

Electrochemical behavior of iron electrode in NaOH solutions

I. ZAAFARANY* and K.S. KHAIROU

Department of Chemistry, Faculty of Applied Science, Umm Al-Qura University,
P.O.Box 118, Makkah Al Mukaramha (Saudi Arabia).

(Received: March 10, 2009; Accepted: May 22, 2009)

ABSTRACT

The electrochemical behaviour of iron electrode in different concentrations of NaOH solution was studied using cyclic voltammograms and A.C. Impedance techniques. Four anodic peaks (A_1 - A_4) were observed in the anodic scan of cyclic voltammograms where two cathodic peaks (C_1 and C_2) were observed in the cathodic scan of cyclic voltammograms. The four anodic peaks due to the formation $\text{Fe}(\text{OH})_{\text{ads}}$ peak (A_1), $\text{Fe}(\text{OH})_2$, peak (A_2), Fe_2O_3 (peak A_3) and formation of more stable $\text{Fe}(\text{III})$ species (peak A_4) and the cathodic scan due to the reduction of species formed on the anodic scan.

Key words: Iron, NaOH, Cyclic voltammograms, A.C. impedance.

INTRODUCTION

Iron is one of the metal used in several fields of industry. Iron and similar metals can be exposed to corrosion in connection with environmental conditions. The corrosion rate varies subject to structure of ions and molecules, kind and concentration of ion, kind of solution and kind of materials^{1,2}.

Oxidation and reduction process taking place on iron electrode in alkaline media are important from the point of view of alkaline accumulators, and many authors³⁻⁵ have dealt with the reaction mechanism, influence of additives, etc.

Extensive studies of the iron electrode in alkaline solution have been presented in numerous publications⁶⁻⁹. Two main reasons of this great interest can be given: one hand, iron electrodes in alkaline solution could be appropriate for various accumulator applications (Fe/NiOOH , Fe/air etc). On the other hand, iron is one of the most important materials in modern technology. Arising corrosion

problems are covering the whole range of pH in aqueous systems from acidic to basic, solutions.

Iron electrodes for batteries are normally placed in concentrated alkali solution 5M KOH. The charged state of the battery in $\text{Fe}(\text{O})$ gained by electrochemical reduction (discharge). The discharge reaction first leads to $\text{Fe}(\text{II})$, which is found to be $\text{Fe}(\text{OH})_2$ ¹⁰. Prolonged discharge leads to the formation of a sludge which was identified by in situ Mössbauer spectroscopy during cyclic galvanostatic oxidation-reduction of iron and found to be mainly FeOOH and unreacted $\text{Fe}(\text{OH})_2$ ¹¹ on numerous occasions, it has been pointed out that the formation of oxides involves soluble $\text{Fe}(\text{II})$ and $\text{Fe}(\text{III})$ species¹².

EXPERIMENTAL

The test electrode was made of pure iron obtained from Saudi iron and steel company and having the following chemical compositions (wt%) (C, 0.052, Mn 0.189, S, 0.011, P 0.008, Si 0.011, Al 0.039, N 0.001, Cr 0.012, Cu 0.04, Mo 0.024, Ni 0.029, and the remaining is iron). Acylindrical iron

rod embedded in aralidite with exposed surface area of 0.5 cm^2 . Prior to each experiment, the surface of iron specimen were mechanically polished with different grades of emery paper, degreased with acetone and rinsed by distilled water. No attempts were made to deareate them. The electrolytic cell was all pyrex and described elsewhere¹³.

Cyclic voltammograms curves (CVs) were performed using auto lab (ECO Chemie) combined with the software package GPES (General Purpose Electrochemical System) was used. This is a computer controlled electrochemical measurements system. It consists of data acquisition system and potentiostat-galvanostat CV's were used to study the electrochemical behavior of iron in different concentrations of NaOH solutions sweeping from hydrogen evolution to oxygen evaluation. All measurements were taken at $25 \pm 1^\circ\text{C}$.

The electrochemical impedance spectroscopy (EIS) was carried out in a conventional three electrodes electrochemical cell. The counter

and reference electrodes were a platinum plate (2 cm^2) and saturated calomel electrode (SCE) respectively. The measurements were recorded using a voltalab PGZ 301. EIS voltammetry system with an accompanying PC and soft ware.

