

Electrochemical behavior of iron electrode in sodium sulphide solutions

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ABSTRACT

The electrochemical behavior of iron electrode in sodium sulphide solutions was studied using cyclic voltammograms technique. The morphology of the surface before and after immersion of iron electrode in Na₂S solution was also studied using scanning electron microscope (SEM) and energy dispersive analysis of X-rays (EDAX). Two anodic peaks were observed in the anodic scan due to the formation of FeS₂, converted to FeS on the surface of electrodes. On the other hand one cathodic peak occurred due to the reduction of FeS in the cathodic branch of cyclic voltammograms. The formation of iron sulphide was supported by SEM photograph and increase of sulphur counts observed in EDAX analysis. The current for peaks (A and B) increases with increasing sodium sulphide concentration and voltage scan rate but the values of peak potential remains unchanged.

Key words: Iron, sodium sulphide, cyclic voltammogram, SEM, EDAX.

INTRODUCTION

The electrochemical behavior of iron in sulphide solutions has been studied both from a fundamental and a practical point of view, especially in relation with the corrosion problems in the pulp and paper industry. The electrochemical behavior of iron in sulphide solution has extensively studied. The first anodic peak in voltammetric sweeps at 0.1V versus a reversible hydrogen electrode (RHE) was attributed to the formation of FeS₂, although others have assigned it to the formation of an iron oxide with FeS being formed in a second anodic peak after dissolution of the oxide film. Perhaps these differences may be due to the different pH values and/or Na₂S concentrations. Salvarezza et al. have explained the behavior of iron in alkaline sulphide solutions on the basis of an initial competitive adsorption between OH⁻, SH⁻ and H₂O with the nature of the products formed and increasing on the concentration of both OH⁻ and SH⁻.

EXPERIMENTAL

Iron electrode having the chemical composition (％) 0.052C, 0.189 Mn, 0.008 P, 0.011 S, 0.011 Si, 0.012 Cr, 0.029 Ni, 0.04 Cu, 0.039 Al and the remainder is Fe, provided by the “Saudi Iron and Steel Company” was used in the present study. The bottom of the rod specimen with a mean surface area 0.52 cm² was successively abraded with 1-, 0- and OO- emery paper, degreased with acetone and dried between two filter papers and then immersed in 50 ml of the test solution. All chemicals used were of Analar quality. The solutions were prepared using double distilled water. No
attempts were made to deareate them. The electrolytic cell was all Pyrex and described elsewhere.

Cyclic voltammetry curves (CVs) were performed using autolab (ECO Chemic) combined with the software, package, GPES (general purpose electrochemical system) was used. It consists of data acquisition system and potentiostat-galvanostat.

Scanning electron microscope (SEM) of the type (XL-30) was used to examine the surface iron electrode in absence and presence of sulphide solution. All micrograph of corroded specimens were taken at a magnification of (X-500). Energy dispersive analysis X-ray (EDAX) examination using a Traktor TV-2000 energy dispersive spectrometer was used in this work.

RESULTS AND DISCUSSION

Cyclic voltammogram of iron in 0.03 M Na$_2$S solution

The cyclic voltammetry technique is useful for identifying the steps involved in the overall reactions resulting in the formation of various films on metallic surface [8,9]. It is particularly useful for distinguishing between products resulting from chemical, electrochemical reactions. Its main limitation is that, it is only useful for examining very thin film formed in relatively short time.

Fig. 1 represents the cyclic voltammograms curves of iron electrode in 0.03 M Na$_2$S solution at sweep rate of 50 mV sec$^{-1}$. From an inspection of the curves in Fig. 1 it is clear that there are two anodic peaks (A and B) and passive region. The first anodic peak (A) located at -0.87V and the second anodic peak (B) located at -0.25V. The first anodic peak was attributed to formation of ferrous sulphide FeS$^0$ which thicken an anodic polarization.

This process can be looked upon as occurring through the ionization of iron metal followed by combination of ferrous ions and sulphide ions with the precipitation of a porous black scale of ferrous sulphide on the iron surface.

