Study of the Behavior of an Organic Coating Applied on Algerian Oil Tanker in Seawater

N. Hammouda, K. Belmokre

Abstract—Paints are the most widely used methods of protection against atmospheric corrosion of metals. The aim of this work was to determine the protective performance of epoxy coating against sea water before and after damage.

Investigations are conducted using stationary and non-stationary electrochemical tools such as electrochemical impedance spectroscopy has allowed us to characterize the protective qualities of these films. The application of the EIS on our damaged in-situ painting shows the existence of several capacitive loops which is an indicator of the failure of our tested paint. Microscopic analysis (micrograph) helped bring essential elements in understanding the degradation of our paint condition and immersion training corrosion products.

Keywords—Epoxy Paints, Electrochemical Impedance Spectroscopy, Corrosion Mechanisms, sea water.

I. INTRODUCTION

THE paints are used extensively today in the industry to protect the metallic structures of the aggressive environments. This work is devoted to the study of corrosion resistance and aging behavior of a paint coating providing external protection for oil tankers in sea water [1].

To avoid problems related to corrosion of these vessels, two protection modes are provided:
- An electrochemical active protection (cathodic protection of the hull).
- A passive protection by external painting.

The paint film is a barrier against aggressive species such as some ions, water and oxygen. However, all paints are more or less permeable to these species and their presence at the metal/coating interface.

Coating experts often say that surface preparation is the most important factor in determining the success of any protective coating system. By this, it is meant that surface preparation affects the performance of the coating more than any other variable.

Electrochemical impedance spectroscopy (EIS) appears to be an excellent technique for the investigation of bulk and interfacial electrical properties of any kind of solid or liquid material connected to or being part of an appropriate electrochemical transducer [2]. Any intrinsic property of a material or a specific process that could affect the conductivity

N. Hammouda is at Department of Matter Sciences, Faculty of Sciences, 20 Août 1955 University, Route d'El Hadaiek, B.P 26, Skikda-Algeria (phone: 00213773864975; fax: 0021338722109; e-mail: hammoudanad@ yahoo.fr).

K. Belmokre is at Department of Matter Sciences, Faculty of Sciences, 20 Août 1955 University, Route d'El Hadaiek, B.P 26, Skikda-Algeria (phone: 00213661155209; fax: 0021338722109; e-mail: belmokre2013@ yahoo.fr).

of an electrochemical system can potentially be studied by EIS. It is a non-invasive technique that does not require complex or expensive instrumentation and is easy to operate, thus allowing its current applications not only in research laboratories but also as a tool for the control of processes such as the performance of batteries, paints, or thin-film technology, or monitoring corrosion [3]. Using EIS, a vast range of coatings have been widely tested as effective barriers against corrosion of metal surfaces in the last few decades. Paints and other organic and inorganic emulsions deposited on the metal surface break down creating pinholes, craters and other defects when corroded. In other words, water and any other existing free ions are allowed to penetrate into the paint. The aim of this work was to determine the protective performance of epoxy coating against sea water before and after damage.

II. THEORETICAL BACKGROUND

EIS measures the impedance of a system (Z) as a function of frequency of an applied perturbation. When working with electrochemical systems, this perturbation is normally an AC voltage of small amplitude (typically 5–10 mV peak-to-peak) and the response is a current that differs in amplitude and phase (phase difference, Ø) with the applied voltage.

The ratio of applied voltage to measured current is the impedance of the system (Z = E/I) which is easily calculated over a wide frequency range, thus giving a spectrum where processes with different kinetics that may occur at the system under study are dominant at different frequency regions.

In this context, dipolar properties will be reflected at high frequencies, whereas bulk and surface properties will be evident at intermediate and low frequencies, respectively. Experimental impedance data of an electrochemical cell can be easily fitted to the impedance of an equivalent circuit mainly comprising resistors and capacitors. In such circuits, a resistance ideally describes a conductive path, such as that generated by the bulk conductivity of the system or the charge-transfer step due to an electrode reaction, whereas a capacitance generally describes space-charge-polarisation regions within the system as well as modification of an electrode surface due to adsorption processes or polymer-layer deposition.

