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Using Electrochemical Impedance Spectroscopy Sinusoidal Potential Amplitude to Assess the Efficiency of Niobium Oxide Based Organic Coating in Oil Wells Produced Water

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The oil industry coexists with damages caused by corrosion of materials in almost all areas of activity. Recent discoveries in Brazil of potential oil reserves at deeper waters, commonly named “pre-salt oil layer”, may represent severe conditions leading to the need in developing new materials and technologies that meet unfavorable prospection demands. In this context, the corrosion protection characteristic of an organic coating based on niobium oxide immersed in water produced by oil wells was evaluated. The evaluation of the coating was carried out by means of electrochemical impedance spectroscopy technique (EIS). Results showed that only with the application of high voltage amplitudes of 350 mV over the OCP it was possible to decrease dispersion in EIS data, with no degradation or delamination of the coating. Despite this, at high voltage sinusoidal signal and raising the agressivity of the medium, it was observed an increase in the corrosion mechanisms leading to lower impedance module values at longer exposure time (144 days), indicating the need for optimization of sinusoidal voltage amplitudes according with the nature, thickness and resistivity of the coating applied.

Keywords: electrochemical impedance spectroscopy, corrosion, organic coating, Nb_2O_5.

1. INTRODUCTION

As of the 1950s, there was an increase in interest in materials containing niobium and, especially, in the development of niobium alloys for applications in various technological fields, being defined as a critical industrial raw material[1]. With more than 90% of the exploitable global reserves of niobium, Brazil is the largest producer and exporter of this rare mineral. Niobium has at least three stable oxides: niobium oxide II (NbO), considered a conductor; niobium oxide IV (NbO_2), a semiconductor and niobium oxide V (Nb_2O_5) an insulator[2]. However, the most common oxide has a +5 oxidation state, with a high melting point, good ductility at room temperature and resistance to corrosion[3].

Organic paints are considered polymeric coatings and are prepared by adding chemical species that prevent or control corrosion processes, acting both as mechanical and electrochemical barrier, due to the action of incorporated pigments[4]. However, the active protection offered by the pigment aims at reducing the corrosion rate when corrosive species get in touch with the substrate due to coating porosity[5]. In order to assess in qualitative and semi-quantitative ways the corrosion protection ability of organic coatings, the electrochemical impedance spectroscopy (EIS), an in-situ, fast and non-destructive technique, can be used. In potentiostatic mode of the EIS technique, it is normally applied an alternate low voltage perturbation (10 mV) at different frequencies on a fixed DC potential, normally the open circuit potential, generating correspondent current values as response. However, for the evaluation of thick coatings, in order to acquire measurable current readings, larger perturbation amplitudes can be used[6]. According to the performance of anti-corrosion coatings, EIS values may change very little in short periods of immersion. Thus, a long exposure is usually necessary to classify these coatings from a corrosion resistance point of view. Therefore, to evaluate protection parameters in a short period of time, which can be correlated with long-term behavior, is one of the greatest challenges of this type of study. In this regard, the corrosion protection action of the niobium oxide based organic coating applied over carbon steel was evaluated by EIS. Due to the coating resistance characteristic, a greater sinusoidal voltage amplitude of 350mV was applied in this study. Water produced by oil wells in the post and pre-salt regions was used as corrosive medium, since Brazil recently started to produce oil located mainly in deep waters below the pre-salt region, transforming the country into an important place for the oil industry[7].

2. MATERIALS AND METHODS

For the tests, AISI 1020 carbon steel test specimens (TS) with 4.0 cm^2 area were used, previously sandblasted and polished up to a 600-grit sandpaper, degreased by soaking in acetone and then dried in hot air. In order to monitor the electrochemical parameters, a copper wire was welded into the test specimens so that electrochemical measurements could be carried out. Subsequently, the TS were embedded in epoxy resin and the carbon steel exposed faces were coated with the niobium oxide based organic coating. The organic coating was prepared according to manufacturer's specifications by mixing 75% $_{wt}$ of component A (white ink with a specific density of 1.57 $g.cm^{-3}$, containing the niobium oxide pigment) with 25% wt of component B (epoxy resin with a specific density of 0.97 $g.cm^{-3}$). The coupons prepared with the paint niobium oxide based showed 800 µm (± 30.0 µm) thick layer after curing.

