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Electrochemical studies of magnetite coating on carbon steel in ascorbic and picolinic acid

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Abstract

Electrochemical impedance and cyclic voltammetric measurements of magnetite coating formed on carbon steel substrates were carried out in deaerated solutions of 1.0×10^{-2} M ascorbic acid and 3.5×10^{-2} M picolinic acid at 28 °C. Impedance data showed that the interaction between magnetite and ascorbic acid is associated with an incubation period, after which reductive dissolution takes place accompanied by oxidation of ascorbic acid. Once the magnetite film loses its thickness and protective properties on prolonged exposure to ascorbic acid, the charge transfer resistance and the capacitance is reduced. Initial dissolution of magnetite in picolinic acid is due to congruent chemical dissolution with little contribution from reduction by the electrons arising from the corrosive attack of acid on the carbon steel. With time the contribution of the latter process increases as more and more of the substrate opens up. Cyclic voltammetric studies showed that there is an adsorption phenomenon leading to the formation of a surface ferric complex that undergoes reduction to the ferrous species and transfers to the bulk solution. The accumulation of the ferrous ion accelerates the dissolution resulting in an increase in current. Dissolution of magnetite in picolinic acid is slow. The better complexing capability of picolinic acid compared to ascorbic acid does not permit the accumulation of the ferrous ion as indicated by the absence of a peak in the voltammogram.

1. Introduction

Carbon steel is widely used as the material of construction in heat transfer systems in the nuclear, petrochemical and chemical process industries. The alkaline and reduced water chemistry in the primary heat transport system of pressurized heavy water reactors (PHWRs) produces an adherent magnetite film on carbon steel. This scale reduces the heat transfer efficiency, impedes flow of coolant and, more importantly, entraps radioactive isotopes resulting in a high radiation field. Therefore, there is a need to remove this film periodically. Soft cleaning solutions consisting of a weak organic acid, a reducing acid and a complexing agent have been found to be advantageous due to their low corrosivity towards carbon steel and lesser post-cleaning complications compared to mineral acids. Mixtures of ascorbic acid and picolinic acid can be used in the removal of magnetite scales in PHWRs [1, 2]; a formulation containing 1.0×10^{-2} M ascorbic acid 3.5×10^{-2} M picolinic acid is very effective. The mechanism of dissolution of magnetite coatings on carbon steel in ascorbic and picolinic acid has not been reported.

Electrochemical impedance techniques find wide application in the study of electrochemical phenomena such as corrosion, coating evaluation, batteries, electrodeposition, electro-organic synthesis, semiconductors and cathodic protection [3]. Since this technique does not involve potential variation during the measurement, it is suited to media of low conductivity. Das et al. have studied the corrosion and inhibition of carbon steel in 3.5×10^{-2} M picolinic acid and 1.0×10^{-2} M ascorbic acid using electrochemical impedance [4]. In cyclic voltammetry, scanned potential accelerates slow reactions, thereby enabling the study of the nature of the interaction with the working electrode. The type of reaction and the product formed which is responsible for a particular peak give an insight into the process. This paper reports results obtained from electrochemical impedance and cyclic voltammetric studies on grown-on magnetite on carbon steel in 1.0×10^{-2} M ascorbic acid and 3.5×10^{-2} M picolinic acid at 28 °C to understand the mechanism of their action on magnetite.

2. Experimental details

Carbon steel specimens of composition (wt %) C 0.3; Si 0.1; P 0.06; Mn 0.05 and balance iron (Fe) were solution-annealed (925 °C for 30 min and furnace cooled). Samples of 10 × 10 mm polished to diamond finish (0.5 μm) were autoclaved in partially deaerated (<50 ppb O_2) LiOH solution of pH 10.5 at 310 °C for 150 days to form magnetite film; the thickness was 3.9 μm. Specimens were stored in an evacuated desiccator to prevent further oxidation in air before the electrochemical measurements. Identification of the scale was carried out by X-ray diffraction. Solutions were prepared by dissolving picolinic acid (Aldrich, 99%) and L-ascorbic acid (s.d.fine-chem, 99%) in double distilled water.

