

STUDIES ON THE $\text{Fe}^{2+}/\text{Fe}^{3+}$ REDOX SYSTEM USING D.C. LINEAR POLARISATION AND IMPEDANCE TECHNIQUES

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Summary

This paper reports experimental data for the solution and polarisation resistances, exchange-current density, and rate constant of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple. To use this couple in redox batteries, it is concluded that the concentrations of Fe^{2+} must be greater than 0.4 M and that of the supporting HCl must be below 2 M.

Introduction

In recent years, redox systems have been considered for use in possible rechargeable batteries for both terrestrial and space applications [1]. For example, during the late 1970s, NASA in the USA commenced studies on the iron-titanium system for the bulk storage of electrical energy in load-levelling applications [2].

Conventional cells generally employ solid materials for the electrodes. These materials can be subject to deleterious changes in morphology during charge/discharge cycling, however. Further, the capacity of conventional cells is limited by the size of the electrodes and, hence, by the content of the active solid materials contained therein. Metals such as zinc, aluminium and magnesium are used as negative electrodes, whereas metal oxides, sulphur, halogens or oxygen serve as positives in different batteries and fuel cell systems. Redox cells have an advantage over conventional types using solid active materials, in that the reactants can be continuously replenished by mechanical, chemical, electrochemical or photoelectrochemical methods. Redox cells are generally low-power systems.

Since the Fe-Ti systems [3] employ relatively inexpensive materials and theoretically exhibit a medium-range cell voltage, further development to give an optimum performance is warranted. Although the $\text{Ti}^{3+}/\text{Ti}^{4+}$ electrode has been the subject of much investigation [4 - 6], the $\text{Fe}^{2+}/\text{Fe}^{3+}$ system has received less attention. Accordingly, a study is reported here of

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the impedance and linear polarisation of the iron redox couple. The results are used to determine the critical composition and concentration of the electrolyte suitable for a redox battery in which the catholyte compartment contains FeCl_2 electrolyte. The studies also provide useful information on other parameters of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ system, *viz.*, solution resistance, polarisation resistance, exchange-current density, and rate constant.

Experimental

Ferrous chloride solutions of 0.1, 0.2, 0.4 and 1.0 M were prepared by dissolving $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Fluka guaranteed reagent) and adding to each litre of solution 30.0 ml of Analytical Reagent grade (AR) hydrochloric acid. A second series of solutions was made from the above-mentioned four mixtures by adding to each a 4 M HCl (AR) solution in the volume ratio of 3:1. Finally, a third set of solutions was prepared by adding 1, 2, 3 and 4 M HCl (AR) to 0.2 M FeCl_2 in the volume ratio of 3:1. All the solutions were made up immediately prior to experiment.

D.C. linear-polarisation studies were carried out using a Princeton Applied Research Corporation Model 350A instrument. Polarisation resistances were measured for seven sweep rates in four different concentrations of FeCl_2 .

Impedance measurements were obtained with Solartron Model 1174 Frequency Response Analyser and Solartron Model 1186 Electrochemistry interface equipment (Fig. 1). The real and imaginary parts of the electrochemical cell were obtained for various concentrations of FeCl_2 at different frequencies.

The test cell consisted of a platinum working electrode (1 cm^2 area) with a silver wire electrical contact, a saturated calomel reference electrode, and a platinised platinum (10 cm^2 area) counter electrode. All experiments were conducted at 28°C . The platinum electrode was degreased with acetone and then cleaned cathodically in 10% HCl solution at 10 mA cm^{-2} for 20 min; it was washed thoroughly with distilled water before each experimental run.

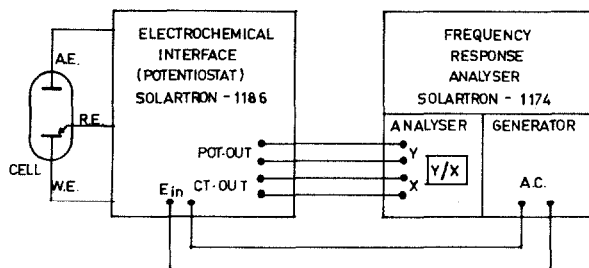


Fig. 1. Impedance set-up.