For the corrosion tests performance, two different media were used, both provided by PETROBRAS S.A.: water produced by oil reservoirs of the post and pre-salt regions. The media were sterilized in an autoclave at 120°C for 15 minutes to avoid the formation of bacterial biofilms, and thus evaluate the corrosion protection ability of the coating without the influence of biocorrosion. The specimens, in triplicate, were then immersed in each production water for 144 days, replenished during the experiment time, so one could evaluate the performance of the coating through EIS measurements. EIS experiments were carried out on coated test specimens, at the beginning (t=0 days) and at the end of immersion time (t=144 days), by application of varying voltage sine wave amplitude (10 mV and 350 mV) in order to get current response. Electrochemical Impedance was measured as a function of immersion time, with potentiostatic regulation over the open circuit potential (OCP) of the specimens. The experiment was conducted in three electrode electrochemical cells placed inside a Faraday cage, and connected to a Potentiostat/Galvanostat AUTOLAB PGSTAT302N, using saturated calomel as reference electrode and a platinum wire as auxiliary electrode.The frequency range applied was 100 kHz to 0.01 Hz and the results obtained are presented in Nyquist and Bode mode diagrams.

3. RESULTS AND DISCUSSION

Organic coatings are widely used to protect metal structures against corrosion, and in this sense, the aggressiveness of the corrosion process depends on the environment to which the material is exposed[8]. Table 1 shows the physical-chemical profile of the water produced by oil wells. According to the results, the water produced in the pre-salt region is characterized by a higher salinity and lower resistivity, indicating a higher aggressiveness, in comparison with the water produced in the post-salt region.

Table 1. Physicochemical properties of water produced in oil reservoirs.

Working Fluid	pH	Conductivity (mS.cm^{-1})	Resistivity (ohm.cm)	Salinity (g.L^{-1})
Post-salt	7.16	213.3	4.69	96.582
Pre-salt	7.18	307.6	3.25	180.282

The electrochemical impedance signals acquired by the potentiostat are usually interpreted as a combination of resistive, capacitive and inductive parameters, thus are used to characterize the actual occurrent mechanisms on the specimens surface. Fig. 1 shows the results of the electrochemical impedance analysis after immersion of the organic coating based on niobium oxide in the water produced by oil wells in the post-salt region. In Fig. 1a, one can see high dispersion in data obtained by the Nyquist diagram, when 10 mV sinusoidal amplitude is applied, right after the coating immersion. As already known, a coating surface is not perfectly flat from a geometric point of view: irregularities can be distinguished at the atomic scale, called “superficial disorders”, as well as at a much larger scale than 10 nm, known as “roughness”[9]. Thus, two theories can be used to explain the dispersive behavior of data:

(i) initially it is assumed that the capacitance of the double electric layer is uniform on the roughened surface of the electrode and because of the cavities and protrusions existent in the coating, there is a difference in the solution resistance values. The synergy of these two factors, i.e., the double electric layer capacitance and the solution resistance, results in the behavior of the overall impedance as a function of the resistive and capacitive elements of the coating interface with the solution, where the interfacial capacitance depends on the analyzed frequency. Thus, this model predicts capacitance values of the electrochemical system at a higher frequency range (kHz to GHz), differing from the values of the actual capacitance. The divergence shown by the theoretical and observed capacitance values generates a large dispersion in the impedance of the electrochemical system studied;

(ii) another theory on the origin of the dispersion shown in the results may be associated with the inhomogeneity at atomic scale, of the electrode surface, leading to changes at the double electrical layer structure, together with the presence of kinetic adsorption processes of specific anions.

