



# NiFeZn codeposit as a cathode material for the production of hydrogen by water electrolysis

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## Abstract

This work describes the development of a composite material, NiFeZn coatings, prepared from the electrodeposition of NiFeZn alloys followed by chemical leaching in KOH solution. A sulphate bath was used to electrodeposit the NiFeZn alloys (55, 1, 44% in atoms, respectively) on a mild steel substrate. The evaluation of this material as electrocatalyst for the hydrogen evolution reaction was carried out in alkaline solutions through steady-state polarization curves. The long term operation at  $135 \text{ mA cm}^{-2}$  showed good stability for up to 200 h. A positive aspect of this cathode is that the polarization behavior of the material shows one Tafel slope over the temperature range 25–80°C. The operational potential of this material in 28% KOH at 80°C is about 100 mV which is significantly lower than that of mild steel (400 mV). © 2000 International Association for Hydrogen Energy. Published by Elsevier Science Ltd. All rights reserved.

## 1. Introduction

The hydrogen evolution reaction (HER) is one of the most important processes in electrochemistry. Fundamental studies that go back to the beginning of the century have helped considerably to establish the foundations of modern electrochemical dynamics. In industrial electrochemistry, the HER is particularly important in commercial water electrolysis, chlor-alkali electrolysis and other important processes.

The production of hydrogen by water electrolysis is of particular interest because of the many industrial applications that require pure hydrogen, like the food industry, the refining of metals, etc. More recently, a growing concern with environmental protection has

seen good possibilities in the use of hydrogen in suitable energy converters like fuel cells. Combined with electrolytic hydrogen this allows the establishment of a totally clean and efficient energy cycle.

The main problem with electrolytic hydrogen is the higher cost when compared with hydrogen produced by vapor reforming of fossil fuels (but here the long-term cost of using fossil fuels for this purpose is not considered). Thus, efforts are being devoted to reduce the cost of electrolytic hydrogen. It has been demonstrated that, apart from the cost of electricity, which is a political issue, the cost of hydrogen is directly proportional to the voltage of operation of the electrolyser [1]. Traditional unipolar electrolyzers operate with mild steel cathodes and nickel plated anodes in 28–30% KOH solution at about 80°C. In bipolar electrolyzers nickel is used for both anode and cathode. Under these conditions the overvoltages for the HER and for the oxygen evolution reaction (OER) may be as high as 400 mV under operating conditions [2].

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Thus, these overvoltages account for more than one third of the operational voltage of the electrolyzer. From this consideration it becomes apparent that one way of reducing the operational voltage is to find materials with good electrocatalytic activity that will present lower overpotentials for the HER and OER.

In the search for electrocatalysts it must be taken into account that the cost of the material has to be consistent with the cost of the technology being proposed. This practically rules out the use of precious metals in ordinary alkaline electrolysis. Several materials have been studied as electrocatalysts for the HER, and significant reductions of the overpotential have been achieved with electrodeposited nickel alloys with transition metals [3]. Another approach has been to produce high active area materials by electrodepositing nickel with a suitable metal like zinc [4–8] and then leaching the zinc in an alkaline solution. One of the materials that were found to have a good electrocatalytic activity for the HER is electrodeposited NiFe [9–12]. Previous works in this laboratory have shown that in spite that NiFe codeposits do not have a high surface area they present a good electrocatalytic activity for the HER in alkaline solutions. This is achieved through an activation process, which consists of a partial oxidation of the electrode in acid solution [11,12].

The purpose in this work is to try to combine the effects of electrocatalysis and high surface area by developing an electrodeposit of Ni, Fe and Zn. Partial removal of the Zn by leaching in alkaline medium should render a high surface area material, which may present the beneficial catalytic effect of NiFe alloys.