Results and discussion

D.C. linear polarisation studies

The relationship between corrosion current (I_C) and polarisation resistance (R_p) is given by the Stern–Geary relationship:

$$I_C = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)R_p} \quad (1)$$

where β_a and β_c are Tafel constants. This equation can be simplified to:

$$I_C = K/R_p \quad (2)$$

where K is a constant for a given system. Since eqn. (2) holds for a small perturbation of voltage (*i.e.*, for an overpotential (ΔE) of less than 20 mV), in the studies reported here, a ΔE value of 20 mV was applied above and below the open-circuit potential. The resulting linear current *versus* voltage polarisation plot obtained in 0.1 M FeCl_2 at a sweep rate of 0.03 mV s^{-1} is given in Fig. 2. The polarisation resistance values ($R_p = \Delta E / \Delta I_c$) obtained for different electrolyte concentrations and different sweep rates are given in Fig. 3. Two important observations can be made from the data. First, the polarisation resistance remains virtually constant at sweep rates above 0.2 mV s^{-1} and then increases sharply at lower rates. Second, the electrolyte concentration has little effect on the polarisation resistance between 1 and 0.4 M, only a slight influence between 0.4 and 0.2 M, but causes a sharp increase in resistance between 0.2 and 0.1 M. These data indicate that FeCl_2 solutions below 0.4 M, and particularly below 0.2 M, are not suitable for use in redox batteries.

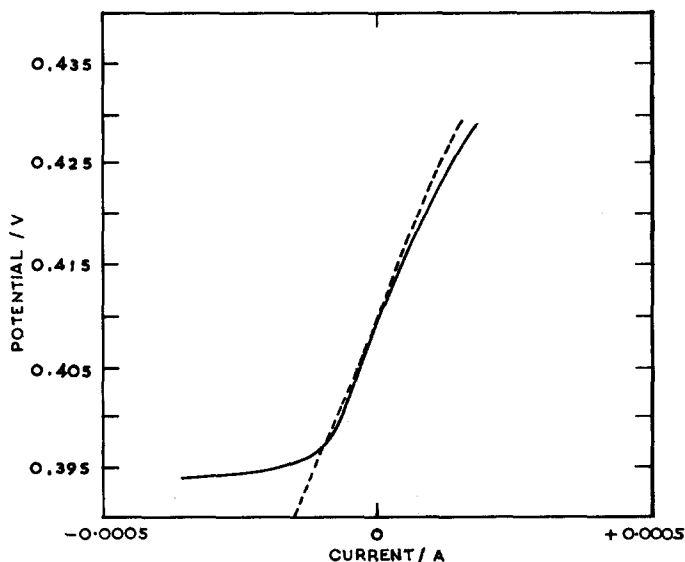


Fig. 2. Typical linear polarisation plot of 0.1 M FeCl_2 at sweep rate of 0.03 mV s^{-1} .

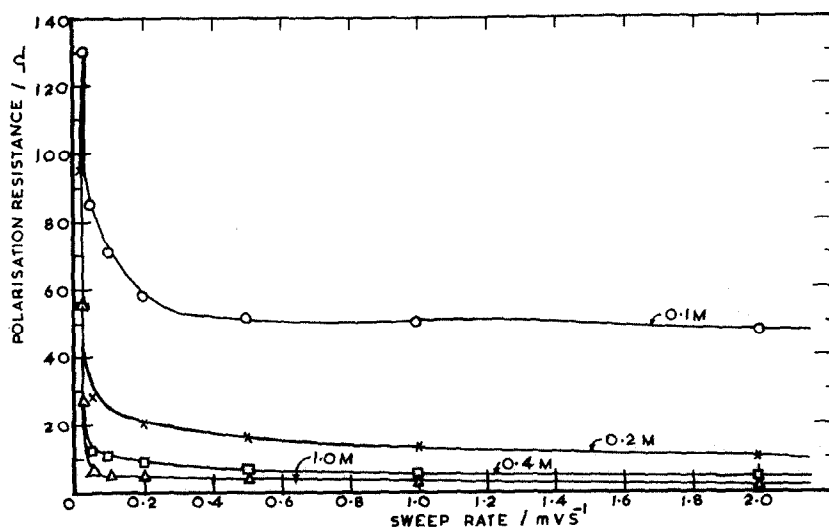


Fig. 3. Polarisation resistance *vs.* sweep rate plots for 0.1, 0.2, 0.4 and 1.0 M FeCl₂.