The Randles circuit is the simplest equivalent circuit that describes an electrochemical cell where a single-step Faradaic process in the presence of diffusion may occur (Fig. 1 (a)). It combines three components, namely the electrolyte resistance between working and reference electrodes (R_e), the double-layer capacitance (C_{dl}) and the Faradaic impedance due to the

charge-transfer process (Z_f) at the working electrode-electrolyte interface. Z_f is normally subdivided into a charge-transfer resistance (R_{ct}) and the so-called Warburg Impedance (Z_w), which reflects the influence of the mass transport of the electroactive species on the total impedance of the electrochemical cell. Thus, for those diffusion-limited processes, Z_w becomes dominant, whereas for those charge-transfer-controlled processes, Z_f is just R_{ct}. All these components can be identified by studying the variation in impedance of σ electrochemical cell over a wide frequency range (normally 100 kHz–0.1 Hz). A common way of showing the resulting data is the complex plane or Nyquist Plot (Fig. 1 (b)), in which the real (Z') versus the imaginary (Z'') components of the impedance are plotted. In this plot, two separate processes are very well differentiated, that is, a semicircle relating to a charge-transfer-controlled process, the intercept of which with the X axis gives R_e and R_{ct} values, and a straight line with a slope of 1 due to Z_w, whose extrapolation to the X axis allows calculation of the Warburg coefficient (σ), from which the diffusion coefficients of the electroactive species can be estimated. From the frequency at the top of the semicircle, where Z'' is maximum, the time-relaxation constant (τ) for the Faradaic process can also be calculated.
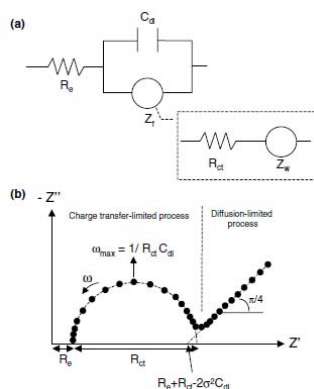

Fig. 1 (a) Randles equivalent circuit and (b) Nyquist Plot that describe impedance behavior of a simple electrochemical cell involving a single Faraday process

III. EXPERIMENTAL PART

A. Sample Material and Preparation

The metallic substrate was X52 carbon steel (according to NF10027 standard) in conformity with the norm API (American Petroleum Industry), used in the tanker, the chemical composition of the tested carbon steel is given in Table I. Before coating application, the metallic substrate was sandblasted to Sa 2.5 (Swedish Standard SIS 05 59 00/67) (roughness Ra 6.2 μm) or polished with emery paper up to G 400. Commercial epoxy was immediately applied onto steel panels using a brush or a roller (Fig. 2). Once cured, the samples were stocked in a desiccator until the moment of testing. The coating thickness was measured using an Elcometer gauge and was found around 80 μm for all panels, the composition of the coating is proprietary information.

TABLE I
CHEMICAL COMPOSITION OF X52 CARBON STEEL (% IN WEIGHT)

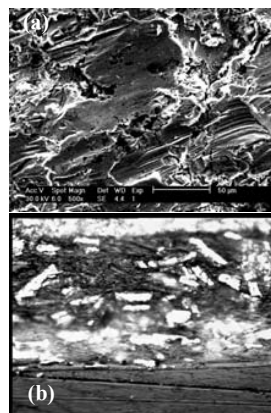| C	Mn	S	P
0.28	1.25	0.03	0.03

Fig. 2 (a) Cross section SEM micrograph on sandblasted Carbon steel (Sa 2.5) (b) Cross-section of the studied epoxy paint

Coated panels were cut out (100 ×60 ×4 mm) and an electrical wire was added in order to allow electrochemical measurements. With the aim to achieve the electrochemical measures in the best conditions it has been suited that the areas of about 15 cm^2 exposed to the electrolytic solution were sufficient. It seemed necessary to use a surface of paint relatively big in contact with electrolytic solution in order to compensate the insulating role of the sample as the thickness of the film grows. Mansfeld reports in a technical document [4] a study of Kendig and Scully suggesting the use of samples covered with a ratio area / thickness of the coating of at least 10^4 to assure satisfactory electrochemical measurement. Samples were exposed under open circuit potential conditions in sea water, for electrochemical impedance.