Impedance and cyclic voltammetric measurements were carried out in a three-electrode corrosion cell with a platinum counter electrode and a saturated calomel reference electrode at 28 °C. Magnetite coated specimens were mounted in cold setting METSET. The test solution was deaerated by bubbling argon gas during the experiment. After 30 min of immersion, the open circuit potential was measured and impedance data were acquired. Measurements were performed at the open circuit potential in the frequency range 10^4 to 10^{-3} Hz using a sinusoidal potential of ±5 mV. Data acquisition was carried out using a Tacussel model Z-computer. The charge transfer resistance (R_t) was obtained from the Nyquist plots by fitting the data to a semicircle in the frequency range 100 Hz to 5 mHz. Capacitance (C) was calculated using the relation [5, 6]:

$$C = \frac{1}{2\pi f R_t}$$

where f is the frequency (Hz) at the maximum of the fitted semicircle (Nyquist plot). Cyclic voltammetric measurements were carried out using magnetite (on carbon steel) of area 1 cm^2. Potential was scanned between ±500 mV vs SCE at a sweep rate of 10 mV s^{-1}.

3. Results and discussion

X-ray diffraction patterns of the coating formed on carbon steel during autoclaving showed the presence of magnetite (Fe_3O_4) (X-ray data file no. 11.0614). Magnetite film grown under identical experimental conditions has been shown to consist of two layers; a thin compact layer of about 0.2 μm under a thick voluminous outer layer [7].

3.1. *Impedance measurements*

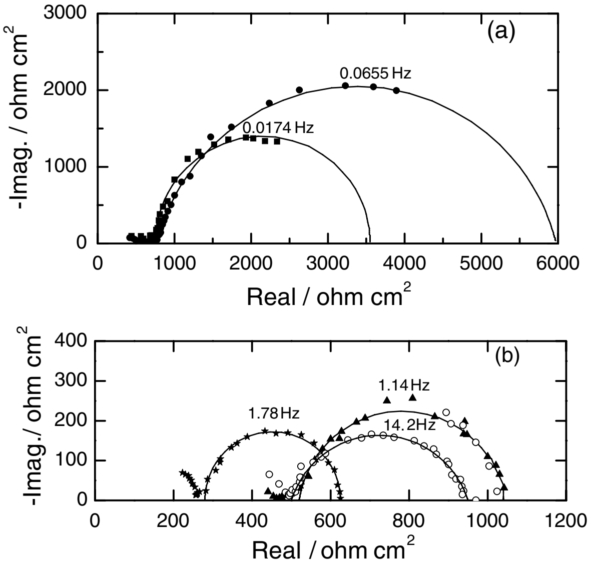

Fig. 1. (a) Nyquist plots of magnetite coating on carbon steel in 1.0 × 10^{-2} M ascorbic acid at o.c.p. at 28 °C after (●) 0.5 and (■) 2 h. (b) Nyquist plots in 1.0 × 10^{-2} M ascorbic acid at o.c.p. at 28 °C of magnetite coating on carbon steel after (▲) 10, and (★) 11 h and (○) carbon steel after 1 h.

Nyquist plots of the magnetite film on carbon steel in 1.0 × 10^{-2} M ascorbic acid solution are shown in Figure 1(a) and (b). For comparison, Figure 1(b) includes the plot for carbon steel in the same media after 1 h of exposure. Exposures of 30 min and 2 h resulted in plots which were incomplete even at low frequencies of 5–10 mHz. This indicates that the presence of initial, less defective and compact magnetite prevents the attack by ascorbic acid by providing a barrier between the reacting species. Corresponding Bode plots are shown in Figure 2. Bode plots have been used for corrosion

