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to $1.E^{07}\Omega\ cm^2$ for both coal tar and tar free epoxy coating which considered as doubtful to faire barrier properties respectively.

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Ecorr (mV)	βa	- βc	Icorr (mA/cm^2)	Corrosion Rate (mpy)	Corrosion Rate (mm/y)
	mV/decade				
728	78.299	147.97	0.04663	0.05404	2.1279

6.0. CONCLUSIONS

In this work, the influence of the electrolyte (natural sea water) on the protective efficiency of paint coating, when applied onto blasted bare and coated mild steel panel was studied. The protective coating performance and the electrochemical properties of all bare and coated mild steel test panels were evaluated by EIS & OCP and the following conclusions were drawn: Bare mild steel corrosion in natural sea water environment can be successfully controlled by complete protective coating epoxy system.

The provided protection efficiency after applying the protective coating has been approximately reached $\approx$100% i.e. the corrosion rate has been decreased by $\approx$100% folds. The Rct (Charge transfer resistance) also has been increased to $\approx$ 100% folds. Quantitative corrosion rate in natural sea water environment of both bare and different type and quality epoxy coated mild steel has been determined using electrochemical impedance spectroscopy.

Bare mild steel behavior in natural sea water environment can be successfully studied using potentiodynamic polarization technique and useful electrochemical polarization parameters could be obtained. Rabid evaluation of organic protective coating performance in natural sea water environment has been performed using electrochemical impedance spectroscopy and the most organic protective coating prosperities have been identified.

Corrosion can be detected beneath the protective costing and quantitatively evaluated using EIS. The achieved qualification range of all studied coated panel test samples in natural sea water are $1.E^{06}$

can be divided into three different regions which are activation, oxygen reduction that is clearly explained by the limiting current and finally hydrogen evolution. Therefore, it could be concluded that the corrosion processes of steel in sea water occurs under oxygen reduction control.

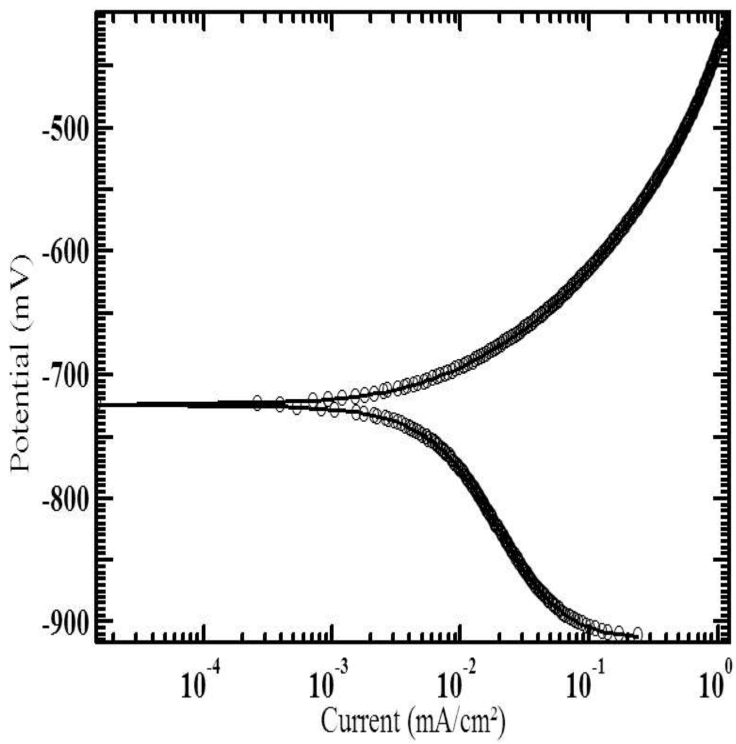


Figure 14: Potentiodynamic polarization curves of mild steel in natural seawater solution.

