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Development of the electrochemical preparation and characterizations of an electrode consisted an electro deposited iron thin film

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ABSTRACT

The deposition by electrochemical way in the form of an iron thin film was studied on a vitreous carbon electrode in various aqueous and organic mediums. The deposit of iron was studied by cyclic voltammeter; the quantity of iron deposited was determined by integration of the cathode and anodic peaks of Fe (0) and Fe (II) of the various mediums.

Key words: Thin film, cyclic voltammetery, electrochemical.

INTRODUCTION

The electrolytic alloy or metal deposits are the subject of an private interest, in particular as regards their use in industry in objectives of decoration of surface or protection of the materials.[1,2]

Pure iron the electrolytic film deposit thin as ferromagnetic component received an special attention, the first studies in the field of iron the electrolytic alloy deposits.[3,4]

R. Krumm and B. Guel have studied for the third time, nucleation and the growth of the metal electrodeposition on NR If (111), whereas Darko Grujicic and Batric Pesic studied the reactions and the mechanisms of nucleation of the electrodeposition of copper.[5] Y. Yoo and S.C.Hernandez have also studied the electrodeposition of FeCoNi in the form of thin films for magnetic devices MEMS.[6]

In the same way, Hirofumi Ebe, and Mikito Ueda have reported the electrodeposition of Sb, Bi, Te and their alloy[7]. E. Jartych and co-workers studied the film electrodeposition of $CuInSe_2$ for the application for the photovoltaic one,[8] Hanna Bryngelsson and Jonas Eskhult electro deposed coatings made up of nanoparticules of Sb and Sb2S3 being used as materials for the anode Li-ion, J. Zarpellon and H. F. Jurca have described the deposit of metal iron on If (1 1 1) by the method of electrodeposition in sulfate and a saccharin sodium solution of ammonium,[9] Y. Recently, Ito and co-workers have studied the effects of the magnetic fields on the electrolytic iron deposit,[10] More recently, J. Zarpellon, H.F. Jurcaont carried out their experiments on the electrodeposition of iron;[11] Olivier Zaouak and co-workers have also deposited bismuth for the development of a microsensor screen prints.[12]

The preparation of metal thin films of transition such as Ni, Co, Cu and Fe drew a considerable attention because of their applications the potential in scientific disciplines and technological.[13]

Moreover Gowand Hutton has studied the electro -deposition of a thin iron film.[14] more recently, several studies feel on the thin film electrodeposition of iron made by F. Lallemand.[15-17]

The aim of this study is to develop a thin layer of iron deposits on a vitreous carbon electrode in different mediums.

EXPERIMENTAL

Chemistry

The chemical reagents used were commercial products used without additional purification: sulphuric acid (96%), acetic acid (99%) and N, N-dimethylformamide were obtained from Fluka products; sodium hydroxide (97%), lithium hydrogenophosphate, lithium hydroxide ; ferrous chloride (97%) and sulfate of hexahydrate ferrous ammonia (extra Pure) were provided by Carlos Erba, Aldrich and Scharlau respectively.

Electrochemical studies

The electrochemical studies were carried out using a potentiostat EEG Model 362 connected to a plotting table X-Y there and Zonen, in a cell with three electrodes. The electrode of work was a stationary disc or vitreous carbon turning 2 mms in diameter. The potentials were measured compared to a reference electrode of saturated calomel (ECS). The auxiliary electrode consisted of a graphite bar. The working electrode was cleaned after each measurement by polishing on abrasive papers of different granulometrys. Deoxygenating was ensured by nitrogen splashing. All measurements were taken at room temperature. The quantities of current were determined by integration.

RESULTS AND DISCUSSION

Voltammetric studies in aqueous medium

The method consists in recording the voltammogrammes cations of iron in mode of stationary convective diffusion to a stationary and revolving electrode. Indeed, this method must make it possible to visualize the consequences which rise from the contacts that the ions with the electrode can have. In order to cover the field of the potentials available in aqueous medium. The voltammogrammes were recorded with sweeping of the potentials being carried out initially towards the negative values then after inversion to dissolve the metal électrodéposé on the electrode (Fig. 3). Tests have been carried out in various aqueous mediums such as the sulphuric acid, the ammonium acetate and the acetic acid. Among these various mediums it is the acetic acid which appeared the best to us.