Results obtained showed high impedance (10^{10} ohm.cm^2) and, considering the experiment assembling as well as the correspondent electrical circuit, one can say that the coating capacitance is in series with the solution resistance, therefore when a very low sinusoidal voltage was applied in this circuit, the fluctuations in the measured data might be related to the difficulty in acquisition of the current signals. On the other hand, when a greater magnitude (350 mV) alternating voltage was applied to the system, a decrease in the dispersion of data obtained was observed (Fig. 1b). Thus, one can infer that the coating capacitance is the main parameter which defines the optimization of alternating voltage amplitude in order to acquire a sensitive response in overall impedance measurements.

Several studies[10, 11, 12, 13] relate the high frequency region (10^5-10^4 Hz) of the impedance diagrams to the capacitance (permittivity) of the coating and the medium-low frequency region (10^3 - 10^{-2} Hz) is assigned to the conducting path and metallic interface phenomena[14]. Figures 1c and 1d show the region of the Nyquist diagram where one can visualize no dispersion in the measured data. By applying a 10 mV signal amplitude, results show no dispersion only in the high frequency region. However, when a 350 mV AC amplitude was applied, results can be measured without dispersion in the regions of high and medium frequencies. The Nyquist graphical profile of these figures also show an almost parallel line to the imaginary axis, characteristic of a high resistivity coating. Furthermore, Figures 1e and 1f confirm this information by presenting increasing values of impedance modulus and phase angle near -90 in the medium and low frequency regions[15].

After 144 days of immersion in water produced from oil wells in the post-salt region, new impedance results were obtained (Figure 2). The Nyquist (Fig. 2a and 2c) and Bode modulus/phase (2e) diagrams acquired for a 10 mV signal amplitude application, showed dispersion behavior only from lower frequency values (2.512 Hz).