RESULTS AND DISCUSSION

Cyclic voltammogram behavior of iron electrode in NaOH solutions

Fig. (1) represents the cyclic voltammograms of iron electrode in different concentrations of NaOH at a voltage scan rate 50 mV/s in the potential range -1300 to $+600 \text{ mV}$. An inspection of this figure four anodic peaks (A_1 - A_4) and two cathodic peaks (C_1 and C_2) are observed. Similar curves were obtained by Burke and Lyons¹⁴.

The general shape of the cyclic voltammograms suggesting that the composition of the film both in the passive and in the active region. The peak A_0 at the upper and of the potential corresponds to the oxygen gas evolution reaction

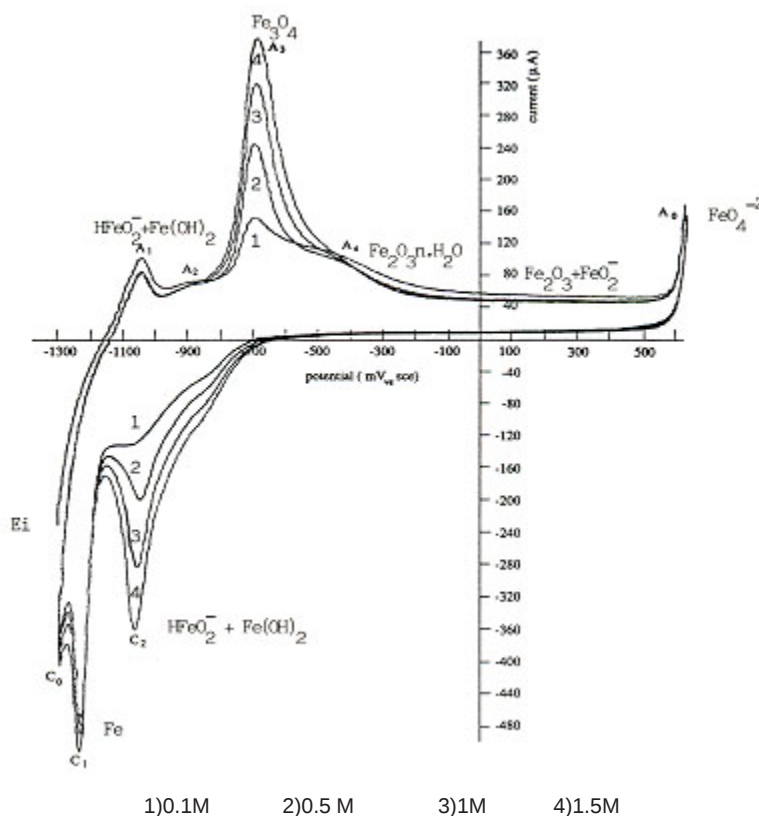


Fig. 1: Cyclic Voltammetry of iron in different concentrations of NaOH solutions at 50 mV/sec

and the peak C_0 at lower end of the potential corresponds to the hydrogen gas evolution reaction, Fig. (1).

There are two anodic peaks or humps A_1 and A_2 at more cathodic potentials than A_3 . From the curves in Fig. 1 suggest that the cathodic peak C_1 conjugated with the anodic peaks A_1 and A_2 . This behavior is in accord with MacDonald and Owen¹⁵.

The hump A_2 which is next to the peak A_3 corresponds to the reaction of $Fe \rightarrow Fe(OH)_2$ only the cited authors [15] assumed the less probable reaction $Fe(OH)_2 \rightarrow Fe_3O_4$, hence the back reaction $Fe(OH)_2 \rightarrow Fe$ proceeds in the peak C_1 . Confusion exists, however, regarding the hump A_1 (which is next to A_2) it has been attributed either to oxidation of adsorbed hydrogen¹⁶ or to oxidation of iron¹⁵ or to both¹⁷. The first step in the oxidation of iron appears more probable than oxidation of hydrogen. This step should be formulated as $Fe \rightarrow Fe(OH)_{ads}$ ¹⁸, contrasting with $Fe \rightarrow Fe(OH)_2$ proceeding in peak A_2 . Further inspection in Fig.1, it is clear that the peak A_2 and C_1 do not increase with the number of cycles distinguishes them well from the peaks A_3

