

Magnetic Field Effect on Electrode Reactions. III. Effects on the Anodic Polarization of an Iron Electrode in an Iron(III) Chloride Solution under Potentiostatic Conditions

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Under potentiostatic conditions, the anodic current through a working electrode of iron in a stirred iron(III) chloride solution increases when exposed to static magnetic fields. This effect depends on the magnetic flux density, the electrode potential, the electrolyte concentration and the stirring rate. The effect occurs only within the prepassive potential range of the iron electrode. Also, a possible interaction mechanism is proposed which indicates that the observed results can be explained in terms of the force on the transport of Fe^{3+} ions to the electrode due to the high discontinuity in the magnetic field strength at the interface between the iron electrode and the test solution.

The purpose of this study is to examine experimentally the effects of static magnetic fields on the anodic polarization of an iron electrode in contact with a stirred iron(III) chloride solution. The hypothesis is that an applied magnetic field will tend to increase the metal dissolution as a result of an increased rate of transfer of Fe^{3+} ions toward the iron electrode. Also, a suggestion of a possible interaction mechanism is given.

Results from experimental and theoretical studies indicate that magnetic fields exert a perceptible influence on the electrode processes in electrochemical cells. The effect has been explained in terms of magneto-hydrodynamics.^{1–9}

The present study is based upon results from two previous experimental studies. Results from the first study show that static magnetic fields increase the rest potential of a ferromagnetic iron electrode in a paramagnetic iron(III) chloride solution under open-circuit conditions. The observed effect increased both with the magnetic flux density and with the electrolyte concentration, and it showed a dynamic behavior.¹⁰ Results from the second study show that static magnetic fields increase both the anodic and the cathodic electrode potentials of the iron electrode in stirred iron(III) chloride solutions under galvanostatic conditions. The increase in the anodic electrode potential was observed only within the pre-passive potential region of the iron electrode, and the increase in the cathodic electrode potential was associated with limiting current density. However, the

observed effects were found not to be explained in terms of magneto-hydrodynamics.¹¹

Preconsiderations

In this section, some considerations concerning polarization of an iron electrode in a stirred iron(III) chloride solution when exposed to a magnetic field, are given. Also, a possible interaction mechanism is proposed.

The electrode is mounted vertically into the solution, and the magnetic field is introduced perpendicular to the iron electrode. A positive x -direction is defined as the perpendicular direction from the electrode into the solution.

Electrochemical aspects. According to the theoretical considerations in the previous study, it is assumed the main anodic and cathodic electrode reactions are^{2,12}



When two or more electrode reactions take place simultaneously, a mixed potential, i.e. a corrosion potential, is developed. The overall electrode reaction is characterized by the polarization (η), which here is defined as the difference between the electrode potential with a net current flow, and the corrosion potential with no net current flow.¹³

The polarization is determined by the slowest of the electrode reactions. Two of the rate-control reactions are the charge-transfer and the mass-transport controlled processes.¹³ The polarization due to the charge-transfer reaction is determined by the hindrance of rate of transfer to charge carriers between the electrode and the solution.¹³ The mass-transfer-controlled polarization is determined by the hindrance of the transport of Fe^{3+} ions from the bulk to the iron electrode where they receive electrons from the electrode. This mass transport involves the existence of a stagnant layer of thickness (δ), the Nernst diffusion layer, near the electrode surface where the Fe^{3+} concentration ($C^{\text{Fe}^{3+}}$) is less than the bulk concentration ($C_b^{\text{Fe}^{3+}}$). In unstirred solutions, $\delta \approx 0.0004$ m. In stirred solutions, δ decreases and the electrode current increases with increasing stirring rate.^{14,15}

The electrode currents due to the metal dissolution in reaction (1) (I_m), and the electron transfer in reaction (2) (I_{corr}), which is controlled by the diffusion, are given by^{11,14}

$$I_m = I_{\text{corr}} \exp\left(\frac{F}{2RT} \eta\right) \quad (3)$$

$$I_{\text{corr}} = -I_L = \frac{FD}{\delta} C_b^{\text{Fe}^{3+}} \quad (4)$$

where I_{corr} is the corrosion current density, which is supposed to be equal to the limiting current density I_L , F is the Faraday constant, R is the universal gas constant, T is the temperature in K, η is the polarization, D is the diffusion coefficient for Fe^{3+} ions, δ is the thickness of the diffusion layer, and $C_b^{\text{Fe}^{3+}}$ is the bulk concentration of Fe^{3+} ions.