B. Electrochemical Impedance Spectroscopy Measurements

The Electrochemical Impedance Spectroscopy (EIS) measurement is carried out in sea water, using a potentiostat/galvanostat EG&G A273. A frequency response analyser Solartron FRA 1260 connected to an electrochemical interface Solartron SI 1287 was used to perform EIS measurements. A filter (Kemo VBF 8) was also employed to improve the signal to noise ratio. The frequency domain covered was 100 kHz to 10 MHz with the frequency values spaced logarithmically (five per decade). The width of the sinusoidal voltage signal applied to the system was 10 mV. All the measurements were performed at the open circuit potential and at different immersion times. The electrolyte was confined in a glass tube which was fixed to the painted surface by an O-shaped ring. The total tested area was 15 cm^2. Platinum gauze of large area was used as a counter electrode. All the potentials in the current article are referred to Ag-Ag-Cl. During the intervals between EIS measurements, the painted specimen was kept in the electrolyte cell without reference electrode. The cell design for EIS measurement was described in detail in a previous work [5].

IV. RESULTS AND DISCUSSION

A. Electrochemical Properties of Sandblasted Carbon Steel in Sea Water

The Electrochemical Impedance Spectroscopy (EIS) measurement is carried out in sea water during 3 days, using sandblasted carbon steel panels (X52). The electrochemical impedance diagrams determined at different immersion times in sea water are shown in Fig. 3. The values of various parameters are summarized in Table II.

They are characterized by a single capacitive loop. As arcs are not centered on the real axis Z for the calculation of R_p was extrapolated "low frequency" at zero frequency portions.
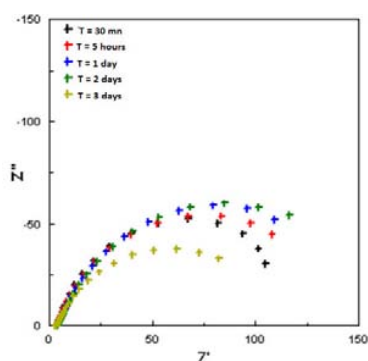

Fig. 3 Evolution of Nyquist diagrams as a function of immersion time in sea water for the sandblasted carbon steel

TABLE II
PARAMETERS VALUES EXTRACTED FROM THE FITTING PROCEDURE

Time	R_e (KΩ.cm^2)	R_{ct} (KΩ.cm^2)	C_{dl} (mF.cm^{-2})
30 mn	50.7	1.815	2.008
5 hours	47.1	2.1498	2.97
1 day	50.7	2.4741	3.50
2 days	52.2	2.5959	3.209
3 days	45.0	1.69505	2.894

Analysis of the various electrochemical parameters shown in Table II, we note a significant increase in the polarization resistance R_{ct} between the first hours of immersion and the second day, beyond this time it drops to a value of 1.69 KΩ.cm^2.The gradual growth of R_{ct} for the first days of immersion (1.815 < t < 2.595), translated the film formation of corrosion products that grows with the immersion time [6] as rust layers consist mainly of hydroxides such as $Fe(OH)_3$ or an iron oxide Fe_2O_3.

The decrease of the R_{ct} after 2nd days of immersion could be due to the penetration of the electrolyte as a function of time through the porosity of the film of corrosion products, thus promoting the attack of the metal substrate.

In contrast, the double layer capacitance C_{dl} varies only slightly with the immersion time, the values are between 2 and 3 mF.cm^2, values that seem very high to be representative capacity double layer C_{dl} which are usually of the order of μF.cm^{-2}. This is attributed to the porous nature of the film of the corrosion products formed abandonment and present at the

metal interface. Through these results, we deduced that the naked steel has a mediocre behavior in this environment.

