Effect of Potentiostatic Passivation on Corrosion Resistance of 304 Stainless Steel in Nace Solution

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Abstract

Stainless steel samples (304) were passivized in 1.0 N sulfuric acid at different passivation potentials. Effect of different holding time on the passivation at corresponding passivation potential was also investigated. Corrosion resistance property of the passivated and the bare samples in NACE solution were measured using Tafel extrapolation method. Electrochemical impedance spectroscopy (EIS) tests were conducted to study the stability of the passive layers. Scanning electron microscope (SEM) images of passivated samples were also examined to understand the extent of protection obtained by passivation. Results obtained showed that potentiostatic passivation could serve as a fairly good tool to fight against the pitting corrosion of 304 stainless steel in NACE.

Keywords: 304 stainless steel, NACE solution, Potentistaticp, Corrosion, Polarization test, EIS, SEM.

Introduction

Austenitic 304 stainless steels are widely used in several industries such as chemical, pharmaceutical and naval for their high corrosion resistance property following the stability of the passive film which forms on their surfaces [1-4]. In spite of their wide use, failures of stainless steel structures in industry due to localized corrosion attack are often reported [2,3]. Pitting corrosion is one of the most dangerous forms of localized attack of stainless steels in chloride media [5,6]. One of the non aggressive anions that reduce the pitting corrosion of stainless steel in chloride ion containing solutions include sulfate ion [7-9].

In the present investigation, based on the experimental findings of number of authors [10] potentiostatic passivation method has been applied on 304 stainless steel and its effect on corrosion resistance property in a high chloride ion containing medium like in NACE solution has been extensively carried out. The electrochemical passivation is done by applying a controlled polarized potential to the specimen. The applied potential is selected from the passive region of the corresponding potentiodynamic polarization diagram of the sample in the specific solution. The potential is applied for a given time for the formation and growth of passive layer on the bare surface. 1.0 N sulfuric acid, a common industrial chemical has been opted

as laboratory electrolyte for potentiostatic passivation of stainless steel since dilute sulfuric acid with nominal unit activity H+ ion has been found to be an effective passive medium for 304 stainless steel samples [11].

Electrochemical impedance spectroscopy tests have been conducted to study the stability of the passive layers. Scanning electron microscopy studies have also been carried out to characterize the passive morphologies and to understand the extent of protection obtained by passivation.

Experimental

Sample Composition and Solution Preparation

AISI 304 stainless steel samples were polished mechanically to a mirror finish using successive grades of emery papers followed by polishing with alumina powder. Then the specimens were washed thoroughly with distilled water, degreased with acetone properly for one hour, cleaned with alcohol & inspected and transferred quickly into the electrochemical cell only after ensuring that there were no pits. For each experiment a cross-sectional area of 0.75 cm2 was exposed in standard electrochemical cell.

NACE solution was chosen as the testing environment and as a passivating sulfate medium 1.0 N reagent grade sulfuric acid was chosen. All solutions were prepared using double distilled water. The composition of NACE solution was sodium chloride-25g/l and glacial acetic acid-2.4ml/l. The pH of the solution was maintained at 4.7 throughout the experiment by adding 6 pieces of pH-7 buffer tablets.

Electrochemical Instruments & Measurements

Standard three electrode system consisting of a calomel electrode as a reference electrode, a graphite rod as a counter electrode and the testing specimen as the working electrode was used for the experiments. The specimens were mounted in a tight Teflon holder so that only one circular end was exposed, making sure that no crevasses occurred between the metal and Teflon holder.

Polarization experiments with scan rate of 1mV/s were carried out as per ASTM ST72 using Gamry Potentiostat. The software used was Gamry Echem Analyst version 4.0. The Icorr and Ecorr values were obtained by Tafel's extrapolation method. In potentiostatic passivation method, current transient curves were obtained by holding the sample for different time intervals at different passivating potentials selected from the corresponding potentiodynamic polarization curves. EIS was carried out in a frequency range of .01 Hz to 106 Hz. The r.m.s. value of the applied alternating signal was 0.01V. The Bode and Nyquist plots were fitted by simplex algorithm supported by the Gamry Echem Analyst software version 4.0.

