



Electrodeposition of iron fragile layer on nickel substrate with emphasis on iron powder production

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Abstract

The study of galvanostatic iron electrodeposition on nickel substrate was carried out in order to establish the most suitable experimental conditions to obtain pure iron fragile layers to be removed and transformed into powder. Under current density of 40 mA cm⁻² the deposits obtained were satisfactory to be transformed into a powder. In the light of the cathodic polarization phenomena and Scanning Electron Microscopy (SEM) graphs an explanation has been offered for the various trends observed during the investigation. The optimum storage conditions for the iron powder was found to be in vacuum using the Schlenk technique. The results led to conclude that the use of stainless steel as anode must be avoided since the presence of Mn is not beneficial for the performance of iron electrodes in charge/discharge reactions in Ni/Fe batteries. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Fragile iron deposits are currently under study in our, as well as in other laboratories [1–6], because of their potential application in the alkaline batteries area [7–11], production of permanent magnets [12–16], various alloys [17] and mixed ferrites [18], which require high purity. Iron fragile deposits can be produced by electrolysis, directed reduction of iron minerium, carbonyl method and by autoclave reduction [19–21]. The advantage in producing iron powder by electrolysis is the high specific area which increases the catalytic activity and its purity. In previous studies, [6] we have described the production of iron films on aluminum cathode using iron chloride solution. The iron deposits obtained were contaminated by 0.1% aluminum which is higher than the acceptable value of 0.01% [22]. It was observed that the presence of aluminum species in the deposit has a detrimental effect especially on the iron electrode. The harmful effect on the capacity and charge retention of iron electrodes is due to the reaction

between Al⁺³ and OH⁻ ions of the electrolytic solution which produces [Al(OH)]₄⁻. In addition to former studies, in this paper the obtainment of fragile iron deposits is reviewed with particular emphasis on the optimization of the experimental conditions, using nickel cathode and stainless steel as anode.

2. Experimental

The electrochemical data were obtained using a PAR model 173 potentiostat/galvanostat and a plotting system recorder. Measurements have been carried out in a 1.5 M FeCl₂ at pH = 1.5 with HCl using a cell containing a normal calomel electrode as reference electrode, stainless steel sheet as auxiliary electrode and a nickel sheet or rotating disc as working electrode. The 304 stainless steel sheet, from Villares, contained ≤ 0.08% C, ≤ 2% Mn, 0.045% P, 0.03% S, ≤ 1% Si, 18.3% Cr and 8.5% Ni. The nickel substrate, from Aldrich, was 99.99% of purity. Plating was performed at room temperature with a magnetic stirrer controlled at about 1000 rpm. The polarization curves were obtained using a nickel sheet with an area of 12 cm². The range of deposition current density was 6–59

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mA cm^{-2} . Potentiodynamic measurements were carried out using a rotating disc electrode of nickel with an area of 0.315 cm^2 inserted in an epoxy resin. Immediately prior to the electrochemical measurements the nickel electrodes surfaces were ground with 600 emery paper and rinsed with distilled water.

Scanning Electron Microscopy (SEM) micrographs were taken with a Carl Zeiss, Model DMS 940A electron microscope with 4 nm of resolution connected to an X-ray microanalysis system, Model AN 10/55S. X-ray analyses were taken with a diffractometer Model HZ64C. The quantitative analysis by Atomic Absorption Spectrophotometry (AAS) was carried out in an Interlab Spectrophotometer Model AA12/1475.

The surface area of the iron powder was determined by the BET method on a CG 2000 instrument using nitrogen.

3. Results and discussion

Fig. 1 shows the polarization curves of iron deposition with and without stirring of the deposition bath. The deposition potential shifts to more positive values when the bath is stirred. These results can be attributed to the decrease in the effective thickness of the diffusion layer which leads to an increase in the diffusion rate. Consequently, the iron ions relative concentration in this layer

