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Electrochemical Studies on the Corrosion Behavior of API X65 Pipeline Steel in Chloride Solutions

El-Sayed M. Sherif[1,3,*], *Abdulhakim A. Almajid*[1,2], *Khalil Abdelrazek Khalil*[2,4], *Harri Junaedi*[2] *and F. H. Latief*[1]

[1] Center of Excellence for Research in Engineering Materials (CEREM), Advanced Manufacturing Institute, King Saud University, P. O. Box 800, Al-Riyadh 11421, Saudi Arabia
[2] Department of Mechanical Engineering, College of Engineering, King Saud University, P.O. Box 800, Al-Riyadh 11421, Saudi Arabia
[3] Electrochemistry and Corrosion Laboratory, Department of Physical Chemistry, National Research Centre (NRC), Dokki, 12622 Cairo, Egypt
[4] Material Engineering and Mechanical Design Department, Faculty of Energy Engineering, South Valley University, Aswan, Egypt
[*]E-mail: esherif@ksu.edu.sa; emsherif@gmail.com

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Electrochemical studies on the corrosion of API X65 pipeline steel after its immersions in 3.5% sodium chloride solutions for 1 h and 24 h have been reported by using open-circuit potential (OCP), cyclic potentiodynamic polarization (CPP), chronoamperometric current-time (CT) at -500 mV vs. Ag/AgCl and electrochemical impedance spectroscopy (EIS) measurements. OCP measurement for 24 h indicated that the potential of X65 steel increases in the less negative direction with time. CPP data revealed that increasing the immersion time to 24 h before measurements decreases the corrosion current density, the corrosion rate and increases the polarization resistance. The CT curves showed that X65 pipeline steel does not suffer pitting corrosion even after applying -500 mV vs. Ag/AgCl on the electrode for 65 min. EIS spectra confirmed that increasing the immersion time increases the surface and polarization resistances of the steel. All measurements were consistent with each other and showed clearly that increasing the immersion time from 1 h to 24 h before measurements leads to decreasing the corrosion rate and the corrosion resistance for the API X65 pipeline steel in the chloride test solutions.

Keywords: API X65 pipeline steel, corrosion, cyclic polarization, electrochemical impedance spectroscopy, sodium chloride

1. INTRODUCTION

Iron and steel alloys have been one of the most important materials in our daily life because of their good properties and their so many applications. The API X65 pipeline steel is characterized by its excellent weldability, high toughness and tensile strength. It is used in the oil and gas industries as one of the primary steels used in pipe [1,2]. The low cost and strength make API X65 pipeline steel much more attractive than other, higher-performing steels since these industries routinely use miles of pipe. The strength of API X65 pipeline steel also means it is a good choice for pressurized lines, where the steel's excellent weldability ensures strong seals.

The corrosion and corrosion inhibition of steel pipelines in harsh environments has been investigated by many investigators [1-6]. Meresht et al. [1] studied the effect of 2-butyne-1,4-diol on the corrosion susceptibility of grade API 5L X65 steel pipeline in 2 M Na_2CO_3/1 M $NaHCO_3$ using electrochemical techniques and weight loss measurements and found that the corrosion of this steel can be inhibited by up to 92% by using 5mM of 2-butyne-1,4-diol as a corrosion inhibitor. They [1] also reported that the water content accompanying the oil production process has been found to be a significant factor in the internal corrosion of steel pipelines because it contains many corrosive agents such as carbon dioxide, hydrogen sulphides, organic acids, and salts. Tian and Cheng [7] have also studied the electrochemical corrosion behavior of X-65 steel in the simulated oil sand slurry and found that the corrosion of the API steel records its minimum when there is no sand because of the formation of an oily layer that covers the steel surface and protects it from being attacked by any aggressive species present in the water, while the presence and the increase of the sand content increases the corrosion rate. Quej-Aké et al. [8] studied the electrochemical and tension behavior of API pipeline steel in a simulated soil solution using electrochemical impedance spectroscopy and slow strain tests and reported that the steel was highly resistant to the stress corrosion cracking.

In the present work we report the corrosion of API X65 pipeline steel after different exposure intervals, 1 h and 24 h, of its immersion in high salinity water that contains 3.5% NaCl solution. Although, the corrosion of this steel in different media has been reported by many investigators [3-6], its behavior and the effect of 3.5% NaCl on its dissolution has very little attention. Our study was carried out using different electrochemical techniques including cyclic polarization, current-time measurements at -500 mV, open-circuit potential and electrochemical impedance spectroscopy.