B. Equivalent Circuit for the EIS Simulation

The interfacial impedance is modeled in terms of equivalent circuit [7]. The electrical circuits that are used to simulate the EIS results are shown in Fig. 4.

The control of the electrochemical kinetics is under charge control, the contribution of the resistance of the electrolyte is simulated by R_e, the charge transfer resistance R_{ct} and the double - layer capacitance C_{dl} respectively. They are characteristic of the substrate.
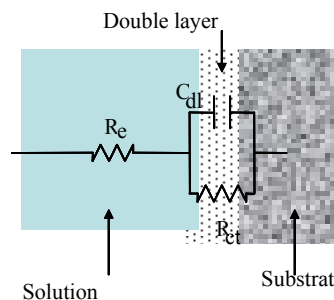

Fig. 4 Electrical circuits used to simulate the EIS results

C. Study of Barrier Properties of non-Damaged Epoxy Paint by Electrochemical Impedance Spectroscopy in Sea Water

It is very difficult to obtain information on the mechanism occurring in coated metal/ electrolyte interface with classic electrochemical technique. The electrochemical impedance spectroscopy offers the advantage of using low amplitude signals without disturbing the measured properties. At the beginning of the immersion period, the impedance measurements made on epoxy paint in a frequency range of 10 kHz–8 mHz revealed a fully capacitive behavior.

The Nyquist impedance diagrams determined at different immersion times in sea water are shown in Fig. 5. The values of various parameters are summarized in Table III.
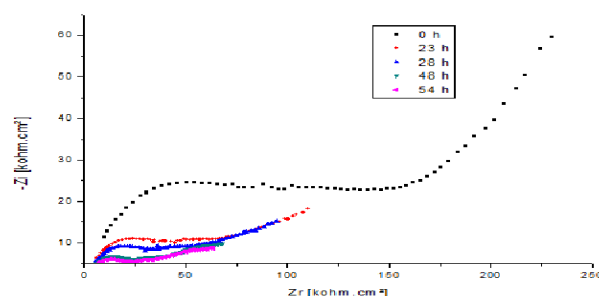

Fig. 5 Evolution of Nyquist diagrams as a function of immersion time in sea water for coated steel. (Z', Z" Ω.cm^2)

We note an evolution of the electrochemical parameters such as: the resistance of the electrolyte in the pores $R_p^°$, the transfer resistance of none covered metal R_{ct}, the capacity of the paint film C_f, and the resistance of diffusion σ.

The evolution of the electrochemical behavior of the covered material by epoxy paint in sea water, permits to conclude the existence of two capacitive loop (two constant of time) followed by a linear straight line inclined to 45°, This is a characteristic of the process of diffusion (WARBURG diffusion).

TABLE III
PARAMETERS VALUES EXTRACTED FROM THE FITTING PROCEDURE.

Time (hours)	0	23	28	48	54
R_1 (kΩ.cm²)	122.1	56.81	45.50	36.86	32.53
CPE_1 (nF/cm²)	3.258	5.602	5.537	6.820	6.141
R_2 (kΩ.cm²)	25.85	76.18	22.95	13.86	48.71
CPE_2 (nF/cm²)	972.4	417.8	346.7	918.2	816.7
R_3 (kΩ.cm²)	-	-	-	110.9	104.8
CPE_3 (μF/cm²)	-	-	-	180.6	191.2
R_d (kΩ.cm²)	0.471	0.177	0.154	-	-

The existence of a diffusionnel control is an indicator of the defective coating; this is confirmed by the decrease in the values of the diffusion resistance (R_d): 0.471 kΩ.cm²; 0.177 kΩ.cm² and 0.154 kΩ.cm². Fig. 6 shows the various electrical circuits related to the metal / paint interface immersed in sea water.
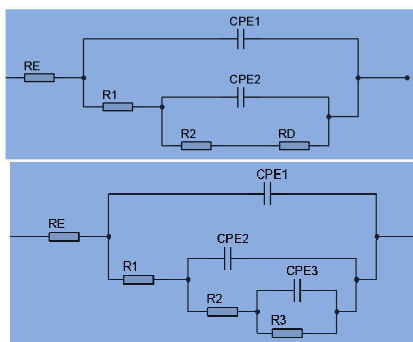

