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The preparation and behaviour of magnetite anodes

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A short review of the methods of preparation of magnetite anodes and the physico-chemical properties of Fe_3O_4 is followed by experimental results using chlorine evolution as a test reaction. Problems arising in the operation of composite magnetite–titanium structures are considered.

1. Introduction

There is not such a wide choice of useable anode materials for aqueous electrochemical processes that one can afford to ignore each possible candidate. While graphite, lead dioxide (whether on Pb or an inert substrate) and the range of precious-metal or precious-metal oxide anodes on inert substrates all have their merits, as do the 'duriron' or MnO_2-coated electrodes, they equally have disadvantages, whether these be poor acid resistance, high cost or lack of mechanical strength.

Magnetite too is a substance which is used in certain circumstances as an anode material in industrial processes, as well as being frequently mentioned in patent literature.

Massive magnetite anodes have long been used in industrial processes. However, they have suffered from two main disadvantages, namely a poor electrical conductivity and an inherent brittleness. One might further add that their method of preparation (subject to what is written below) required that they be cast in very thick sections and in a form poorly compatible with the engineering of modern electrochemical reactors.

Their brittleness was reported in 1917 [1] as being the reason the electrodes were being replaced with duriron. Since then there have been but few reports of work to improve either problem. The most popular engineering approach has been to make the electrodes hollow and then apply a coating of a good conductor like copper on the inside. The resulting structure has improved electrical conductivity and also better mechanical properties. Magnetite coatings on ferrous basis metals were prepared by the direct oxidation of the iron to magnetite. However, the coating was usually porous and of poor adhesion so that the underlying iron was not protected and corroded. This led to the development of magnetite coatings on an inert substrate, usually titanium.

The literature on magnetite electrodes is mainly concerned with their manufacture. Although no kinetic study has been reported using magnetite as the anode material, the electrochemical oxidation and reduction of magnetite has been extensively studied because of its relevance to the corrosion and passivation of iron. This is of particular importance in the field of boiler corrosion, especially at high temperature, where iron is converted to magnetite by the action of steam. However, this paper is concerned only with the use of magnetite as an anode material in electrochemical cells. Other useful references relating to electrical or physico-chemical properties are [2–4].

2. Manufacture of massive magnetite anodes

Three general methods have been reported for the manufacture of bulk magnetite anodes, both flat sheets [5–7] and hollow cylinders [8–12]. They are: (a) casting molten magnetite [1, 8, 11–18]; (b) sintering magnetite powder [5–7, 9, 19–21]; (c) oxidizing iron to magnetite, usually to produce thick coatings [10, 22–24]. The effect of chemical composition on electrical conductivity [1, 15, 25, 26], brittleness [1, 15, 27] and corrosion resistance [1, 15] has also been reported.

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3. Manufacture of magnetite-coated anodes

By making an anode with an electrocatalytic outer layer of magnetite deposited on an inert but electrically conducting substrate, it is possible to create electrodes at once thin in section, yet strong and lightweight, and thus better suited to modern cell-designs with their finer tolerances. In practice, however, difficulties arise due to loss of electrical contact between the magnetite and the substrate. As Wabner [28] has pointed out for the PbO_2–Ti anode, the juxtaposition of two- or three-valent iron with a fully reduced metal (e.g. Ti) invites a situation where mutual oxidation–reduction takes place. In principle, there are two ways of producing this type of electrode. One is to apply magnetite powder directly to the substrate material and the other is to apply a coating of iron, usually by electroplating, and then oxidize it to magnetitie.

Direct coatings of magnetite have been applied by plasma spraying [29, 30], explosive bonding [31] or simply by heating a mixture of magnetite powder and a paraffin wax in an inert atmosphere [32].

Oxidation of iron films was first patented by De Nora [33] as a means of protecting platinum from anodic dissolution during the electrolysis of NaCl solutions. The iron is oxidized to magnetite in an atmosphere consisting of a mixture of CO_2 and/or H_2O and/or air with an inert gas, preferably argon at a temperature of 600–900° C. It is claimed that the coating has better adhesion if the iron is first allowed to diffuse into the substrate by being heated in an inert atmosphere at about 700° C. A variation of this by Japanese workers [34, 35] is to immerse the iron in ammonium ferric oxalate solution under reduced pressure before heating at around 600° C in an atmosphere of 20% hydrogen/steam.

