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# THE DIFFERENTIAL CAPACITANCE OF MAGNETITE

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## Summary

Results from impedance measurements on a polycrystalline magnetite electrode in  $\text{NaClO}_4$  solution are presented as plots of capacitance and resistance against potential. In order to explain the curves semiconductor properties of the electrode must be taken into account. Mott-Schottky plots indicate a change in semiconductor behaviour.

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## 1. Introduction

The electrochemical properties of magnetite ( $\text{Fe}_3\text{O}_4$ ) are of considerable interest owing to its importance as a product in the corrosion of iron and steels. We have already reported some of the electrochemistry of magnetite [1]. In the course of this investigation we verified that the surface of the material is sensitive to oxidation. Only when magnetite electrodes are maintained at potentials characteristic of stoichiometric  $\text{Fe}_3\text{O}_4$  [2] can this precise composition be assumed as that on the electrode side of the interphase.

To date, no a.c. impedance measurements characteristic of magnetite have been recorded in the literature although we have reported [3] measurements on an iron electrode covered with oxide. These measurements were complicated because the composition of the electrode surface changed with potential.

Investigations of the integral capacitance and surface charge of magnetite powders have been made by both titrimetric [4] and electrokinetic [5] methods. Ahmed and Maksimov [4] concluded that the oxide was negatively charged owing to acidic dissociation of surface OH groups. At high negative charge density cations were found specifically adsorbed on atoms of the surface metal through an  $\text{O}^{2-}$  bridge. These results agree with those of Anderson [5] who found the interfacial structure to be sensitive to pH with a pronounced tendency to the adsorption of other ions.

A recognition that under certain circumstances the semiconductor properties of magnetite complicate the electrochemical behaviour has followed from a detailed electrode kinetic study of the material [6]. The semiconductor properties have the effect of imposing a second network of components in the equivalent electrode analogue in addition to the network characteristic of the electrode-electrolyte interphase. It was therefore considered of interest to investigate the impedance of the magnetite in aqueous solution with the object of identifying the presence of these semiconductor effects; this paper describes the results.

## 2. Experimental

The electrode impedance was measured using a modified Schering bridge and electrolytic cell which have been described elsewhere [7]. The electrode consisted of fused polycrystalline magnetite\* which was sheathed in polyethylene to leave one face exposed to the electrolyte. The embedded part of the electrode contained a contact to a stout copper contact made with conducting Araldite. Measurements on this electrode junction showed that this contact had a negligible resistance.

The electrolyte solutions investigated were  $\text{NaClO}_4$  ( $1 \text{ mol dm}^{-3}$ ) adjusted to the required pH with  $\text{HClO}_4$  and  $\text{NaOH}$  which were passed over purified activated charcoal for 48 h prior to any data acquisition. Measurements were made under nitrogen by manually balancing the bridge, and the electrode impedance was obtained as a series combination of resistance and capacitance.

## 3. Results

Figure 1 shows the differential capacitance curves for magnetite in 1 M  $\text{NaClO}_4$  solution at pH 1 at a series of frequencies. The experimental range of potential within which reproducible data were obtained was from about  $-600 \text{ mV}^{**}$  to about  $1750 \text{ mV}$ ; these potentials mark the reduction of the lattice with attendant hydrogen evolution and evolution of oxygen respectively. At these limits the occurrence of the respective redox reactions gives rise to considerable pseudo-capacitance which cannot be accurately measured.

A well-defined capacitance peak which shows a considerable amount of frequency dispersion occurs at about  $250 \text{ mV}$ . At approximately  $900 \text{ mV}$  there is evidence of a much smaller capacitance peak which is amplified by low frequency measurements.

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\*This material was kindly donated by Dr. B. Case of the Central Electricity Research Laboratories.

\*\*All measurements were made with reference to the saturated sodium calomel electrode and converted to the standard hydrogen scale.