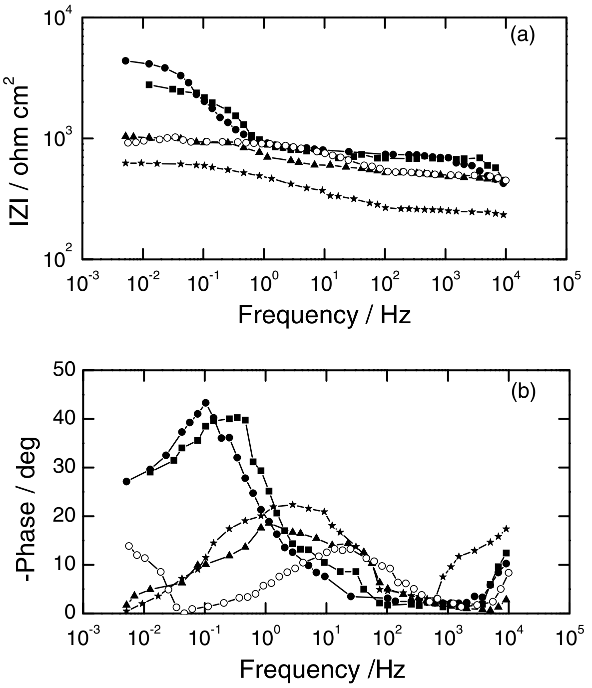

Fig. 2. Bode plots in 1.0 × 10^{-2} M ascorbic acid at o.c.p. at 28 °C of magnetite coating on carbon steel after (●) 0.5, (■) 2, (▲)10 and (★) 11 h and (○) carbon steel after 1 h, (a) Impedance and (b) phase angle.

Table 1. Resistance (R_{HF}), charge transfer resistance (R_t) and capacity (C_T) of magnetite coating in two chelating acids

Time /h	Ascorbic acid(1.0×10^{-2} M)			Picolinic acid (3.5×10^{-2} M)	
	R_{HF} /Ω cm^2	R_t /Ω cm^2	C_T /μF cm^{-2}	R_t /Ω cm^2	C_T /μF cm^{-2}
0.5	775	5200	1759	2500	821.4
2.0	764	2800	867.8	–	–
10.0	520	525	265.9	1850	147.56
11.0	280	345	259.2	–	–

evaluation of coated materials for its advantages over Nyquist plots [8]. The impedance plot recorded after 30 min reveals a relaxation process characterized by a phase angle of about 45° (slope −0.47) occurring at 100 mHz. The presence of a second process in the higher frequency region is also indicated. On increasing the exposure time to 2 h, the phase angle is lowered and the maximum shifts to higher frequency. Various parameters have been determined from the Nyquist plots. To ascertain the reaction responsible for the Nyquist plots, it is useful to compare the open circuit potential recorded before the impedance run with thermodynamic potentials of various electrochemical equilibria in the Pourbaix diagram of iron [9]. The measured potential after 30 min was −71 mV vs SCE. Two reactions of magnetite that need to be considered here are its oxidation to ferric oxide (Fe_2O_3) and reduction to ferrous ion (Fe^{2+}) according to Reactions 1 and 2.

$$2\,Fe_3O_4 + H_2O = 3\,Fe_2O_3 + 2\,H^+ + 2\,e^- \tag{1}$$

and

$$Fe_3O_4 + 8\,H^+ + 2\,e^- = 3\,Fe^{2+} + 4\,H_2O \tag{2}$$

The calculated equilibrium reduction potentials (E_0) are −207 and +527 mV vs SCE for Reaction 1 and 2 at pH 3.14 in 1×10^{-3} M ascorbic acid assuming $[Fe^{2+}] = 10^{-6}$ M, respectively [9]. Although both reactions are favoured, the latter dominates due to its more positive standard reduction potential. The reduction potential E_0 for ascorbic acid corresponding to the reaction

$$C_6H_6O_6 + 2\,H^+ + 2\,e^- = C_6H_8O_6 \tag{3}$$

is +171 mV vs SCE [10] and hence can act as a reducing agent for magnetite. The potential of the system consisting of magnetite in ascorbic acid solution is expected to be between +171 and +527 mV vs SCE. At −71 mV, oxidation of ascorbic acid and hence the reduction of magnetite (Reaction 2) is favoured. All the potentials mentioned above are those under ideal conditions when the substrate is not participating in the reaction and the overvoltage for the reactions is zero. In the present study iron (carbon steel) also takes part in the overall dissolution process and therefore, the potential measured is the result of different surface processes. Impedance measurements on carbon steel in deaerated 1×10^{-3} M ascorbic acid resulted in a single depressed semicircle with a characteristic frequency at 14.2 Hz after 1 h exposure (Figure 1(b)) and a corresponding phase angle of 13° at 25 Hz (Figure 2(b)). The charge transfer resistance (R_t) and the differential capacity (C_T) are given in Table 1. The resistance R_{HF} shown in the table is the real part of the impedance at the high-frequency end of the Nyquist plot. This is the sum of the solution resistance R_Ω and pore resistance R_p due to electrolyte penetration [11]. The latter parameter could not be determined due to insufficient and scattered data points in the high frequency region. R_{HF} is 775 Ω cm^2 for magnetite compared to 500 Ω cm^2 for carbon steel in ascorbic acid. The semicircle with a characteristic frequency at 17.4 mHz recorded after 2 h of exposure of magnetite to ascorbic acid can be attributed to Reaction 2. Upon increasing exposure, the open circuit potential shifts to a more active value of −436 mV after 2 h due to the loss of protection by the magnetite film. There is no change in the reaction as is evident from the identical Nyquist plot with a characteristic frequency at 65.5 mHz and phase angle of 40° at 343 mHz. At this stage, the reaction