Surface morphologies of some selective samples were examined by scanning electron microscope (SEM), model no. JSM 6360.

Results and discussion

The Icorr & Ecorr values of as received sample in 1.0 N sulfuric acid and in NACE solution as given in Table 1, are derived from Figure 1. In both the situation Icorr values are in the μA/cm2 range. However, in terms of nobility, Ecorr value is much higher in sulphuric acid since it does not contain the damaging chloride ions. Interestingly, although in both the cases the sample exhibits a passive behaviour and the passive range is longer in 1.0 N sulfuric acid. Moreover in case of NACE solution the passive region is found to break up abruptly indicating pitting tendency. The manifestation is typical as reported earlier [12,13].
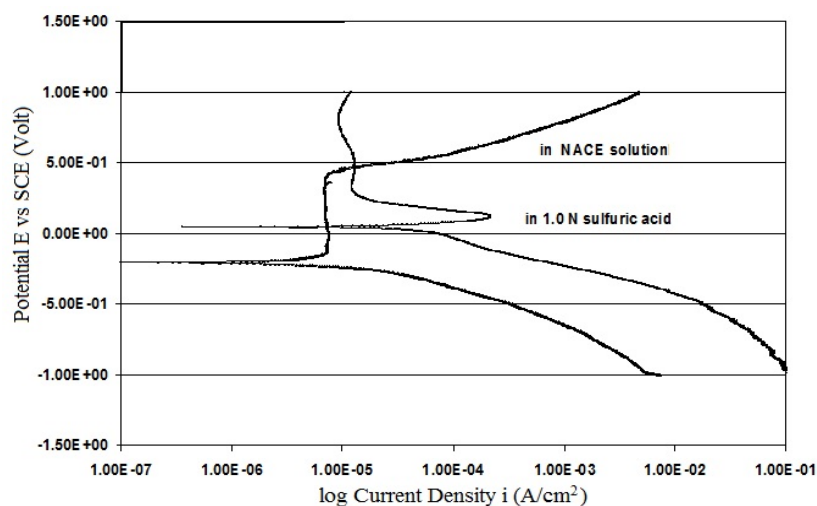
Figure 1: Polarization curves of as received 304 stainless steel in 1.0 N sulfuric acid and in NACE solution.

Electrolyte	$i_{corr}(\mu A/cm^2)$	$E_{corr}(V)$
1.0 N sulfuric acid	28.5	0.059
NACE solution	3.82	-0.181

Table 1: Corrosion data of as received sample.

Figures 2-4 show the current transient curves of the as received sample in 1.0 N sulfuric acid at different passivating potentials, namely at 350, 550 and 750 mV respectively for three different holding times, specifically for 10, 20 and 30 minutes at each passivating conditions. According to these curves, the passive film growth, over the sample, increases with the increasing passive potential and also with longer time of passivation at a given potential as indicated by lower steady state current densities [14,15] in the corresponding figures.
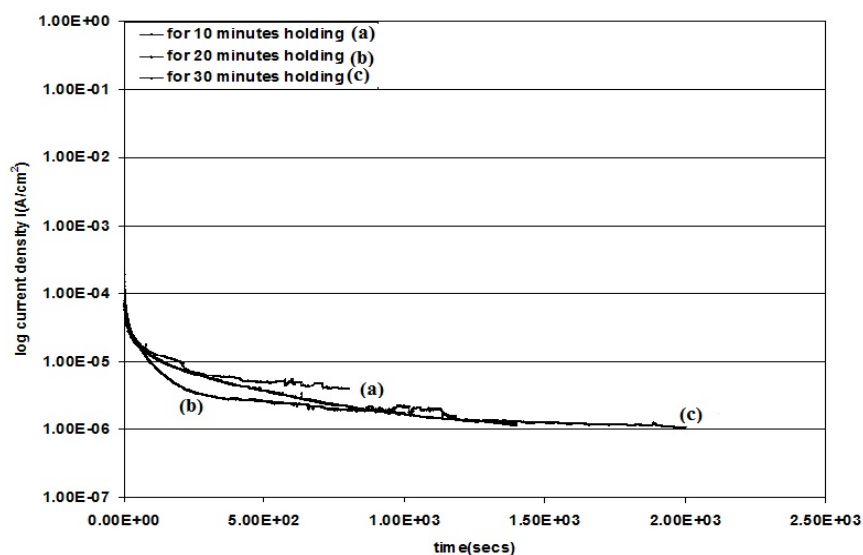