4. Uses of magnetite electrodes

Magnetite anodes were in use early this century for the production of chlorate [36]. They were still in use in 1971 at the Japan Carlit plant in Japan [36]. The rate of anode loss is very small a loss of 5 mm on the external diameter of 60 mm after four years of continuous operation is reported [8] – and is not affected by temperature, thus permitting operation at 70° C with an increased current efficiency. Magnetite anodes were also in use early this century in Chile for the electrolysis of acid $CuSO_4$ solutions. However, by 1917 they had almost all been replaced by duriron because of their extreme brittleness [1]. Various other uses have been proposed for magnetite anodes, for example as anodes in the following electroplating baths: chromium [37], sulphamic acid [38], metal–ammonia complexes [39, 40]. Water treatment uses that have been reported are electrolysis of sewage [41], desalination of water [42], cyanide destruction [43], and water disinfection [44]. Electrolysis of sodium acetate solutions to acetic acid has been studied [45, 46] and a patent covers the electrolysis of solutions of alkali metal salts of lower fatty acids [47]. Cathodic protection has also been suggested [21, 48–50]. Its use as an inert substrate on which to apply a coating of platinum metals has been patented by De Nora for chlorine production [51], whereas Yamamoto and co-workers [52] have studied the formation of perchlorate on platinum-plated magnetite. This reaction is not possible on magnetite itself probably because of the low oxygen overvoltage on magnetite in chlorate solution [53]. An interesting suggestion has been the use of a lead–magnetite bielectrode [54]. It is claimed that if magnetite particles are embedded in a lead electrode, the electrode can be used as an anode in the electrolysis of brine. For electrochemical manufacture of magnetite powder see [55–57].

5. Electrochemical data

Matsumura *et al.* [8] have reported polarization results for chlorine evolution on magnetite in 5·3 M NaCl at 25° C. They obtained a Tafel slope of 73 mV $decade^{-1}$ over a current density range of 1–40 mA cm^{-2}. The exchange current density for the reaction was approximately 16×10^{-6} A cm^{-2}. The slope was hardly affected by change in purity of the magnetite (which was made from haematite) or by additions of $NaClO_3$ to the electrolyte. Eguchi [45, 46] compared various anode materials for the electrolysis of sodium acetate solutions to yield acetic acid. Magnetite gave good current efficiency with a low corrosion rate.

Nagai and Takei [58, 59] found that the more anodic the potential, the greater was the corrosion rate of magnetite anodes in NaCl solutions and $NaClO_3$ solutions. In the NaCl solution the potential decreased as the solution concentration was increased but the opposite effect was obtained with the $NaClO_3$ solutions.

In 1949 Yoneda [60] reported the activation energy for oxygen evolution in NaOH solution to be 14 kcal on platinum and 26 kcal on magnetite. It was decided to investigate the chlorine evolution reaction on magnetite supported on a substrate of titanium in these laboratories.

6. Experimental

6.1. *Electrode preparation*

Magnetite electrodes were made by plating iron on to a titanium substrate and then oxidizing the iron to magnetite. A chloride–sulphate bath was found to give a good quality plate at reasonably high current densities and, therefore, short plating times. It consisted of [61] $FeSO_4 \cdot 7H_2O$, 250 g l^{-1}; $FeCl_2 \cdot 4H_2O$, 42 g l^{-1}; NH_4Cl, 20 g l^{-1}. When 1 cm squares of titanium were used as substrates the magnetite coating had a tendency to crack and lift; this was overcome by using titanium wire, 1 mm diameter (Koch Light Ltd). Immediately prior to the plating of the iron, the titanium was etched for 30 min in 10% oxalic acid solution at 95–100° C. A coating of iron nominally 20 μm thick was applied at a current density of 60 mA cm^{-2}. In some cases the wires were first plated with approximately 6 μm of platinum from a 4% solution of chloroplatinic acid. Conversion of the iron to magnetite was initially by the method of de Nora [33] in which the iron is oxidized in an atmosphere of 50% Ar, 50% CO_2 at 800° C. However, this did not bring about complete conversion of the iron and so oxidation in steam at 800° C was adopted. The magnetite electrodes were prepared for testing by being spot-welded on to a titanium wire sealed in a glass tube with epoxy-resin. Alkathene (courtesy of ICI Ltd) was applied in a semi-molten state to the electrode and used to cover the titanium wire and the epoxy-seal and all but a short length of the magnetite.