Behavior of Fe^{2+}

The study of 5.10^{-3} mol.L^{-1} in a medium of $1.1O^{-1}$ mol.L^{-1} acetic composition of acid, sodium acetate 1.1O-1mol.L^{-1} shows that during sweeping with 100 mV/S and between -1,4V/ECS and +1,0 V/ECS Fe (0) oxidizes with - 0,65 V/ECS and that Fe (II) oxidizes have + 0,7 V/ECS. On the other hand, the Fe reduction (III) is to +0, 04 V/ECS and that of Fe (0) is in extreme cases of the cathodic current - 1, 4 V/ECS (Fig. 1).

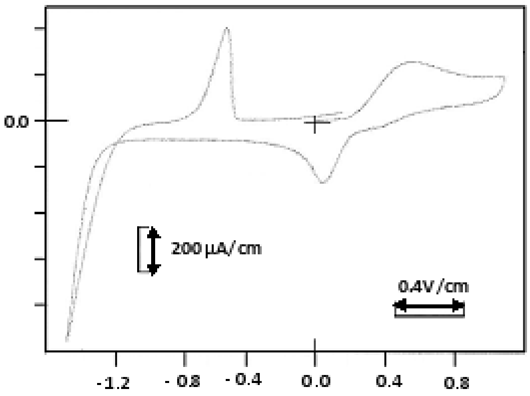

Fig.1: Cathodic current - 1, 4 V/ECS

Response of a modified vitreous carbon modified electrode

The method consists in first of all preparing an iron electrode on vitreous carbon by electrodeposition of an iron film starting from an acetic solution containing a ferrous salt; the formed electrode is then plunged in an acetic solution deprived of iron ions. Voltammogrammes of the deposit of film of iron (fig. 2) and its dissolution (fig.3) were recorded. The reduction in the current observed on the voltammogrammes of anodic dissolution repeated successively clearly shows the electrodeposition of iron on vitreous carbon.

This Voltammogramme (Fig.2) corresponds to the following reactions:

$$\text{Fe (II)} + 2e^- \rightarrow \text{Fe (0)}$$
$$\text{Fe (0)} \rightarrow \text{Fe (II)} + 2\text{nd}$$

The deposit of iron was studied on an electrode in C.V in a solution of composition CH_3CO_2H to 1.10^{-1}mol. L^{-1}, CH $_3CO_2Na$ with 1.10-1 mol. L^{-1}contenant 5.10^{-3} mol. L^{-1} de $FeCl_2$, after deoxygenating of the solution by nitrogen during ten minutes. The électroactivite of iron on a stationary vitreous carbon electrode is represented on (figure 2). The electrodeposition of iron begins to – 1, 20 V/ECS and quickly reaches a stage of diffusion during the cathodic sweeping of the potentials. The vitreous carbon electrode recovers iron, during sweeping return; the ferrous ions are reduced more easily on this iron cathode. Électrodéposé iron is oxidized during anodic sweeping with -0, 3 V/ECS what appears by an anodic peak and a rapid decrease of the current until its cancellation (figure 2). The electrode obtained is an iron electrode on vitreous carbon. The study reveals that during sweeping with 10mV/S between – 0,3 and – 1,4 V/ECS Voltammogramme presenting a peak of Fe(0) deposit on the electrode of C.V have -1,4 V/ECS (fig.2). This deposit is confirmed by the electrochemical study of the electrode in C.V modified in a solution of 1. 10^{-1} mol.L^{-1} composition. Acetic acid 1. 10^{-1}mol. L^{-1} of Sodium acetate 1.10^{-1} mol. L^{-1} free from $FeCl_2$. In order to dissolve iron, we carried out a sweeping of potential of - 0, 9 to + 1, 0 V/ECS then with -1.4 V/ECS. The voltammogrammes comprised a peak of dissolution of Fe (0) (fig.3) quite symmetrical which appears with the potential – 0, 3 V/ECS followed by another peak more spread out to the potential + 0, 12 V/ECS corresponding to Fe(II) oxidation out of Fe(III). The many sweepings carried out in return ticket from – 1,0 to + 1,0 V/ECS and a return to - 1,4 V/ECS make it possible to note a decrease of the current until it becomes null (fig.3). After graphic integration in one notes that the report of the quantities of anode current and cathodic Qa/Qc is of 0, 41 relatively far away from the theoretical value 1. The important variation compared to the theoretical value is not has a phenomenon of passivation which would block the oxidation of électrodéposé iron. This weak Qa/Qc could be explained, except error of integration, by a cathodic current of hydrogen formation partially confused with the Fe (II) reduction could be at the origin of an error of integration in the calculation of the quantities of electricity.