2. EXPERIMENTAL PROCEDURE

2.1. Materials and chemicals

An API X65 pipeline steel electrode contains the following additions: 0.10% C, 0.35% Si, 0.005% S, 0.15% P, 0.015% N, and 1.5% maximum Mn. The API X65 pipeline steel had a rectangular shape with dimensions of 1x1 cm. A stock solution of 3.5% sodium chloride (NaCl, Merck, 99%) was prepared by dissolving 35 g of NaCl in 1 L glass flask.

2.2. Electrochemical cell

An electrochemical cell with a three-electrode configuration was used; the API X65 pipeline steel rod; a platinum foil, and an Ag/AgCl electrode (in the saturated KCl) were used as the working, counter, and reference electrodes, respectively. The working electrode for electrochemical measurements was prepared by welding a copper wire to a drilled hole was made on one face of the rod; the rod with the attached wire were then cold mounted in resin and left to dry in air for 24 h at room temperature. Before measurements, the other face of the working electrode, which was not drilled, was first grinded successively with metallographic emery paper of increasing fineness up to 1200 grit. The electrode was then cleaned using doubly-distilled water, degreased with acetone, washed using doubly-distilled water again and finally dried with dry air.

2.3. Electrochemical methods

For all electrochemical experiments, an Autolab Potentiostat (PGSTAT20 computer controlled) operated by the general purpose electrochemical software (GPES) version 4.9 was used to perform the electrochemical experiments. The open-circuit potential (OCP) of the API X65 pipeline steel was measured versus time for 1350 min. The cyclic potentiodynamic polarization curves were obtained by scanning the potential in the forward direction from -1.200 V to 0.250 V against Ag/AgCl at a scan rate of 0.003 V/s. For the back scan, the potential was reversed in the backward direction at the same scan rate in order to understand the possibility of the occurrence of pitting corrosion. Chronoamperometric current-time experiments were carried out by stepping the potential of the steel samples at – 0.50 V vs. Ag/AgCl for 4000 sec. The electrochemical impedance spectroscopy (EIS) tests were performed at corrosion potentials (OCP) over a frequency range of 100 kHz to 100 mHz, with an ac wave of ± 5 mV peak-to-peak overlaid on a dc bias potential, and the impedance data were collected using Powersine software at a rate of 10 points per decade change in frequency. All experiments were carried out at room temperature in a cell contains 100 ml of the freely aerated stagnant NaCl solutions.

3. RESULTS AND DISCUSSION

3.1. Cyclic potentiodynamic polarization (CPP) measurements

In order to report the corrosion parameters such as corrosion potential, corrosion current, polarization resistance and corrosion rate, for API X65 pipeline steel after its immersion in the chloride test solution for 1 h and 24 h, CPP measurements were carried out. Fig. 1 depicts the CPP curves obtained for API X65 pipeline steel after its immersion for 1 hour in aerated stagnant 3.5 wt% NaCl solution. The same measurements were carried out for API X65 pipeline steel after 24 hours immersion in the chloride solution and the curve is shown in Fig. 2. The values of cathodic (βc) and anodic (βa) Tafel slope, corrosion potential (E_{Corr}), corrosion current density (j_{Corr}), pitting potential (E_{Pit}), pitting current density (j_{Pit}), protection potential (E_{Prot}), polarization resistance (Rp), and corrosion rate (K_{Corr}) obtained from the polarization curves shown in Fig. 1 and Fig. 2 are listed in Table 1. The values of all these corrosion parameters were obtained as has been reported in our previous studies [9-12].