Fig. 6 Electrical circuits used to simulate the EIS results

D. Study of the Electrochemical Behavior in Sea Water of Epoxy Paint Damaged in –situ

It is very difficult or impossible to obtain information on the mechanism occurring at the coated metal/ electrolyte interface with conventional electrochemical techniques. Electrochemical impedance spectroscopy offers the advantage of using low-amplitude signals without disturbing the measured properties thus; it provides a convenient way to evaluate the performance of a coated metal system [8].

We studied the electrochemical behavior of epoxy paint that has been damaged in situ (tanker), Epoxy paints have the ability to actively protect the metal substrate.

Damage is found by the formation on the paint layer of red rust due to the presence of oxide iron. The values of the parameters obtained through the EIS measurements on our damaged paint immersed in seawater are summarized in Table IV; Fig. 7 shows the evolution of the impedance spectra.

The impedance spectra represented in the Nyquist plane permits to conclude the existence of two capacitive loops followed by a linear straight line. According to the Nyquist diagrams, several authors assign the loop at high frequencies to the intact part of the paint. Under the low frequencies, the processes become more and more slow. Thus, in some cases, the transfer resistance can be determined [9], [10]. At the limit of the low frequencies, a straight line is attributed to Warburg, interpreting this way the electrolyte diffusion phenomenon through the paint layer.
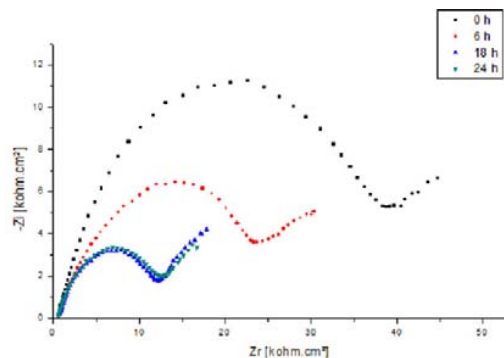

Fig. 7 Evolution of Nyquist diagrams as a function of immersion time in sea water for damaged (in-situ) paint

TABLE IV
PARAMETERS VALUES EXTRACTED FROM THE FITTING PROCEDURE

Time (hours)	0	6	18	24
R_e (Ω.cm²)	223	562.8	520.4	429.6
R_f (kΩ.cm²)	42.49	26.68	13.05	13.86
C_f (μF /cm²)	187.2	596.2	2.438×10^3	3.627×10^3
R_{ct} (kΩ.cm²)	9.680	25.26	20.61	-
C_{dl} (μF/cm²)	164.4	199.0	972.8×10^3	-
R_d (kΩ.cm²)	2.714	0.386	-	0.333

According to the values of R_d and R_{ct} after 24 hours of immersion, we find that we are in the presence of a mixed system (diffusion- charge transfer). It is possible that it is a cyclical phenomenon if we have traced the curves for longer periods. These redox processes are well known to dominate the electrochemistry of iron at neutral or alkaline environment [11] the corrosion process of iron:

$$Fe(OH)_2 + OH^- \longrightarrow Fe(OH)_3 + e^- \qquad (1)$$
$$2Fe_3O_4 + 2OH^- \longrightarrow 3Fe_2O_3 + + H_2O + 2e^- \qquad (2)$$
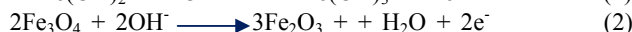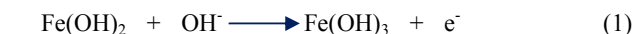
From the results of Table V, we note a decrease in the values of the diffusion resistance, they spend from ≈ 2.714 kΩ.cm² to ≈ 333 Ω.cm², and this decrease reflects the failure of our epoxy paint. The increase or decrease in R_d, is due to a phenomenon of clogging and unclogging or creation of new pores in the paint.