The corrosion current density, i_{corr}, was calculated from the intersection of anodic and cathodic Tafel lines. The values of the electrochemical polarization parameters, corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic and cathodic Tafel slope βa, and βc for bare mild steel in seawater are shown in table (3).

Table 3: Electrochemical polarization parameters for steel in seawater.

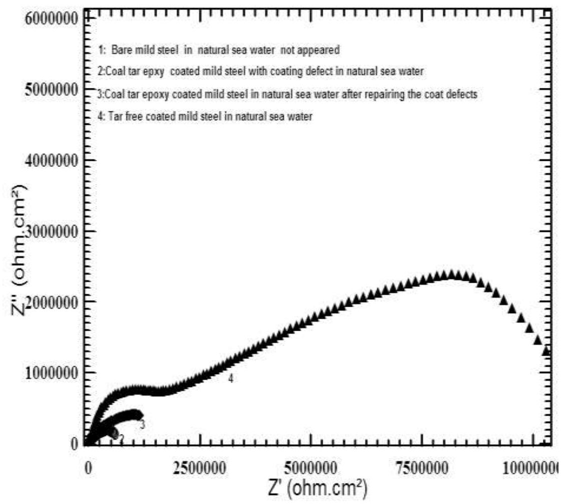


Figure 12: Comparison of Nyquest plots between bare and different type of coated steel.

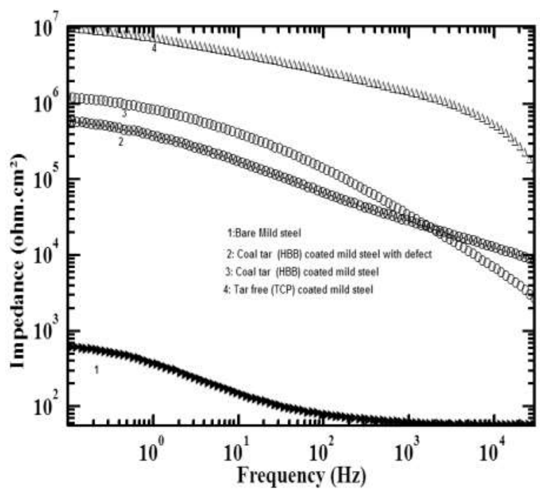


Figure 13: Comparison Between Bode Plot Of Bare And Different Type And Condition Of Epoxy Coated Mild Steel.

5.0. *Pc*

5.1. *Bar*

Figure 14 shows the potentiodynamic polarization curves for the bare mild steel in natural seawater. The anodic part of the polarization curves indicates spontaneous dissolution of steel with raise of the anodic potential. On the other hand, the cathodic part of the curves

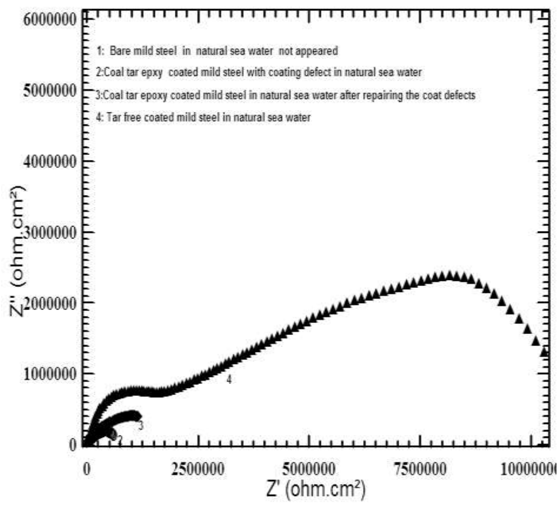


Figure 11: Comparison of Nyquest plots between bare and different type of coated steel.