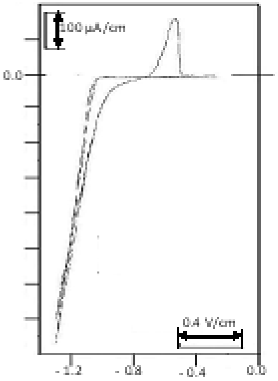

Fig. 2: Voltammogramme of the Fe electrodeposition on an electrode out of C.V in a solution of 1.10^{-1} mol. L^{-1} acetic acid and 1.10^{-1}mol. L^{-1} sodium acetate containing 1.10^{-2} mol. L^{-1} de $FeCl_2$; stationary electrode out of C.V (Ø = 4 mm, scanning rate: V = 10 mV.s^{-1}. Thickness of the iron deposit is of 23.78 µm.

The deposit of iron formed on the electrode has quite precise potentials after sweeping

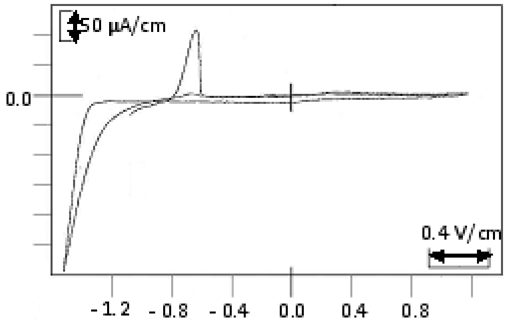

Fig.3: Voltammogramme of the dissolution of iron in a solution of composition: 1.10^{-1} mol. L^{-1} acetic acid and 1. 10^{-1} mol. L^{-1} sodium acetate; electrode out of C.V modified (Ø =4 mm, scanning rate of the potentials: V= 100 mV. S^{-1}).

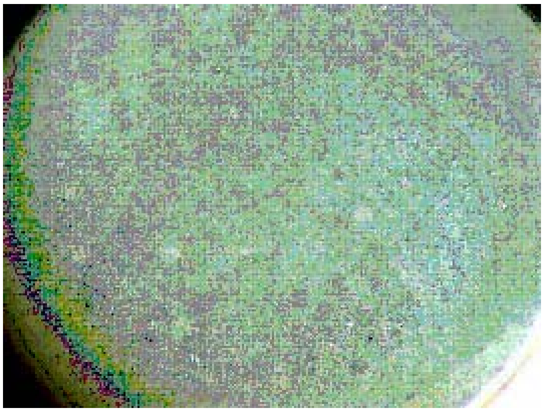

Image 1: Image of deposit of iron on an electrode in revolving C.V, in a medium of composition 1.10^{-1} mol.L^{-1} from acid acetic and 1.10^{-1} mol.L^{-1} of sodium acetate containing $1.1O^{-1}$ mol.L^{-1} ferrous chloride (Fecl2): (Ø = 2 mm, number of revolutions W =1600 tr.p.m, scanning rate of the potentials=5mV.s-1).