$$Fe = Fe^{2+} + 2\,e^- \tag{4}$$

also takes place to some extent but does not appear as a second charge transfer loop. While R_t decreased, indicating an increase in the rate of reaction, R_{HF} remains changed.

After prolonged exposure, the underlying metal comes into contact with the ascorbic acid due to the removal of magnetite film from the surface. As a result, the base metal starts to dissolve, according to Reaction 4 to a greater extent, resulting in a potential of −610 mV after 10 h exposure. The cathodic process taking place is hydrogen evolution

$$2\,H^+ + 2\,e^- = H_2 \tag{5}$$

with thermodynamic potential of −427 mV at pH 3.1. The absence of any reaction other than Reactions 4 and 5 resulted in a single charge transfer process at 1.14 Hz as shown in Figure 1(b) with corresponding phase angle of around 20° (slope of −0.1) in the Bode plot. This frequency is closer to that observed for carbon steel in ascorbic acid, which suggests that Reaction 4 is responsible for the semicircle and the reduction of magnetite has become less significant. Both R_t and R_{HF} are lowered, resulting in the enhancement of reaction rate. Further increase in exposure time to 11 h did not affect the nature of the Nyquist and the Bode plots. The values of R_t and R_{HF} are lowered with the latter falling below 500 Ω cm^2. As the film dissolves, the contribution of R_p, which depends on the porosity of the magnetite film, becomes increasingly small. Upon complete removal, the resistance should be equal to the solution resistance.

However, further lowering of the solution resistance in long duration experiments is attributed to increased conductivity of the solution in the presence of dissolved ionic iron species. The capacity of the electrode decreases with time as shown in Table 1. The total capacity of the composite electrode C_T is given as [12]

$$C_T = \frac{[A_{Fe}C_{Fe} + A_{mag}C_{mag}]}{[A_{Fe} + A_{mag}]} \tag{6}$$

where C_{Fe} and C_{mag} are the metal–solution and magnetite–solution interface capacity respectively. The area of metal and the magnetite, A_{Fe} and A_{mag}, respectively, are time-dependent. For a perfect and defect free film C_T is equal to the capacity of the magnetite–solution interface. Dissolution of the magnetite film increases the area of the exposed metal. Upon complete removal of the magnetite, the measured capacity stabilises at a value corresponding to the metal/solution capacitance. High values for the capacity are due to the relatively thick magnetite film. As the dissolution proceeds, the capacity continues to decrease and remains unchanged after 10–11 h at about 260 μF cm^{-2}. However, this value is still very high compared to 24.9 μF cm^{-2} obtained for the carbon steel/ascorbic acid system. This is probably due to its pseudo nature resulting from the hydrogen evolution during oxide dissolution.

Figure 3 shows the Nyquist plots for magnetite in deaerated solutions of 3.5×10^{-2} M picolinic acid at 28 °C. A single capacitive loop with a characteristic frequency 77.5 mHz is observed after 30 min exposure. The relaxation process appears with a phase angle of 30° at 140 mHz in the Bode plot, shown in Figure 4. Data obtained for carbon steel exposed for 1 h in same media are included in both the figures for comparison. The depressed semicircle has a characteristic frequency of 23.5 Hz with phase angle of 11°, as shown in Figure 4. The measured open-circuit potential of the magnetite film in picolinic acid was −524 mV after 30 min immersion. According to Pourbaix [9], Reaction 2 can only take place at this potential. The nature of the Nyquist plot in picolinic acid is different from that in ascorbic acid after similar duration of exposure. This can be attributed to the fact that ascorbic acid is a reducing acid and has inhibiting properties while picolinic acid is non-reducing. However, chemical dissolution can take place in both the media according to the reaction

