

ELECTROCHEMICAL BEHAVIOR OF IRON ELECTRODE IN NaOH SOLUTIONS

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(Received: 6 / 8 / 2008)

ABSTRACT

The electrochemical behavior of iron electrode in different concentrations of NaOH solution was studied using cyclic voltammograms and AC 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 $Fe(OH)_{ads}$ peak (A_1), $Fe(OH)_2$ peak (A_2), Fe_2O_3 (peak A_3) and the formation of more stable $Fe(III)$ species (peak A_4). The cathodic scan due to the reduction of species formed on the anodic scan.

Key words: Fe, NaOH, Cyclic voltammograms, AC impedance.

INTRODUCTION

Iron is one of the metals used in several fields of industry. Iron and similar metals can be exposed to corrosion in connection with environmental conditions. The corrosion rate varies with structure of ions and molecules, kind and concentration of ions and kind of solutions and materials [Erbil et al., (2005) and Zor et al., (2002)].

Oxidation and reduction processes taking place on iron electrode in alkaline media are important from the point of view of alkaline accumulators, and many authors [Cerny et al., (1989); Ojefors et al., (1976) and Castro et al., (1994)] have dealt with the reaction mechanism, and influence of additives.

Extensive studies of the iron electrode in alkaline solution have been presented in numerous publications [El-Sayed et al., (1993); Anderson et al., (1976); Macdonald et al., (1973) and Beck et al.,

(1976)]. 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 of 5M KOH. The charged state of the battery in Fe(O) gained by electrochemical reduction (discharge). The discharge reaction first leads to Fe(II), which is found to be Fe(OH)₂ [Silver et al., (1970)]. 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 Fe(OH)₂ [Geronov et al., (1974)] on numerous occasions, it has been pointed out that the formation of oxides involve soluble Fe(II) and Fe(III) species [Hurlen et al., (1963)].

The present work aims to study the electrochemical behavior of iron electrode in sodium hydroxide solutions using cyclic voltammograms and AC impedance techniques.

EXPERIMENTAL METHODS

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, S0.011, 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). A cylindrical iron rod embedded in araldite with exposed surface area of 0.5 cm². 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 elsewhere [Shams El-Din et al., (1973)].

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 evolution. 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 Volta Lab PGZ 301. EIS voltammetry system with an accompanying PC and software.

RESULTS AND DISCUSSION

1. 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 scan rate 50 mV/s in the potential range -1300 to $+600\text{ mV}$. Inspection of these 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 Lyons [**Burke et al., (1986)**].

The general shape of the cyclic voltammograms suggesting that the composition of the film is in the passive and the active region. The peak A_0 at the upper end of the potential corresponds to the oxygen gas evolution reaction 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 . The curves of Fig. 1 suggest that the cathodic peak C_1 conjugated with the anodic peaks A_1 and A_2 . This behavior is recorded by MacDonald and Owen [**MacDonald et al., (1985)**].