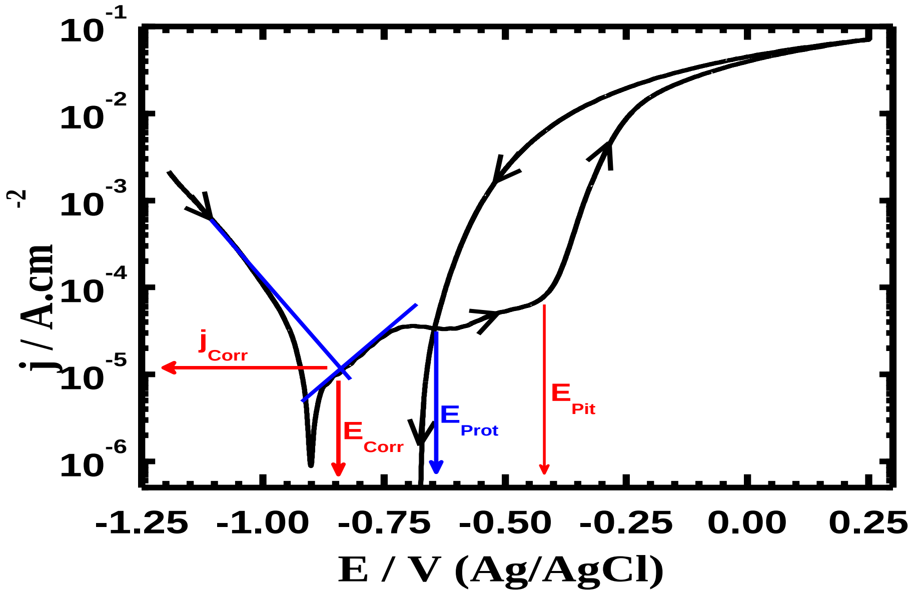

Figure 1. Cyclic potentiodynamic polarization curves for API X65 pipeline steel electrode after its immersions in aerated stagnant 3.5 wt% NaCl solution for 1 hour.

It is well know that the cathodic reaction for metals and alloys in near neutral solution is primarily the oxygen reduction as reported in our previous work [9]. On the other hand, the anodic reaction for iron and its alloys is the dissolution to ferrous cations and further to ferric cations [13,14]. It has been reported [13-15] that this dissolution is accelerated by the presence of oxygen due to the increased consumption of the produced electrons by the anodic reaction at the cathodic one. Fig. 1 depicts that the steel electrode shows a passive potential region between -900 mV and -450 mV vs. Ag/AgCl as a result of the formation of passive layer of iron oxides and/or corrosion products on the electrode surface. Oh et al. [16] has reported that iron can develop up to nine different oxide phases on its surface; in this case the possible oxides that might form at these conditions can be represented according the following reactions [15];

$$Fe + ½ O_2 + H_2O \rightarrow Fe(OH)_2 \quad (1)$$

$$3Fe(OH)_2 + ½ O_2 \rightarrow Fe_3O_4 + 3H_2O \quad (2)$$

The formed ferrous hydroxide, Eq. (1), reacts with more oxygen to form the top layer of corrosion product, Fe_3O_4 (magnetite). The presence of such oxide partially protects the steel surface from further dissolutions and leads in turn to the appearance of a passive region on the polarization potential-current behavior. The passive region dissolves under the influence of chloride ions attack and pitting corrosion occurs as indicated by the rapid increases in the current values for steel with increasing potential and by the appearance of the wide hysteresis loop in the area between the forward and backward directions for potential in the anodic branch shown in Fig. 1.

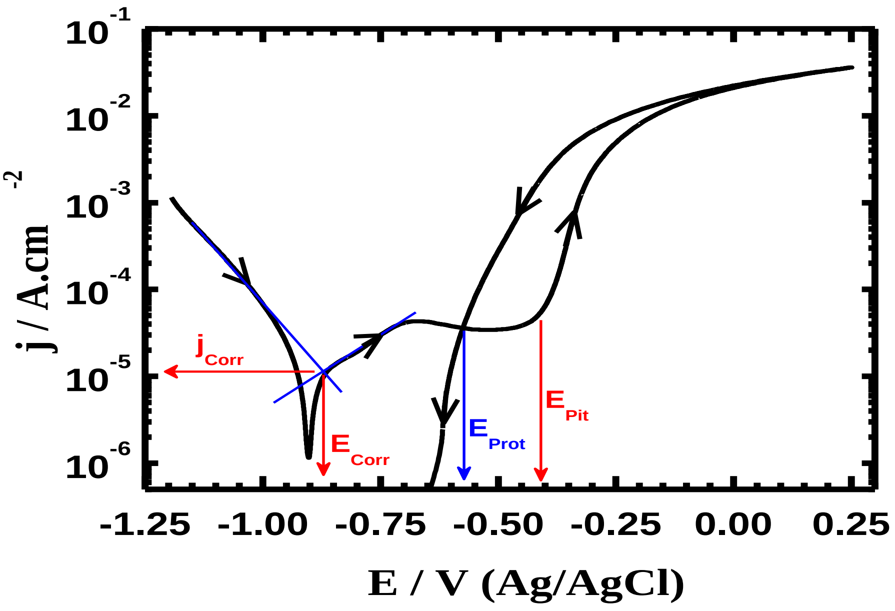

Figure 2. Cyclic potentiodynamic polarization curve for the API X65 pipeline steel after its immersion in aerated stagnant 3.5% NaCl solutions for 24 hour.