$$Fe_3O_4 + 8\,H^+ = 2\,Fe^{2+} + Fe^{3+} + 4\,H_2O \tag{7}$$

Picolinic acid forms three complexes with iron with formation constants (log K) of 4.9, 9.0 and 12.0 compared to 0.21 and 1.99 for the iron–ascorbic acid complexes [13]. Therefore, Reaction 7 will occur at a faster rate in picolinic acid than ascorbic acid, even though the pH of both solutions are similar. Magnetite reduction in picolinic acid through Reaction 2 would require electrons supplied by Reaction 4, which can take place only when the film becomes porous and the base metal is exposed. Thus the magnetite dissolution in picolinic acid is initially a purely chemical dissolution in the absence of an external reducing agent. Once the bare metal is exposed, Reaction 4 takes place unabated as the ferrous ion is removed through complexation and rapid dissolution of oxide takes place. However, the time constants for Reactions 2 and 4 are not resolved in the initial stage as shown in Figure 3. R_t, R_{HF} and C_T values are given in Table 1. R_t and R_{HF} are 2500 and 1220 Ω cm^2 for magnetite compared to 720 and 565 Ω cm^2 for carbon steel.

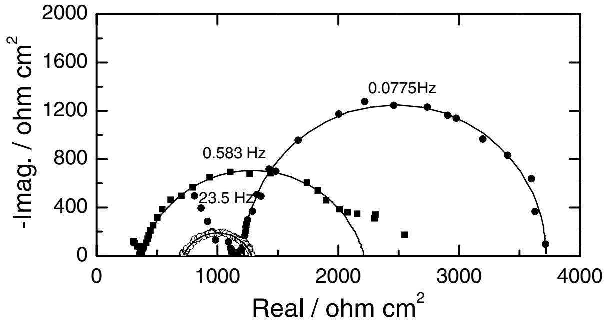

Fig. 3. Nyquist plots in 3.5×10^{-2} M picolinic acid at o.c.p. at 28 °C of magnetite coating on carbon steel after (●) 0.5 and (■) 10 h and (○) carbon steel after 1 h.

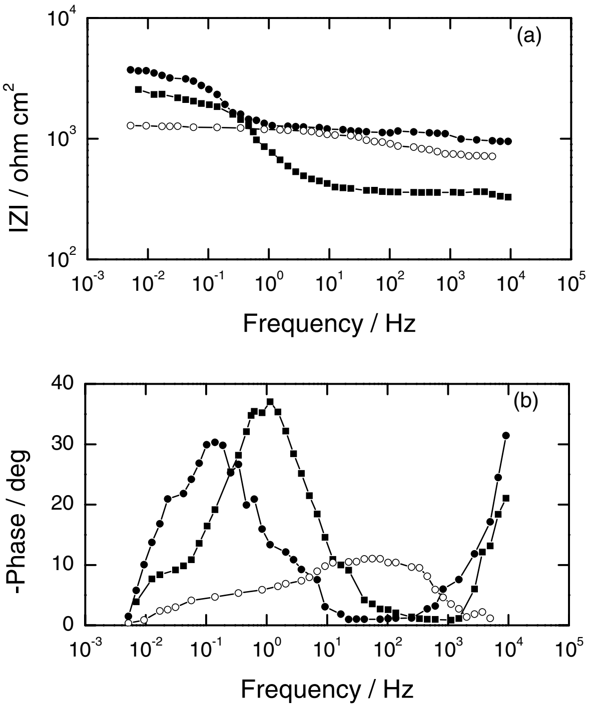

Fig. 4. Bode plots in 3.5×10^{-2} M picolinic acid at o.c.p. at 28 °C of magnetite coating on carbon steel after (●) 0.5 and (■) 10 h and (○) carbon steel after 1 h. (a) Impedance and (b) phase angle.