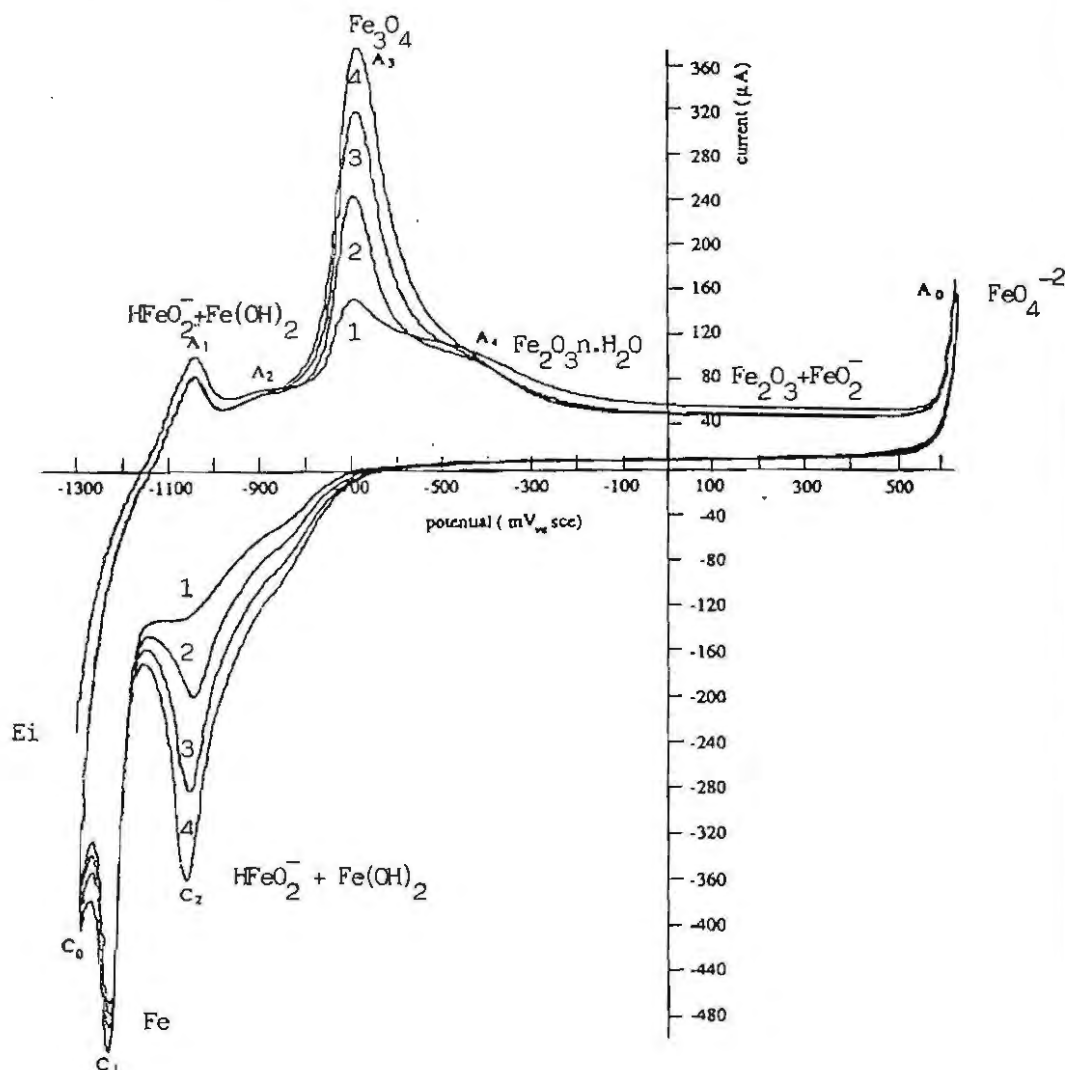


Fig. (1): Cyclic Voltammetry of iron in different concentrations of NaOH solutions at 50 mV/sec. 1) 0.1 M 2) 0.5 M 3) 1 M 4) 1.5 M

The hump A₃ which is next to the peak A₃ corresponds to the reaction of $\text{Fe} \rightarrow \text{Fe(OH)}_2$ only the cited authors assumed the less probable reaction of $\text{Fe(OH)}_2 \rightarrow \text{Fe}_3\text{O}_4$, hence the back reaction $\text{Fe(OH)}_2 \rightarrow \text{Fe}$ proceeds at the peak C₁. Confusion exists, however, regarding the hump A₂ (which is next to A₂) it has been attributed either to oxidation of adsorbed hydrogen [Muralidharan et al., (1985)] or to oxidation of iron

or to both [Armstrong et al., (1972)]. The first step in the oxidation of iron appears more probable than oxidation of hydrogen. This step can be formulated as $\text{Fe} \rightarrow \text{Fe(OH)}_{\text{ads}}$ [Burke et al., (1986)], contrasting with $\text{Fe} \rightarrow \text{Fe(OH)}_2$ 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 mechanism. By contrast, the "classical" passivity of iron occurs at more anodic potential [Lorbeer et al., (1987)] and is due to the formation of non-porous film of Fe(III) oxides [Hunny et al., (1985)]. 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 Burke [21] it is much more probable that the peak A_3 involves oxidation of both Fe(OH)_2 and Fe to Fe(III). 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 C_2 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 and Fe_3O_4 . The peak at A_3 represents the formation of the magnetite or FeOOH .

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

AC 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 plot [Stimming et al., (1979)].

Figs. (2-4) show the typical complex plane and Bode plots for passive film on 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 deviates 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° .