It is clearly seen from Fig. 2 that the API steel after 24 hours in the chloride solution before measurement shows a wider passivation region with lower passivation current and lower currents at all applied potential values. This was quantified as listed in Table 1, which confirms that increasing the immersion time of steel to 24 hours decreases the values for j_{Corr} and K_{Corr}. This effect was also found to increase the values for the cathodic and anodic Tafel slopes (β_c and β_c) and highly increases the polarization resistance, Rp. This is due the fact that to increasing the immersion time of API steel in chloride solution allows it to develop a layer of corrosion products and/or oxides that protect its surface from being attacked by the aggressive chloride ions and leads in turn to decreasing the corrosion parameters and thus decreases both the uniform and pitting corrosion.

Table 1. Parameters obtained from cyclic potentiodynamic polarization curves shown in Fig. 1 and Fig. 2 for API X65 pipeline steel after 1 and 24 h immersion in 3.5% NaCl solutions.

Immersion time	Parameter								
	E_{Corr}/ mV	j_{Corr}/ μAcm^{-2}	β_c/mV dec^{-1}	β_a/mV dec^{-1}	E_{Pit}/ mV	j_{Pit}/ μAcm^{-2}	E_{Prot}/ mV	R_p/ kΩcm^2	K_{Corr}/ mmy^{-1}
1 hour	- 835	13	120	165	- 445	50	-650	2.32	0.151
24 hours	- 870	11	140	190	- 430	75	-580	3.19	0.128

3.2. Chronoamperometric current-time (CT) measurements

Figure 3 shows the CT curves obtained at -500 mV for the API X65 pipeline steel electrode after its immersion in the aerated stagnant 3.5% NaCl solution for (1) 1 h and (2) 24 h before measurements. These experiments were carried out to shed more light on particularly the pitting corrosion the API X65 pipeline steel electrode in chloride solutions after 1 h and 24 h. The recorded after 1 h immersion, Fig. 3 (curve 1), showed rapid increases in its value in the first few minutes of applying the constant potential. This might be due to the dissolution of an oxide film (see Eq. (1) and Eq. (2)) was developed on the steel surface during its immersion in the solution. The current then slightly decreases with increasing time up to almost 40 min after which the current decreases and increases till the end of experiment.

Increasing the immersion time to 24 h before measurements, curve 2, greatly decreases the initial current from about 400mAcm^{-2} after 1 h (curve 1) to circa 60mAcm^{-2} after 24 h immersion. The current then slightly increases with increasing time up to the end of the run. The initial decrease in the current values for steel after 24 h immersion before applying the constant potential is most probably due to the formation of corrosion products and/or oxide films on the steel surface, which get thicker with further with time. This effect also decreased the absolute current values for steel after 24 h immersion compared to those obtained after 1 h immersion. The CT measurements thus confirm that the uniform corrosion of API X65 pipeline steel decreases with increasing immersion time as well as this steel grade does not suffer pitting corrosion at the applied potential value, -500 mV even after 24 h immersion. This aggress with the data obtained by polarization measurements, Fig. 1 and Fig. 2, and confirms that elongating the immersion time for API X65 pipeline steel before measurements allows the surface to go through oxide films and/or corrosion products formation that resist the chloride ions attack, which in turn lowers the obtained current values.