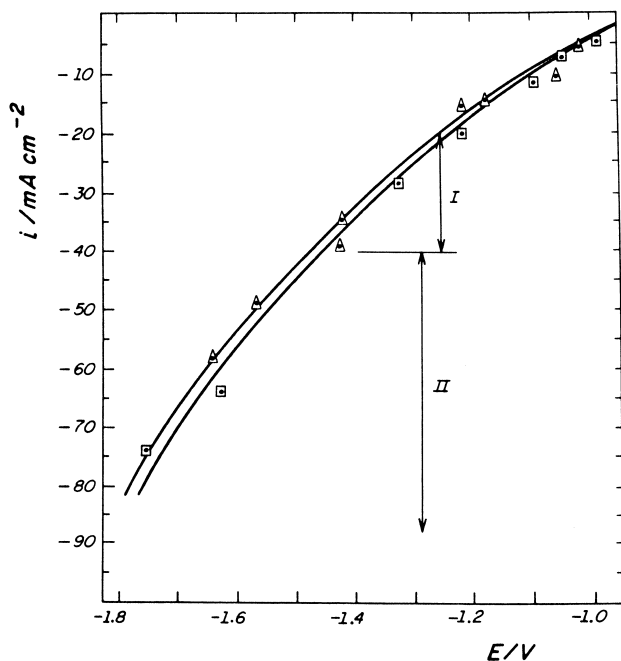


Fig. 1. Steady state polarization curves for the Fe electrodeposition from $1.5 \text{ M FeCl}_2 \cdot 4\text{H}_2\text{O}$ at pH 1.5 with HCl solutions (Δ) without, (\square) with magnetic stirring (1000 rpm).

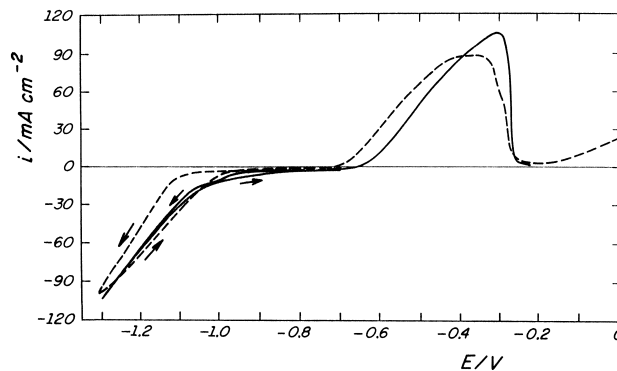


Fig. 2. E/i Potentiodynamic profiles of iron electrodeposition/electrodissolution process, $v = 10 \text{ mV cm}^{-1}$; electrolytic solution $1.5 \text{ M FeCl}_2 \cdot 4\text{H}_2\text{O}$ at pH 1.5, (---) without, (—) with magnetic stirring (1000 rpm).

increases, suggesting that the process is controlled by mass transport. Adherent iron films were obtained by low current densities (region I) but above 40 mA cm^{-2} the films were fragile (region II).

The iron deposition voltammogram shown in Fig. 2 presents typical features of a nucleation process: an increase in current after an induction time and a current loop between the forward and reverse direction. By increasing the bath stirring the iron deposition overpotential (η_d) was shifted towards less negative values from -0.45 V to -0.35 V . The observed changes show that the deposition process is controlled by mass transport in agreement with the results obtained in Fig. 1.

From the above results the value of current density of 0.18 A cm^{-2} has been chosen to verify the best storage conditions of the iron powder. The fragile film obtained at 0.18 A cm^{-2} was washed with doubly distilled acetone and dried under an N_2 atmosphere. The iron powder was obtained by grinding the fragile iron in an agata mortar under an N_2 atmosphere. Subsequently, the iron powder was submitted to three storage methods: (1) in 3.0 M NaOH solution, (2) in 3.0 M NaNO_3 solution and (3) under vacuum using the Schlenk technique. In the first method, the iron oxidation was observed after 25 days of storage while in the second one the oxidation was observed after 1 day. The optimum storage condition for the iron powder was under vacuum using the Schlenk technique. In this condition, the powder was kept stable.

Fig. 3 shows the physical characterization of the electrodeposited iron film at 0.18 A cm^{-2} and stored under vacuum by SEM graphs. It can be seen that the iron deposit presents a nodular structure (Fig. 3a) with many cracks in the nodules (Fig. 3b). The cracks were found to be the result of high tension present during the formation of the iron layer probably due to the presence of Cl^- ions in the electrolyte [19].

Fig. 4 shows that the region between the nodules present needles like structures.