6.2. *Electrochemical tests*

Polarization curves were obtained galvanostatically in 2 M and 5 M NaCl solutions saturated with chlorine at temperatures of 30, 55 and 80° C. When the electrolyte was stationary the potential fluctuated considerably at current densities above a few mA cm^{-2}, making the readings of dubious value. These fluctuations are caused by the formation and release of gas bubbles and the same problem has been experienced on ruthenium [62] and RuO_2/TiO_2 [63] electrodes. To overcome this problem the electrolyte was pumped over the electrode in a direction perpendicular to the axis of the wire. The electrolyte was pumped by an Iwaki M15 magnetically-coupled pump at a rate of 1·5 l min^{-1}.

The polarization sweep was first in the cathodic direction and then in the anodic. Between each sweep the electrode was polarized at approximately 1 A cm^{-1}.

Several electrodes were also tested by continuous polarization at 250 mA cm^{-2} in 2 M NaCl at room temperature with the electrolyte stationary.

Polarization curves were also obtained potentiodynamically at room temperature at a sweep rate of 5 mV s^{-1}. The potential limits were 0 and 2·2 V versus SCE. Fig. 1 shows the results uncorrected for ohmic drop (ohmic-free data obtained by the method of [64] is shown in Fig. 2). The hysteresis at low potentials is thought to be due to chemical changes in the magetite layer but this aspect was not pursued further.

7. Results

7.1. *Continuous polarization*

The potential–time relationship usually showed a slow linear increase in potential followed by a linear region of faster potential increase, itself followed by a sudden rise in potential (Fig. 3). This latter region usually occurred at night with the consequence that by the morning the electrode, including the titanium, had disappeared. The electrodes with a platinum interlayer exhibited a steady linear increase in potential for several hundred hours before the (arbitrary) end of the experiments.

7.2. *Potential cycling*

Ohmic correction was by a computational method

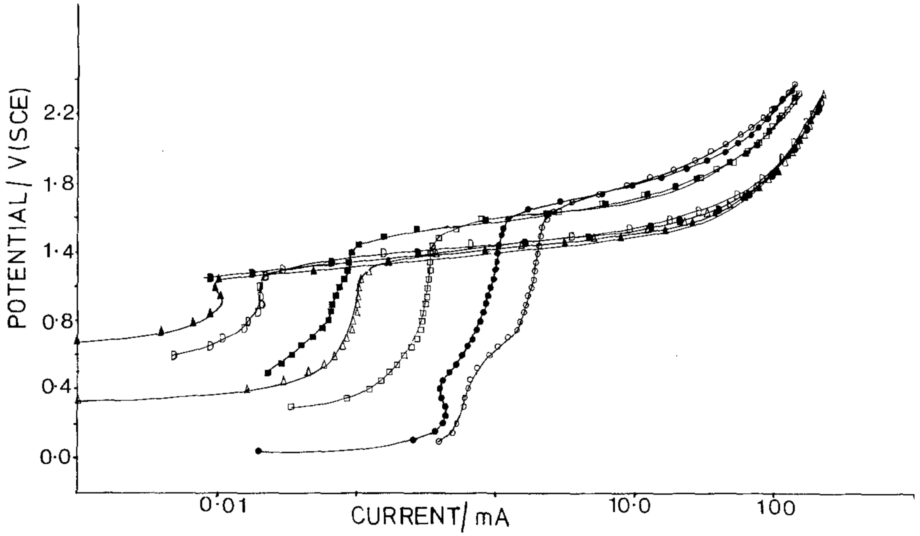

Fig. 1. Potentiodynamic E versus log i uncorrected for ohmic drop. 2 M NaCl room temperature, 5 mV s^{-1}. Open points, anodic sweep; solid points, cathodic sweep. ○, ● – 1st cycle; □, ■ – 10th cycle; △, ▲ – 20th cycle; ◑, ▸ – 35th cycle.

described elsewhere [64]. The values of b were found to vary considerably from sweep to sweep and from electrode to electrode. However, the following general conclusions can be made.

(a) Electrodes without the platinum interlayer experienced a fairly rapid increase in resistance from approximately 5 Ω to several tens of ohms: 162 Ω has been obtained although most tests were stopped at about 40 Ω. In contrast, the electrodes with a platinum interlayer showed a resistance change of only 1 Ω.