After prolonged exposure of 10 h, Reactions 2 and 4 are resolved appearing as two semicircles in the Nyquist plots shown in Figure 3. The characteristic frequency shifts to 583 mHz and the phase angle increases slightly to 37°. The potential of the electrode was −616 mV, which is close to the equilibrium potential of Reaction 4. Although, both R_t and C_T decrease with time, as shown in Table 1, the values are still higher than those for carbon steel; the capacity is 12 μF cm^{-2} for carbon steel in 3.5×10^{-2} M picolinic acid. This indicates the existence of magnetite film even after 10 h. However, R_{HF} is 365 Ω cm^2 which is much less than that obtained for carbon steel in picolinic acid. This is due to the increased conductivity of the solution resulting from the dissolved magnetite.

3.2. *Cyclic voltammetric measurements*

Figure 5 shows the cyclic voltammograms of magnetite film on carbon steel in 1.0×10^{-2} M ascorbic acid recorded with continuous cycling at a scan rate of 10 mV s^{-1}. The first cycle was initiated from −500 mV. Raw data with no correction for ohmic drop are shown in the figure, which otherwise would be shifted without any additional features. Since the study is restricted to the mechanism of dissolution and is not intended for quantitative information, no ohmic-drop correction was made. The higher current observed in the cathodic scan in the first cycle is due to adsorption/desorption phenomena and surface complexation [14]. In the second cycle, the forward (anodic scan) current becomes greater than the reverse current above +236 mV. This can be attributed to the oxidation of ferrous hydroxide [$Fe(OH)_2$], formed during the first cathodic scan, to ferric oxide (Fe_2O_3), in addition to adsorption and complex formation. Increased exposure and cycling resulted in further increase in current and a plateau region appeared between +50 to +200 mV without current reversal in the 25th cycle. At this stage, the adsorption and complexation phenomena became less dominant. Incomplete reduction of $Fe(OH)_2$ at −500 mV results in its accumulation and then conversion to Fe_2O_3. With further potential sweep, the plateau developed into a peak at +200 mV in 38th cycle and the difference between the forward and the reverse currents increased. Increasing exposure with cycling caused the peak to shift anodically, accompanied by its split, as shown in the 58th cycle. On reverse scanning, a peak also appears at +200 mV. The nature of the voltammogram recorded after 18 h exposure in ascorbic acid is similar to that of the first cycle, but the currents are very high. The electrode surface consists of bare metal and loose porous oxide film, which is different from the initial magnetite film. The adsorption of ascorbic acid on the surface accounts for the higher reversal current.