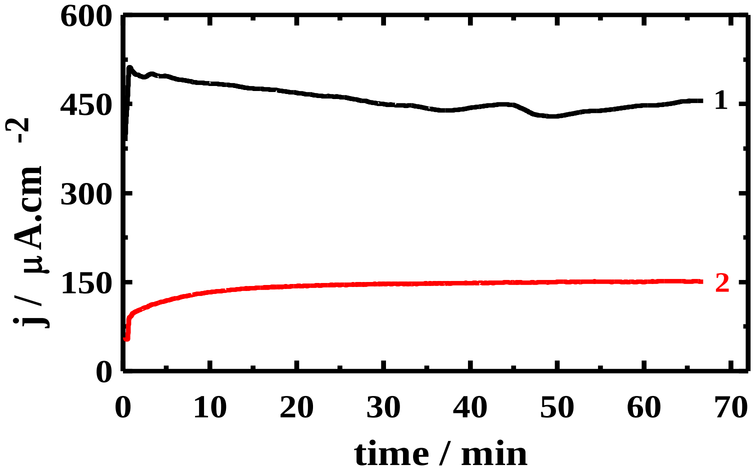

Figure 3. Chronoamperometric current-time curves obtained at -500 mV for API X65 pipeline steel electrodes after its immersion in aerated stagnant 3.5% NaCl solutions for (1) 1 h and (2) 24 h, respectively.

3.3. Open-circuit potential (OCP) and Electrochemical impedance spectroscopy (EIS) measurements

Figure 4 shows the OCP curves obtained for API X65 pipeline steel in aerated stagnant 3.5 wt% NaCl solutions. It is seen from Fig. 4 that the potential of the steel increased towards the more negative values from the first moment of electrode immersion as a result of the dissolution of an air oxide film was formed on the electrode before its immersion in the solution. The potential then abruptly shifted from -0.645 V to -0.460 V within only an hour time. This rapid positive potential shift indicates on the passivation of the steel surface due to the formation of an oxide film. Further increasing the time of the experiment led to a rapid negative potential shift, which might have resulted from the dissolution of the formed oxide film under the influence of the aggressive chloride ions attack. After almost 260 min, the potential of API X65 pipeline steel started to very slowly decrease and shows almost a stable change for current with time at circa -0.565 V vs. Ag/AgCl, indicating that the steel surface was under equilibrium between its dissolution and its protection via the formation of an oxide film and/or a layer of corrosion products.

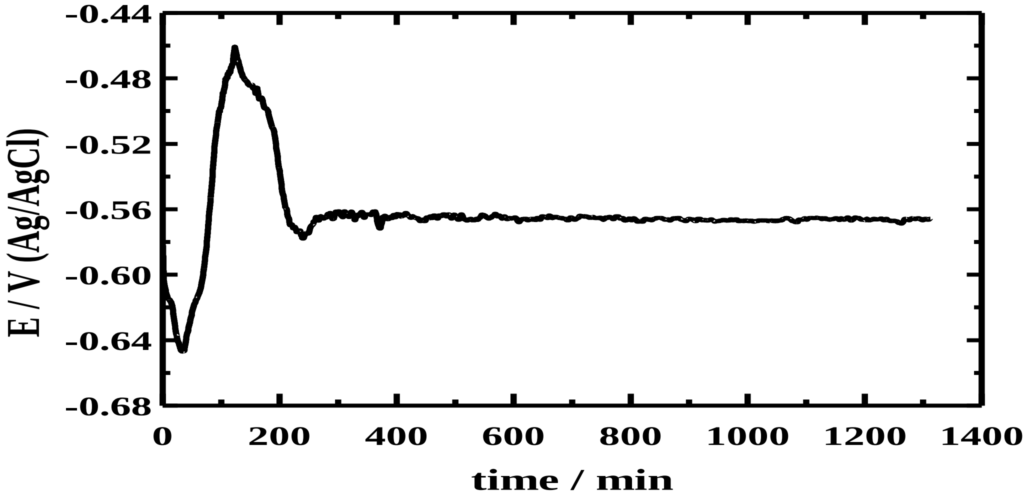

Figure 4. Open-circuit potential curves obtained for API X65 pipeline steel in aerated stagnant 3.5% NaCl solution.

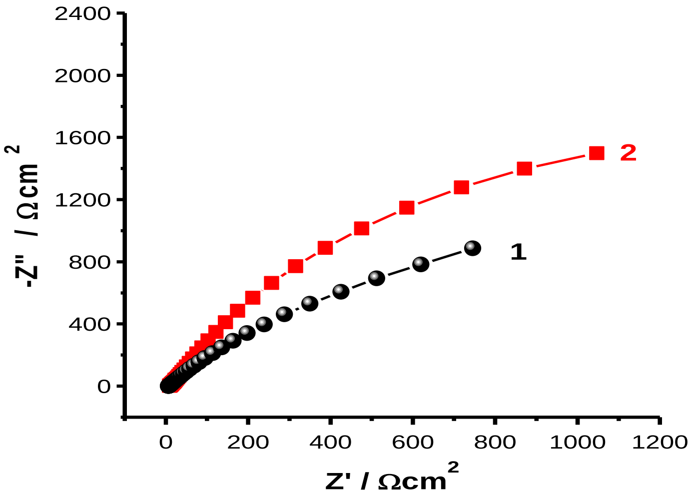

Figure 5. EIS Nyquist plots for API X65 pipeline steel electrode after its immersion in aerated stagnant 3.5% NaCl solution for (1) 1 h and (2) 24 h, respectively.