Figure 12 shows the comparison between bode plot curves of bare and different type and condition epoxy coated panels in natural sea water environment of the same obtained data in figure 13. The X-axis represents the log. of impedance values, whilst the Y-axis represents the log. of frequency values. The obtained impedance values indicated from curves (1, 2, 3 & 4) at low frequencies (0.1Hz) were $1.E^{03}$ $ohm.cm^2$ for bare mild steel, $\geq 1.E^{06}$ $ohm.cm^2$ for coal tar epoxy (HBB) defected /undefeated coated mild steel respectively, whilst the maximum obtained impedance value is $1.E^{07}$ $ohm.cm^2$ for tar free epoxy coated mild steel. The bare mild steel different achieved protection levels (corrosion resistance) could due to the protective coating barrier properties. It is clear that the bare mild steel impedance has been dramatically increased from less than 1000 to 10000000 $ohm.cm^2$ after complete coating system application i.e. 9999000 impedance folds has been achieved**.**

steel, compared with bare steel in same environment, this can be clearly seen in figure 10 by comparison between impedance bode plot curves of both bare (1 and 2) respectively.

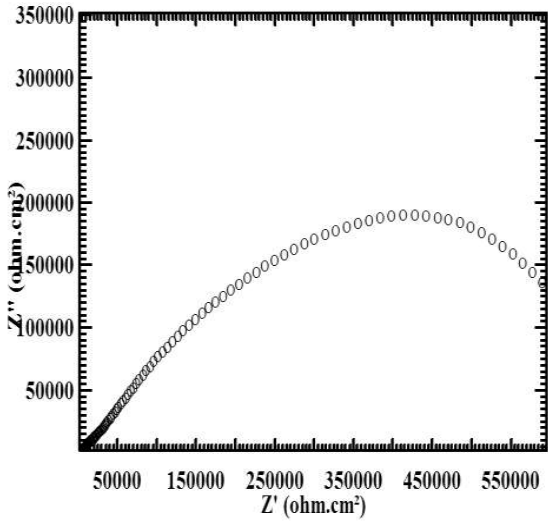


Figure 9: Nyquist plot of epoxy coated mild steel in natural seawater solution

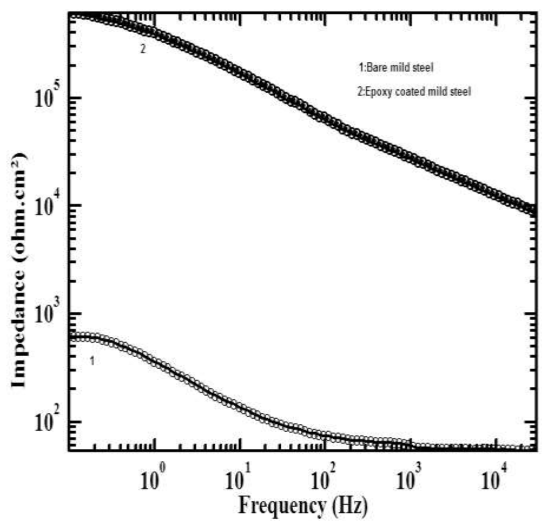


FIGURE 10: COMPARISON BETWEEN IMPEDANCE BODE PLOT OF BOTH BARE AND EPOXY COATED MILD STEEL.

Figure 11 shows Nyquest plots comparison between bare and different type and condition of coated mild steel in natural sea water environment, the X-axis represents the real values of the log. of impedance (Z') whilst the Y-axis represents the log. of imaginary values of the impedance (Z").The semi-circle diameter is inversely proportional to the corrosion rate, it is clear that the bare steel Nyquest plot disappeared (not appeared in figure 11) during presenting of other associated Nyquest plot curves of different type and condition of coated mild steel in natural seawater environment, this could be attributed to small value of it is impedance compared to the epoxy coated mild steel ones.

represents the coating resistance or Rp which represents polarization (corrosion rate of the metal substrate beneath the coating) and it's inversely proportional to the corrosion rate.