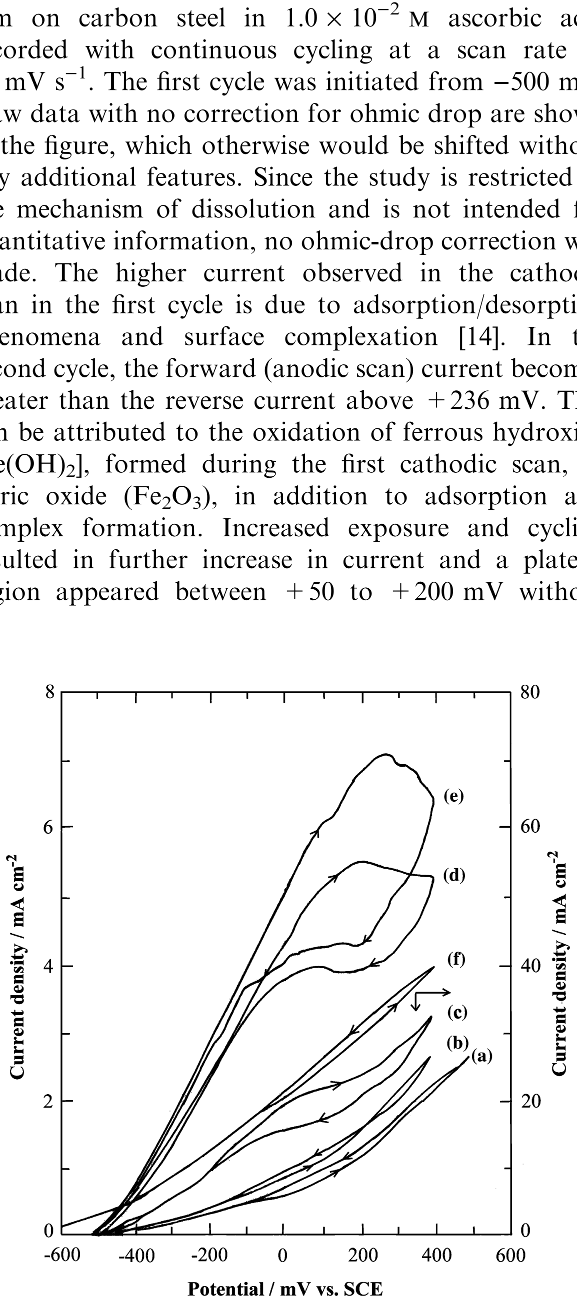

Fig. 5. Cyclic voltammograms of magnetite coating on carbon steel in 1.0×10^{-2} M ascorbic acid at 28 °C. Scan rate 10 mV s^{-1}. Cycle: (a) 1st, (b) 2nd, (c) 25th, (d) 38th and (e) 58th, and (f) after 18 h.

As discussed earlier, the dissolution of the oxide film may be either a purely chemical or a reductive or combination of both the processes. The reductive dissolution can be caused either by an externally added reducing agent or by the electrons generated during the base metal dissolution (oxidation). Gilbert and Ouellet have proposed that the dissolution of magnetite particles in acidic solutions containing EDTA/citric acid and hydrazine proceed by adsorption of chelating agents at the solid–solution interface which weakens the bond between the iron atom and oxygen atom of the crystal lattice and leads to the release of the complex to solution [15]. The hydrazine reduced ferric ions through surface complexation. An alternate dissolution reaction proposed by the author is Reaction 7 or Reaction 2 in the presence of reducing agent. For the dissolution of metal hydrous oxide powders in chelating acids, Torres et al. have also proposed a sequence of reactions in which the ferric surface complex ($-Fe_s^{III}-$) undergoes an electron transfer reaction to form ferrous ion in solution (Fe_{aq}^{2+}) which can also reduce $-Fe_s^{III}-$ to $-Fe_s^{II}-$ inside the oxide lattice releasing soluble ferric ion (Fe_{aq}^{3+}) [16]. A similar mechanism is valid in the present study. Since ascorbic acid is easily oxidisable, the reduction of Fe_s^{III}-ascorbate can occur at a faster rate thereby releasing Fe^{2+} ions in solution. Once ferrous ions have accumulated in the solution, they can reduce the lattice Fe_s^{III}-ascorbate to Fe_s^{II}-ascorbate. Moreover, there is an additional source of ferrous ions through base metal dissolution and this can produce an enhanced rate of magnetite dissolution. Relatively higher current obtained in the cathodic scan in the first few cycles is attributable to the adsorption of ascorbate at the magnetite surface.

The cyclic voltammogram of the magnetite film in picolinic acid (3.5×10^{-2} M) under deaeration is shown in Figure 6. The magnitude of the current during the initial scan and the increase in current in subsequent scans were low compared to ascorbic acid. This suggests that the attack by picolinic acid was much slower compared to ascorbic acid. The current was similar in the anodic and cathodic scans. No characteristic peak or plateau was observed, even after prolonged exposure.

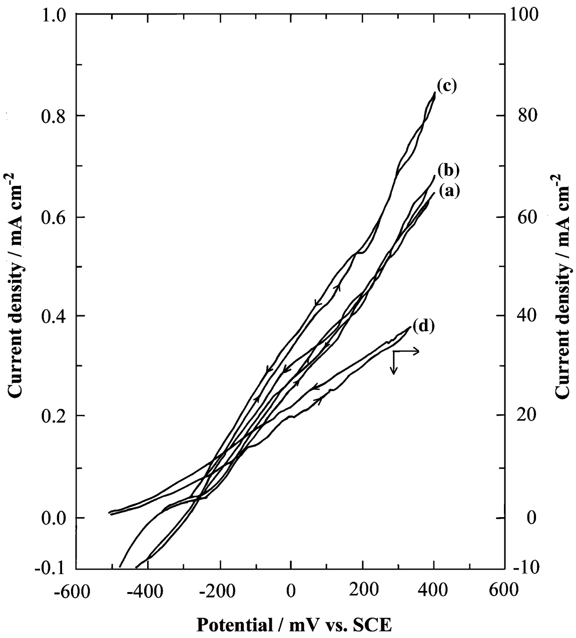

Fig. 6. Cyclic voltammograms of magnetite coating on carbon steel in 3.5×10^{-2} M picolinic acid at 28 °C. Scan rate 10 mV s^{-1}. Cycle: (a) 1st, (b) 2nd and (c) 4th, and (d) after 18 h.

