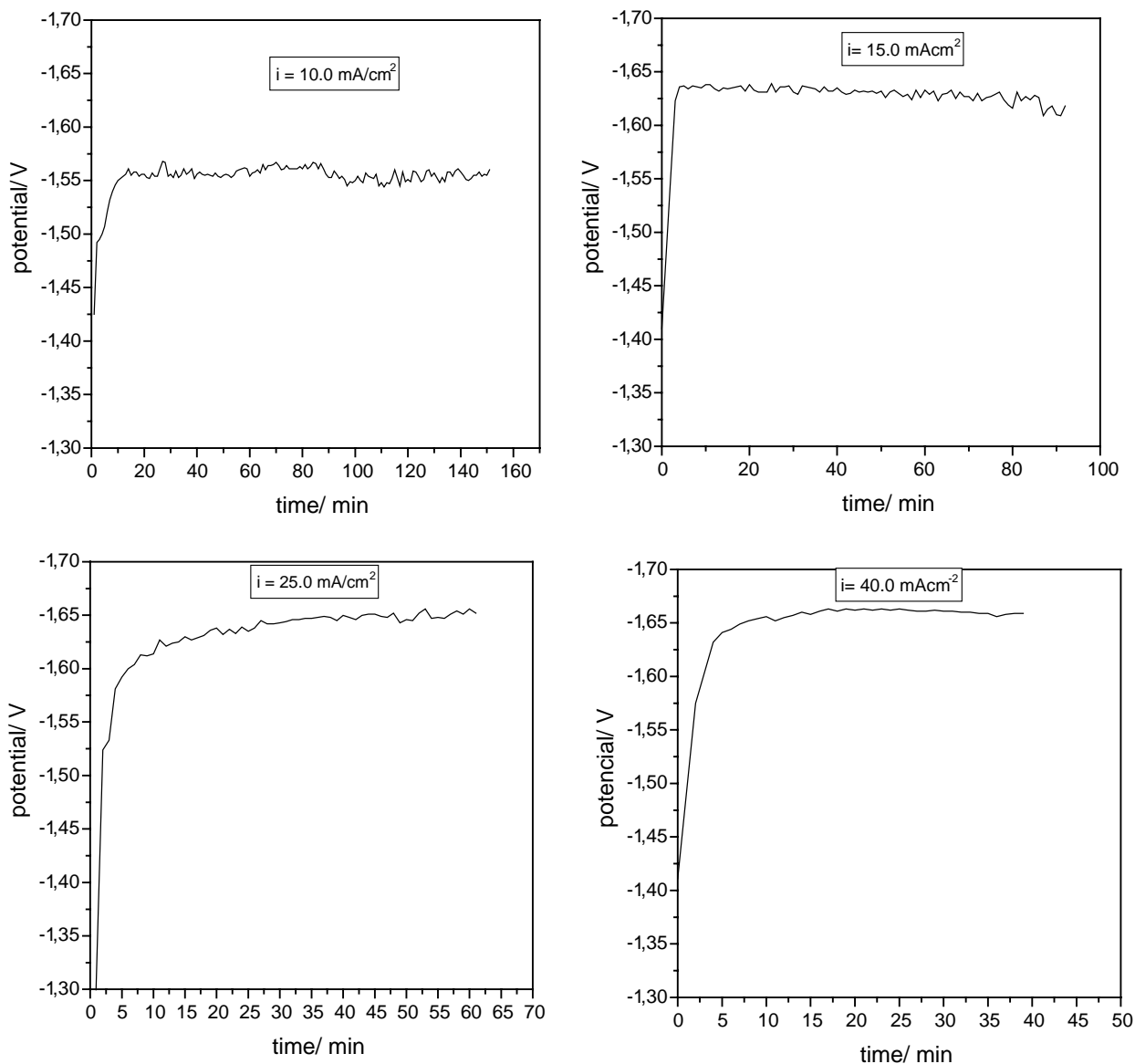


Fig. 6. Typical chronopotentiogram for zinc electrodeposition in alkaline solutions, pH 13.0, 298 K, without stirring, $q_{\text{applied}} = 90.0\text{ C cm}^{-2}$.

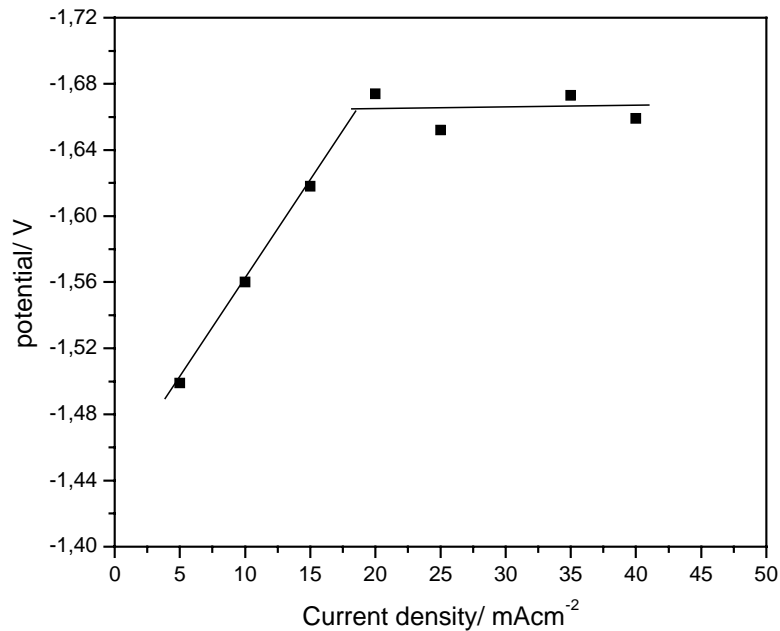


Fig. 7. Potential vs current density for zinc electrodeposition in alkaline solutions, pH 13, 298 K, without stirring, $q_{\text{applied}} = 90.0 \text{ C cm}^{-2}$.