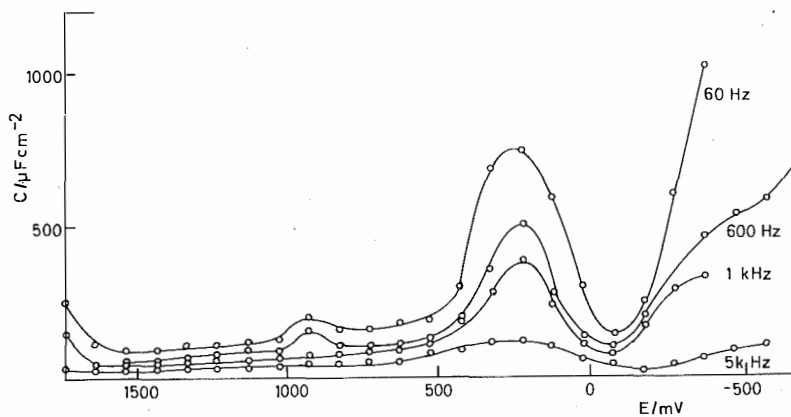


Fig. 1. Capacitance-potential curves for magnetite in 1 M NaClO<sub>4</sub> solution at pH 1 and 23 °C: electrode area, 0.125 cm<sup>2</sup>; frequencies, as marked.

The corresponding electrode resistance is shown in Fig. 2. These curves contain contributions from the electrolyte and the electrode itself in addition to that of the interphase. However, the difference between the resistance curves at the two frequencies indicates that at the potentials of capacitance maxima the resistance is reduced as the double layer becomes shunted by a faradaic impedance corresponding to an electrode reaction.

Figure 3 shows the effect of pH on the differential capacitance curves. The capacitance peak at approximately 250 mV (at pH 1) has an interesting pH dependence for it shifts to more negative potentials at higher pH values. The intensity of the dependence amounts to about 90 mV per pH unit over at least 10 pH units. The faradaic process leading to this dependence arises from the interconversion of Fe(II) and Fe(III). This reaction stabilizes the equilibrium stoichiometry under the continuing dissolution of Fe(II) from

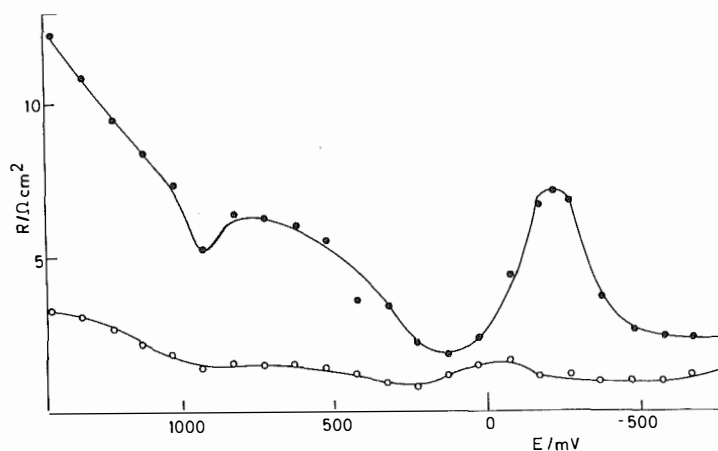


Fig. 2. An electrode resistance-potential curve (conditions as for Fig. 1): ●, 50 Hz; ○, 5 kHz.

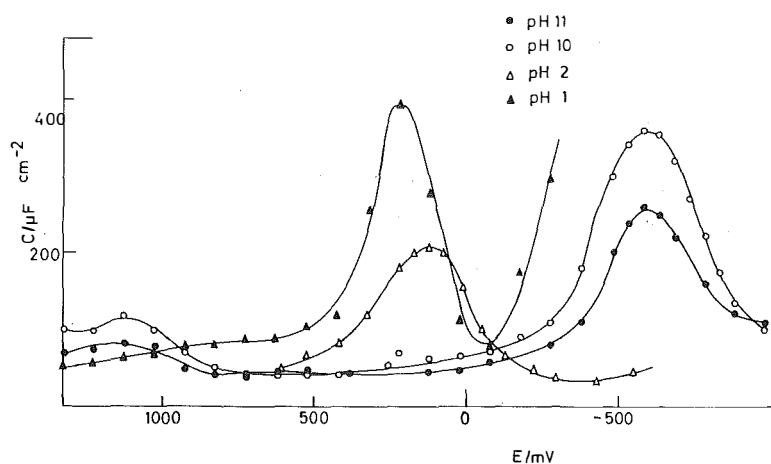
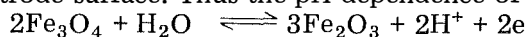
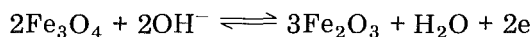


Fig. 3. Capacitance-potential curves for magnetite in 1 M NaClO<sub>4</sub> solution at various pH values: frequency, 1 kHz.

