Electrodeposition of Iron from Aqueous Ferrous Sulphate Solutions

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Effect of iron concentration, temperature and pH on the cathodic polarization curves at iron cathode in pure $FeSO_4$ solutions has been studied. The current efficiency for iron deposition was determined as a function of ferrous ion concentration, temperature and pH of the elctrolyte, cathodic current density and addition of Fe^{3+} ions to the catholyte. Based on these, optimum conditions for the electrodeposition of Iron have been proposed.

Practically whole of iron and its alloys, at present, are being produced by pyrometallurgical process. Iron thus produced invariably contains varying amount of impurities like C,S,P and Si. Pure iron (99.95%) can be produced by electrolytic methods. Metal so produced has a number of valuable properties such as high degree of plasticity, high magnetic permeability and is very valuable for industries like electronics and telecommunications, powder metallurgy etc.

Electrodeposition of iron has been studied over a century(1,2). Kudryavtsev(3) obtained metallic iron from a bath of composition, $FeSO_4$ $7H_2O$ 70 g/l NaCl 110 g/l,pH 4.5-5.3,T = 70-80°C, c.d. 10-40 A/dm . Different baths based on Sulphate-chloride mixtures or entirely chlorides have been tried (4-9). The authors claimed the purity of the metal to be 99.9%. The main drawback of the chloride bath is the evolution of chlorine at the anode which pollutes the atmosphere and makes the working conditions harmful and aggressive.

Study of cathodic process during the electrolysis of aqueous $FeSO_4$ solutions was undertaken with a view to find out optimum conditions for the electroproduction of iron.

EXPERIMENTAL

Polarization measurements were conducted in a H-type glass electrolytic cell, with a porous diaphragm. The capacity of the cell is 200 ml. The electrodes were cut from a cylindrical steel rod of 10 mm diameter. These were inserted in the rubber corks closing tightly the side tubes of the electrolysis cell. The working surface of the electrode was ground and polished before use. The electrolysis cell along with reference electrode (SCE) was kept in a water thermostat controlled to ±0.5°C. The temperature correction of the calomel electrode was made using data from the Hand book of Analytical Chemistry by Ju.Lurie, 1975.

The working surface of the electrode was covered by electrolytically deposited iron from 1 M $FeSO_4$ solution at 60°C and at c.d of 350 A/M^2 . The electrode potentials were measured on OSAW.VP 6995 potentiometer with an accuracy upto 10^{-4} volt.

The current efficiency was determined in the same cell using a platinum cathode which was earlier covered with a compact layer of electrolytic iron. A steady d.c was drawn from a lead accumulator. Current consumption was determined from the increase in platinum cathode weight. Platinum wire served as an anode and 1 N Na_2 SO_4 as an anolyte.

The chemicals used were all analytical grade. The solutions were prepared by dissolving solid salts in distilled water. The pH adjustments were made by ammonium hydroxide and sulphuric acid additions.

RESULTS AND DISCUSSION

POLARIZATION CURVES

Examination of polarization curves (Fig. 1A) shows that the discharge of Fe^{2+} takes place earlier than that of H^+ ions. With the increase of iron concentration, the cathodic potential moves to more + ve direction.

The two electrochemical reactions taking place are :

$$Fe^{++} + 2\,e \rightleftharpoons Fe \;; \qquad E^\circ = -0.44\ V$$

$$2H^+ + 2\,e \rightleftharpoons H_2\,(g); \qquad E^\circ = \pm 0.000\ V$$

During the electrodeposition hydrogen ion discharge potential not only depends upon the aH^+ but also on the over potential of hydrogen discharge on iron. Hydrogen potential at a given current density (i) at 25°C is

$$E_H = +0.059 \log a_{H^+} \quad — \quad (a + b \log i)$$

where $b = 2.3\,RT/\alpha F = 0.118$ and 'a' is a constant the value of which depends upon the nature of metal. The reults in fig. 1a shows that the over

potential of iron deposition is less than the hydrogen over potential on iron.

In Fig 1B is shown the effect of pH on the cathodic polarization curves. With the increase in pH of the electrolyte, the cathodic potential shifts to more positive values. The rate of potential shift ($\partial E/\partial$ pH) is 0.04 V per pH unit. At lower pH values, the evolution of hydrogen is observed to be higher.