of water decomposition, a zinc hydroxide film forms. This superficial film of Zn(OH)_2 inhibited current passage [13]. Therefore, there is an increase in the polarisation resistance $(d\eta/di)_q$. The charge efficiency ($\alpha = Q_{\text{deposition}}/Q_{\text{applied}}$) is independent of the current density in the interval between 10.0 and 27.0 mA cm^{-2} and decreases for current density larger than 27.0 mA cm^{-2} (Fig. 5). The charge efficiency is totally compatible with the change of the polarisation resistance.

3.2. Recycling of zinc from alkaline solutions

The type of zinc electrodeposits and the overpotential for hydrogen evolution on metallic zinc depends on the current density [14]. Experiments confirmed that fact. As can be seen in Fig. 6 there are oscillations in the potential. The number of oscillations decreases with the increase in the current density. These oscillations appear as the result of irregular growth of the deposit [14]. The reaction

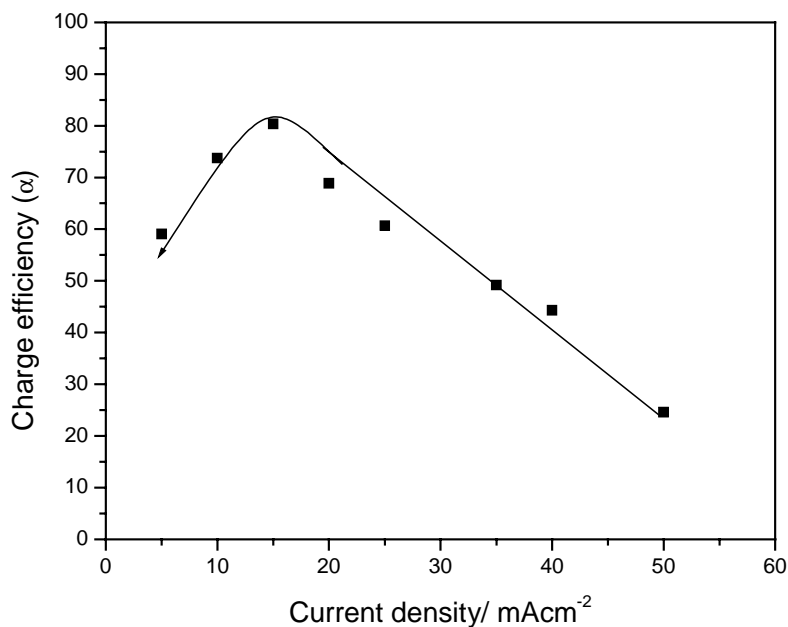


Fig. 8. Charge efficiency vs current density for zinc electrodeposition, alkaline solution pH 13.0, 298 K, without stirring, $q_{\text{applied}} = 90.0 \text{ C cm}^{-2}$.

potential (measured for constant charge density) is a function of the current density (Fig. 7). It is activation controlled for a current density smaller than 15.0 mA cm^{-2} and becomes mass-transport controlled for current density larger than 20.0 mA cm^{-2} . The angular coefficient $(d\eta/di)_q$ represents the polarisation resistance for zincate electrodeposition on zinc. It is the main reaction in this interval. The polarisation resistance $(d\eta/di)_q$ is practically constant for current density larger than 20.0 mA cm^{-2} . In this case, the hydrogen evolution on metallic zinc becomes the main reaction. The zinc deposit always is formed with concurrent hydrogen evolution, as shown in Fig. 8. The charge efficiency ($\alpha = Q_{\text{deposition}}/Q_{\text{applied}}$) for zincate electrodeposition from alkaline solution has a maximum point for current density equal to 15.0 mA cm^{-2} . The increase of the hydrogen evolution on metallic zinc reduces the charge efficiency for zinc recovery. The decrease of the charge efficiency with the increase of the current density is more abrupt in alkaline than in acid solution. For the same current density, the reaction potential is more cathodic for zinc electrodeposition from alkaline than from acidic solution. The displacement of the reaction potential to more cathodic values demonstrates that the activation energy is larger for zinc electrodeposition from alkaline than from acidic solution.

4. Conclusions

The electrochemical recycling of zinc should reduce the amount of exhausted Zn–MnO₂ batteries in the garbage and protect the environment from contamination with toxic metals. The maximum charge efficiency is equal to 80.0%. Therefore, electrochemical recycling is also viable economically. The charge efficiency decrease occurs due to the

increase of the polarisation resistance (acidic solution). A parallel reaction of hydrogen evolution reduces the charge efficiency for zinc recovery from alkaline solution. The mechanisms zinc recovery from spent Zn–MnO₂ batteries depend on whether the solution is acid or alkaline. In acidic solutions, the adsorbed hydrogen catalyses the Zn²⁺ electrodeposition. In alkaline solutions, hydrogen evolution tends to block zincate electrodeposition.

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