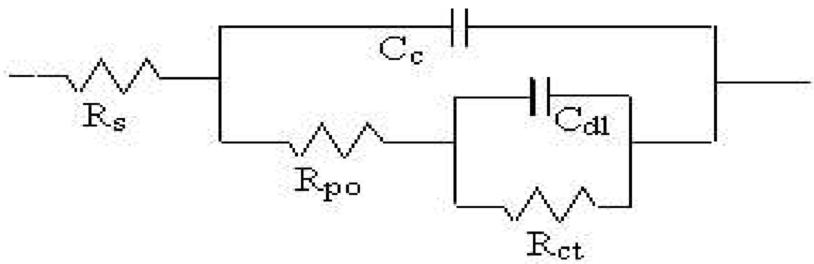


Figure 8: Equivalent Circuit for a Failed

Coating capacitance (Cc), which is an important parameter, to measure during coating failure.
Equation 1 has been used for calculation of protection efficiency achieved by applying organic protective coating to the mild steel in natural sea water environment.

$$PE\ (\%)=100\ (BS_{CR0}-CS_{CR})\ /\ BS_{CR0}^{2} \qquad \text{Equation 1}$$

It can be seen from the table 1 that the provided protection efficiency after applying the protective coating has been approximately reached ≈100% i.e. the corrosion rate has been decreased by ≈100% folds. The Rct (Charge transfer resistance) also has been increased to ≈ 100% folds. Cdl(Double layer capacitance) capacitance which represents the coating barrier water uptake which inversely proportional to the decrease of coating the capacitance.
Figure 9 Shows the Nyquist plot of epoxy coated mild steel in natural seawater solution for the same data obtained in table 1 circuit and revealed the dramatically increase in the impedance of the coated

resistance, i.e. solution resistance between the counter and reference electrodes.

Table 2: Comparison of bare and different type of epoxy coated mild steel (EIS) parameters and achieved protection efficiency

	$E_{corr.}$ (-mV)	$I_{corr.}$ (mA/cm^2)	CR (mpy)	CR (mm/y)	Rct (Ohms.cm^2)	Cdl (µF)	Protection efficiency (PE)%
Bare steel	634	2.411E-02	1.100E+01	2.794E-01	1.082E+03	825.3	99.932
Epoxy (HBB) coated steel	528	1.631E-05	7.444E-03	1.891E-04	1.599E+06	.25310	
Epoxy (TCP) coated steel	578	1.286E-06	5.867E-04	1.490E-05	2.029E+07	0.05371	99.994

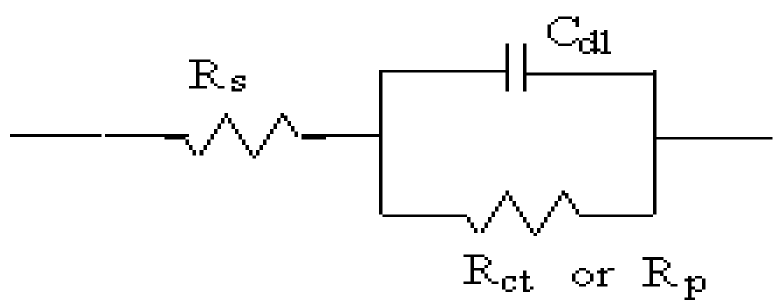


Figure 7 :The equivelent ciruit of the Nyquist obtained plot of bare mild steel

Double layer (C_{dl}) exists at the interface between an electrode and its surrounding electrolyte. Charge transfer resist
ance (Rct) represents an electrode reaction indicative of its inherent speed i.e. a large charge-transfer resistance indicates a slow reaction. Figure 8 indicates the failed coated steel equivalent circuit elements as previously described in addition to the followings: Rpo. this

represent the electrochemical behavior of the coating and the metal substrate. Impedance spectroscopy is a non-destructive technique and so can provide time dependent information about the properties but also about ongoing processes such as corrosion or the discharge of batteries and e.g. the electrochemical reactions in fuel cells, batteries or any other electrochemical process. When we plot the real and imaginary components of impedance in the complex plane (Argand diagram) [1], we obtain a semicircle or partial semicircle for each parallel RC Voigt network.