and C_2 and implies a passivity property of Fe(II) hydroxide film formed. This probably has a low porosity and thus hinders the diffusion of ions necessary for its growth. The film is formed in NaOH solution-precipitation mechanism¹⁷. By contrast, the "classical" passivity of iron occurs at more anodic potential¹⁹ and is due to the formation of non-porous film of Fe(III) oxides²⁰. Since the anodic charge corresponding to the humps A_1 and A_2 is considerably smaller than that corresponding to the peak A_3 , it is obvious that the latter can not be due merely to one electron oxidation of the film formed is the proceeding sites as suggested by Burke²¹ it is much more probable that the peak A_3 involves oxidation of both $Fe(OH)_2$ and Fe to $Fe(III)$ ¹⁵. Peak A_3 always lies in the region where oxidation of $Fe(OH)_2$ (either to Fe_3O_4 or to $FeOOH$) takes place. The conjugated peak $C2$ logically corresponds to the back reaction. The composition of the oxidation product may depend on the experimental conditions, the following compound have been considered by various authors, $Fe(OH)_3$ or $FeOOH$ or Fe_2O_3 [15] and Fe_3O_4 ¹⁷. The peak at A_3 represents the formation of the magnetite or $FeOOH$.

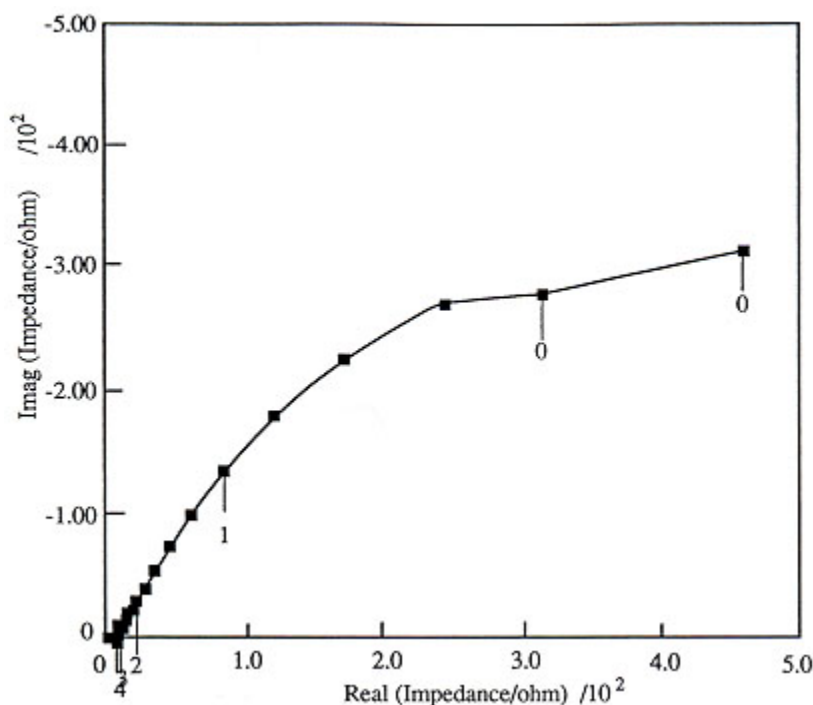


Fig. 2: Complex plane of passive film on iron in 1M NaOH in low potential (-1.2V)