(b) The value of b was usually in the range 90 ± 20 mV.

(c) At 30° C the value of b for the anodic scan was higher by 5–10 mV than that for the cathodic scan. At 55° C and 80° C the situation was reversed.

(d) There was no significant difference in either b_{cathodic} or b_{anodic} with change of temperature or electrolyte concentration.

8. Conclusions

There does not seem to be any obvious way of further developing the massive magnetite anode beyond what has been described above, and apart from its poor mechanical properties, there seems no reason why it should not be seriously considered for applications where low current densities prevail. Our investigation has, we believe,

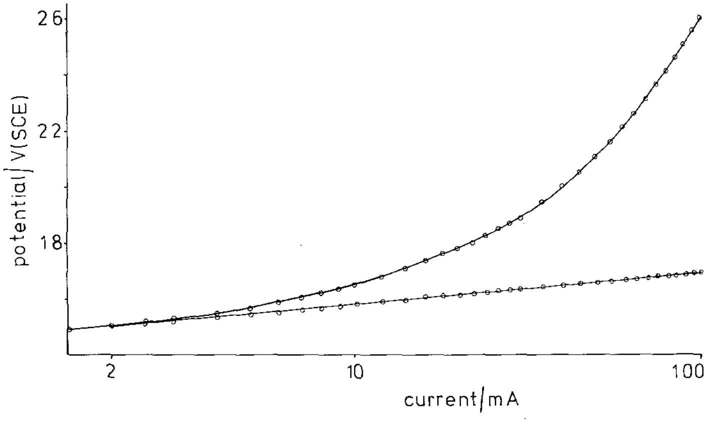

Fig. 2. Ohmically-corrected current–voltage plot. Conditions: 5 mV s^{-1} 2 M NaCl, room temperature.

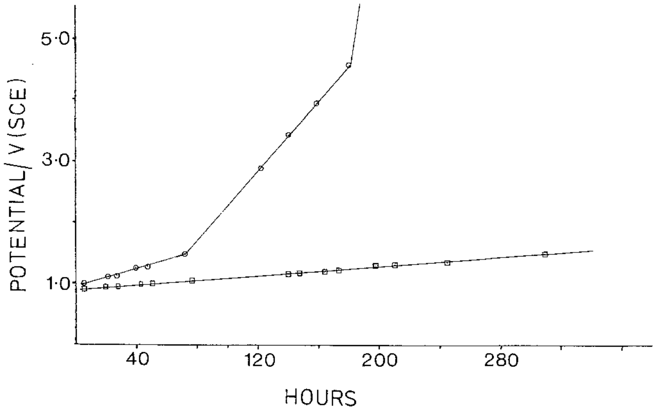

Fig. 3. Potential–time relationship for magnetitie anodes ⊙ without Pt interlayer; ⊡ with 6·6 μm Pt between Ti and magnetite; 2 M NaCl, room temperature, 250 mA cm^{-2}.

highlighted the problems in the use of magnetite–titanium composite anodes, and these are, perhaps unsurprisingly, found to be much the same as [65] those with the PbO_2–Ti composite. In respect of the latter, there is disagreement in that one school of thought (represented by the manufacturers of these anodes) believes them to be viable at least in chloride-containing media. The school of Wabner [28], on the other hand, maintains that (at least in sulphate media) such anodes fail within 100 hours or so, unless a special pre-treatment is applied to the Ti surface prior to coating. This pre-treatment is claimed to repress the growth of TiO_2 between the metal and the overlying oxide film. Clearly with Pt-coated Ti, such problems are absent, as our investigations broadly show. On the other hand, once one is forced to use the precious metals, much of the rationale underlying a magnetite coating disappears, though not all, since one might use much thinner layers of Pt (as interlayers to prevent oxide formation) than would be possible if the same metal were exposed to the electrolyte. In the same way too, the poor acid resistance of normal Pt-coated Ti would be less important when coated with magnetite. An area that remains unexplored is to create a stable magnetite anode, on Ti whether coated or treated to prevent oxidation, and then to seek to promote the electrocatalytic activity of the magnetite by incorporation of small amounts of either precious metals or their oxides, or some other oxides such as those found by Tseung and Jasem [66] to be catalytically active.

In such a form, one can see no reason why the ‘promoted magnetite’ anode should not make a useful contribution to technology.

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