

Full Paper

Electrochemical Behaviour of AISI 410 Stainless Steel at Open Circuit Potential in Acidic Solutions

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Abstract- In this study, the electrochemical behaviour of AISI 410 stainless steel at open circuit potential (OCP) in acidic solutions was investigated. For this purpose, the passivation parameters and semiconductor properties of passive films were derived from potentiodynamic polarization, Mott–Schottky analysis and electrochemical impedance spectroscopy (EIS). The potentiodynamic polarization curves suggested that AISI 410 stainless steel showed excellent passive behaviour in HNO₃ solutions. Also, the polarization curves showed that the corrosion potential and corrosion current density of AISI 410 stainless steel increased with the increase in the concentration of solutions. For all HNO₃ solutions, Mott–Schottky analysis showed two positive slopes in the main passive region (n-type behaviour). Also, this analysis indicated that the donor densities (N_{D1} and N_{D2}) for the passive films formed on AISI 410 stainless steel are in the range 10^{21} cm⁻³ and increased with HNO₃ solutions. EIS results showed that the reciprocal capacitance of the passive film is directly proportional to its thickness which increases with decreasing HNO₃ concentration. It is thus clear that dilute HNO₃ solutions offer better conditions for forming passive films with higher protection behaviour, due to the growth of a much thicker and less defective films.

Keywords- Stainless steel, Polarization, EIS, Mott–Schottky, Donor density

1. INTRODUCTION

Martensitic stainless steels are used for applications where high mechanical performance is required. However, due to their low chromium content, these steels are relatively sensitive to corrosion. The corrosion resistance of stainless steel is due to the presence of passive films formed on the surface. Generally, the substrate, the environment and also specific experimental conditions affect both the chemical composition and the structure of the passive layer [1,2].

Generally, an increase in solution concentration has significantly effects on the corrosion behaviour of stainless steels. It is reported [3] that HNO_3 concentration has a significant effect on the corrosion behaviour of stainless steel. In the other study [4], the anodic polarization curves showed that no significant changes in corrosion potential even with increase in HNO_3 concentration in presence of oxidizing ions. For austenitic stainless steel in HNO_3 solutions, it is found [5] that the passive film consists of platelet-like structures at lower concentrations of HNO_3 . This study also showed that at higher concentrations of HNO_3 , the platelet-like structures disappear. Also, it is found that the variation in passive film morphology (For austenitic stainless steel) occurs depending upon the concentration and time of immersion [6]. The present study was designed to obtain a better knowledge of the electrochemical behaviour of AISI 410 stainless steel (AISI 410) in HNO_3 solutions. The aim of this work was to investigate the influence of HNO_3 concentration on the passivation parameters and semiconductor properties of AISI 410 using the potentiodynamic polarization, Mott-Schottky analysis and EIS.

2. EXPERIMENTAL

The chemical composition of AISI 410 used in the present investigation is shown in Table 1. All samples were polished mechanically by abrading with wet emery paper up to 2000 grit size on all sides and then were embedded in cold curing epoxy resin. After this, the stainless steels were degreased with acetone, rinsed with distilled water and dried with a stream of air just before immersion. Aerated acidic solutions (without purging oxygen or any gas) with seven different concentrations were used and the compositions were 0.1, 0.3, 0.6, 0.9, 1.5, 1.8 and 2.0 M HNO_3 , respectively. All solutions were made from analytical grade 67% HNO_3 and distilled water, and the tests were carried out at 25 ± 1 °C.