According to the cathodic reaction (2), and the anodic metal dissolution, there will be a decrease in the Fe^{3+} concentration within the solution. Assuming that Fe^{3+} ions are consumed at their diffusion limited rate, the change in the Fe^{3+} concentration with time, is given by¹⁵

$$\frac{dC_b^{\text{Fe}^{3+}}(t)}{dt} = -D \frac{A}{V_e} \frac{C_b^{\text{Fe}^{3+}}(t)}{\delta} \quad (5)$$

where A is the electrode area, and V_e is the volume of the electrochemical cell.

Integration of eqn. (5) between $t = 0$ and t gives the Fe^{3+} concentration in the cell solution as a function of time:

$$C_b^{\text{Fe}^{3+}}(t) = C_b^{\text{Fe}^{3+}}(t=0) \exp - \frac{AD}{V_e \delta} t \quad (6)$$

The bulk concentration of Fe^{3+} ions ($C_b^{\text{Fe}^{3+}}$) in eqn. (4) is replaced by the expression in eqn. (6).

Without exposure to a magnetic field, the mass transport takes place by three principal mechanisms: diffusion, migration (transport by an electric field) or convection

(transport by stirring).¹⁶ The total rate of transfer in the x direction (mol per s per unit area perpendicular to x), is given by

$$N_t = N_m + N_d + N_c = cu \frac{\partial U}{\partial x} - D \frac{\partial c}{\partial x} + vc \quad (7)$$

where the subscripts m, d and c indicate rate of transfer due to migration, diffusion and convection, c is the Fe^{3+} concentration, u is the mobility, U is the potential, D is the diffusion coefficient for Fe^{3+} ions, and v is the velocity of the bulk fluid due to stirring.

According to the hypothesis, the applied magnetic field will tend to increase the rate of transfer of Fe^{3+} ions toward the iron electrode (N_{mag}). The total rate of transfer will be

$$N_t = N_m + N_d + N_c + N_{\text{mag}} \quad (8)$$

The rate of transfer due to the applied magnetic field may be written as^{17,18}

$$N_{\text{mag}} = cF_{\text{mag}}u \quad (9)$$

where c is the concentration (mol per unit volume), F_{mag} is the magnetic driving force, and u is the mobility (velocity per unit force).

Magnetical aspects. The magnetic susceptibility of the ferromagnetic iron electrode is much greater than the paramagnetic iron(III) chloride solution.^{19,20} Consequently, when the electrochemical system is exposed to the magnetic field, there will be discontinuity in the magnetic field strength in the interface between the iron electrode and the solution. Suppose that 1 mol of Fe^{3+} ions are transferred from the bulk, through the diffusion layer, to the iron electrode when exposed to a magnetic field. The magnetic field strengths within the solution and the electrode are H_s and H_e , respectively. the change in the potential energy (ΔW_{mag}) for the Fe^{3+} ions due to the magnetic field, is given by²⁰⁻²³

$$\Delta W_{\text{mag}} = \frac{1}{2}(1 + \kappa)\mu_0(H_e^2 - H_b^2)V \quad (10)$$

where κ is the magnetic volume susceptibility for 1 mol of Fe^{3+} ions in solution, μ_0 is the magnetic permeability of vacuum, and V is the volume per mol of Fe^{3+} ions.

Introducing the term magnetic flux density (B), the change in the potential energy is written as²⁰

$$\Delta W_{\text{mag}} = \frac{1 + \kappa}{2\mu_0} \left[\frac{1}{(1 + \kappa_e)^2} - \frac{1}{(1 + \kappa)^2} \right] B^2 V \quad (11)$$

where

$$B = (1 + \kappa_e)\mu_0 H_e = (1 + \kappa)\mu_0 H_b$$

The magnetic driving force (F_{mag}) which tends to move ions a distance Δx , is given by²⁰

$$F_{\text{mag}} = \frac{\Delta W_{\text{mag}}}{\Delta x} = \frac{1 + \kappa}{2\mu_0 \Delta x} \left(\frac{1}{(1 + \kappa_e)^2} - \frac{1}{(1 + \kappa)^2} \right) B^2 V \quad (12)$$

Considering $\kappa_e \gg \kappa$, the magnetic force (F_{mag}) in eqn. (12) is negative. According to this, the paramagnetic Fe^{3+} ions within the bulk will experience a force that tends to increase the ion transport from the bulk through the diffusion layer, to the electrode surface where charge-transfer takes place.

Experimental

The apparatus and preparation procedure used in this study are described in the previous study.¹⁰

The potentiostat/galvanostat (Wenking MP87) was switched into the potentiostatic mode. The working electrode, the counter electrode and the reference electrode were connected to the potentiostat in conjunction with two digital multimeters (Fluke 87).