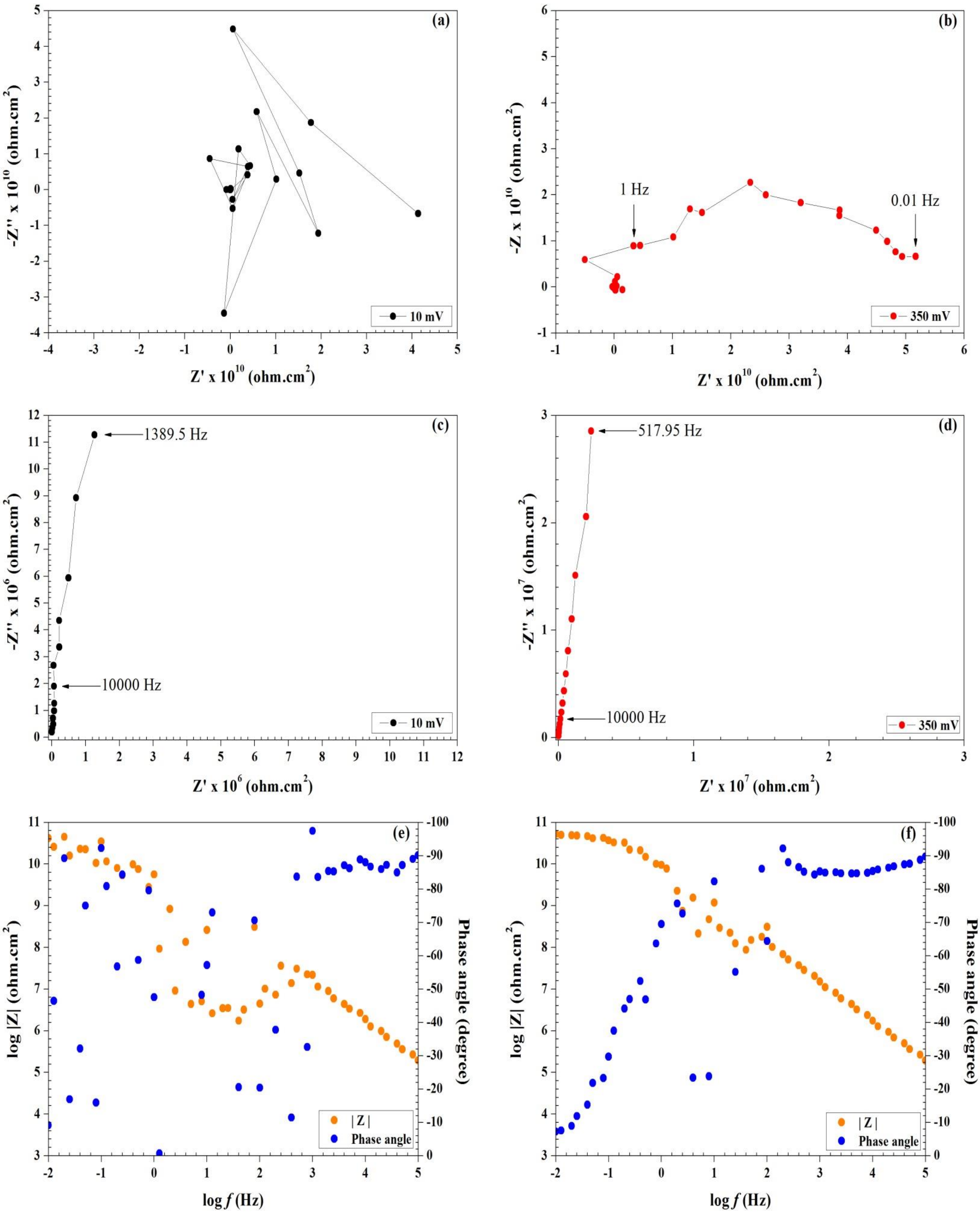

Figure 1. Nyquist (1a, 1b, 1c and 1d) and Bode modulus/phase (1e and 1f) diagrams of the niobium oxide based organic coating immersed in water produced from oil wells in the post-salt region (t = 0 days), obtained with different alternating signal amplitudes (10 and 350 mV).