Table 1. Chemical compositions of AISI 410 stainless steel

Elements	Cr	Ni	Mo	Mn	Si	C	P	Cu	S	Fe
AISI 410 / wt%	12.5	0.17	0.02	0.31	0.5	0.07	0.02	0.04	<0.003	Bal

All electrochemical measurements were performed in a conventional three-electrode cell under aerated conditions. The counter electrode was a Pt plate, and all potentials were measured against Ag/AgCl in saturated KCl. All electrochemical measurements were obtained using METROHM AUTOLAB potentiostat/galvanostat controlled by a personal computer. Prior to all electrochemical measurements, working electrodes immersed at OCP for 900 s to form a steady-state passive film. Potentiodynamic polarization curves were measured potentiodynamically at a scan rate of 1 mV/s starting from -0.25 V (vs. E_{corr}) to 1.2 V. Mott-Schottky analysis was carried out on the passive films at a frequency of 1 kHz using a 10 mV ac signal and a step potential of 25 mV, in the cathodic direction.

3. RESULT AND DISCUSSION

3.1. OCP measurements

In Fig. 1(a) and (b), changes on OCP of AISI 410 in HNO_3 solutions are shown. At the start of immersion, the open circuit potential is directed towards positive amount.

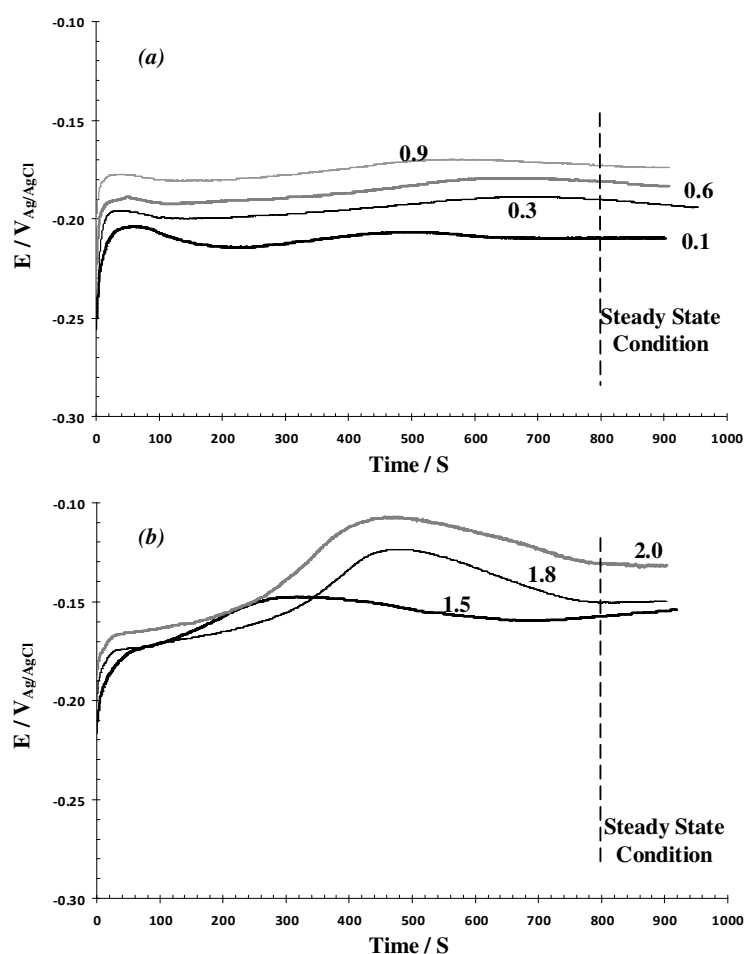


Fig. 1. OCP plots of AISI 410 in HNO_3 solutions

This trend is also reported for austenitic stainless steels in acidic solutions which are indicative of the formation of passive film and its role in increasing protectivity with time. Fig. 1(a) and (b) also indicates that after 800 s a complete stable condition is achieved and electrochemical tests are possible.

3.2. Potentiodynamic polarization measurements

Fig. 2(a) and (b) shows the potentiodynamic polarization curves of AISI 410 in HNO₃ solutions. For all curves, it was observed that before the electrode was transferred to a passive state an active current peak occurred, which could be attributed to the oxidation of Fe²⁺ to Fe³⁺ ions in the passive film [7,8].