Figure 6 Shows the Nyquist plot of bare mild steel in natural seawater, the X-axis represents the real values of the impedance (Z') whilst the Y-axis represents the imaginary values of the impedance(Z").

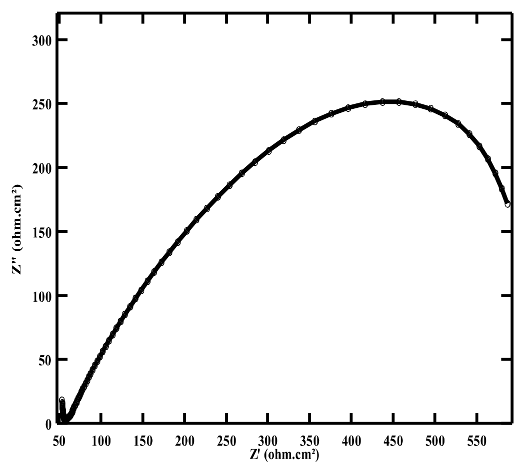


Figure 6: Nyquist plot of bare mild steel in natural seawater solution.

In order t ... ied by fitting electroch... results using commercially available software. The obtained results are indicated in table 2, the most important data includes corrosion current density, corrosion rate, double layer, charge transferee resistance, which can be clearly represented by equivalent circuit in illustrated in figure 7, the equivalent circuit elements in which Rs represent the cell solution

Figure 5 shows the comparison between the open circuit potential OCP(Y- axis) carves vs. time (X- axis) of bare and epoxy coated mild steel in natural seawater. It can be seen that the OCP of coated steel has been shifted to the positive direction see (figure 6) leading to more corrosion protection as expected and exhibiting a steady state potential with respect time which could be attributed to function of the coating achieved barrier between the steel surface and the electrolyte (seawater), whilst the bare steel behavior (curve 1) revealed variation of OCP with respect time leading to clear shift of the OCP to the negative direction more corrosion and less steady state OCP as also expected due to the direct contact of the steel surface with the corrosive environment(natural seawater).

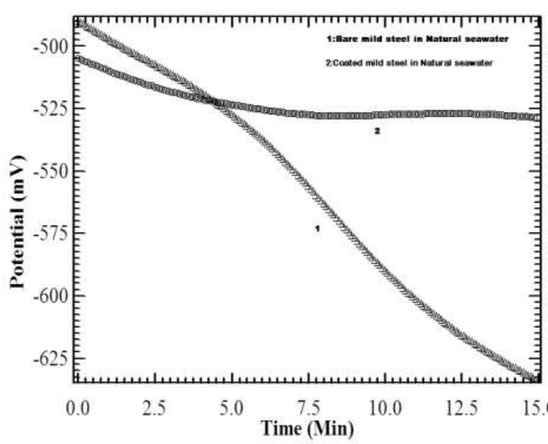
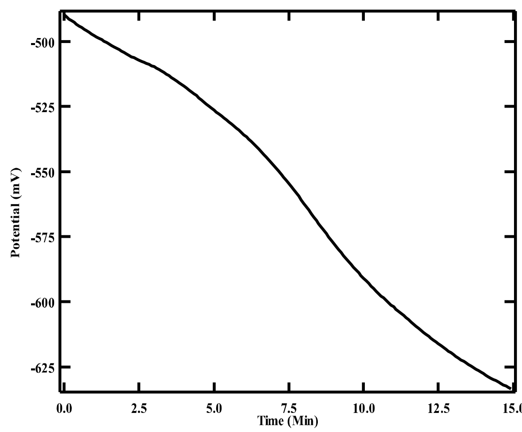


Figure 5: Comparison between bare and coated mild steel OCP in natural seawater.