Figure 2: Current Transient curves of as received 304 stainless steel in 1.0 N sulfuric acid at 350 mV vs SCE for different holding times.
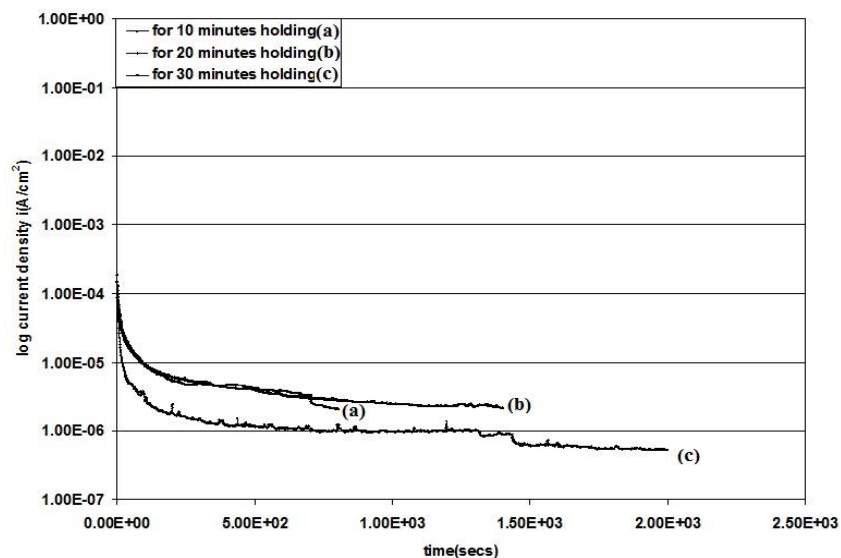
Figure 3: Current Transient curves of as received 304 stainless steel in 1.0 N sulfuric acid at 550 mV vs SCE for different holding times.
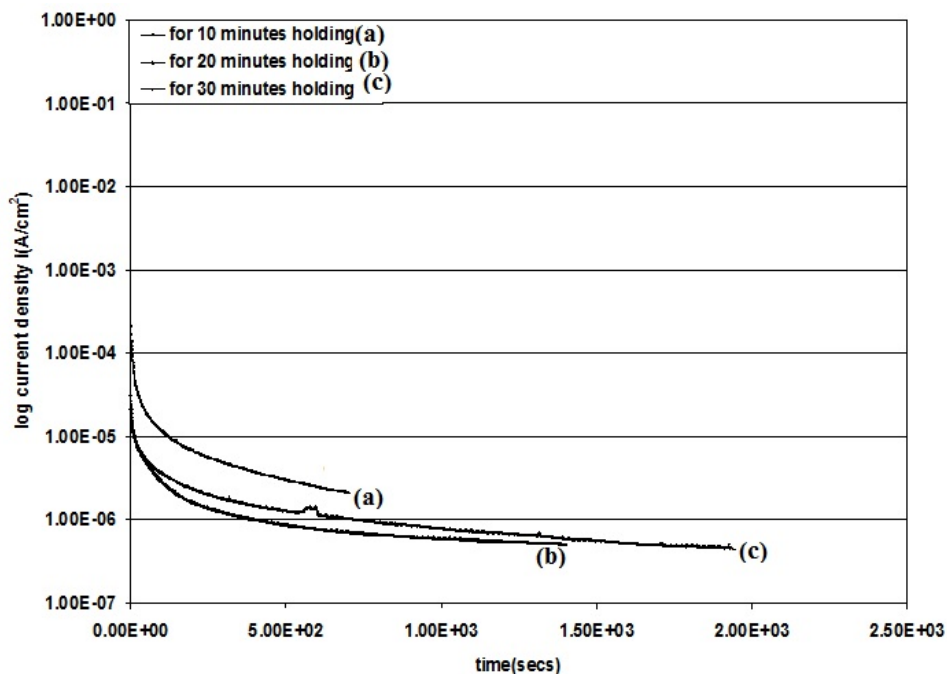

Figure 4: Current transient curves of as received 304 stainless steel in 1.0 N sulfuric acid at 750 mV vs SCE for different holding time.