Three different kinds of experiments were carried out during this study.

(1) Current measurements as a function of the applied potential difference (-300 to 100 mV), at specified rotation speeds (0 – 2000 r.p.m.) and magnetic flux densities (0 , 400 or 800 mT). The exposure schedule for each applied potential difference was 0 , 400 , 0 or 0 , 800 , 0 mT. The time elapsed at each magnetic flux density was 1 min. The working electrode used was made of iron, and the electrolytes were 0.5 and 1 M iron(III) chloride.

(2) Current measurements as a function of the magnetic flux density (0 – 800 mT), at a specified rotation speed (120 r.p.m.) and applied potential difference (-300 , 0 , 300 mV). The exposure schedule was: 0 , 140 , 0 , 270 , 0 , 400 , 0 , 510 , 0 , 600 , 0 , 710 , 0 , 800 , 0 mT. The time elapsed at each magnetic flux density was 1 min. The working electrode of iron, and 1 M iron(III) chloride was used.

(3) Current measurements as a function of time, at specified potential differences (-300 , 0 , 300 mV), rotation speed (120 r.p.m.) and magnetic flux density (800 mT). The exposure schedule was 0 , 800 , 0 , etc. mT. The time elapsed at each magnetic flux density was 1 min. The working electrode of iron, and 1 M iron(III) chloride was used.

Each series of experiments lasted for about 40 min. Several experiments were carried out at each set of experimental conditions.

For all the experiments, the temperature was 25 ± 1.5 °C.

Results and discussion

Figure 1 shows the electrode current as a function of applied electrode potential at rotation speeds 0 , 120 and 960 r.p.m., without exposure to magnetic fields. The working electrode was made of iron, and the electrolytes were 0.5 and 1 M iron(III) chloride.

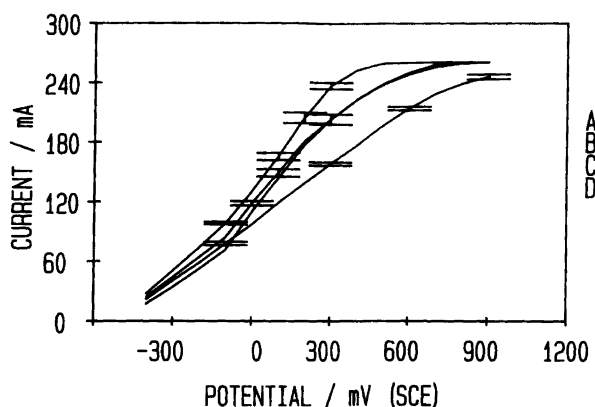


Fig. 1. The measured electrode current as a function of applied potential without magnetic field, for iron in 1 M iron(III) chloride at rotation speeds of 960 (A), 120 (B) and 0 (C) r.p.m., and in 0.5 M iron(III) chloride at 120 r.p.m. (D). Each curve represents the mean of 10 measurements.

At a specified electrode potential, the electrode current increases with increasing Fe^{3+} concentration and rotation speed, which indicate that the transport of Fe^{3+} ions toward the electrode surface, where reaction (2) occurs, is one of the potential determining factors. According to the mixed-potential theory, an increase in the reaction (2), must be followed by an increase in reaction (1), i.e. an increased metal dissolution.^{24,25} The measured saturation current was 261 mA, and with an electrode area of 4 cm², the current density is ca. 65 mA cm⁻², which is associated with the passivation phenomenon of the iron electrode.²⁵

Figures 2 and 3 show the change in the anodic electrode current as a function of applied electrode potential due to 400 and 800 mT magnetic field, at rotation speeds 120 and 960 r.p.m., respectively.

The results show an increase in the anodic current due to the magnetic field, only within the active and prepassive potential range of the iron electrode. The results indicate that the magnetic field causes an increase in the

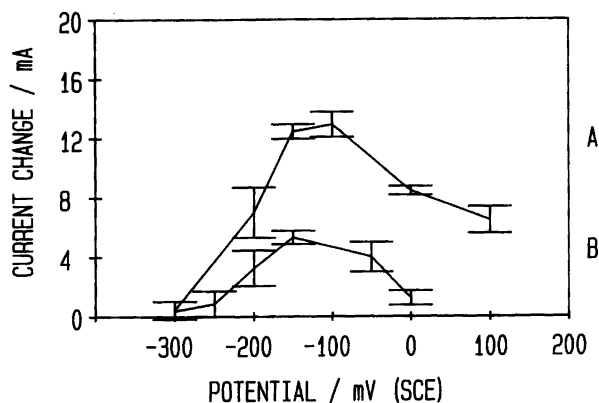


Fig. 2. The measured change in the electrode current as a function of applied potential at magnetic fields of 800 mT (A) and 400 mT (B) for iron in 1 M iron(III) chloride at the rotation speed of 120 r.p.m. Each curve represents the mean of three measurements.