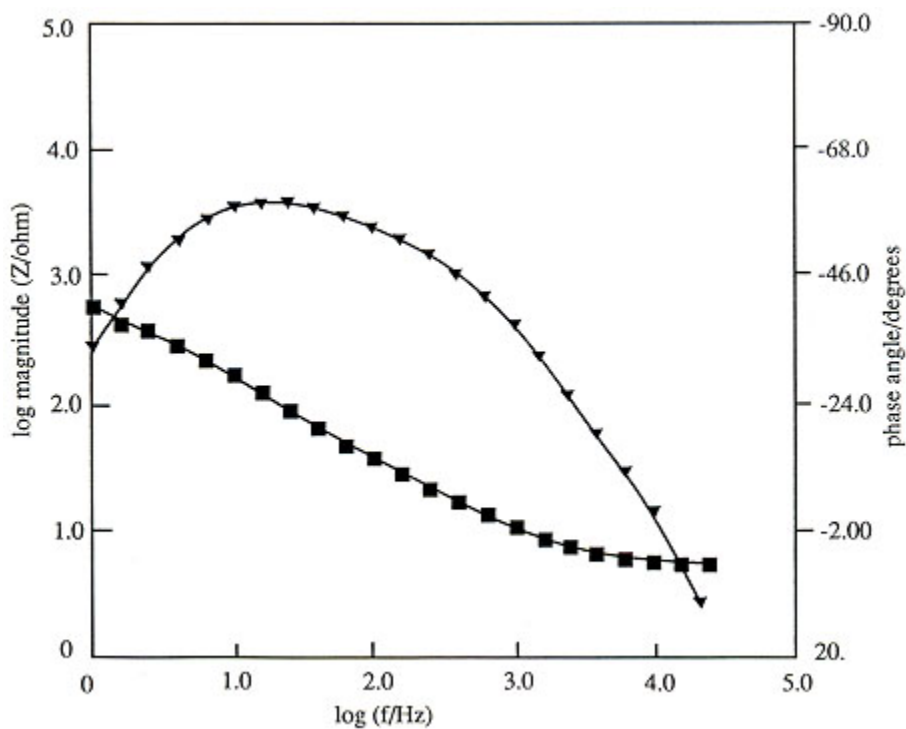


Fig. 3: Bode plots of passive film on iron in 1M NaOH in low potential (-1.2V)

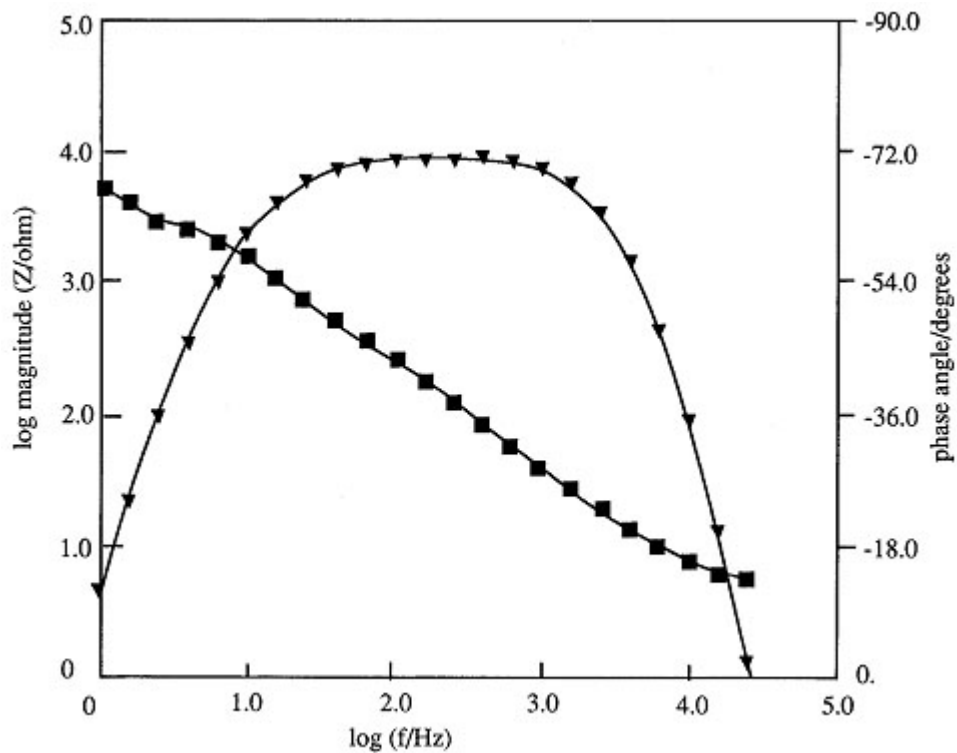


Fig. 4.: Bode plots of passive film on iron 1M NaOH in intermediate potential -0.5 to +0.5V

The hump A_4 , which is more anodic than the peak A_3 , is observed it might correspond to the formation of more stable Fe(III) species than that formed in the peak A

A.C. Impedance behavior of iron in alkaline solutions

Impedance measurements were made of the passive film on pure iron from the dissolution potential to a potential of oxygen evolution. The analysis of the experimental impedance data is based on the Bode plots which emphasize aspects of the response while are not readily apparent from the analysis of the impedance in the complex plane plot²².