## 2. Experimental

Mild steel foil of 2 mm thickness was used to make the substrates for the cathodes. The composition of the steel (apart from Fe) was: C, 0.102%, Si, 0.05%, Mn, 0.62%, P, 0.019% and Mg, 0.016%. The foils were mounted into epoxy resin, which through extensive testing in this laboratory was found to be highly resistant to hot concentrated alkali. The exposed geometrical area of the electrode was 0.5 cm<sup>2</sup>. Prior to the electrodepositions the surface was polished with emery paper and cleaned with diluted HCl and acetone. The codeposition of NiFeZn was done on this surface using a bath containing nickel sulphate (300 g l<sup>-1</sup>), zinc sulphate (0.7 g l<sup>-1</sup>), and ferrous ammonium sulphate (10 g l<sup>-1</sup>). The electrolysis time was 30 min at 27°C under a current density of 10 mA cm<sup>-2</sup>.

After the electrodeposition, the activation of the electrodes were made by treating the deposit with 6 M KOH solution at room temperature until no more hydrogen bubbling was observed. This treatment pro-

motes a partial leaching of the Zn present in the deposit.

Electrochemical measurements were carried out in a three-compartment glass cell. A platinum sheet of about 2 cm<sup>2</sup> served as auxiliary electrode and a Hg/HgO/HO<sup>-</sup> system, joined to the main compartment through a Luggin capillary, as a reference electrode. Steady-state polarization curves were obtained galvanostatically in the range of 0.001–0.4 A with a PAR 273A potentiostat/galvanostat provided with iR compensation. The working solutions were 1 M NaOH prepared with pa reagents and water purified in a Milli-Q (Milli Pore) system.

Chemical analyses of the electrodeposits were carried out with atomic absorption spectroscopy (Hitachi Z-8100). The deposits were also characterized through X-ray diffractograms (Rigaku Rotaflex RU 200B). The morphology of the surface was examined by SEM (ZEISS DSM 960) and the chemical composition determined by EDX (LIMK QX 2000). For these experiments the electrodeposits were prepared on a copper substrate to avoid the unwanted interference of iron from substrate.

## 3. Results and discussion

### 3.1. Characterization of the electrodeposits

The bulk composition of the NiFeZn alloy was characterized by atomic absorption spectroscopy in a solution obtained by complete dissolution of the electrodeposit in a 3:1 HNO<sub>3</sub>/HCl followed by the evaporation of HNO<sub>3</sub>. The results of these analyses for Ni–Fe–Zn were 31:1:68 (atom %) before and 49:1:50 (atom %) after the treatment to remove Zn. Although the percentage of Zn diminishes substantially after the alkaline treatment, the amount remaining is still significant. On the other hand, the fundamental parameter in an operational electrode is the surface composition. True surface compositions could be obtained in ultrahigh vacuum equipment with Auger spectroscopy, but this technique was not readily available. However, an indication of this surface composition can be obtained with EDX analysis. Due to the penetration of the X-rays the results can be considered as representing only approximately the surface composition. The results of the EDX analysis for Ni–Fe–Zn were 25:0:75 (atom %) before and 55:1:44 (atom %) after removal of the Zn, so the results can be considered consistent with those obtained for the bulk electrodeposit by atomic absorption. This means that for this type of the electrodeposit the composition of a surface layer is essentially similar to that of the bulk. It is interesting to note that the amount of Fe in the electrodeposit is

rather small, and according to the EDX results after removal of the Zn it is present mainly on the surface. Several attempts to increase the contents of Fe by increasing the amount of ferrous ammonium sulphate in the electrodeposition bath were carried out, but this led to non-adherent deposits.

Micrographs obtained with a SEM equipment show that the morphology of the surface changes significantly after the leaching of Zn. Fig. 1(a) and (b) shows the micrographs of the NiFeZn codeposit before leaching, and Fig. 1(c) and (d) the corresponding images

after the removal of Zn at two magnifications. It can be observed from these pictures that initially the deposit presents a compact and uniform structure on the surface. But, after the removal of Zn a great number of cracks and pores appear, which indicates a substantial increase in the active surface area. So, it is probable that the small content of Fe observed from the EDX analyses only after the leaching, is mainly present on sublayers exposed on the activation process.