During the 24 hours the capacity of our film does increases (187.2 μF/cm² to 3.627×10^3 μF/cm²) this increment would be due to the penetration of the electrolyte through the pores or the coating defect [12]. The values of the resistance of electrolyte through the pores Rp° decrease with immersion time (42.49 kΩ.cm² to 13.86 kΩ.cm²) allow us to conclude that the film of corrosion products put on the interface metal/solution, through the pores is becoming unstable and

that the coating is very porous, or even discontinuous. In other words, the inevitable porosity through which the electrolyte reaches the steel encourages the attack of metal [13].

E. Equivalent Circuit for the EIS Simulation

As the diagrams of Nyquist, make to appear, the importance of the parameters $Rp°$, and C_f characterizing the performance of the coating for steel paints (Fig. 8), the impedance response of the coated electrode can be modeled by an equivalent electrical circuit simulating the interface coated metal/ electrolyte, corresponding.
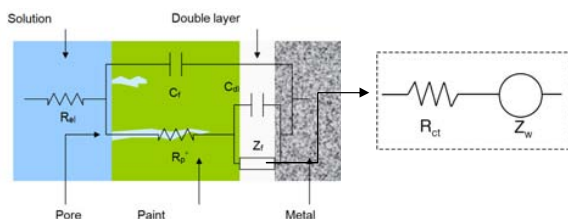

Fig. 8 Equivalent electrical circuit for a defective organic coating

F. Micro-Raman Spectroscopy

In order to understand the behavior of epoxy paint, complementary analyzes were carried out. Raman spectroscopy analyzes were performed after immersion of the epoxy paint in seawater. This technique allows identifying locally zinc corrosion products inside the coatings. Representative spectra obtained for our sample are shown in Fig. 9, a characteristic peak was observed at 543 cm^{-1} which was attributed to a non-stoichiometric oxide $Zn_{1+x}O$ [14], which is detected on some particles of zinc to some micrometers of the electrolyte/ coating interface whereas only the metallic zinc is detected on the other particles. This shape of the non-stoichiometric zinc oxide $Zn_{1+x}O$, where zinc ion is in interstitial position had been observed by [15]. Other corrosion products were detected inside the coatings and their characteristic wavenumbers. We detected additional peaks at 240.5 and 409.7 cm^{-1} attributed to simonkolleïte [4Zn (OH)$_2$·ZnCl$_2$·H$_2$O] The band around 667 cm^{-1} is related to the Magnetite (Fe$_3$O$_4$) [16].
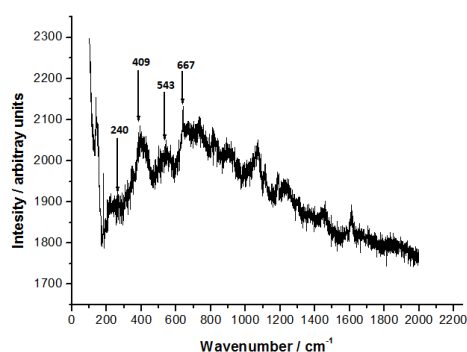

Fig. 9 Raman spectrum of the damaged paint at the interface film/electrolyte after immersion in seawater

G. SEM Analysis

Cross section S.E.M. micrograph of damaged epoxy paint is shown in Fig. 10. It was clearly observed that the coating presented zones which did not contain zinc particles. Moreover, it can be seen that the zinc particle shape varied significantly from spherical to elongated forms. Most of the zinc particles were not in direct contact with the substrate. The oxidation of zinc in the coating creates the so-called "white corrosion"; the shapes of damage were under Cracks and scaling damage. White insoluble corrosion products are visible on the surface, the sample also presents a blister. The scheme outlines the possible reactions at the appearance of oxidation zinc products; these products are of alkaline nature and can manifest themselves in the neutralization protection mechanism [17].
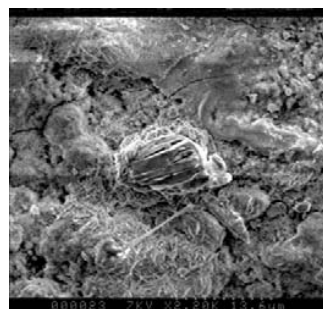

Fig. 10 SEM picture of the damaged epoxy paint in seawater

V. CONCLUSION

Epoxy paint was characterized using EIS, immersed in sea water. In this work is shown the approach of electrochemical impedance data interpretation by equivalent electrical circuits of organic coated metals.