These results can be explained considering that picolinic acid is only a complexing agent and is not easily oxidisable. As a result, reduction of the surface complex (Fe_s^{III}-picolinate) to soluble ferrous ion would be slow. Until the base metal is exposed, Reaction 7 is the only source of ferrous ions that can reduce the surface complex Fe_s^{III}-picolinate to Fe_s^{II}-picolinate. Therefore, the dissolution of magnetite in plain picolinic acid would take place mainly through Reaction 7. Once the base metal starts dissolving, the released electrons participate in reductive dissolution of magnetite. The better complexing ability of picolinic acid compared to ascorbic acid prevents accumulation of reaction products, such as $Fe(OH)_2$ on the electrode surface and no peak is observed in the cyclic voltammogram of the magnetite film in picolinic acid.

4. Conclusions

(i) Impedance measurements in ascorbic acid show that the interaction between magnetite and ascorbic acid is associated with an incubation period when the film acts as a diffusion barrier. The electrons required for reductive dissolution of magnetite are supplied through the oxidation of ascorbic acid. On prolonged exposure, the coating loses its protective properties and base metal dissolution provides necessary electrons for reduction.

(ii) Magnetite coating exhibits less coherent and compact behaviour in picolinic acid than ascorbic acid. Initial dissolution in picolinic acid occurs by direct acidic dissolution. The contribution of reductive dissolution increases with the availability of base metal for acid attack.

(iii) Cyclic voltammetry indicates the surface adsorption of ascorbate ion onto the oxide surface. The ferric surface complex undergoes reduction to soluble ferrous species and is transferred to the bulk solution. The accumulation of the ferrous ion accelerates the dissolution resulting in an increase in current.

(iv) The slow dissolution of magnetite results in lower currents in picolinic acid. The absence of any characteristic feature in the voltammogram is attributable to the better complexing capability of picolinic acid compared to ascorbic acid which prevents the accumulation of ferrous ions on the electrode surface.

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References

1. G.R. Srinivasan, NPCIL (1992), (personal communication).
2. S. Dutta, S. Ramabhadran and R.S. Shetiya, BARC Report, BARC/1993/1/025 (1993).
3. F. Mansfeld, *Electrochim. Acta* **35** (1990) 1533.
4. ChintamaniDas, M. Sudersanan and M.K. Totlani, *in* A.S. Khanna, K.S. Sharma and A.K. Sinha (Eds), 'Emerging Trends in Corrosion Control: Evaluation, Monitoring, Solution's, Vol 1, (Akademia Books International, New Delhi, 1999), p. 145.
5. S. Rengamani, S. Murlidharan, M.A. Nathan and S.V. Iyer, *J. Appl. Electrochem.* **24** (1994) 355.
6. S. Rengamani, S. Murlidharan, M. Ganesan and S.V. Iyer, *Indian J. Chem. Technol.* **1** (1994) 168.
7. K.B. Gaonkar, 'Studies on Formation and Characterization of Magnetite on Carbon steel in High Temperature Water', PhD thesis, Mumbai University (1993).
8. F. Mansfeld, *Corrosion* **44**(8) (1988) 556.
9. M. Pourbaix, 'Atlas of Electrochemical Equilibria in Aqueous Solutions' (Permagon, 1966), p. 307.
10. W.M. Clark, 'Oxidation–Reduction Potentials of Organic Systems', (Robert E. Krieger Publishing, Huntington, New York, 1972).
11. F. Mansfeld, M.W. Kendig and S. Tsai, *Corrosion* **38**(9) (1982) 478.
12. I.H. Plonski, *Mater Sci. Forum.* **185–188** (1995) 649.
13. A.E. Martell and R.M. Smith, 'Critical Stability Constants' (Plenum Press, London, 1974).
14. P. R. Singh, P.K. Chauhan and H.S. Gadiyar, *J. Electrochem. Soc. India* **30**(4) (1981) 322.
15. R. Gilbert and L. Ouellet, *Nucl. Technol.* **68** (1985) 385.
16. R. Torres, M.A. Blesa and E. Matijevic, *J. Colloid Interface. Sci.* **134** (475) 1990.