... (1)

... (2)

The mechanism of film formation under peak (A) can be readily account for on the basis of specific adsorption of OH$^-$ and S$^{2-}$ or (HS$^-$) on the metal surface.

The second peak (B) appears at about -0.25V is thought to correspond to the partial transformation of the thick corrosion product Fe$_2$S formed under peak A to FeS (pyrite) according to the following reaction.

... (3)
Some FeS may also be formed by the direct combination between Fe$^{2+}$ ions and sulphide ions which could black some pores in the sulphide-type film.

$$\text{Fe}^{2+} + \text{S}^2^- \rightleftharpoons \text{FeS} + 2\text{e}^- \quad \ldots(4)$$

On the reversing scan, there is only one defined cathodic (reduction) peak. This peak was attributed to the reduction of ferrous sulphide.

**Effect of cyclization**

Fig. 2 represents the cyclic voltammograms of iron electrode in 0.1M Na$_2$S solution recorded in three successive sweeps 1, 2 and 3 at voltage scan rate of 50 mV/sec. The numbers on the curves correspond to the sweep number. The observed difference in the curves can be attributed to different initial states of the electrode surface and can be recognized along both the anodic and cathodic branches of the cyclic voltammograms. The initial state of the electrode surface determines to an important extent the shape of the resulting cyclic voltammograms. It is of interest to remark that the second and third sweeps give essentially similar voltammograms.

The quantity of electricity integrated under the whole anodic branch of the voltammogram is
relatively highly enlarged in value with the increasing the number of sweep. This behavior could be attributed to the activation of the metal surface and the continuous formation of different ferrous sulphide species along the whole anodic-branch of cyclic voltammograms. It is noteworthy that the presence of (OH-) ions may bring about partial activation of the formed sulphide layer possibly due to the formation of hydroxyl complex ion through the interaction of OH- ions with the metal in the pores of sulphide layer9.

In summary, one concludes that pre-condition of the metal surface in the second sweep (activation) interferes with normal formation and growth of the protective oxide film during the second sweep. Moreover, the initial corrosion is high and remained high over a wide range of potential covering peaks A and B.

**Effect of sodium sulphide concentration**

The cyclic voltammograms of iron electrode in different concentrations of sodium sulphide at voltage scan rate of 50mV/sec was studied. Similar curves to figs (1 and 2) were obtained (not shown). But the values of peak current density of peaks (A and B) are changed. The values of peak potential for peaks A and B are almost constant (at the same potential -0.87V and -0.25V for peaks A and B respectively).

Fig. 3 (a and b) represents the plots between the peak current Ip and the molar concentration of sodium sulphide on a double logarithmic scale for anodic peaks A and B respectively. Straight lines relationship were obtained satisfying the following equation.
where, \( a \) and \( b \) are constants depend on the type of electrode used.

**Effect of voltage scan rate**

The cyclic voltammograms of iron electrode in 0.8M \( \text{Na}_2\text{S} \) solution at different voltage scan rate was studied. Similar curves to figures 1 and 2 were obtained (not shown). The values of peak potential for peaks A and B are almost constant. But the values of peak current (\( I_p \)) increases with increase the voltage scan rate.

**Surface analysis**

The layer formed after immersed the iron electrode in 0.03M \( \text{Na}_2\text{S} \) solution was investigated using scanning electron microscope (SEM) and energy dispersive analysis of X-rays (EDAX).

**CONCLUSION**

1. Two anodic peaks were observed in the cyclic voltammograms of iron electrode in 0.03M \( \text{Na}_2\text{S} \) solution.
2. The first anodic peak is due to the formation of FeS\(_2\) while the second anodic peak is due to the transformation of FeS\(_2\) to FeS.
3. The peak current for peaks A and B increases with increasing \( \text{Na}_2\text{S} \) concentration and voltage scan rate, but the peak potential remain unchanged.
4. SEM and EDAX analysis emphasizes the formation of sulphide ion on the surface of iron electrode.

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