Some general information about the morphology

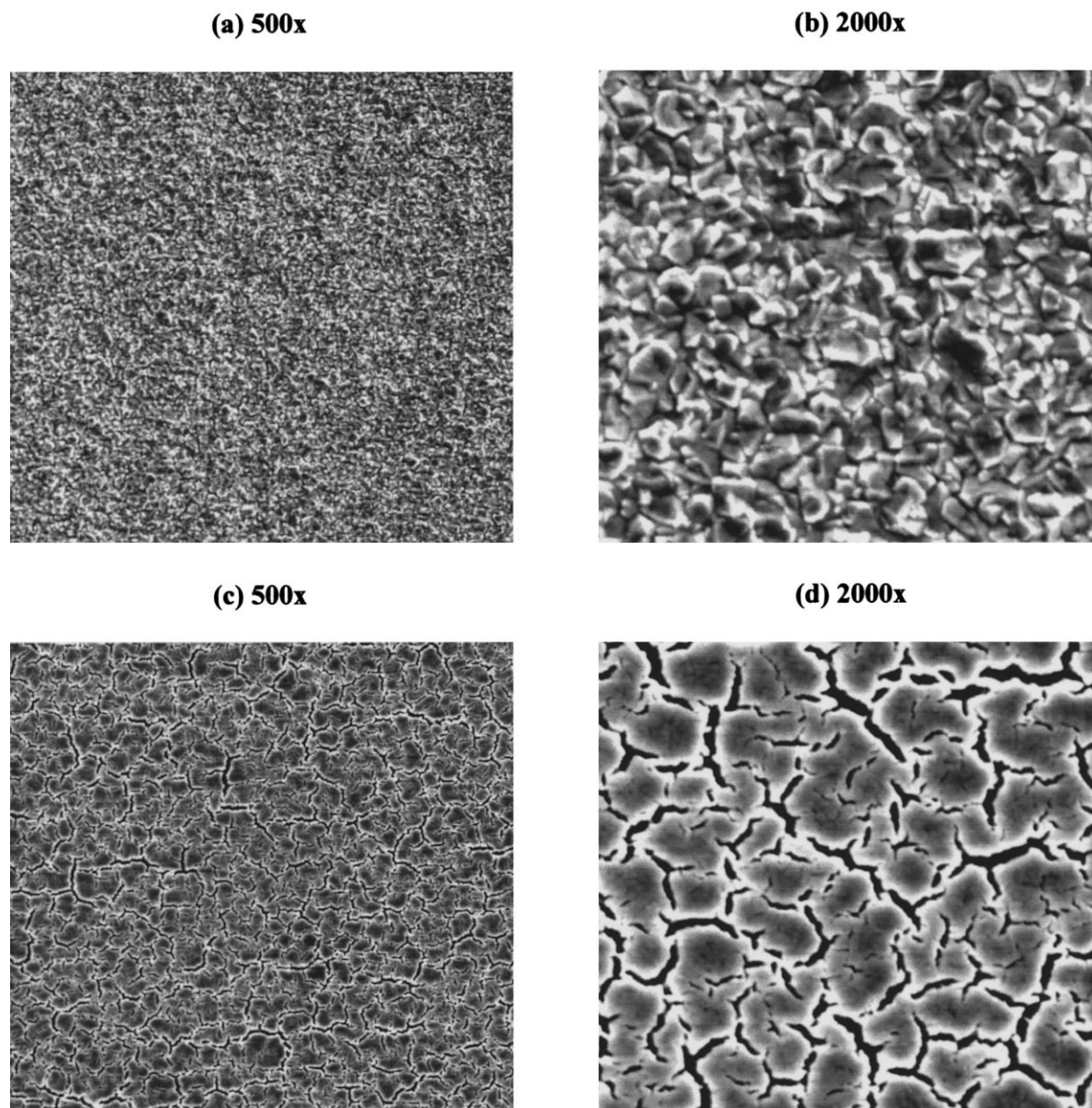


Fig. 1. SEM micrographs for electrodeposited NiFeZn, (a) and (b) before activation, (c) and (d) after activation.