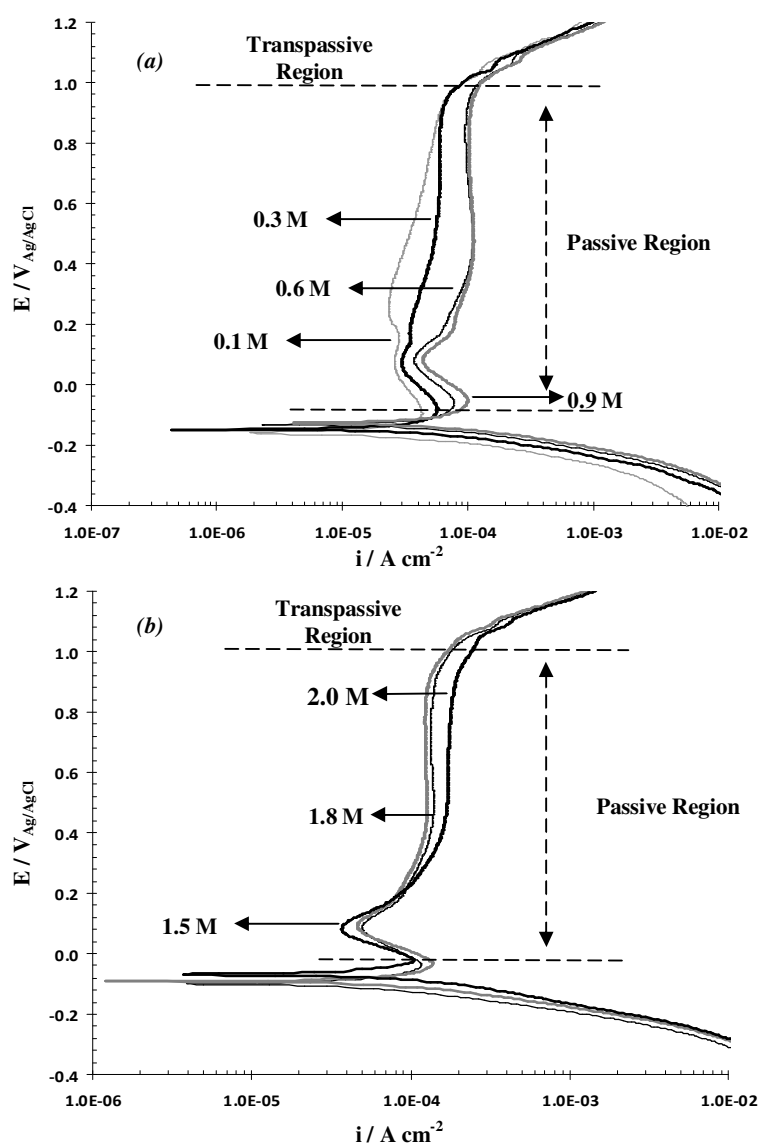


Fig. 2. Potentiodynamic polarization curves for AISI 410 in HNO₃ solutions

Fig. 3 shows the corrosion potential and corrosion current density of AISI 410 in HNO₃ solutions. It is evident from this figure that the corrosion potentials were found to shift slightly towards positive direction with an increase in solution concentration. Also, the results revealed that the corrosion current density increased with the increase in the concentration of HNO₃ solutions. It is also clear in the passive potential region, the passive current density increased with the increase in the concentration of HNO₃ solutions.