Figures 5-7 are the potentiodynamic polarization curves of the passivated samples in NACE solution and Table 2 gives the corresponding Icorr and Ecorr values of these samples. Clearly the corrosion rate decreased with increasing passivating potential and also with the increase in the time of passivation. All the Icorr values are well below the corrosion rate of the as received sample. The lowest possible Icorr value ~13nA/cm2 was achieved at 750 mV with 30 minutes passivation time.
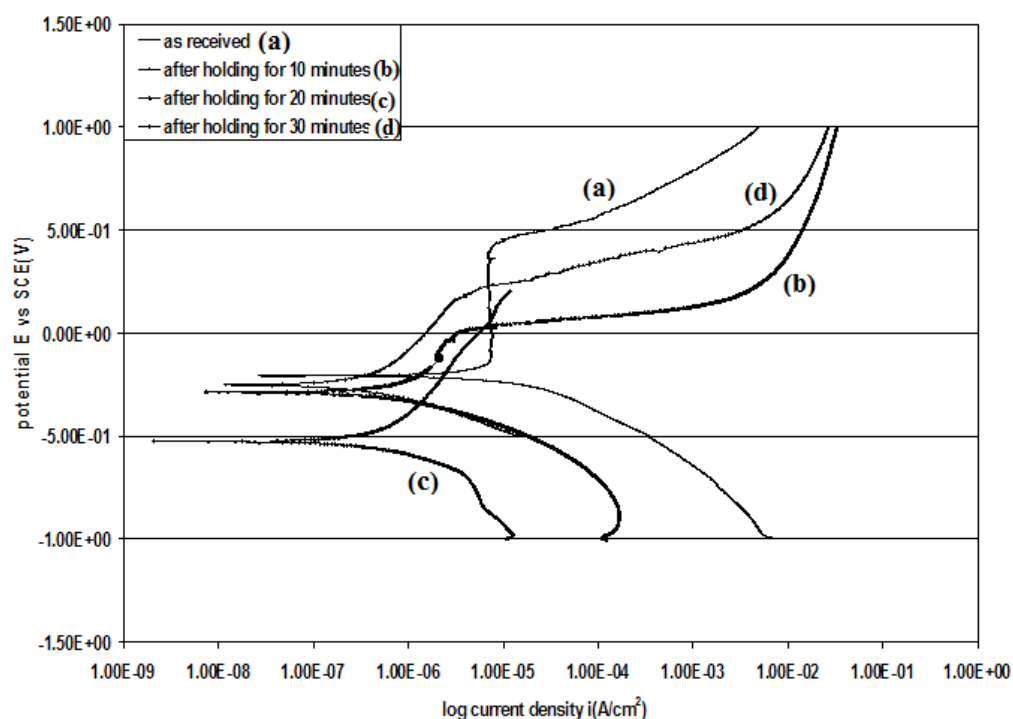
Figure 5: Polarization curves of as received and passivated (by potentiostatic passivation method in 1.0 N sulfuric acid at 350mV vs SCE passivating potential and for different holding times) 304 stainless steel in NACE solution.
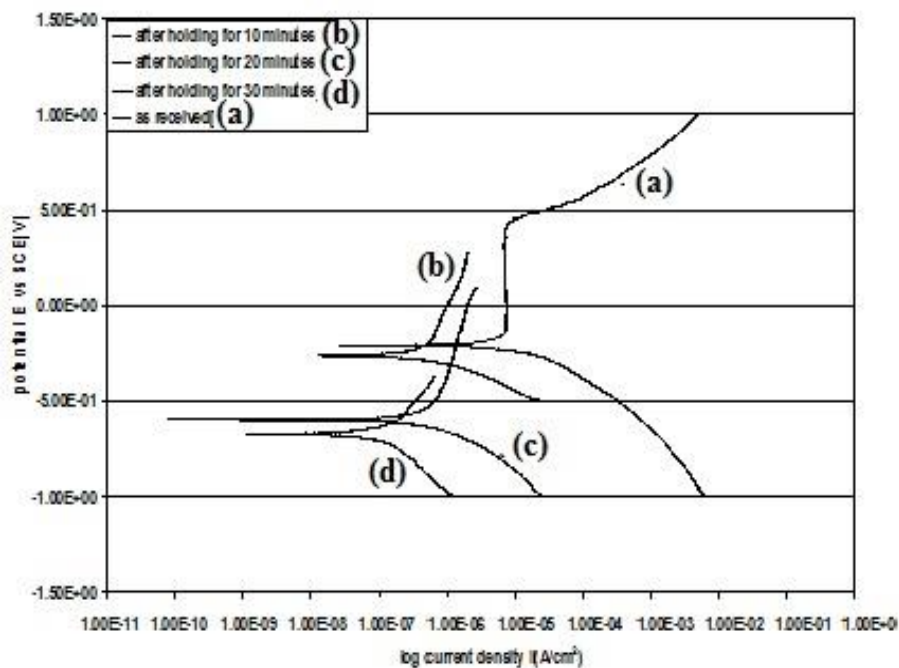