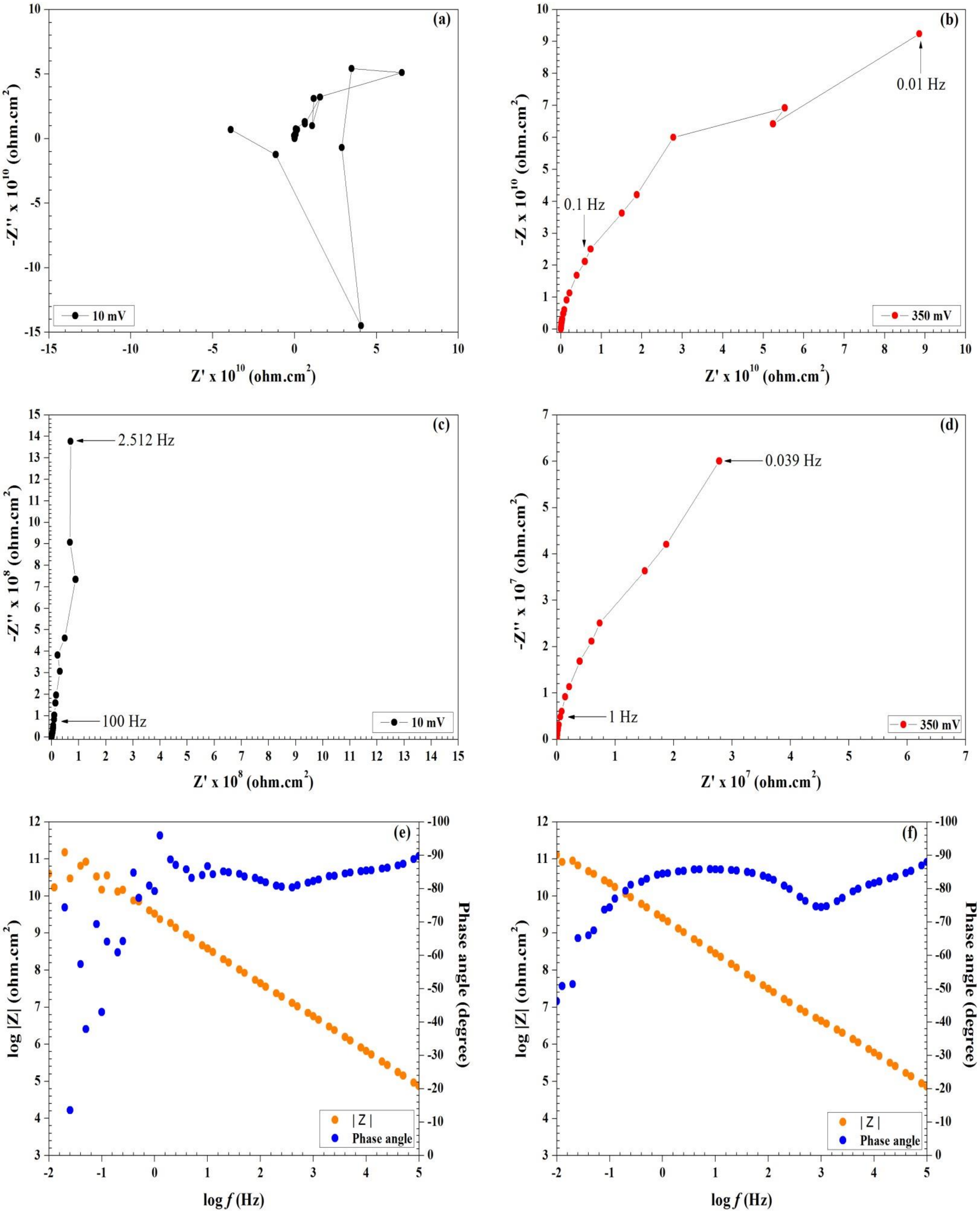

Figure 2. Nyquist (2a, 2b, 2c and 2d) and Bode modulus/phase (2e and 2f) diagrams of the niobium oxide based organic coating immersed in water produced from oil wells in the post-salt region (t = 144), obtained with different alternating signal amplitudes (10 mV and 350 mV).

This might indicate that the coating had its resistivity lowered during immersion time. On the other hand, Nyquist diagrams acquired by application of a 350 mV signal amplitude (Figures 2b and 2d) showed no dispersion over almost all frequency range, but unlike the t=0 results, it was observed a less capacitive behavior throughout the stable frequency range (Figure 2d) corroborating with the idea that there is a straight relation between coating degradation and the minimum EIS AC potential signal which must be applied, allowing acquisition of impedance values and still causing no harm for the specimen. Likewise, the Bode modulus/phase diagram (2f) showed no dispersion at 350 mV signal amplitude, although phase angle measurements show a stable second time constant over medium/low frequencies, which is not so clear at lower signal amplitude, indicating that the application of a higher signal over the coated specimen immersed for 144 days in post-salt produced water, somehow influenced the corrosion mechanisms evolution on the test specimen, supposedly facilitated by the coating natural resistivity decay over time. In fact, the impedance modulus values at low frequencies were slightly higher than the ones observed at t=0. This corroborates with the possible change in the coating structure, lowering its pore resistance, favoring fluid percolation towards the metallic interface. Therefore there can be an establishment of an electrical double layer on the metallic interface, getting along with a charge transfer which helps clogging the inner pores of the coating. This phenomenon can explain the slight increase observed for the values of the impedance module at lower frequencies for 350 mV sinusoidal amplitude application at t=144 days.

The Nyquist (Fig. 3a, 3b, 3c and 3d) and Bode modulus (Fig. 3e and 3f) diagrams obtained after immersing the niobium oxide based organic coating in the water produced by oil wells in the pre-salt region showed the same initial behavior of the results when the coating was immersed in water produced in the post-salt region, notwithstanding the signal amplitude applied. However, after 144 days of immersion in this higher corrosivity medium, the coating showed some water permeation, as evidenced by the slight increase in capacitance. On the other hand, Nyquist and Bode plots (Fig. 4) show decrease on the low frequency impedance module and also of the phase angle values, along with characterization of two time constants independently of the sinusoidal signal applied. Despite this result, one can observe that at higher sinusoidal signal a clearer resistive behaviour is set up which might be explained by the percolation of fluid along with establishment of a corrosion mechanism on metal/coating interface.