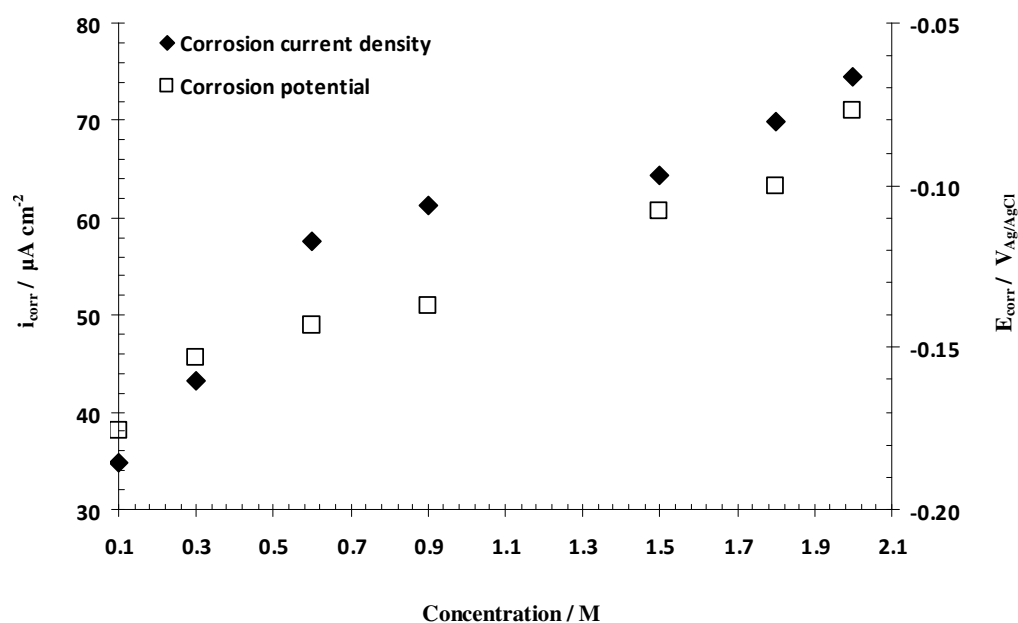


Fig. 3. Corrosion potential and corrosion current density of AISI 410 in HNO₃ solutions as a function of concentration

3.3. Mott-Schottky analysis

The outer layer of passive films contains the space charge layer and sustains a potential drop across the film. The charge distribution at the semiconductor/solution is usually determined based on Mott-Schottky relationship by measuring electrode capacitance C , as a function of electrode potential E [9-12]:

$$\frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 e N_D} \left(E - E_{FB} - \frac{kT}{e} \right) \quad \text{for n-type semiconductor} \quad (1)$$

$$\frac{1}{C^2} = -\frac{2}{\epsilon\epsilon_0 e N_A} \left(E - E_{FB} - \frac{kT}{e} \right) \quad \text{for p-type semiconductor} \quad (2)$$

where e is the electron charge (-1.602×10^{-19} C), N_D is the donor density for n-type semiconductor (cm^{-3}), N_A is the acceptor density for p-type semiconductor (cm^{-3}), ϵ is the

dielectric constant of the passive film (usually taken as 15.6 [9-12]), ϵ_0 is the vacuum permittivity (8.854×10^{-14} F cm⁻¹), k is the Boltzmann constant, T is the absolute temperature and E_{FB} is the flat band potential. Flat band potential can be determined from the extrapolation of the linear portion to $C^{-2}=0$.

Fig. 4(a) and (b) shows the Mott-Schottky plots of AISI 410 in HNO₃ solutions. It should be noted that for all concentration, C^{-2} clearly decrease with solution concentration. In all plots, the positive slopes in the main passive region are attributed to a n-type behaviour, probably due to the presence of Cr₂O₃ and FeO on the passive films [13].