The above conclusion can be quantified in terms of both exchange current density (I_0) and rate constant (k_0). These parameters were calculated from polarisation resistance data using the following expressions:

$$I_0 = \left[\frac{RT}{nF} \right] \frac{I}{R_p} \quad (3)$$

and

$$k_0 = \frac{I_0}{nFC} \quad (4)$$

The resulting values for I_0 and k_0 are given in Tables 1 and 2, respectively.

Linear polarisation experiments were reported for FeCl₂ solutions containing 4 M HCl. Data were obtained at a low sweep rate of 0.03 mV s⁻¹, a condition under which appreciable changes in the polarisation resistance

TABLE 1

Exchange-current density, I_0 ($\times 10^{-4}$ A cm⁻²) (linear polarisation)

FeCl ₂ (M)	Sweep rate (mV s ⁻¹)						
	0.03	0.05	0.1	0.2	0.5	1.0	2.0
0.1	1.0	1.51	1.82	2.21	2.52	2.52	2.69
0.2	1.34	4.49	4.86	5.97	7.90	9.61	11.99
0.4	2.27	10.35	11.13	13.46	18.31	22.15	26.61
1.0	4.99	19.79	21.97	25.17	28.36	31.30	33.11

TABLE 2

Rate constant, k_0 ($\times 10^{-5}$ cm s $^{-1}$) (linear polarisation)

FeCl ₂ (M)	Sweep rate (mV s $^{-1}$)						
	0.03	0.05	0.1	0.2	0.5	1.0	2.0
0.1	1.03	1.57	1.88	2.29	2.61	2.62	2.79
0.2	0.70	2.33	2.52	3.09	4.09	4.98	6.21
0.4	0.59	2.68	2.88	3.49	4.74	5.74	6.89
1.0	0.52	2.05	2.28	2.61	2.94	3.24	3.43

TABLE 3

Polarisation resistance, R_p (Ω); exchange-current density, I_0 ($\times 10^{-4}$ A cm $^{-2}$) and rate constant, k_0 ($\times 10^{-5}$ cm s $^{-1}$) (linear polarisation); sweep rate 0.03 mV s $^{-1}$

FeCl ₂ (M)	FeCl ₂			FeCl ₂ + 4 M HCl		
	R_p	I_0	k_0	R_p	I_0	k_0
0.1	130.00	1.00	1.03	163.00	0.79	0.82
0.2	96.54	1.34	0.70	112.54	1.15	0.60
0.4	57.17	2.27	0.59	59.82	2.17	0.56
1.0	25.97	4.99	0.52	30.07	4.31	0.45

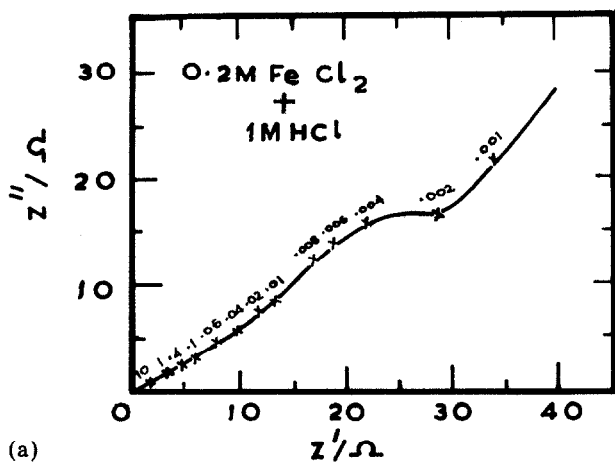
were expected. The results are presented in Table 3. The data show that the addition of 4 M HCl causes an increase in polarisation resistance rather than a decrease, despite the increase in ionic concentration. This may be due to the formation of complex iron species between FeCl₂ and HCl, thereby reducing the concentration of Fe²⁺, i.e.,