Figure 6: Polarization curves of as received and passivated (by potentiostatic passivation method in 1.0 N sulfuric acid at 550mV vs SCE passivating potential and for different holding times) 304 stainless steel in NACE solution.
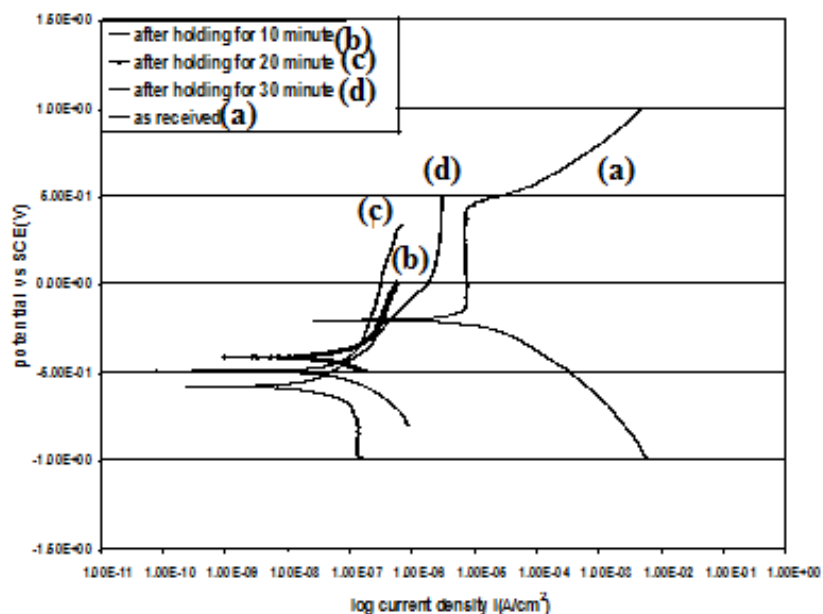
Figure 7: Polarization curves of as received and passivated (by potentiostatic passivation method in 1.0 N sulfuric acid at 750mV vs SCE passivating potential and for different holding times) 304 stainless steel in NACE solution.

At lower potentials like 350 mV or 550 mV and for smaller passivation times like 10 and 20 minutes, the passive layers formed on the sample surface presumably were not too compact to lower the corrosion rate to a significant extent.

Passivation Potential (mV)	Time of Passivation (mins)	i_{corr} (μA/cm2)	E_{corr} (V)
350	10	0.292	-0.272
	20	0.170	-0.509
	30	0.101	-0.240
550	10	0.215	-0.243
	20	0.152	-0.582
	30	0.043	-0.655
750	10	0.041	-0.397
	20	0.023	-0.482
	30	0.013	-0.056

Table 2: Corrosion data of passivated sample.

Though in all cases the Ecorr values were in the active side as compared to the as received one (0.059V Vs. SCE), which might possibly due to long range non-stability of the passive layer.