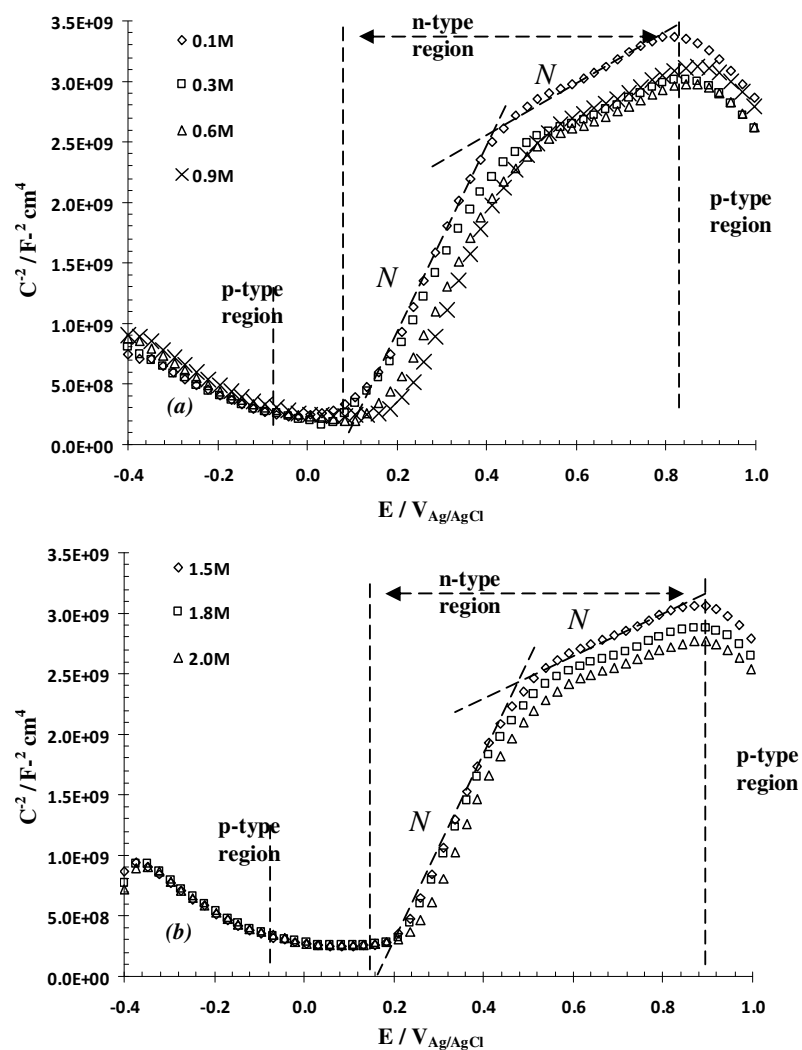


Fig. 4. Mott-Schottky plots of AISI 410 in HNO₃ solutions. The electrodes are immersed at OCP for 900 s to form a steady-state passive film

According to Schmucki et al., the Mott-Schottky plots obtained for bulk metal oxides like Fe_2O_3 show no breakdown of linearity, and the n-type semiconductivity is unambiguously attributed to the presence of Fe^{2+} ions that act as donor levels [14]. For passive films formed on stainless steels or pure iron, the origin of the two slopes obtained in the anodic domain appears to still be subject to debate [15,16]. As reported by Hakiki et al., the first and second slopes are attributed to Fe^{2+} located, respectively, in the tetrahedral and octahedral sites of a spinel type structure [17]. Sikora et al. [15] found these levels to oxygen vacancies and Fe^{2+} in octahedral sites. However n-type semiconductivity was observed with passive films formed on ferritic stainless steels, in spite of their low Fe^{2+} content.

According to Eq. (1), donor density has been determined from the positive slopes in the main passive region. Fig. 5 shows the calculated donor densities (N_{D1} and N_{D2}) for the passive films formed on AISI 410 in HNO_3 solutions. The orders of magnitude are around 10^{21} cm^{-3} and are comparable to those reported in other studies.