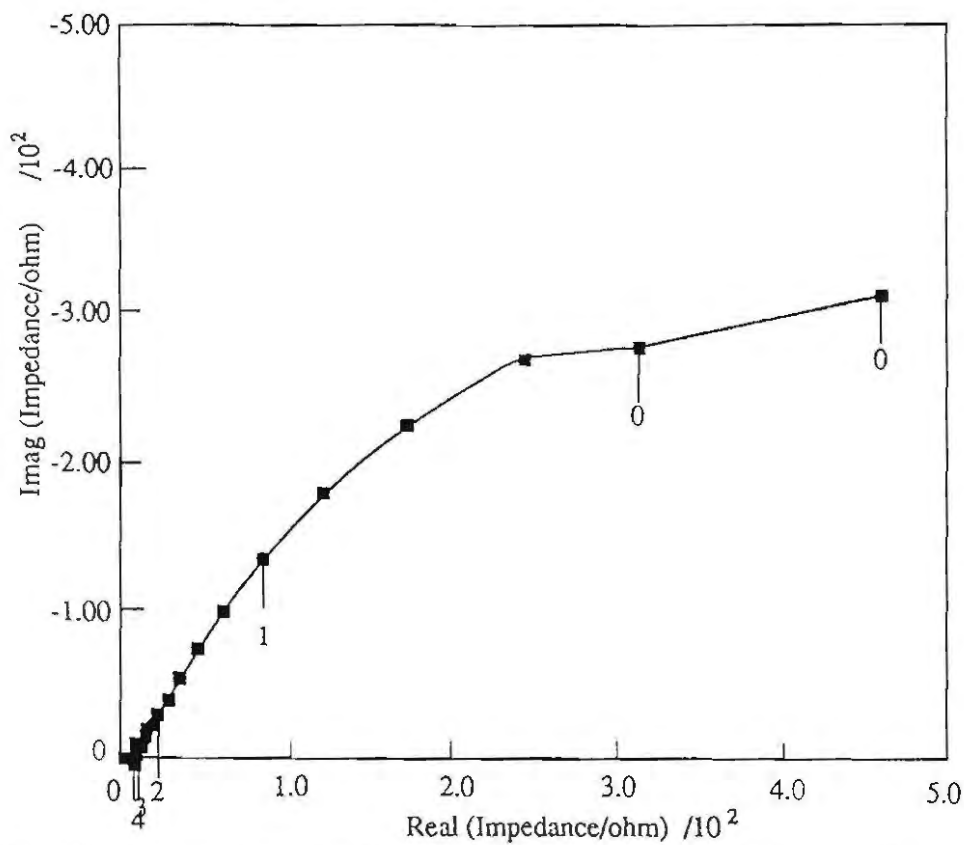


Fig. (2): Complex plane of passive film on iron in 1M NaOH at low potential (-1.2V)