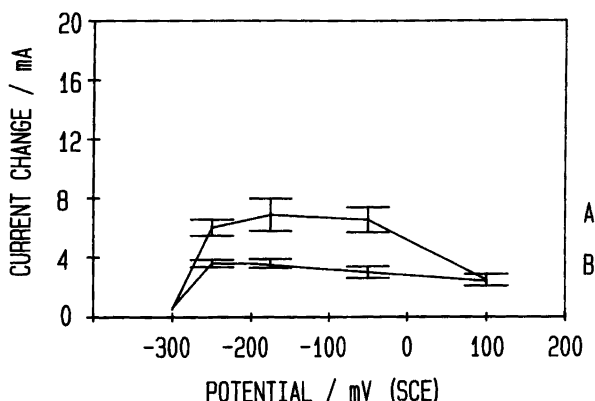


Fig. 3. The measured change in current as a function of applied potential at magnetic fields of 800 mT (A) and 400 mT (B) in 1 M iron(III) chloride, at a rotation speed of 480 r.p.m. Each curve represents the mean of three measurements.

transport of Fe^{3+} ions towards the iron electrode, where ferric ion reduction occurs, and hence an increase in the iron dissolution. This is in accordance with eqn. (12), which predicts that the paramagnetic Fe^{3+} ions within the bulk will experience a force that tends to increase the ion transport from the bulk to the electrode surface where charge-transfer takes place. Also, the results are in accordance with similar results obtained by Bhatnagar and Mathur where they observed that the reduction of ferric chloride solution containing hydrochloride with iron was accelerated by a magnetic field.²⁶ In addition, the experimental results show that the magnetic field effect depends on the electrolyte concentration, which is in accordance with eqn. (9).

However, results from all experiments show a maximum in the change in the electrode current. The maximum changes in the electrode current due to the magnetic fields at rotation speeds up to 2000 r.p.m., and at 0.5 M and 1 M iron(III) chloride, are given in Table 1.

The results in Table 1 indicate a decrease in the mag-

netic field effect with increasing stirring rate. An increase in the stirring rate will cause a decrease in the thickness (δ) of the diffusion layer, and hence an increase in the total electrode current, eqn. (4). Consequently, the relative contribution of the magnetic field effect to the total electrode current decreases with increasing stirring rate. However, according to the large variations in the measured electrode currents, and because the electrochemical behavior of iron in the prepassive potential range is not fully understood,^{12,26} no conclusions concerning any relationship between the magnetic field exposure and stirring rate can be drawn.

Figure 4 shows an increase in the electrode current as a function of magnetic flux density, at electrode potentials of 0, 300 and -300 mV. The working electrode was made of iron, the electrolyte was 1 M iron(III) chloride, and the rotation speed was 120 r.p.m.

At electrode potential of -300 mV, the net electrode current is small. At small electrode currents, the accuracy of the potentiostatic measurements is low. Consequently,

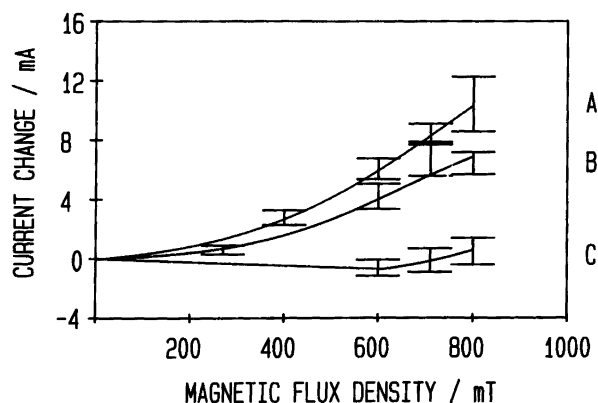


Fig. 4. The measured change in current as a function of the magnetic flux density at electrode potentials of 0 (A), 300 (B) and -300 (C) mV for iron in 1 M iron(III) chloride at a rotation speed of 120 r.p.m. Each curve represents the mean of 10 measurements.

Table 1. Mean electrode current (I) and max increase in the electrode current (ΔI_{max}) due to 400 and 800 mT magnetic fields at different FeCl_3 concentrations and stirring rates. The electrode area was $4 \times 10^{-4} \text{ m}^2$.