Energy dispersion X-ray (EDX) analyses show that the nodular (Fig. 5a) and needle like structures (Fig. 5b) of the iron deposit present Cr, Mn, Ni, Cl and S as impurities. The contaminant species Cr, Ni, S and Mn were produced by the anode dissolution while the source of Cl species was the deposition bath. The AAS analyses showed that the iron powder impurities were consisted of 0.06% Mn, 5.2% Cr and 0.56% Ni. The presence of Mn in the iron is not beneficial for the Fe/NiOOH battery plates since it can produce self-discharge in the iron electrode [9]. On the

other hand the Ni presence has not damaged on the iron electrode since the negative plate substrate of this battery consists of nickel. There is no evidence that Cr has a harmful effect on the batteries. Even in the literature, the harmful effects of Cr have never been described [22]. The presence of S in the iron is favorable for a better work electrodes due to its important role as an activating agent [9]. The Cl species are supposed to be detrimental to the nickel oxide electrode since chloride corrodes the inactive supporting parts of such electrode. Nevertheless, it has

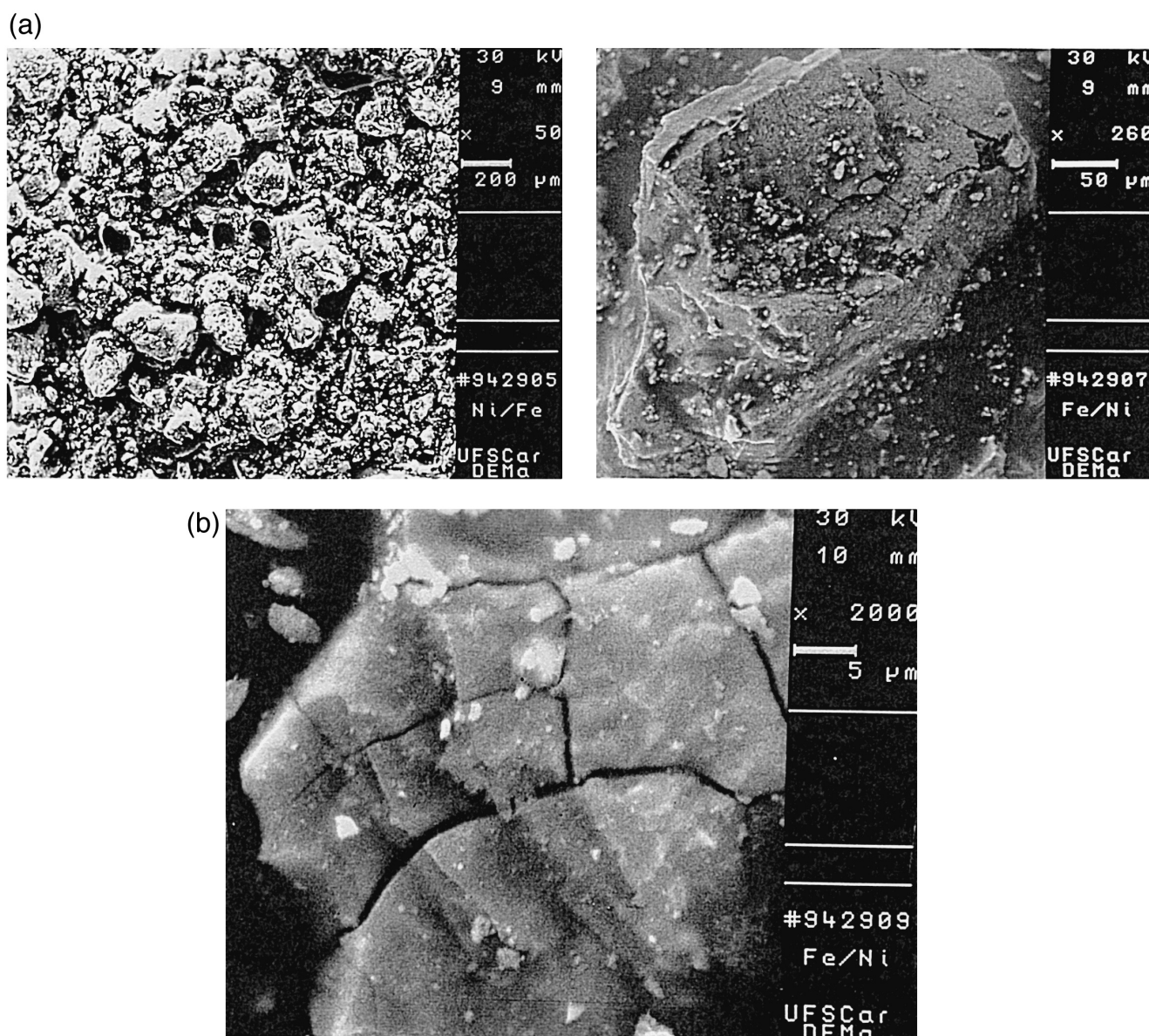


Fig. 3. SEM graphs of powder iron in the nodular region; electrolytic solution 1.5 M $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ at pH 1.5, $i_d = 0.18 \text{ A cm}^{-2}$. (a) Nodular structure, (b) nodular structure with cracks.

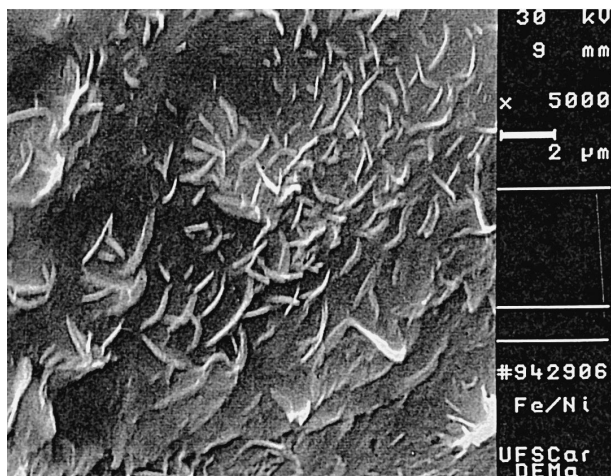


Fig. 4. SEM graphs of powder iron in the needles region; electrolytic solution 1.5 M $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ at pH 1.5, $i_d = 0.18 \text{ A cm}^{-2}$.

been reported that as much as 10 g KCl l^{-1} has no significant effect on the cycle life of nickel–iron batteries [22].