The capacitance evaluation of an immersed coating is used to indicate the occurrence of the water absorption phenomenon, because this process changes the dielectric constant of the polymer. The capacitance evaluation is an important parameter in the study of corrosion protection coating performance, since permeation of water and electrolytes through the coating may trigger the corrosion process[16]. Thus, the greater the capacitance value, the higher the water permeation in the coating. Table 2 shows the capacitance values of the niobium oxide based coating (C_c), obtained after applying 10 mV and 350 mV sinusoidal amplitude in different corrosive media, calculated using equation (1) where *f* is the applied alternate voltage frequency and |Z| is the impedance modulus and θ is the phase angle:

$$C_c = \frac{1}{2\pi\, f\, |Z|\, \sin\, \theta} \qquad (1)$$

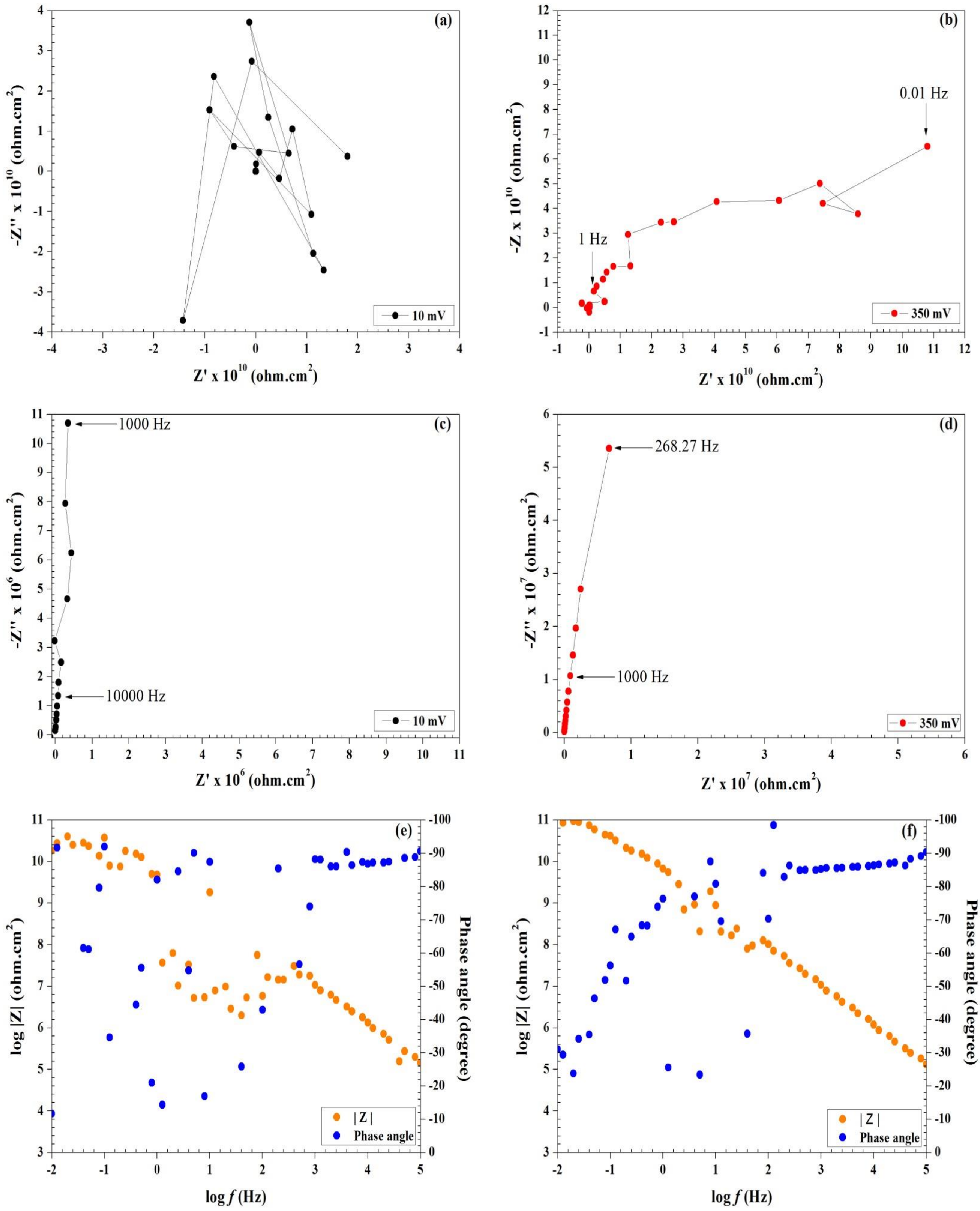

Figure 3. Nyquist (3a, 3b, 3c and 3d) and Bode modulus (3e and 3f) diagrams of the niobium oxide based organic coating immersed in water produced from oil wells in the pre-salt region (t = 0 days), obtained with different alternating signal amplitudes (10 mV and 350 mV).