4.0. Electrochemical impedance spectroscopy

Behavior of a coating on a metal when in salt water is required, by the appropriate use of impedance spectroscopy, a value of resistance and capacitance for the coating can be determined through modeling of the electrochemical data. The modeling procedure uses electrical circuits built from components such as resistors and capacitors to



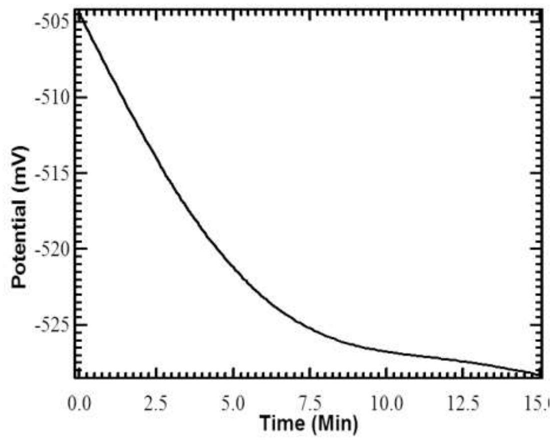


Figure 3: Potential (OCP) vs. time of bare mild steel in natural seawater with respect to Ag/AgCl.

Figure 4: Potential vs. time of epoxy coated mild steel in natural seawater with respect to g/AgCl.

The comparison of OCP for both panels is also represented in Figure 5. The evolution of the curves is clearly related to differences in the surface characteristics. The more noble values for coated steel panel (CSP) than bare steel panel (BSP) were due to the barrier properties of the paint films. During exposure time, the OCP values varied between - 490 to -630mV for BSP with a continuous decreasing trend toward more –ve potential which was the direct indication of active corrosion process.

While the OCP values for CSP panel were varying between -505 to -528mv with a decreasing trend. The rapid decrease in OCP from -505 to -528mV in first 15min may be due to the adsorption of water in the paint film.

was 45 cm^2. Copper wire was used for the electrical connection. Before applying the coat to the steel surface, surface preparation was performed using grit blasting according to Swedish standard (ST 2 1/2) (up to near white metal surface). The coat was applied according to the manufactures instruction and specifications using conventional spray (C. spray) nozzle method, coat thickness measurements was performed using a coating thicken gauge, DeSelsko 6000 model 6000-1 coat, the total obtained dray film thickness (D.F.T) is 500-600μm.

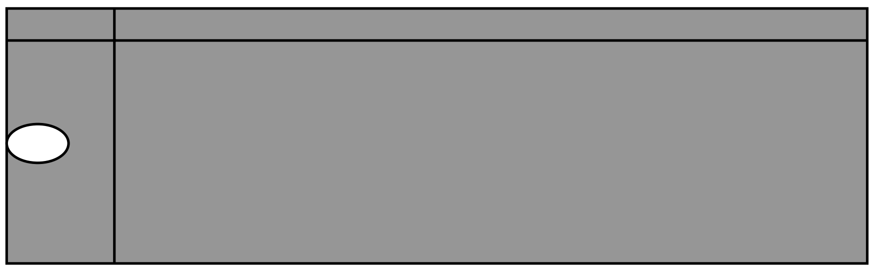


Figure 2: schematic diagram of the coated steel specimen.

3.0. RESULTS AND DISCUSSION

3.1. Open circuit potential (OCP)

Figure 3 shows the open circuit potential (OCP) function of time of bare mild steel behavior, in natural seawater. Measuring the variation of the (OCP) with time for the investigated working electrode is important in defining domains of test sample free corrosion behavior. The OCP measurement also is a simple additional tool that provides complementary information to EIS results regarding the corrosion undergone by the steel substrate after exposure to aggressive solutions (*Ramirez et al., 2005).* The variation of OCP over time for bare steel panel (BSP) and coated carbon steel (CSP) panels are shown in Figures 3 & 4 respectively.

2.1. Working electrode

2.1.1. Bare mild steel

Bare Steel samples of 1cm diameter were used. The chemical composition of these specimens is given in Table1.