EIS measurements are seen to be useful for studying the progress of corrosion in coatings of essentially epoxy paint .It is suggested that ion transport in the coating might be controlling the corrosion process unlike at the beginning.

With regard to our tests, the capacitive arc corresponding to the coating decreases while it deteriorates: R_f decreases when C_f increases. The evaluations of these two parameters permits to affirm that the primer tested present a strong porosity. This means that the base metal is in direct contact with the electrolyte. We conclude that the primer that we tested is of a less quality.

REFERENCES

[1] D. Aylor, Sewater. In Corrosion Tests and Standards: Application and Interpretation. Philadelphia: ASTM, P. 307, 1995.
[2] A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamental and Applications, Wiley, New York, USA, 1980.
[3] J.R. McDonald, Impedance Spectroscopy: Emphasizing Solid Materials and Systems, Wiley, New York, USA, 1987.
[4] F. Mansfeld, J. B. Lumsden, S. L. Jeanjaquet, S. Tsaï, Evaluation of surface pretreatment methods for application of organic coatings, Corrosion Control by Organic Coatings, H. Leidheiser, Jr. - Editor NACE 1981, pp. 227-237.
[5] X .R. Novoa, M. Izquierdo, P. Merino and L. Espada, Mater. Sci.Forum 44 & 45, 223 (1989).

[6]   J. M. R. Genin, D. Rezel, Ph. Bauer, A. Olowe, A. Beral, Electrochem. Methods in Corrosion Research, 8, p.477-490 (1986).

[7]   N. Azzouz, Thèse, LCTS, univ. Franche, compté, France (1992).

[8]   W. Strunz, Dielectric relaxation in banier coatings, volume 39, issue 1, 2000, daudes 49-60.

[9]   M. Keddam, O. R.Mattos, H. Takenouti, Electrochem. Soc. 1981, 128,257.

[10] C. Gabrielli, Identification of electrochemical process by frequency response analysis, Solartron Schlumberger, 1984.

[11] conversation privée avec M. keddam, directeur du laboratoire de physique des liquides et électrochimie, U.P.R.15 du C.N.R.S, Paris-Jussieu, décembre 2001.

[12] K. Belmokre, F. Kermiche, J. Pagetti, Bull. Soc. Chim. Belg. 1997, 106, 177.

[13] E. P. M. Van Westing, G. M. Ferrari, J. H. Dewit, Corros.Sci. 1994, 36, 957.

[14] M. Tzolov, N. Tzenov, D. Dimova-Malinovska, M. Kalitzova, C. Pizzuto, G. Vitali, G. Zollo and I. Ivanov, "Vibrational Properties and Structure of Undoped and Al-Doped ZnO Films Deposited by RF Magnetron Sputtering," Thin Solid Films, Vol. 379, No. 1-2, 2000, pp.28-36.

[15] C. Cachet, et al., "EIS Investigation of Zinc Dissolution in Aerated Sulphate Medium. Part II: Zinc Coatings," Electrochimica Acta, Vol. 47, No. 21, 2002, pp. 3409- 3422.

[16] D. L. A. De Faria, S. V. Silva, et al., "Raman Microspectroscopy of Some Iron Oxides and Oxyhydroxides," Journal of Raman Spectroscopy, Vol. 28, No. 11, November 1997, pp. 873-878.

[17] P. Kalenda, "Effects of Particle Sizes and Shapes of Zinc Metal on the Properties of Anticorrosive Coatings," Progress in Organic Coatings, Vol. 46, No. 4, 1993, pp. 324-332.