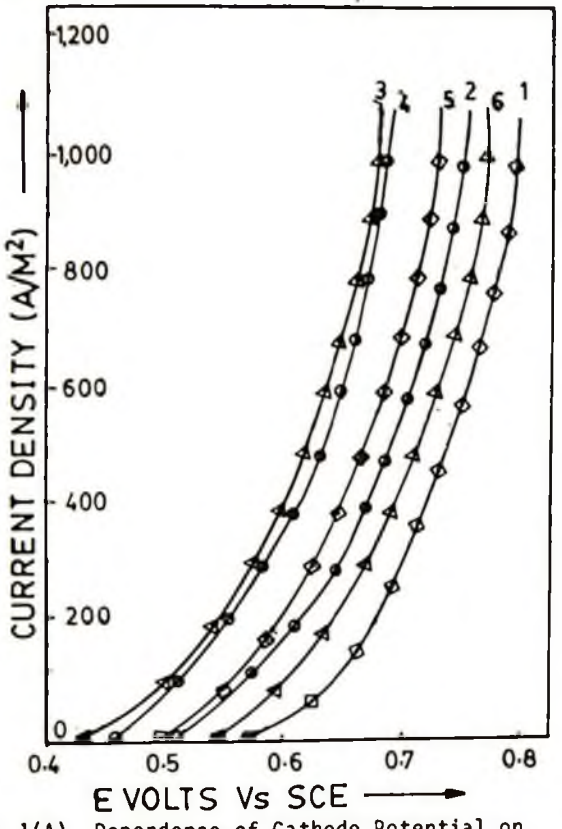


Fig. 1(A) Dependence of Cathode Potential on Current Density, pH and concentration of ferrous sulphate

Temp. 20°C pH (for 1,2,3) : 2.5

1 : 1 m/l Na_2SO_4
2 : 0.1 m/l $FeSO_4 7H_2O$
3 : 1 m/l $FeSO_4 7H_2O$
4 : pH 1.0
5 : pH 2.5
6 : pH 3.5

Fig. 1C, shows that the iron cathodic potential shifts to more + ve values with rise in temperature. The rate of potential shift ($\partial E / \partial t$) is 0.048 V/°C.

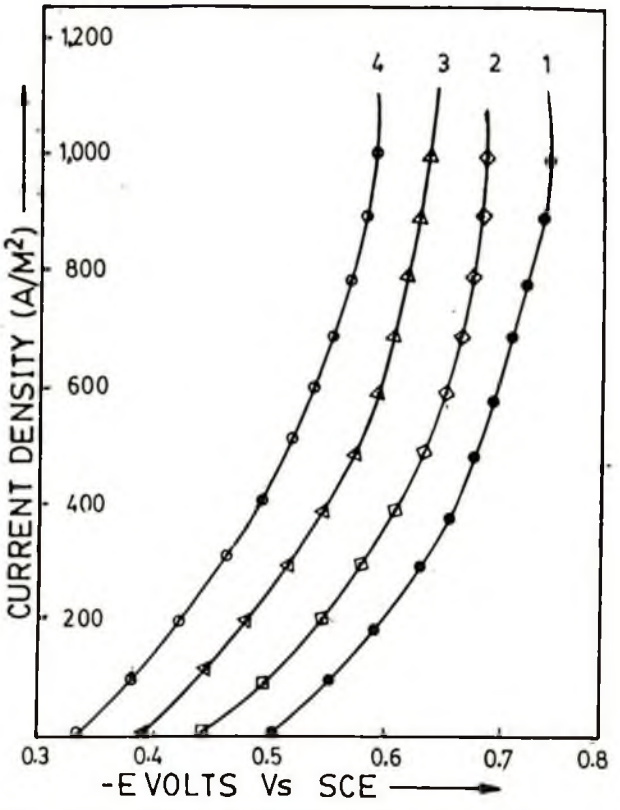


Fig. 1(B) Effect of Temperature on Cathodic Potential at pH = 2.5 and concentration of ferrous sulphate 0.1 m/l
1 = 20°C 3 = 60°C
2 = 40°C 4 = 80°C

CURRENT EFFICIENCY OF IRON DEPOSITION

Maximum iron current efficiency was attained in $FeSO_4$ (1 m/l) solution without any added electrolytes. With the decrease of Fe^{2+} concentration, cathodic polarization increases. cathodic potential shifts to more negative values which facilitates the simultaneous discharge of H^+ ions; at very low iron concentrations (<0.05M $FeSO_4$) the process of hydrogen ion discharge plays significant role and the current efficiency does not cross 50% while at concentration (~1.0 m/l) it is 93% (fig 2). Current efficiency slightly decreases as $FeSO_4$ concentration is raised above 1.0 m/l. This is perhaps due to the lowering of activity of iron ions and to the increase in the viscosity of solutions.

Simultaneous discharge of hydrogen ions along with iron ions, affects the properties of the deposit. According to Baimakov (10) hydrogen gets dissloved in iron and forms solid solutions and also gets adsorbed on the boundaries of crystals. Uneven distribution of hydrogen in the deposited iron creates internal stress which makes the deposits brittle. The hydrogen adsorbed on the iron.