Voltammetric studies in organic mediums

The method consists in recording the voltammogrammes cations of iron in mode of convective diffusion to a stationary and revolving electrode. Indeed, this method must make it possible to visualize the consequences which rise from the contacts that the ions with the electrode can have. In order to cover the field of the potentials available in organic medium. The voltammogrammes were recorded with sweeping of the potentials being carried out initially towards the negative values then after inversion to dissolve the metal électrodéposé on the electrode **(Fig.4).**

Behavior of Ferrous salt

a. On a stationary electrode

The voltammetric study was carried out on a stationary electrode of vitreous carbon in contact with $FeCl_2$ 5.10^{-3}mol. L^{-1} in 30 ml of N,N-diméthylformamide and an electrolyte tetrabutylammonium hexa-fluorophosphate with 1.10^{-1}mol. L^{-1}. The voltammogrammes recorded during sweeping with 100 mV/S between -1,6 and +1,0 V/ECS present two peaks of oxidation observed to -0,5 and +0,24V and two peaks of reduction observed with -0,04 and -1,6V. The weak difference between the quantities of electricity Qa and Qc calculated by integration of the peaks of reduction of Fe (II) and Fe oxidation (0) watch that the quantities of iron deposited and dissolved are close.

Qa = $1.18.10^{-4}$ Coulomb;
Qc = $1.54.10^{-4}$ Coulomb;
40µA/Cm **µµµµA/cm
0.4 V/cm
Qa/Qc = 0,77

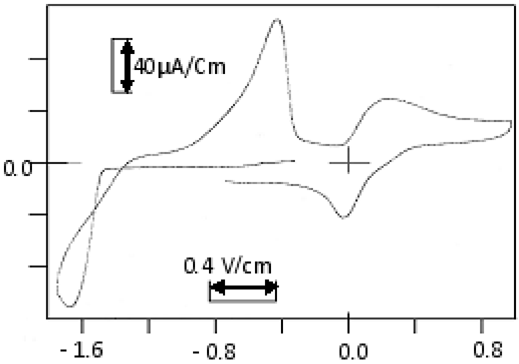

Fig.4:**The voltammogrammes**

b. On a revolving electrode

This study was carried out under the same conditions as the preceding one put aside the stationary electrode which is replaced by a revolving electrode. The experiment was made with a number of revolutions of the revolving electrode equal to 1600 tr/min and a scanning rate of 50 mV/S. the voltammogrammes recorded (fig.5) in field -1,6 with +0,9V presents only two peaks of which one corresponds to the reduction of Fe (II) and the other to the oxidation of Fe (0). The weak difference between the quantities of electricities Qa and Qc calculated by integration of the peaks of reduction of Fe (II) and Fe oxidation (0) watch that the quantities of iron deposited and dissolved are close.
Qa = $3.75.10^{-4}$ Coulomb
Qc = $4.65.10^{-4}$ Coulomb
Qa/Qc = 0, 80

It is noticed that the Qa/Qc reports/ratios obtained with the two types of electrodes are almost equal what means that the électrodéposées and dissolved quantities of iron obtained with these two electrodes are very close.

Revolving electrode in C.V (Ø = 2 mm, number of revolutions W = 1600 tr. token entry,

Scanning rate of the potentials: V = 200 mV.s-1).

The current I (A) verses the speed (m/s) and the Q (coulomb) verses the time T (s) are given in **(Fig-6)** and **(Fig-7).**