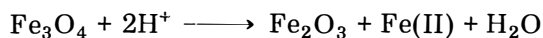
the lattice. The dissolution process itself is pH dependent since the flux of dissolution products (Fe(II) and OH<sup>-</sup>) led to local changes in pH at the electrode surface. Thus the pH dependence of the redox reaction



or



which requires a 60 mV decade<sup>-1</sup> dependence is increased since the actual pH at the electrode is modified by the dissolution



This will be discussed further in a later paper.

#### 4. Discussion

Our data agree well at negative potentials with the data reported by Farr and Zubillaga [8] for oxide and spinel films on certain irons and steels. At more positive potentials, however, the detailed structure found by Farr and Zubillaga [8] is absent. The large capacitance peak can be attributed fairly certainly to the faradaic reaction (1) (or (2)); however, a smaller but nonetheless well-defined capacitance peak exists in the region 500 - 1500 mV which cannot be attributed to any electrochemical effect. This peak is dependent on the frequency of measurement and shows a pronounced frequency dispersion. The frequency dispersion might be due to a number of causes; however, the most probable are surface roughness, adsorption or semiconductor properties. Surface roughness is unlikely to cause an undue

amount of frequency dispersion and can therefore be ruled out. Adsorption at these potentials is also unlikely in the absence of any organic species. We are forced therefore to the conclusion that the presence of surface states is the major factor responsible for the frequency dispersion at these potentials.

We can readily test this hypothesis in a Mott-Schottky plot. Such plots have been used successfully to identify semiconductor effects by Farr and Zubillaga [8] (steel in acid solution) and Lee and Yeager [9] (for the case of NiO in acid solution). The relation between the potential and capacitance is given by

$$\phi - \phi_{fb} = \frac{k}{e} T + \frac{e\epsilon_1 N_i}{\delta \pi} \frac{1}{C^2} \quad (4)$$

where  $\phi$  is the potential,  $\phi_{fb}$  the flat band potential,  $k$  the Boltzmann constant,  $\epsilon$  the permittivity of the magnetite and  $N_i$  the number of charge carriers. Figure 4 shows that two straight lines result from plotting our data in the form of eqn. (4). In the potential region 500 - 1000 mV the Mott-Schottky slope for the system at pH 1 is  $5.6 \times 10^3 \text{ V } \mu\text{F}^2 \text{ cm}^{-4}$  with an intercept at 100 mV. In the range 1000 - 1500 mV the slope is  $2.04 \times 10^3 \text{ V } \mu\text{F}^2 \text{ cm}^{-4}$  with an intercept at 700 mV. This gives values of the carrier concentration  $N_i \approx 9 \times 10^8 \text{ cm}^{-2}$  in the potential region 500 - 1000 mV and  $N_i \approx 3.2 \times 10^8 \text{ cm}^{-2}$  in the potential region 1000 - 1500 mV. These values can be compared with values of  $(0.3 - 0.4) \times 10^3 \text{ V } \mu\text{F}^2 \text{ cm}^{-4}$  observed by Farr and Zubillaga [8] at 312 Hz.

(1)

(2)

(3)

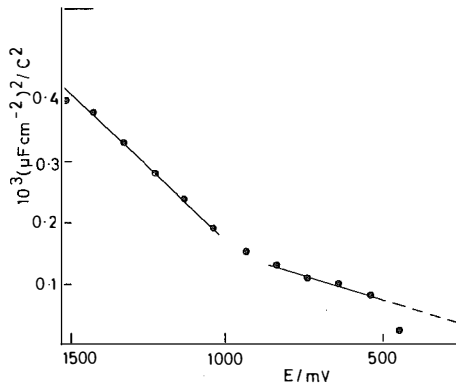


Fig. 4. A Mott-Schottky plot ( $E$  vs.  $1/C^2$ ) for magnetite: frequency, 1 kHz; pH 1.

The change in slope observed in the Mott-Schottky plot for our data is interesting since it indicates that we may be moving from one type of semiconductor to another. We suggest that in this case the intrinsic semiconductor of  $\text{Fe}_3\text{O}_4$  has given way at positive potentials to the n-type semiconductor of  $\text{Fe}_2\text{O}_3$  [10].

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