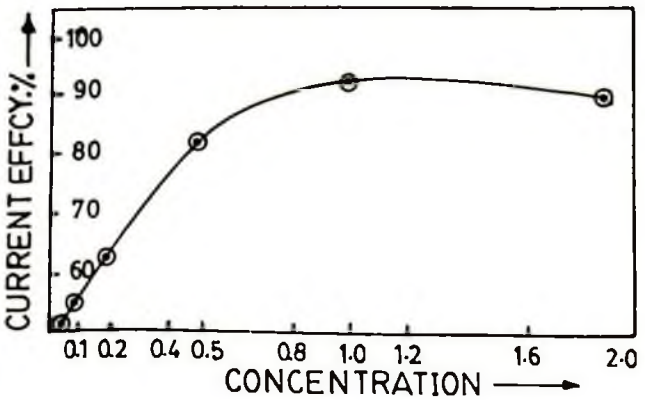


Fig. 2 Effect of concentration of ferrous sulphate on current efficiency during iron deposition at T = 20°C ; c.d = 350 A/M pH = 2.5°C

crystal boundaries is expelled by vaccum heating. The removal process of hydrogen from the solid phase starts at 700°C and is completed at 850-900°C.

The effect of temperature on iron current efficiency is given in Table 1

TABLE 1

ELECTROLYTES 1.0 m/l $FeSO_4$; c.d. = 350 A/M^2 ; pH = 2.5

Temperature°C	20	35	50	70
Current Efficiency %	93	95	96.5	98

The iron current efficiency rises with temperature. The cathodic deposit obtained from hot solutions is more dense and bright.It contains much less adsorbed and dissolved hydrogen. The current efficiency increases due to the increase in conductance of the solution. Hence it is advantageous to conduct electrolysis at 60°C, particularly so since no special preheating is required. The electrolyte under factory scale production conditions is preheated by electrolysis current. As the temperature rises, there is a drop in bath voltage, both as a result of the + ve shift in cathodic potential by about 0.1 V, and also because of the reduction in the potential drop in the electrolyte.

The effect of current density on iron current efficiency is given in Table 2.

TABLE 2

$FeSO_4$ 1.0 m/l; T = 25°C ; pH = 2.5

Current density A/M^2	100	200	300	400	500	600
Current efficiency%	65	83	92	95	97	98

The iron current efficiency increases with the increase in cathodic current density. It seems that the overpotential of hydrogen ion discharge at iron cathode at higher cathodic current density increases more than that for iron ion discharge. Probably this fact favours the increase in iron current efficiency.

The effect of pH and addition of Fe^{+++} ions to $FeSO_4$ electrolyte is shown in fig. 3. Iron current

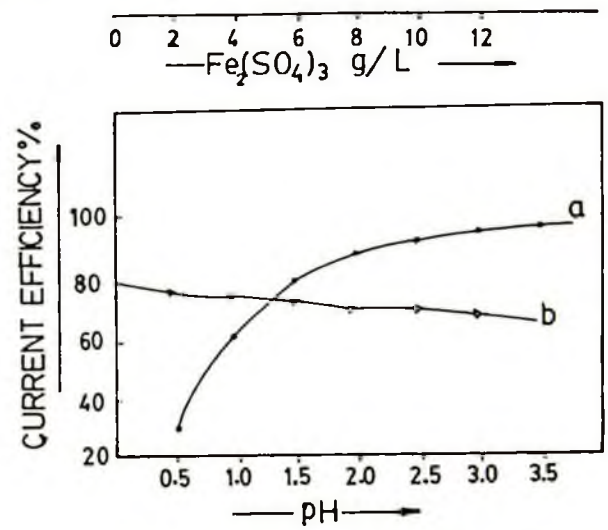


Fig. 3 Effect of pH (a) and Fe addition (b) on current efficiency during electrodeposition of iron at T = 20°C; c.d = 350A/M^2 ; pH = 2.5 and concentration of $FeSO_4$ $7H_2O$ = 1M/L

efficiency increased with pH from 30% at 0.5 pH to 95% at 3.5 pH. This is partially due to the +ve shift in the cathodic potential at higher pH values. However, the pH of the electrolyte could not be raised beyond 3.5 because of the hydrolysis of $FeSO_4$ solution.

During elctrolysis of $FeSO_4$ solutions, every effort was made to avoid oxidation of Fe^{++} to Fe^{+++} Nevertheless aereal oxidation did take place. Although anode compartment containing Na_2 So_4 solution was separated from the catholyte, it has been observed that small amounts of $FeSO_4$ diffused to anode compartment and got oxidized to ferric ions. On backward diffusion to the cathode compartment, the ferric ions must be first reduced to ferrous and then to metallic iron.

From the fig. 3, it is evident that ferric ions decrease the current efficiency significantly. It is advisable to separate anodic and cathodic compartments so as to avoid the presence of ferric ions around cathode while electrolysing $FeSO_4$ solutions.

CONCLUSIONS

On the basis of experimental results it can be concluded that iron should be electrodeposited under the following conditions :

$FeSo_4$ concentration = 1.0 m/l ; c.d. 350-600 A/M^2, $t° = 50°C$,, pH = 3.5; Anodic and Cathodic compartments should be separated by a porous diaphragm.

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