Stirring rate/r.p.m.	400 mT		800 mT	
	$\Delta I_{\text{max}}/\text{mA}$	I/mA	$\Delta I_{\text{max}}/\text{mA}$	I/mA
Conc. = 0.5 M				
60	2.9 ± 1.4	87.0 ± 4.0	8.1 ± 0.4	79.1 ± 16.4
120	3.4 ± 0.2	99.2 ± 1.8	10.0 ± 1.8	87.1 ± 19.0
480	3.3 ± 0.7	86.7 ± 13.4	7.1 ± 0.1	101.2 ± 1.0
2000	3.3 ± 2.3	94.9 ± 2.1	5.5 ± 2.5	109.7 ± 0.7
Conc. = 1.0 M				
0	12.9 ± 4.2	106.4 ± 18.6	12.1 ± 0.5	173.8 ± 12.3
60	7.0 ± 0.2	138.6 ± 28.0	14.7 ± 0.3	144.8 ± 10.4
120	6.2 ± 1.4	123.6 ± 12.9	13.1 ± 1.5	130.5 ± 17.9
240	7.0 ± 0.3	90.0 ± 0.6	12.4 ± 0.2	105.4 ± 10.2
480	3.6 ± 0.1	85.4 ± 5.6	8.9 ± 1.1	124.0 ± 9.0
960	4.4 ± 0.1	116.0 ± 6.8	7.8 ± 0.7	121.4 ± 3.4
2000	2.7 ± 0.1	122.3 ± 1.2	6.8 ± 1.1	117.4 ± 19.2

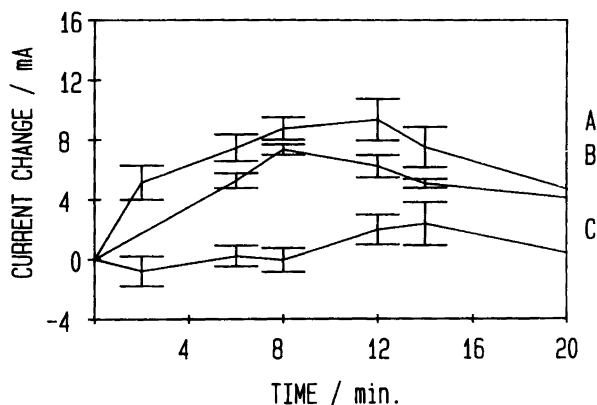


Fig. 5. The measured change in current as a function of time at a magnetic field of 800 mT and electrode potentials of 0 (A), 300 (B) and -300 (C) mV for iron in 1 M iron(III) chloride at a rotation speed of 120 r.p.m. Each curve represents the mean of 10 measurements.

small variations in the electrode current due to the magnetic field are not detectable.

Figure 5 shows the change in the electrode current due to a 800 mT magnetic field as a function of time, at electrode potentials 0, 300 and -300 mV. The working electrode was made of iron, the electrolyte was 1 M iron(III) chloride, and the rotation speed was 120 r.p.m.

The results show that the effect of the magnetic field decreases after an exposure of 12–14 min. According to eqn. (2), there will be an increase in the Fe^{2+} concentration and a decrease in the Fe^{3+} concentration within the test volume. Consider eqn. (6), and suppose that the electrode area (A) = 4 cm^2 , the test volume (V_e) = 3 cm^3 , the diffusion constant (D) = $10^{-9} \text{ m}^2 \text{ s}^{-1}$ and the thickness of the diffusion layer (δ) = $4 \times 10^{-4} \text{ m}$, the time (t) elapsed the $C_b^{\text{Fe}^{3+}}(t) = 1/2 C_b^{\text{Fe}^{3+}}(t=0)$ is ca. 35 min. According to this, and taking the duration of each experiment (which was 40 min) into the consideration, the decrease in the magnetic field effect with time is explained in terms of the small test volume used in the experiments.

Also, the results show great variations in the magnetic field effect during the first 3 min. Therefore, the current measurements started 3 min after adding the electrolyte to the exposure chamber.

To summarize, the results obtained in this study show an increase in the anodic electrode current when exposed to static magnetic fields. The magnetic field effect which is observed only within the prepassive potential range of the iron electrode increases with increasing Fe^{3+} concentration, and decreases with increasing stirring rate. Further, it is observed that the magnetic field effect decreases with time, which is associated with the ferric reduction in the small test volume. Also, a possible interaction mechanism is proposed which indicates that the observed results can be explained in terms of the magnetic force on the transport of Fe^{3+} ions to the electrode due to the high discontinuity in the magnetic

field strength at the interface between the iron electrode and the test solution.

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