The EIS results of as received sample in 1.0 N sulfuric acid and in NACE solutions are given in Figures 8 and 9, and summarized parameter values are given in Table 3. In both the cases the fitting model was CPE. The impervious and continuous passive nature of the bare sample in 1.0 N sulfuric acid could be established by the wide range of the

corresponding Nyquist plot and by the high Rp ~ kohm, according to the corresponding Bode Plot. The excessively low Ru ~ μohm for the as received sample in NACE solution might be due to the high mobility of Cl- ion present in the solution.
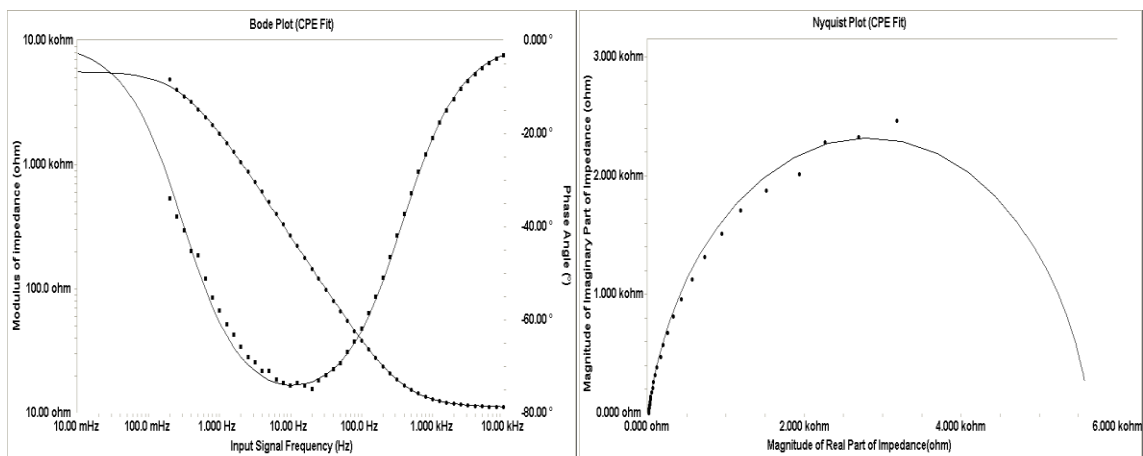

Figure 8: EIS plots of as received 304 stainless steel in 1.0 N sulfuric acid.

EIS parameters of the passivated samples in NACE solution, as shown in Table 4, were generated from Figures 10-18. These results show progressive increment in the Rp values with increasing passivating potentials and time. These values were however well below the kohm range which might serve as the cross proof of the deterioration of the nobility of the sample. The best possible was ~329.4 ohm, observed with the combination of 750 mV passivating potential and 30 minutes of time of passivation, and this was in accordance with the corresponding DC corrosion test results. All the fitting models were the CPE models and degree of fitting became better and better with increasing passivating potential and holding time as indicated by the parameter namely the goodness of fit.
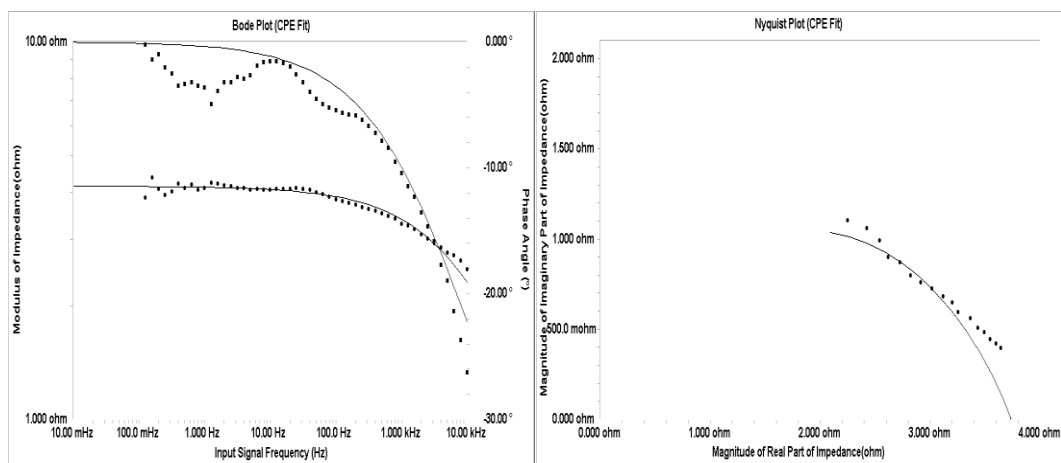