Fig. 6 shows X-ray diffraction patterns of iron powder. In Table 1, the main experimental and theoretical [23–25] results of the iron powder interplanar distances (d) have been compiled for comparison. These results show that the iron powder consists principally of α -Fe but the presence of Fe–Ni alloy can not be refused. The peaks $d = 1.174$ ($I/I_0 = 20\%$) and $d = 1.174$ ($I/I_0 = 27\%$) were attributed to α -Fe while the peak at $d = 0.906$ ($I/I_0 = 12\%$) was attributed to the Fe–Ni alloy. Otherwise the peak at $d = 2.048$ ($I/I_0 = 100\%$) can be attributed to α -Fe $d = 2.030$ ($I/I_0 = 100\%$) or to nickel $d = 2.034$ ($I/I_0 = 100\%$).

BET specific surface area shows that the iron powder has an area of $2.1 \text{ m}^2 \text{ g}^{-1}$ which is a reasonable value for the optimization of the experimental conditions for the manufacture of the Fe/NiOOH battery negative plates [10].

4. Conclusions

Galvanostatic results have shown that the use of current density equal or higher than 40 mA cm^{-2} leads to the

Table 1

Experimental interplanar distances (d_{exp}) of the X-ray diffraction peaks of iron powder and the corresponding theoretical interplanar distances (d_t) [23–25]

| d_{exp} | $(I/I_0)_{\text{exp}}$ (%) | α -Fe | | Fe/Ni | | Ni | |
|------------------|-------------------------------|--------------|--------------------|-------|--------------------|--------|--------------------|
| | | d_t | $(I/I_0)_t$ (%) | d_t | $(I/I_0)_t$ (%) | d_t | $(I/I_0)_t$ (%) |
| 2.048 | 100 | 2.030 | 100 | 1.270 | 50 | 2.034 | 100 |
| 1.174 | 20 | 1.170 | 30 | 0.900 | 30 | 1.246 | 21 |
| 1.174 | 27 | 1.170 | 30 | 0.900 | 30 | | |
| 0.906 | 12 | 1.170 | 30 | 0.900 | 30 | 0.8810 | 4 |

successful production of fragile iron layers when the nickel electrodes are polarized in a $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ deposition bath.