of the electrodeposits was obtained through X-ray analysis of the surfaces, before and after the activation procedure. For these analyses the electrodeposits were prepared onto copper substrates, to avoid the interference of elements present in the mild steel substrate, notably Fe. Fig. 2(a) and (b) shows the X-ray diffractograms of activated and non-activated NiFeZn codeposits, respectively. Apart from lines due to the copper substrate, some lines due to individual metals and intermetallic compounds can be detected. Although some of the lines are quite sharp, many of them suggest some degree of amorphicity in the deposits. A more detailed analysis would be required to fully characterize the crystallographic structure of the alloys.

### 3.2. Polarization measurements

As the first step in the electrochemical evaluation of this material, the HER on NiFeZn was studied by steady state current-potential experiments in alkaline solutions at different temperatures. Fig. 3 shows the Tafel diagrams at different temperatures, and the Tafel parameters are presented in Table 1. It is interesting to note that the results in Fig. 3 show only one Tafel slope with a value of 52–67 mV dec<sup>-1</sup> depending on temperature. In this sense, the behavior is nearer that of the NiZn codeposits [7] than that of the NiFe codeposits [12], particularly because of the fact that the last material presents two Tafel slopes. For many materials based on Ni, it has been observed that the Tafel slope

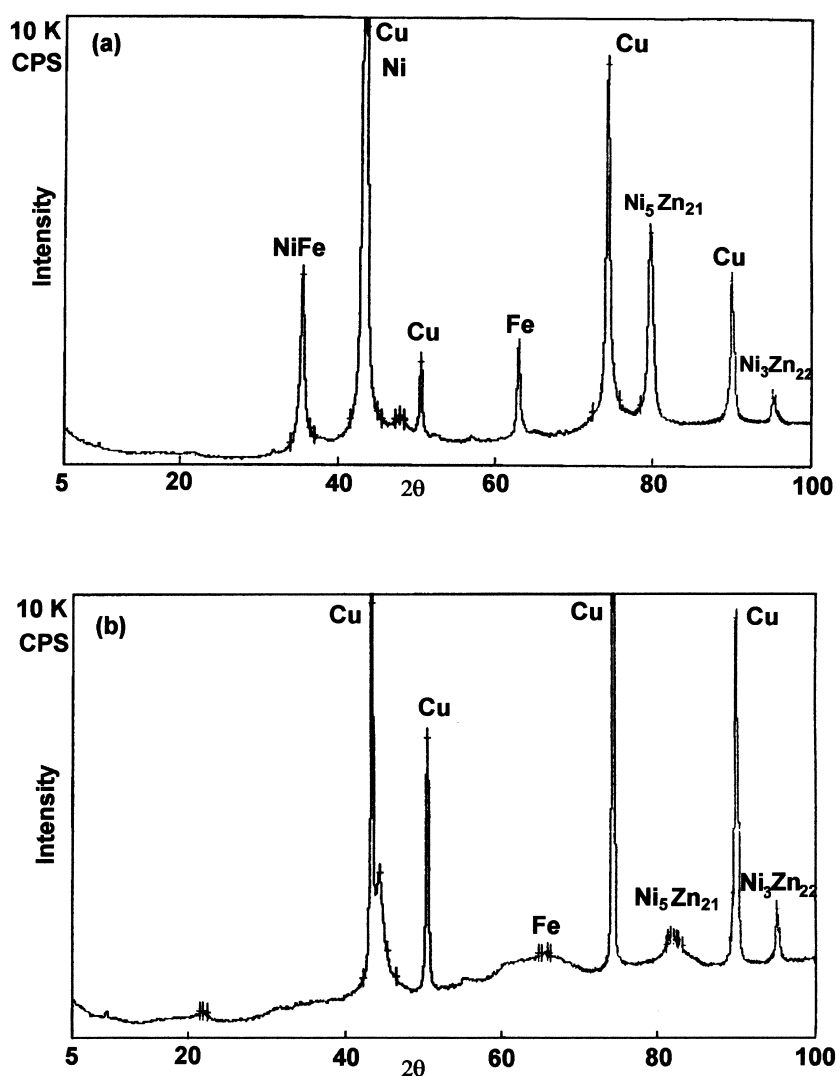


Fig. 2. X-ray diffractograms for NiFeZn electrodes: (a) before and (b) after leaching.

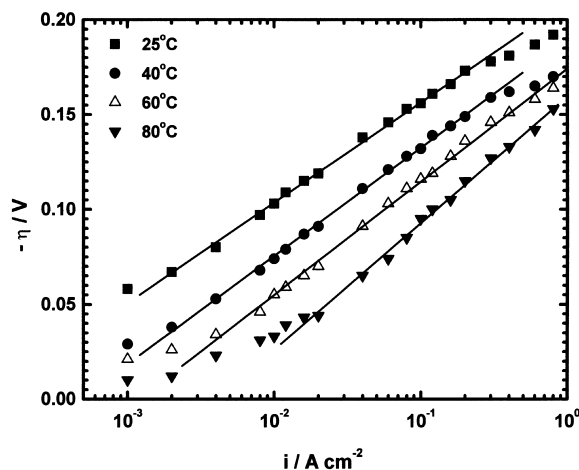


Fig. 3. Tafel plots in 1 M NaOH for different temperatures for NiFeZn.

is almost independent of temperature or even decreases with increasing temperature [7,9,12,13]. This behavior can be considered anomalous in the sense that classical electrochemical theory (Butler–Volmer equation) predicts that the Tafel slope for a single electron transfer should increase with temperature. Here the Tafel slopes on NiFeZn