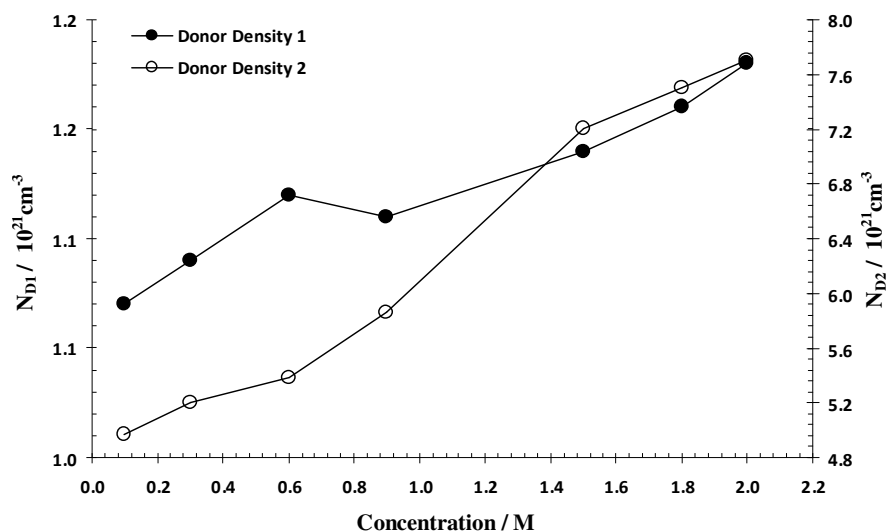


Fig. 5. Donor density of the passive films formed on AISI 410 in HNO_3 solutions

According to Fig. 5, the donor densities increase with solution concentration. Changes in donor densities correspond to the non-stoichiometry defects in the passive film. Therefore, it can be concluded that the passive film on AISI 410 is disordered and becomes more visible at higher concentration. Based on Point defect model (PDM) [18] the donors or acceptors in semiconducting passive layers are point defects. According to the PDM, the flux of oxygen vacancy and/or cation interstitials through the passive film is essential to the film growth process. In this concept, the dominant point defects in the passive film are considered to be oxygen vacancies and/or cation interstitials acting as electron donors.

The p-type semiconductivity observed for stainless steel in cathodic region is generally related to the presence of Cr_2O_3 in the inner part of the film [16,19]. According to Virtanen et al., chromium vacancies or excess oxygen can be related to this p-type semiconductor behavior of chromium oxide in passive films [20].

3.4. EIS measurements

The EIS response of AISI 410 in HNO_3 solutions was performed and the results are presented as Nyquist and Bode plots in Figs. 6 and 7. The Nyquist and Bode plots show a resistive behavior at high frequencies, but in the middle to low frequency range there was a marked capacitive response. The Bode-phase curves show one time constant (only one maximum phase lag at the middle frequency range).