The optimum storage conditions for the iron deposit were obtained by washing with doubly distilled acetone, drying under an N_2 atmosphere and stored under vacuum using the Schlenk technique. Physical and chemical characterization methods have shown that the iron deposit has been contaminated by stainless steel anode. Since the Mn presence in the stainless steel anode is not beneficial for

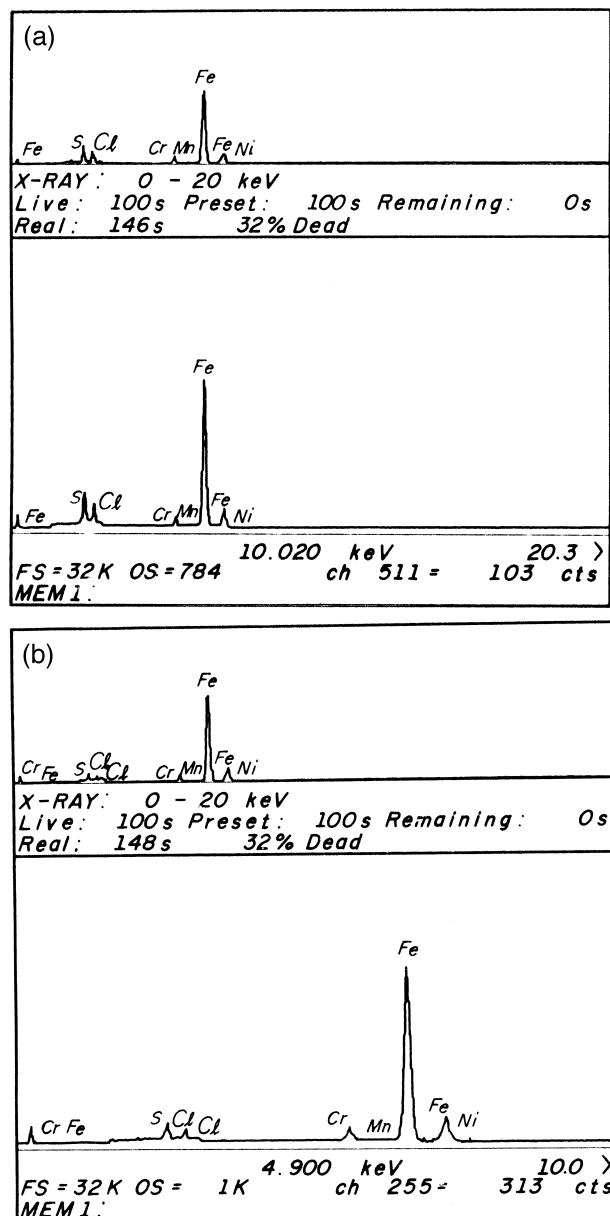


Fig. 5. EDX analysis of powder iron in the region of (a) the nodular section; (b) the needle-like structure. Electrolytic solution: 1.5 M $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$; pH = 1.5; $i_d = 0.18 \text{ A cm}^{-2}$.

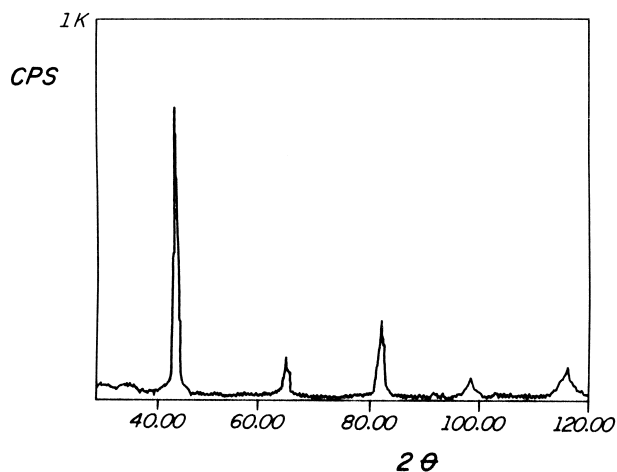


Fig. 6. X-ray analysis of powder iron; electrolytic solution 1.5 M $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ at $\text{pH} = 1.5$, $i_d = 0.18 \text{ A cm}^{-2}$.

the performance of iron electrodes, in Ni/Fe batteries it must be avoided.

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