definitely increase with temperature as predicted by theory. Tafel slopes for NiFeZn are similar to those observed for NiFe at low current densities [12], but on this last material there is a marked increase in the slope at higher current densities ( $> 100 \text{ mA cm}^{-2}$ ) in the operational region of the cathode. As a whole, the Tafel behavior is similar to that reported for NiZn [7]. On this material only one slope is observed but, in contrast, there is a much smaller dependence with temperature for NiFeZn. These comparisons show that although the Fe content of the deposits is small, its presence in the deposit is important enough to produce differences in the observed Tafel slopes, which are beneficial in the operating current density region of the material in water electrolysis.

The appreciable electrocatalytic activity of this ma-

terial for the HER is revealed by the Tafel plot at  $80^\circ\text{C}$  shown in Fig. 3. This plot shows that at  $135 \text{ mA cm}^{-2}$  the overpotential is only 104 mV which compares very favorably with the value of more than 400 mV observed for mild steel under the same conditions [11]. The comparison is still favorable for this material with respect to other nickel alloys investigated previously: NiS, 208 mV at  $70^\circ\text{C}$ ; NiSn, 260 mV at  $70^\circ\text{C}$ ; NiFe, 155 mV at  $70^\circ\text{C}$  [14].

From the values of the exchange current density ( $i_0$ ) presented in Table 1 for different temperatures, an Arrhenius plot was constructed, as shown in Fig. 4. From this plot, the activation energy for the HER was calculated as being  $62 \text{ kJ mol}^{-1}$ . This value is much higher than the value for both NiZn ( $39 \text{ kJ mol}^{-1}$ ) [7] and NiFe ( $31 \text{ kJ mol}^{-1}$ ) [12] and shows that the mechanistic characteristics of the HER on this material cannot be deduced from those of the corresponding binary codeposits. The implications of this higher value of the energy of activation could only be evaluated if the details of the kinetics and mechanism of the reaction were known.