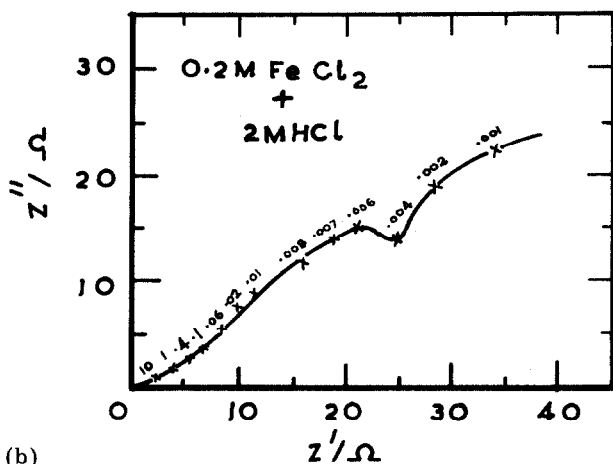
This conclusion has been verified by collecting data of polarisation resistances with respect to 0.2 M FeCl₂ mixed with 1, 2 and 3 M HCl (Fig. 4). The data indicate a continuous increase of diffusion polarisation with increase in HCl concentration.

A.C. impedance studies

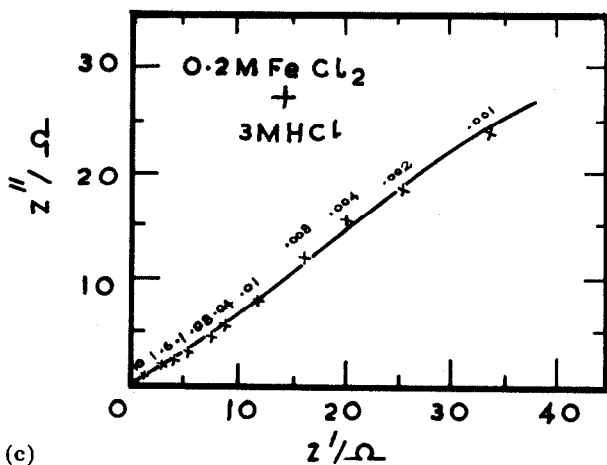
Since a simple electrochemical system consists of double layer capacitance, solution resistance, and activation polarisation resistance, the use of an a.c. signal can provide information additional to that obtained from a d.c. polarisation technique. The impedance locus diagram is obtained by applying a 20 mV rms sinusoidal potential between the working and reference electrodes through a potentiostatic circuit; the potential/current function gives the impedance value. The magnitude (Z)/phase (θ) relation of the impedance is given by: $Z' = Z \cos \theta$ for the real part and by $Z'' = Z \sin \theta$ for the imaginary part. In the impedance diagram, the diameter of the circle gives the polarisation resistance, R_p , and the intercept on the X axis at the



(a)



(b)



(c)

Fig. 4. Impedance plot for 0.2 M FeCl₂ with (a) 1 M HCl; (b) 2 M HCl; (c) 3 M HCl.

higher frequencies gives R_s , the solution resistance. The nature of the curve indicates whether the system is activation controlled (a semi-circle), diffusion controlled (a 45° straight line), or a combination of both.

Impedance diagrams for 0.1, 0.2, 0.4 and 1 M FeCl_2 , with and without 4 M HCl , are presented in Fig. 5. The resulting solution resistances are given in Table 4. It can be seen that the curves for FeCl_2 , in the absence and presence of HCl , approach one another with increase in FeCl_2 concentration from 0.1 - 0.2 M, merge into one another at 0.4 M, and separate again at 1 M. Examination of the intercept on the X-axis shows that the solution resistance of FeCl_2 , both with and without HCl , becomes almost the same at a concentration of 0.4 M and beyond. This finding is in agreement with that obtained from d.c. linear polarisation measurements.