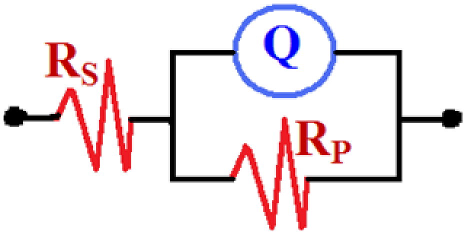

Figure 6. The equivalent circuit model used to fit the experimental data shown in Fig. 5.

The EIS technique has been one of the most used methods to report the mechanism of corrosion and corrosion protection of metals and alloys in aggressive media [17-21]. The Nyquist plots obtained for the API X65 pipeline steel electrodes at an open-circuit potential after their immersion in 3.5% NaCl solutions for (1) 1 h and (2) 24 h are shown in Fig. 5. The spectra represented in these figures were analyzed by best fitting to the equivalent circuit model shown in Fig. 6. The EIS parameters obtained by fitting the equivalent circuit shown in Fig. 6 are listed in Table 2.The parameters of the equivalent circuit model shown in Fig. 6 can be defined according to the usual convention as follows; R_S represents the solution resistance, Q is the constant phase elements (CPEs), and Rp is the polarization resistance. It is seen from Fig. 5 that the API steel showed only one semicircle its diameter gets wider with increasing the immersion time to 24 h before measurements; wider diameter of the semicircle reflects on a better corrosion resistance [18,19-21]. It is clearly seen from Table 2 that the resistances, R_S and Rp recorded higher values for the pipeline steel that was immersed for 24 h before measurements. The constant phase elements (Q, CPEs) with its n values almost 0.8 for all samples represent double layer capacitors with little porosities [9-12]. This is because and depending on the value of n, CPE can represent capacitance (Z(CPE) = Cdl, n = 1), Warburg impedance for (n = 0.5), or resistance (Z(CPE) = R, n = 0). Hence, the CPE for the API steel is substituted for a capacitor to fit the semicircle more exactly [12].

Table 2. EIS parameters obtained by fitting the Nyquist plots shown in Fig. 5 with the equivalent circuit shown in Fig. 6 for API X65 pipeline steel after 1 h and 24 h immersion in 3.5% NaCl solutions.

Immersion time	Parameter			
	R_S / Ω cm^2	Q (CPEs)		R_P / Ω cm^2
		Y_Q / F cm^{-2}	n	
1 hour	9.04	$69E10^{-6}$	0.77	2715
24 hours	11.06	$67E10^{-6}$	0.78	3373

Figure 7 and Figure 8 show respectively the Bode impedance and Bode phase angle plots for API X65 pipeline steel electrode after its immersion in aerated stagnant 3.5% NaCl solution for (1) 1 h and (2) 24 h. It is clearly seen from Fig. 7 that the impedance of the interface for the steel increases with increasing frequency and increasing the immersion time from 1 h to 24 h led to higher impedance values along the whole frequency range. It has been reported [22,23] that the high impedance at lower frequency values indicates on the passivation of the surface. This means that increasing the immersion time increases the corrosion resistance of the steel in the chloride test solution. The impedance of a CPE can be defined as following, respectively [9,24,25];