Table.1: Chemical composition of low alloy steel specimens

Cr	Mn	Si	C	Mo	S	P	Fe
1.1	0.9	0.35	0.33	.0.25	0.04	0.035	Balance

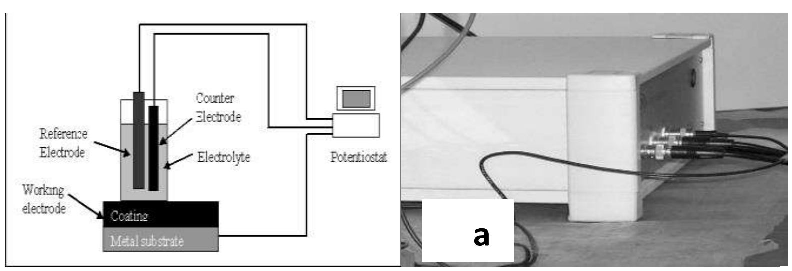
The working electrodes of bare samples were fabricated, cut and shaped, in cylindrical and rectangular Shapes. A long screw fastened to one end of the cylindrical working electrodes for electrical connection The Teflon gasket thereby forms water – tight seal with the specimen electrodes that prevents ingress of any electrolyte and thus avoiding crevices effect. During EIS and potentiodynamic polarization measurements, the exposed area of samples to the corrosive seawater was only 0.785cm^2 for cylindrical, and was 45 cm^2 for the rectangular one. The exposed area was mechanically abraded with a series of emery papers of variable (320-600) grades, starting with a coarse one and proceeding in steps to the finest (600) grade up to a mirror finish. The samples were then washed thoroughly with double distilled water, followed with acetone and finally with distilled water, just before insertion in the cell.

2.1.2. Coated steel

Steel samples of dimensions 0.3 x 3 x 7 cm were used, of the same composition given in Table 1. Figure 2 shows schematic diagram of the coated steel specimen. Two types of epoxy coating were applied to the steel surface such as tar free epoxy; the exposed area

2.0. EXPERIMENTAL

EIS measurements of coated steel panels and polarization curves for bare steel in natural seawater were collected by connecting the electrochemical cell, figure.1.a to Gil ACM Instrument, figure 1.b. The instrument was controlled by personal computer for data logging and data analysis for EIS measurements. Usually, 100 points were measured for each decade of frequency that ranged between 30 kHz - 0. 1 Hz. The amplitude of the superimposed a.c potential was 10 mV. Polarization curves measurements were carried out at scan rate 20 mV/min. Impedance and polarization measurements were carried out employing the three-electrode mode, at the rest potential. Saturated calomel electrode (SCE), and/or Silver/Silver (Ag/AgCl), ware used as reference electrodes (R). A platinum wire 0.5 mm in diameter acted as a counter electrode (C). The polarization cells and their components were carefully cleaned after each experiment to insure cleaning from any possible foreign residues such as metallic products formed during polarization process. The cell and all electrodes were cleaned by distilled water after and before performing each experiment.



b

Figure 1: Electrochemical Cell of EIS a, Gill ACM connected instrument

small fraction of the exposure time required for those changes to be detectable by the traditional mechanical or visual methods.[2-3] The barrier properties of organic coatings create a high electrical resistance across the coating thickness.[4] As coatings age, the interconnecting network of pores within the epoxy matrix eventually becomes saturated with water, salts, etc., exposing the metal substrate to a corrosive environment. The saturation of the pores also creates lower resistance paths through the coating itself. Aged organic coating systems also possess other electrical properties. For instance, dielectric properties cause coatings to act as capacitors to an electrical current. Corrosion occurring at a metal surface possesses related to the corrosion rate, and an electric double layer also behaves as a capacitor. Since Bacon, Smith, and Rugg released their pioneering work in the late 1940s, coatings with impedance>10^9 Ωcm^2 at 0.1 Hz are said to provide excellent corrosion protection; in contrast, those possessing <10^6 Ωcm^2 are said to provide poor corrosion protection.