TABLE 4

Solution resistance, R_s (Ω) (impedance method)

FeCl_2 (M)	FeCl_2	$\text{FeCl}_2 + 4 \text{ M HCl}$
0.1	11.00	3.00
0.2	6.00	2.00
0.4	1.35	1.30
1.0	1.30	1.30

The plots in Fig. 5(a) and (b) approximate to straight lines whereas those in Fig. 5(c) and (d) are curved, thus indicating that the processes in 0.1 and 0.2 M FeCl_2 are largely diffusion-controlled, whereas those in 0.4 M FeCl_2 and beyond are largely activation controlled. This fact can be readily understood as lower concentrations are bound to involve diffusion-controlled processes.

Using Fig. 5(c) and (d) and extrapolating the curves to cut the X-axis, the polarisation resistance of the metal/solution interface is determined approximately from the chord of the arc thus obtained. These values are given in Table 5. The polarisation resistances for 0.1 M FeCl_2 , with and without HCl , have also been obtained and the values are also presented in Table 5, together with exchange-current density and rate constant data. The values obtained by the impedance method are found to be close to the values obtained by the d.c. polarisation technique.

Chen *et al.* [8] obtained rate constants, k_0 , for an $\text{Fe}^{3+}/\text{Fe}^{2+}$ system in 2 M HCl , 0.5 M H_2SO_4 and 3 M H_2SO_4 on platinum or graphite electrodes. The values were 1.9×10^{-3} , 1.6×10^{-3} and 1.2×10^{-2} cm s^{-1} , respectively. Our values (Tables 2, 3, 5) are two orders lower than those reported by previous workers. This difference may be due to that fact that the experiments reported here were carried out at extremely low sweep rates ($0.03 - 2 \text{ mV s}^{-1}$) and at low overpotential limits, with the intention of disturbing the equilibrium conditions to the minimum extent. This also explains a

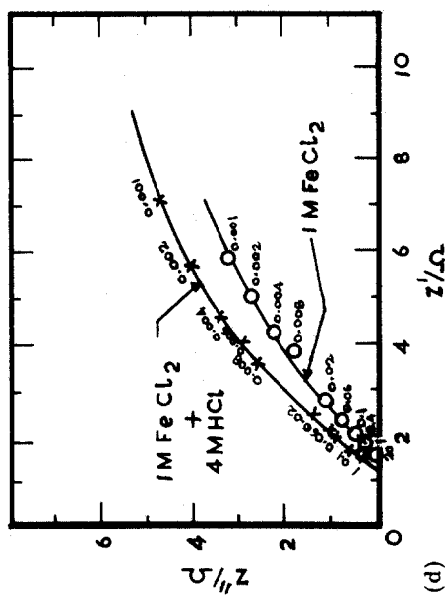
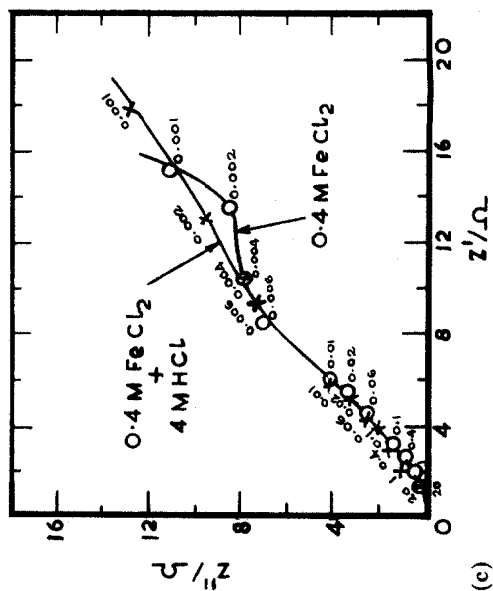
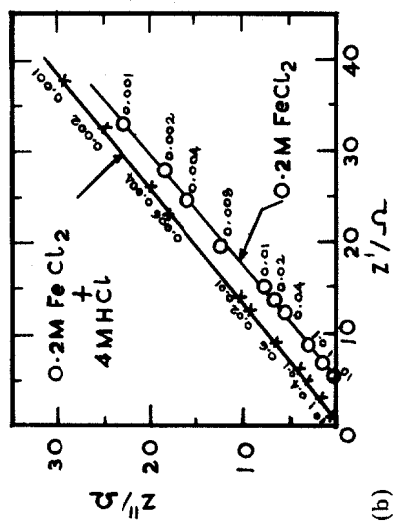
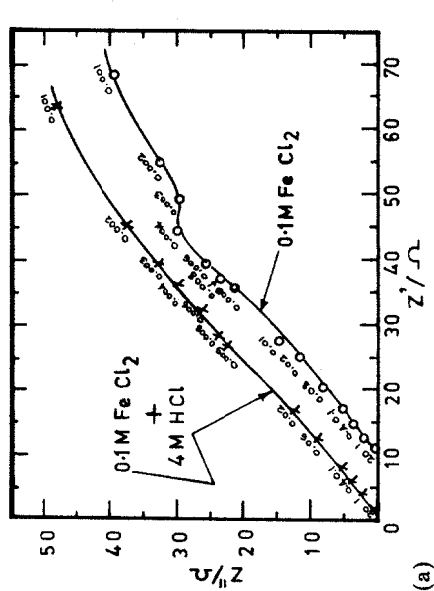