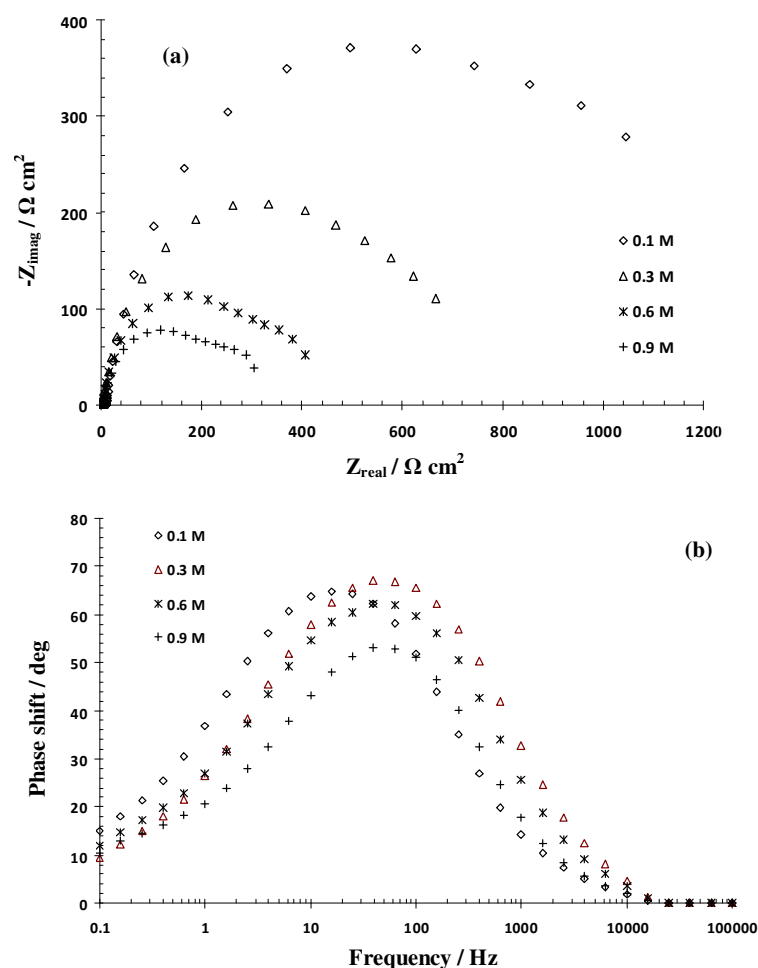


Fig. 6. (a) Nyquist and (b) Bode plots of AISI 410 in 0.1, 0.3, 0.6 and 0.9 M HNO_3 solutions at OCP

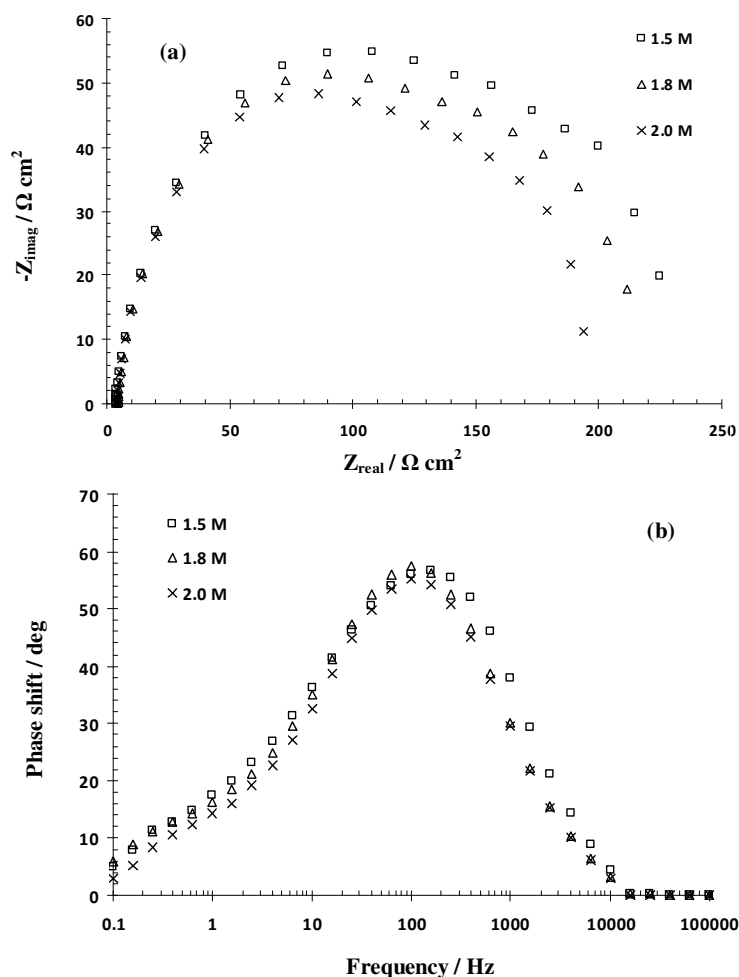


Fig. 7. (a) Nyquist and (b) Bode plots of AISI 410 in 1.5, 1.8 and 2.0 M HNO₃ solutions at OCP

The phase angles values remained very close to 90 °C. This evolution revealed the formation and growth of a passive film. Also, there was a decrease of the low frequency impedance with the solution concentration. Indeed, the capacitive impedance is the least in 2.0 M HNO₃ solution and increases with dilution.