Even though the Tafel plots (Fig. 5) demonstrate clearly the good catalytic activity of the material, a continuous operation test is necessary to evaluate the stability of the codeposit. For this purpose, the material was operated as a cathode for 200 h at a current density of  $135 \text{ mA/cm}^2$  at room temperature, in a cell similar to that used for the electrochemical studies. The result is shown in Fig. 5. Apart from a slight loss of activity during the first few hours, which shows signs of recovery at longer times, the overpotential was stable for the duration of the experiment. The value of the overpotential is greater than that observed from the Tafel plots because in the continuous operation test only the stability was under consideration and the

Table 1  
Tafel parameters for the HER on a NiFeZn electrode, in 1 M NaOH at different temperatures<sup>a</sup>

$T$ ( $^\circ\text{C}$ )	$b$ ( $\text{mV dec}^{-1}$ )	$i_0$ ( $\text{A cm}^{-2}$ )	$\eta_{135}$ (V)
25	52	$6.618 \times 10^{-5}$	0.162
40	54	$3.634 \times 10^{-4}$	0.140
60	62	$1.211 \times 10^{-3}$	0.122
80	67	$3.778 \times 10^{-3}$	0.104

<sup>a</sup>  $b$  is Tafel slope,  $i_0$  is exchange current density,  $\eta_{135}$  is overpotential at  $135 \text{ mA cm}^{-2}$ .

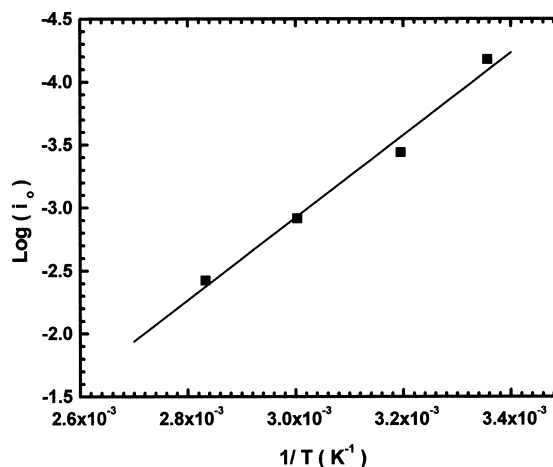


Fig. 4. Arrhenius plot from the values of  $i_0$  obtained from the plots of Fig. 3.

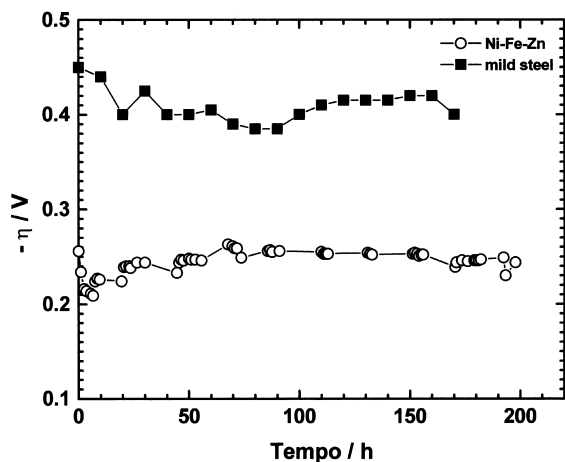


Fig. 5. Potential–time characteristics for (○) NiFeZn in 1 M NaOH at 25°C and (■) mild steel in 6 M KOH at 70°C, under a cd of 135 mA cm<sup>-2</sup>.

ohmic drop was not compensated in a cell with a very unfavorable geometry. In spite of this, the overpotential is significantly lower than the value of ~400 mV observed for mild steel at 70°C, shown for comparison at the same figure.

#### 4. Conclusions

This work shows that there are some practical difficulties in electrodepositing a ternary alloy NiFeZn with substantial amounts of Fe from the baths used in this work. However, even with low contents of Fe, the alloy shows promising results when examined as a cathode in alkaline water electrolysis. The overpotential for the HER is significantly lower than that observed on the traditional materials (mild steel, Ni) and the deposit presents good stability.

#### Acknowledgements

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