Figs. (2-4) show the typical complex plane and Bode plots for passive film iron between -1.2 V to 0.6 V (SCE). Above approximately +0.6V (SCE), the shape of the impedance curves is significantly different from that observed of low potential. In this region, as the potential is increased a very definite inflection appears which moves the curve downward Fig. (3).

In the medium potential region (+0.5 V to -0.5 V) the impedance decreased as the potential was changed to less anodic values. The change of the impedance diagram was not linearly dependent on potential and this effect increased as the potential

was changed to more negative values. The log Z versus log f curves was very straight over a wide frequency range but the slopes were apparently less than -1, (Fig. 4). In the potential region where the film starts to dissolve, there was a clear separation of the impedance curves at various potential values and the slope of these lines becomes significantly less than -1 accompanied by phase angle decreases (Fig.3).

At low frequencies, the impedance showed a straight line with a slope close to -1 which corresponds to the capacitance. At high frequencies the curves become flat with a slope approaching zero which corresponds to a pure resistance. When the potential was removed from the rest potentials the log Z measured at low frequencies decreased linearly with potential, which means that the resistance decreased exponentially with the over potential increase.

In the impedance diagrams, the most sticking characteristic is the straightness of the log impedance versus log frequency curve and the fact that the slope of these lines deviate from -1. This important features precludes the possibility that the oxide can be represented by a pure capacitor, because in a Bode plot, the impedance of a "perfect capacitor" should be represented by a straight line with a slope of -1 and a phase angle of -90 °.

REFERENCES

1. S. Zor, B. Yazici and M. Erbil: *Corros. Sci.*, **47**: 2700 (2005).
2. S. Zor. Turkish: *J. Chem.* **26**: 403 (2002).
3. J. Cerny and K. Micka: *J. of Power Sources* **25**: 111 (1989).
4. L. Ojefors: *J. Electrochem. Soc.* **123**: 1691 (1976).
5. E.B. Castro: *Electrochim. Acta*, **14**: 2117 (1994).
6. A. El-Sayed: *Revue Roumaine de chimie*: **38**(2): 139 (1993).
7. B. Anderson and L. Ojefors: *J. Electrochem. Soc.* **123**: 814 (1976).
8. D.D. Macdonald and D.Owen: *J. Electrochem. Soc.*, **120**: 317 (1973).
9. F. Beck, R. Kaus and M. Oberst: *Electrochim Acta* **30**(2): 173 (1985).
10. H.G. Silver and E. Leaks: *J. Electrochem. Soc.*, **117**: 5 (1970).
11. Y. Geronov, I. Tonov and S. Georgiev: *J. Appl. Electrochem.*, **5**: 351 (1974).
12. T. Hurlen, *Electrochim. Acta*, **8**: 609 (1963).
13. A. M. Shams El-Din and S.M. Abd El-Haleem, *Werkst. Korros.*, **24**: 389 (1973).
14. Z.D. Burke and M.E.G. Lyons: *J. Electroanal. Chem.* **198**: 347 (1986).
15. D.D. MacDonald and Owne: *J. Appl. Electrochem.* **15**: 675 (1985).

16. V.S. Muralidharan: *J. Appl. Electrochem.* **15**: 675 (1985).
17. R.D. Armstrong and I. Baurhoo: *J. Electroanal. Chem.* **40**: 325 (1972).
18. Z.D. Burke and M.E.G. Lyons: *J. Electroanal. Chem.* **198**: 347 (1986).
19. P. Lorbeer and W.J. Lorenz: *Corros. Sci.* **21**: 79 (1981).
20. Z.Q. Hunny and J.L. Ord: *J. Electrochem. Soc.* **132**: 24 (1985).
21. Z.D. Burke and M.E. G. Lyons: *J. Electroanal. Chem.* **198**: 347 (1986).
22. U. Stimming and J.W. Schultze: *Electrochim Acta* **24**: 859 (1979).