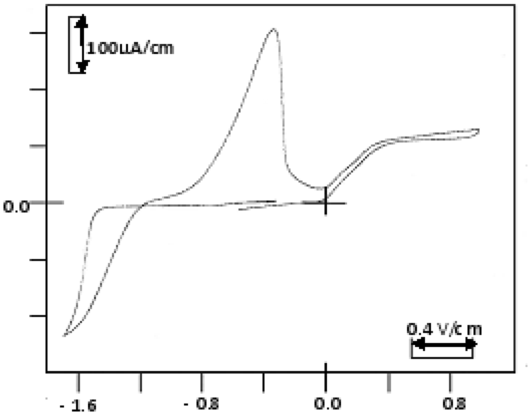

Fig. 5: Voltammogramme of a solution of N,N-dimethylformamide container

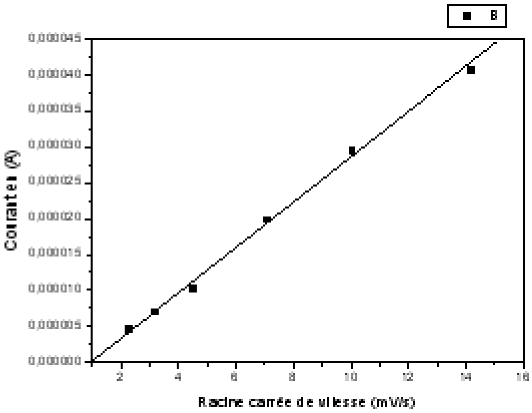

Fig.6: Current (A) *VS* V (m/s)

CONCLUSION

In this study, this chapter related to the iron deposit on vitreous carbon in different mediums aqueous and organic.

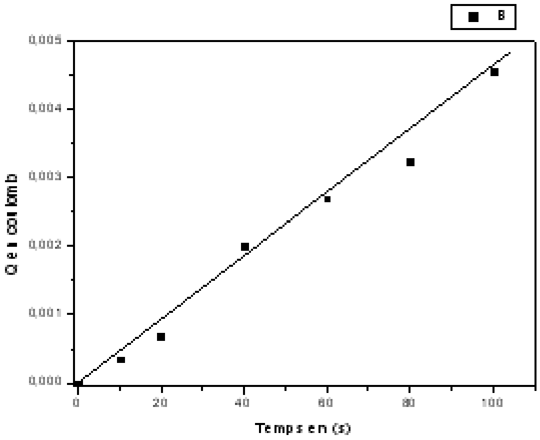

Fig-7: Q (coulomb) *VS* T (s)

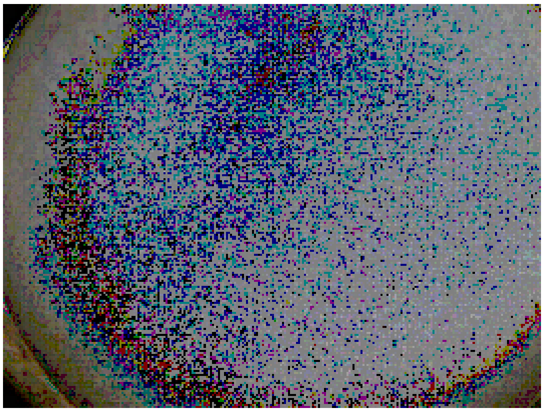

Image-2 :. Image of the iron deposit on a revolving electrode in C.V in a medium of D.M.F + 1.10^{-1} mol. L^{-1} of tetrabutylammonium hexafluorophosphate container 510^{-1}mol. L^{-1} Ferrous chloride ($FeCl_2$): (Ø = 2 mm, number of revolutions W =1600 tr. Token entry, scanning rate of the potentials: V= 5mV.s^{-1})

It was notes that in the case of the aqueous medium when the kinetics of deposit of iron is slow, the simultaneous formation of iron and hydrogen is possible with the risk of insertion of hydrogen in metal and possibly of inclusion of hydroxide $Fe(OH)_2$ in the deposit if the interfacial pH increases sufficiently. The reduction of hydrogen prevented the well electrodeposed of iron in aqueous medium of 23.78 µm

In the case of the organic medium, it was notes some is the kinetics of deposit of iron the problem of insertion of hydrogen is not posed and lay down it iron deposits on the vitreous carbon electrode in organic mediums is much more important than that deposits in the aqueous mediums. The electrodeposed of iron in the organic medium of 54.89μm.

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