The impedance modulus at low frequency (|Z|) is an appropriate parameter for characterizing the protective properties of the coatings.[5] The impedance data will demonstrate the changes in capacitance and resistances. The higher the value of coating capacitance, the more current is conducted passing through the capacitor. This response shows a capacitive behavior.

Polyaniline has been widely used as components of nanocomposite coating formulation due to catalytic activity to form a passivating oxide layer [6]. On the other hand, the addition of nanosilica in the nanocomposite coating increases the superiority of polyaniline as a passivating layer in anticorrosion formulations[7]. EIS equivalent circuit model-fitting has been used as a powerful technique that allows electrical fingerprinting providing an insight into properties and behavior of a large verity of materials[8-10].

الملخص

تم إجراء التحليل الطيفي للمقاومة الكهروكيميائية (EIS) وكذلك إمكانات الدائرة المفتوحة (OCP) لكل من الألواح الفولاذية الطرية المطلية بنظام الايبوكسي العاري والكامل، في بيئة مياه البحر الطبيعية. تم الحصول على جميع معلمات التحليل الطيفي للمعاوقة الكهروكيميائية مثل كثافة تيار التآكل (.icorr) ، وإمكانية التآكل Ecorr ، ومعدل التآكل الكمي (CR) ، ومقاومة نقل الشحنة (Rct)، وسعة الطبقة المزدوجة (Cdl) لكل من الألواح الفولاذية الخفيفة العارية والمغلفة. مقارنة ومناقشة وعرض. تم رسم وتقديم مقارنات بين منحنيات الدائرة المفتوحة المحتملة، ومؤامرات Nyquist و bode لكل من الظروف العارية والمختلفة من الفولاذ الطري المطلي بالإيبوكسي. تم أيضًا إجراء قياسات الاستقطاب الديناميكي الفعال، على الفولاذ الطري العاري وتم تقديم جميع المعلمات الكهروكيميائية التي تم الحصول عليها. تم حساب الفولاذ الطري العاري الذي حصل على كفاءة الحماية من التآكل (PE) باستخدام الطلاءات الواقية العضوية ووجد أنه حوالي 100٪.

الكلمات المفتاحية: مطياف المعاوقة الكهروكيميائية، جهد الدائرة المفتوحة، الطلاء.

1.0 INTRODUCTION

Water, ions, and oxygen are the three main agents responsible for the corrosion of metals under coatings. Their diffusion processes through coatings play an important role in corrosion processes. Therefore, it is vital to study their diffusion behavior through coatings to clarify the present understanding of the corrosion mechanism of the metal underneath[1]. EIS allows one to quantitatively determine several coating properties without affecting the coating and its performance. It also facilitates detection of changes in a coating's behavior at a

Corrosion protection of mild steel in natural sea water, by protective organic coatings and rapid assessment using an electrochemical impedance spectroscopy (EIS)

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Abstract

Electrochemical impedance spectroscopy (EIS) as well as open circuit potential (OCP) of both bare and complete epoxy system coated mild steel panels, have been conducted in natural sea water environment. All obtained electrochemical impedance spectroscopy parameters such as corrosion current densities ($i_{corr.}$), corrosion potential E_{corr}, quantitative corrosion rate (CR), charge transfer resistance (Rct) and double layer capacitance (Cdl) of both bare and coated mild steel panels have been compared, discussed and presented. Comparisons between open circuit potential curves, Nyquist and bode plots of both bare and different conditions of epoxy coated mild steel have been plotted and presented. Potentiodynamic polarization measurements have been also performed, on bare mild steel and all obtained electrochemical parameters are presented. The bare mild steel obtained corrosion protection efficiency (PE) % using the organic protective coatings has been calculated and found to be approximately 100 %.

Key Words: Electrochemical impedance spectroscopies, open circuit potential, coating