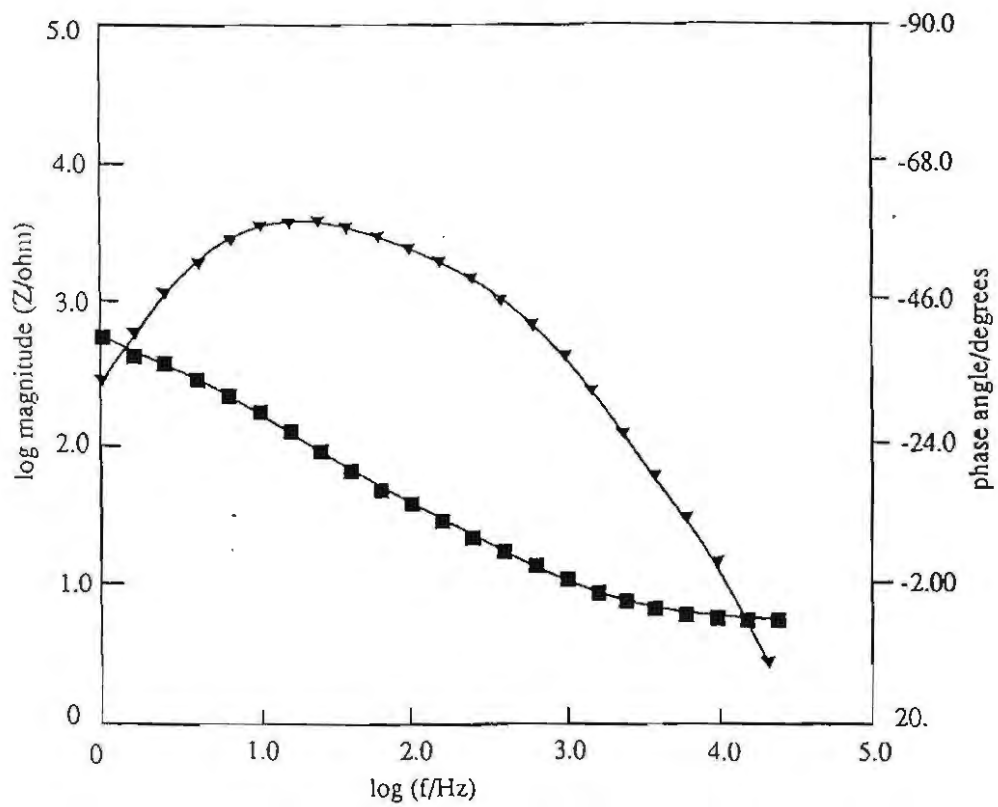


Fig.(3): Bode plots of passive film on iron in 1M NaOH at low potential (-1.2V)

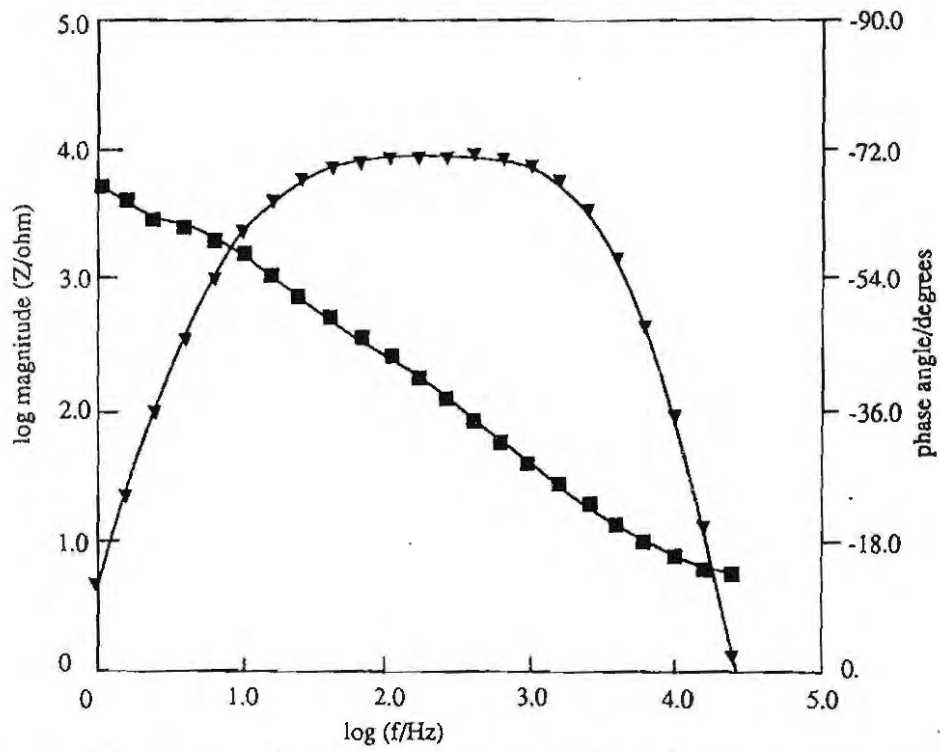


Fig. (4): Bode plots of passive film on iron in 1M NaOH at intermediate potential -0.5 to +0.5V

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السلوك الكهروكيميائي للحديد في محاليل هيدروكسيد الصوديوم

تم دراسة السلوك الكهروكيميائي للحديد في تركيزات مختلفة من هيدروكسيد الصوديوم باستخدام الفلتامترية الدائرية و المعاوقة الكهربية . و قد لوحظ ظهور اربعة قمم في منطقة المصعد و قمتان في منطقة المهبط و قد دلت هذه القمم الاربعة على تكوين $Fe(OH)_{ads}$, $Fe(OH)_2$, Fe_2O_3 and $Fe(III)$