Based on these results, the equivalent circuit shown in Fig. 8 was used to simulate the measured impedance data of AISI 410 in HNO₃ solutions. This equivalent circuit is composed of: R_s – solution resistance; Q_{pf} – constant phase element corresponding to the capacitance of the passive film; R_{pf} – resistance of the passive film [21]. In the investigated frequency range (100 kHz– 100 mHz) contribution of the double layer, or reaction of oxygen evolution has not been detected and the capacitance and the resistance of the passive film dominate the overall process in the passive film. This equivalent circuit composed by one

time constant as proposed by Pardo et al. [21] to describe the behaviour of AISI 304 and 316 stainless steels in H₂SO₄ solutions.

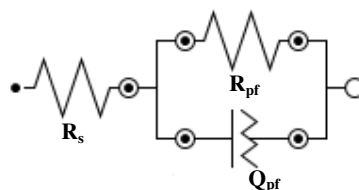


Fig. 8. The best equivalent circuit tested to model the experimental EIS data with one time constant [21]

Table 2 presents the best fitting parameters (with an average error of less than 5%) obtained for the impedance data of AISI 410 in HNO₃ solutions. As can be seen, R_{pf} increases with decrease in HNO₃ concentration while C decreases. This behaviour indicates that grown passive film on AISI 410 surface is liable to dissolve in high HNO₃ concentration, since R_{pf} is inversely proportional to the corrosion current density.

Table 2. Best fitting parameters for the impedance spectra of AISI 410 in HNO₃

HNO ₃ Solution (M)	0.1	0.3	0.6	0.9	1.5	1.8	2.0
R _s (Ω cm ²)	16.1	13.10	9.31	6.31	4.96	4.20	2.67
R _{pf} (Ω cm ²)	1184	671	377	251	212	188	165
C _{pf} (μF cm ⁻²)	244	215	352	366	296	373	305
n _{pf}	0.85	0.89	0.83	0.81	0.87	0.86	0.88

According to the equivalent circuit shown in Fig. 8, the passive film thickness (d) can be calculated using the Eq.(3) [22]:

$$d = \frac{\varepsilon \varepsilon_0 A}{C} \quad (3)$$

Where C is the total capacitance of the passive film, ε the relative permittivity of the passive film, ε_0 is the vacuum permittivity (8.854×10^{-14} F/cm), and A the area in cm². Generally, a change in the total capacitance of the passive film (C) can be used as an indicator for change in the passive film thickness (d). Therefore, the reciprocal capacitance of the passive film (1/C) is proportional to its thickness which increases with decreasing HNO₃ concentration. It is clear that dilute HNO₃ solutions give better conditions for forming the

passive films with higher protection behaviour, due to the growth of a much thicker and less defective passive films [23].

4. CONCLUSIONS

The electrochemical behaviour of AISI 410 in HNO₃ solutions was investigated in the present work. Conclusions drawn from the study are as follows:

1. The OCP plots showed that the open circuit potential is directed towards positive amount, which are indicative of the formation of passive film and its role in increasing protectivity with time.
2. The potentiodynamic polarization curves suggested that AISI 410 showed excellent passive behaviour in all HNO₃ solutions.
3. Also, the potentiodynamic polarization curves showed that the corrosion current densities increase with the increase in the concentration of HNO₃ solutions.
4. Mott–Schottky analysis showed two positive slopes (n-type behaviour) for passive films formed on AISI 410 stainless steel in all HNO₃ solutions.
5. Based on the Mott–Schottky analysis, it was shown that donor densities (N_{D1} and N_{D2}) are in the range of 10^{21} cm⁻³ and increased with HNO₃ solutions.
6. EIS results showed that the reciprocal capacitance ($1/C$) of the passive film is directly proportional to its thickness which increases with decreasing HNO₃ concentration.
7. Also, EIS results showed that dilute HNO₃ solutions offer better conditions for forming passive films with higher protection behaviour, due to the growth of a much thicker and less defective films.

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