$$Z_{CPE} = (1/Y_0)\,(j\omega)^{-n} \qquad (3)$$

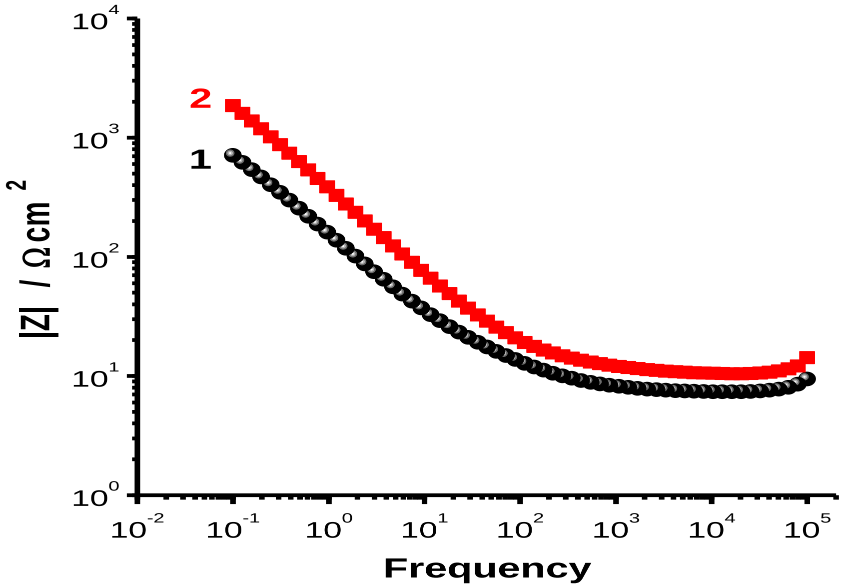

Figure 7. Typical Bode impedance plots for API X65 pipeline steel electrode after its immersion in aerated stagnant 3.5% NaCl solution for (1) 1 h and (2) 24 h, respectively.

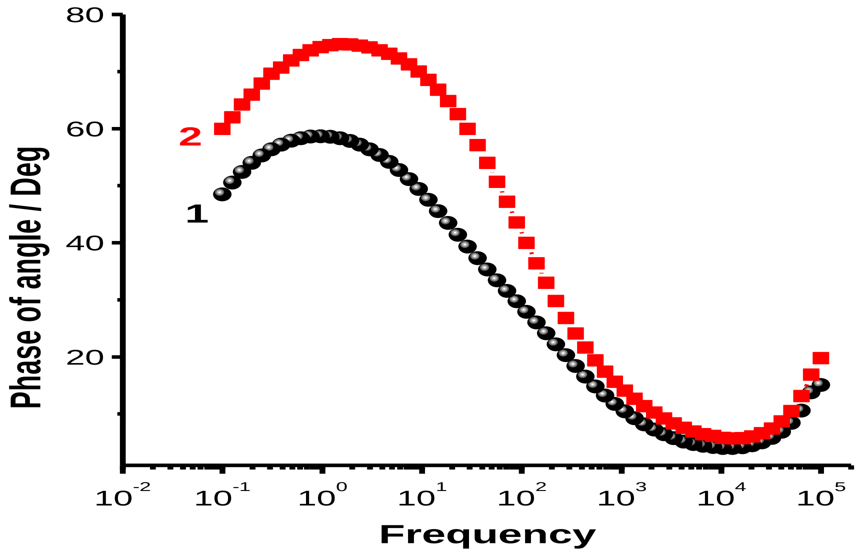

Figure 8. Bode phase angle plots for API X65 pipeline steel electrode after its immersion in aerated stagnant 3.5% NaCl solution for (1) 1 h and (2) 24 h, respectively.

Where, Y_0 is the modulus, ω is the angular frequency, and n is the phase. It is seen from Fig. 8 also that the increase of the immersion time to 24 h before measurements increases the maximum degree of the phase angle (curve 2). The EIS data thus in good agreement with the data obtained by polarization and chronoamperometric current-time measurements that increasing the exposure period for the API X65 steel in the chloride solution before measurements increases its corrosion resistance.

4. CONCLUSIONS

The corrosion of API X65 pipeline steel in 3.5% sodium chloride solutions after 1 h and 24 h immersion has been reported. The study was performed using a variety of conventional and nonconventional electrochemical techniques such as cyclic potentiodynamic polarization, chronoamperometric current-time at -500 mV vs. Ag/AgCl and open-circuit potential (OCP) along with electrochemical impedance spectroscopy (EIS) measurements. It has been found that increasing the immersion time from 1 h to 24 h before measurement decreases the corrosion current, the absolute current obtained at -500 mV vs. Ag/AgCl and the corrosion rate for the API steel as was indicated by polarization and chronoamperometric measurements. This effect was also found to increase the steel’s surface and polarization resistances, the impedance of the interface as well as the maximum phase angle as was shown by the electrochemical spectroscopy data. Results together were consistent to each other confirming that the increase of the immersion time decreases both uniform and pitting corrosion for the API X65 steel in the aerated stagnant 3.5% NaCl solutions.

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