Fig. 5. Impedance plot for FeCl_2 with and without 4 M HCl. (a) 0.1 M; (b) 0.2 M; (c) 0.4 M; (d) 1.0 M.

TABLE 5

Polarisation resistance, R_p (Ω); exchange-current density, I_0 ($\times 10^{-4}$ A cm^{-2}) and rate constant, k_0 ($\times 10^{-5}$ cm s^{-1}) (impedance method)

FeCl ₂ (M)	FeCl ₂			FeCl ₂ + 4 M HCl		
	R_p	I_0	k_0	R_p	I_0	k_0
0.1	115	1.13	1.17	120	1.08	1.12
0.4	24	5.40	1.40	26	4.98	1.29
1.0	16	8.10	0.84	17	7.62	0.79

continuous increase in the values of k_0 from, say, 0.59×10^{-5} cm s^{-1} (in the case of 0.4 M electrolyte solution) to 6.89×10^{-5} cm s^{-1} , when the sweep rate is changed from 0.03 to 2 mV s^{-1} (Table 2). Previous authors have conducted experiments with sweep rates as high as 20 - 500 mV s^{-1} and polarisation of the electrode system as high as 180 mV, whereas the present experiments were restricted to the low range of 20 mV perturbation (linear polarisation range).

Conclusion

Results from d.c. polarisation and a.c. impedance studies on FeCl₂ solutions, in the presence and absence of HCl, show that FeCl₂ concentrations < 0.4 M yield a high polarisation, resulting in apparently low exchange-current densities. This is largely due to the influence of diffusion-controlled processes. The addition of > 2 M HCl increases the polarisation resistance of the system. In the light of these facts, it is concluded that the electrolyte solution should have a concentration > 0.4 M with respect to FeCl₂ and < 2 M with respect to HCl in a redox battery in order that the battery should offer minimum polarisation during charging or discharging. Use of higher concentrations of HCl is not beneficial to the system.

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References

- 1 K. D. Beccu, *Chem. Ing. Tech.*, 46 (1974) 95.
- 2 K. Michaels and G. Hall, *NASA-CR-165260*, Final Report, 1980.
- 3 L. H. Thaller, *Proc. 9th Intersoc. Energy, Conv. Eng. Conf.*, 1974, p. 924.
- 4 R. F. Savinell, *Ph.D. Dissertation*, Univ. Pittsburgh, Pittsburgh, Pennsylvania.
- 5 C. C. Liu, R. T. Galasco and R. F. Savinell, *J. Electrochem. Soc.*, 128 (1981) 1755; 129 (1982) 2502.

- 6 L. H. Thaller, *Ext. Abstr. No. 85, Electrochem. Soc., Proc. Vol. 77 - 2, Atlanta, 1977*, p. 229.
- 7 J. Giner, L. Swette and K. Cahill, *NASA Rep., No. NASA 19760*.
- 8 Y-W-D. Chen, K. S. V. Santhanam and A. J. Bard, *J. Electrochem. Soc.*, 128 (1981) 1460.