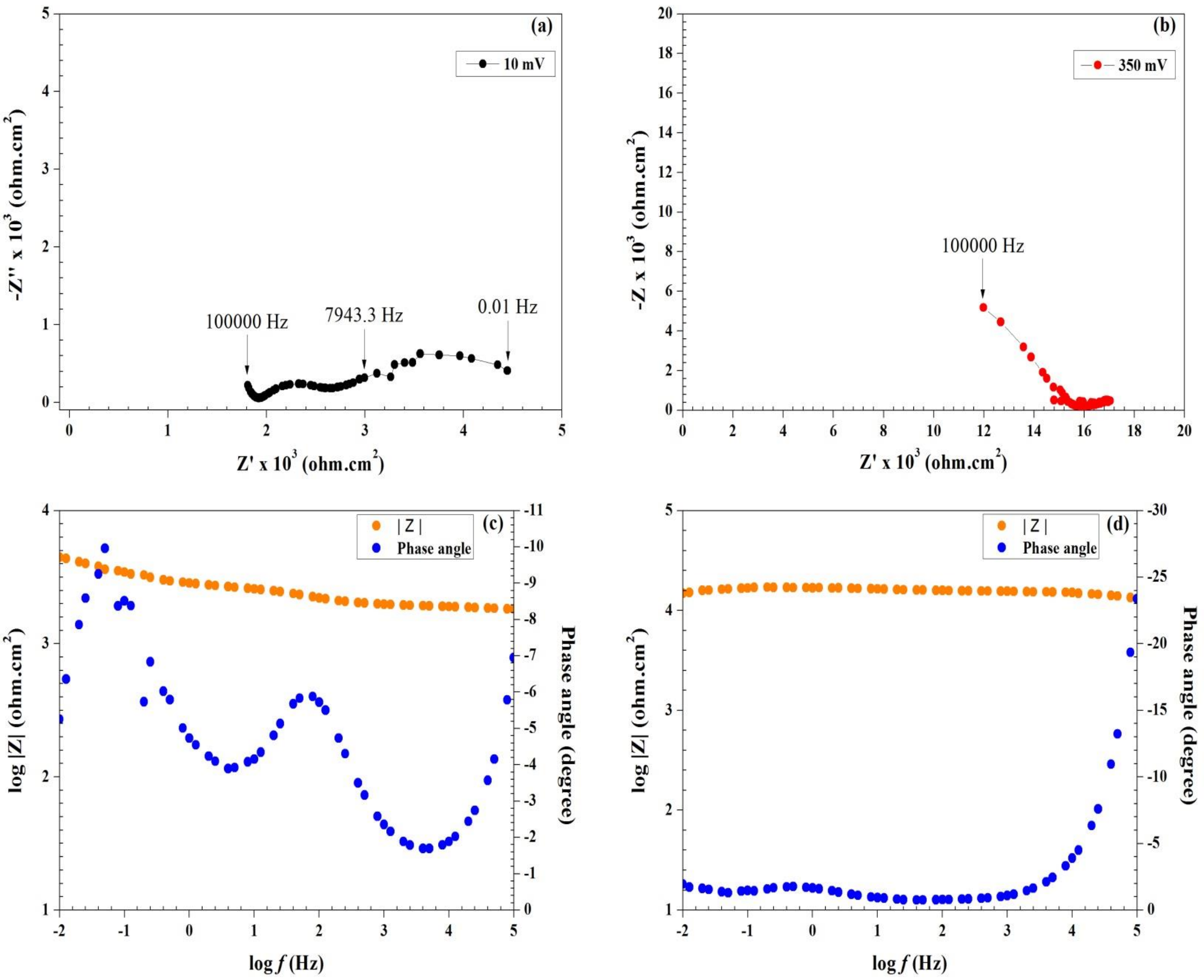

Figure 4. Nyquist (4a, 4b, 4c and 4d) and Bode modulus (4e and 4f) diagrams of the niobium oxide based organic coating immersed in water produced from oil wells in the pre-salt region (t = 144 days), obtained with different alternating signal amplitudes (10 mV and 350 mV).

Table 2. Capacitance in Farads (F) of the niobium oxide based coating at 100 kHz in both corrosive media, different EIS signal amplitudes at initial (t=0 days) and final immersion time (t=144 days).

	Post-salt produced water		Pre-salt produced water	
	10 mV	350 mV	10 mV	350 mV
$Cc_{t=0}$	8.175×10^{-12}	8.235×10^{-12}	1.101×10^{-11}	1.201×10^{-11}
$Cc_{t=144}$	2.151×10^{-11}	2.230×10^{-11}	7.218×10^{-9}	3.577×10^{-10}

Although showing a slight increase between the initial and final immersion time, the capacitance values observed remained between the range of intact coatings[17]. On the other hand, considering the higher agressivity of the pre-salt produced water, the coating capacitances calculated for this condition are a little higher than for the ones calculated for the post-salt condition, indicating a strong relation with water uptake at more agressive conditions, even at early immersion times. Assuming the initial thickness of the coating (≈ 800 μm) and the capacitance values obtained both for small and high sinusoidal potential application over the OCP, one can say that the highest excitation signal (350 mV) was not able to apply a dielectric breakdown on the coating, although favoring to speed up the electrochemical mechanism kinetics specially at final immersion time. This behavior was confirmed by dispersion reduction in EIS data acquired.

