

## CYCLIC VOLTAMMETRY STUDY OF THE EFFECT OF POLYANILINE ONTO IRON IN $K_2SO_4$ MEDIUM

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### ABSTRACT

Corrosion inhibition of iron in  $K_2SO_4$  medium at pH = 5.3 with polyaniline was investigated by cyclic voltammetry. Well-defined cyclic voltammograms showing the growth of polyaniline were observed during each cycle. It was found that this procedure yielded adherent polymer and prevented significantly the degradation of iron.

**Keywords :** *Polyaniline, iron, cyclic voltammetry, electrodeposition, corrosion inhibition.*

### RÉSUMÉ

**Étude par voltammétrie cyclique de l'influence de la polyaniline sur le fer en milieu  $K_2SO_4$ .**

L'inhibition de la corrosion du fer en milieu  $K_2SO_4$  à pH = 5,3 avec la polyaniline, a été réalisée par voltammétrie cyclique. Les voltammogrammes bien définis, montrent la croissance de la polyaniline durant chaque cycle. La polyaniline ainsi formée, adhère à la surface du métal et empêche considérablement la dégradation du fer.

**Mots-clés :** *Polyaniline, fer, électrodéposition, voltammétrie cyclique, inhibition de corrosion.*

## I - INTRODUCTION

Polyanilines have attracted a great deal of research interest because of their inhibition properties [1-5] The inhibitive property of polyaniline can mainly be attributed to the presence of plenty of  $\pi$ - electron clouds coexisting with quaternary nitrogen atom [6,7]. The larger molecular size ensures the greater coverage of the metallic surface and lesser adsorption of  $\text{SO}_4^{2-}$  ions on the metal surface leaving more and more space for the organic molecules to get absorbed. Different metals and alloys such as the iron [8,9], aluminium [10], mild steel [11,12] and steel [13] were used for some deposits. In the present study, cyclic voltammetry technique was employed as main method to obtain well adherent conducting of polyaniline onto iron surfaces.

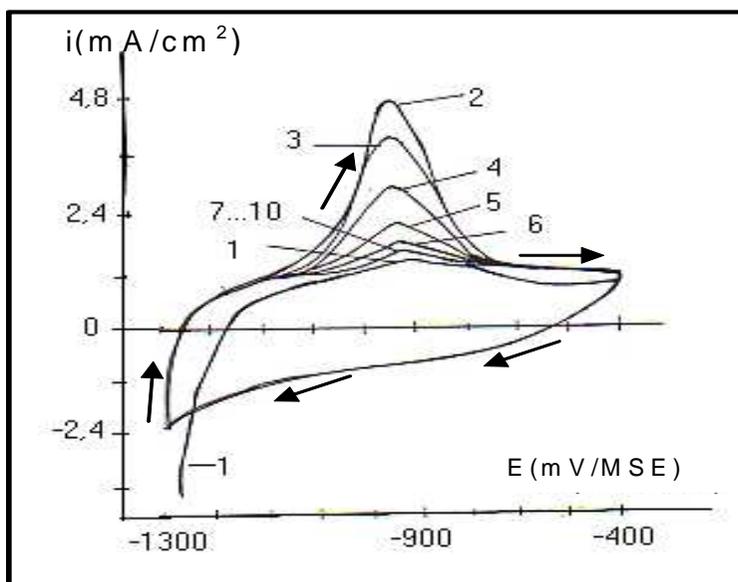
## II - EXPERIMENTAL

Corrosion solution of 0.1 M  $\text{K}_2\text{SO}_4$  is acidified to pH 5.3 by sulphuric acid. The synthesis of the polyaniline was performed by cyclic voltammetry with linear variation of potential. Voltammetric measurements were performed with a conventional three-electrode cell, a vitreous carbon plate as counter-electrode, a mercury / mercurous sulphate electrode (MSE) as reference electrode, an iron plate as working electrode.

The working electrode was polished before and after each experiment, rinsed smoothly with ultra pure water (Milli -Q, Millipore system) and wiped. All measurements were performed with a Wenking VSG72 voltage scanner, a Wenking 68FR05 potentiostat, a LINSEIS LY17200 X-Y recorder. The potential was scanned from – 1300 mV/MSE to – 400 mV/MSE, and the scan rate was 50 mV/s. All measurements were carried out at  $T = 298 \text{ K}$ .

## III - RESULTS AND DISCUSSION

Conducting polymer films of polyaniline were deposited onto pure iron using cyclic voltammetry techniques. The well-defined cyclic voltammogram curves are shown in *Figure 1*.



**Figure 1 :** Cyclic voltammograms during electropolymerization of 0.1 M aniline on the iron in 0.1 M  $K_2SO_4$  up to 10 cycles at 50mV/s and at 25°C

The first sweep is characterized by a slight anodic peaks at approximately – 825 mV vs. MSE which is consistent with the beginning of the oxidation of iron. After, the current density decreased from 1.25 to 0.85 mA/cm<sup>2</sup>. During the back sweep, the current density decreased markedly and no reduction peak is observed. In the second sweep, the density increased rapidly and reached a maximum at 4.8 mA/cm<sup>2</sup> and a new anodic peak at the same potential appears.

This behaviour indicates the maximum of the oxidative polymerization of aniline. At higher potentials, the density current decreased as an iron layer formed which passivated the surface. The constancy of the current density marks the end of the inhibition process by passivation of the surface of the electrode; therefore there is a blocking of the surface. During the reverse cycle no cathodic peak appears.

After the second cycle, the peak current at - 825 mV vs. MSE decreased gradually on increasing the cycle number. When all the active sites of iron were covered by the products of polymerization, the oxidation reaction of aniline ceased, and it follows a decrease of the peak which starts from the 3<sup>th</sup>

cycle to the 10<sup>th</sup> potential cycle and by a decrease of the current density from 4.8 to 1.2 mA/cm<sup>2</sup>. One can see that no changes were produced in the coating during the reverse negative scan. This indicates that the reactivation of the Fe do not occur [14]. On the other hand, the deposited polymer is not undergoing degradation and is capable of preventing the reaction.

This is due to the fact that the passivating character of PANI is so effective that a slight amount released is sufficient to produce a passivating and insulating layer that prevent charge transfer at the metal/polymer interface. This may be a sign of stabilization of the iron oxide substrate due to the formation of an adherent PANI film, which indeed shows a well-defined electrochemical response.

As already pointed out by *Bernard et al.* [15], this last oxidation of the surface is due to a phenomenon of acidification with the formation of oxyhydroxide FeOOH according to the reaction :



Or according to the reaction of Ogura [16]



According to *Gottesfeld et al.* [17] the large cathodic peak located between -600 and -400 mV vs. MSE, can be ascribed to the weak change in the film resistivity from the insulating form to the conductor form of PANI.

#### IV - CONCLUSION

Corrosion protection of iron in K<sub>2</sub>SO<sub>4</sub> 0.1M medium at pH 5.3 with polyaniline was investigated by cyclic voltammetry. Well-defined anodic peaks were obtained at -825 mV vs. MSE which indicated the growth of polyaniline with the maximum at the second sweep. No cathodic peak appears during the reverse negative scan. This fact indicates that the deposited polymer is not undergoing degradation and is capable of preventing this reactivation reaction. In these conditions, the polyaniline provides corrosion inhibition of the iron with substantial efficiency.

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