Table 3 shows the impedance modulus values at 0.01 Hz which may be associated to the specimen polarization resistance. After 144 days of immersion in the pre-salt water, the coating showed a significant reduction in the impedance value, indicating a lower corrosion resistance. Although the niobium oxide coated specimen subjected to the 350 mV sinusoidal amplitude shows a greater impedance when compared with the 10 mV alternate signal values, this might be due to corrosion mechanisms speed up inferred by the high voltage alternate signal, leading to a decrease in corrosion resistance of the coated specimen.

Table 3. Electrochemical impedance values obtained at a frequency of 0.01 Hz.

	Post-salt		Pre-salt	
	10 mV	350 mV	10 mV	350 mV
$Z_{t=0}$ (ohm.cm^2)	4.188×10^{10}	5.211×10^{10}	1.838×10^{10}	1.261×10^{11}
$Z_{t=144}$ (ohm.cm^2)	3.957×10^{10}	1.279×10^{10}	4464.08	14805.2

4. CONCLUSION

The corrosion protection behavior of the niobium oxide based organic coating immersed in water produced from oil wells could be assessed by electrochemical impedance spectroscopy at different sinusoidal signal amplitudes. Results indicate that the application of high amplitudes during EIS tests can be used to evaluate thick and high resistivity coatings, once they reduce data dispersion associated with difficult current acquisition. The sine wave potential must be optimized according to the resistivity of the coating applied so that the coating is not damaged or delaminated. Besides, the niobium oxide based organic coating showed no change in corrosive property after 144 days of immersion in water produced from oil wells in the post-salt region. However, when the coating was exposed to water produced by wells of the pre-salt region, i.e., with twice as much salinity, the coating corrosion protection performance was impaired, indicating that it can be used in media where salinity is lower than 90 g.L^{-1}, thereby increasing the useful life of metallic substrates.

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