Figure 9: EIS plots of as received 304 stainless steel in 1.0 NACE solution.
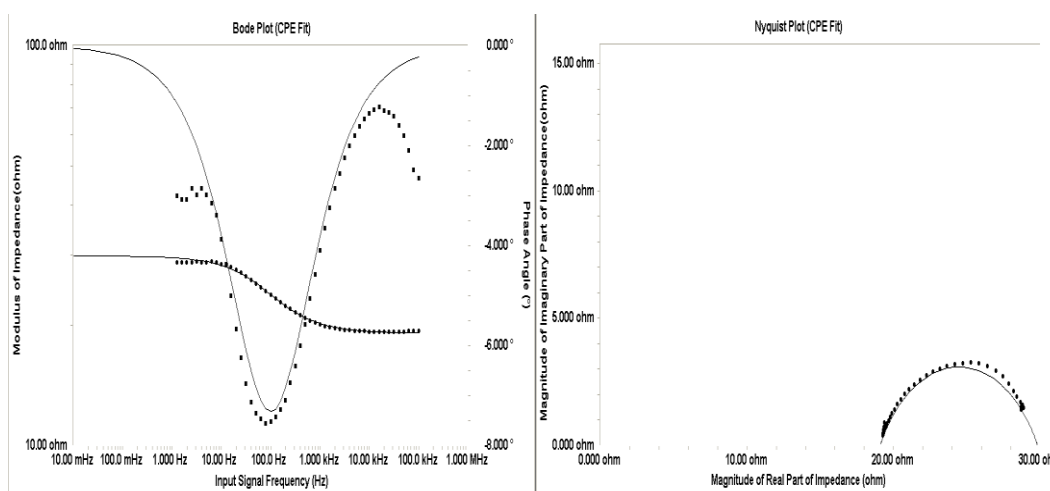
Figure 10: EIS plots of passivated (by potentiostatic passivation method in 1.0 N sulfuric acid at 350mV vs SCE passivating potential and holding for 10 minutes) 304 stainless steel in NACE solution.
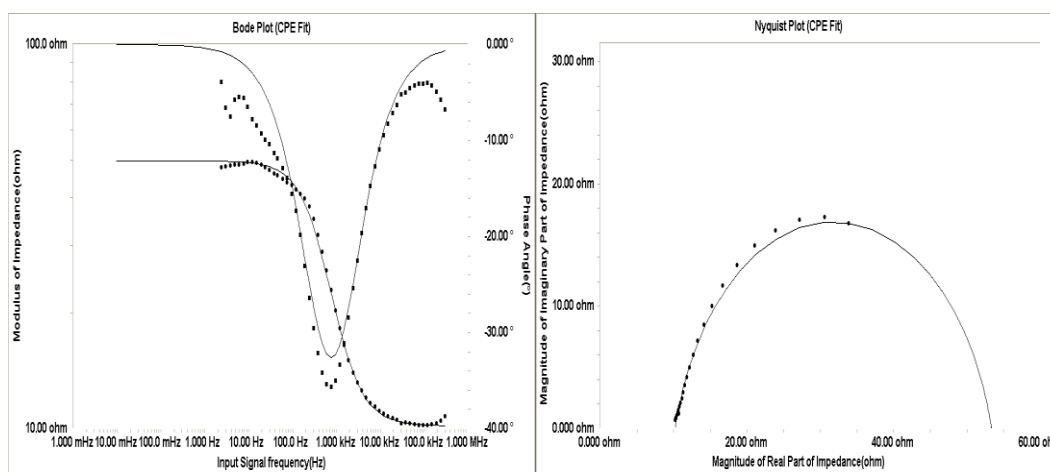

Figure 11: EIS plots of passivated (by potentiostatic passivation method in 1.0 N sulfuric acid at 350mV vs SCE passivating potential and holding for 20 minutes) 304 stainless steel in NACE solution.
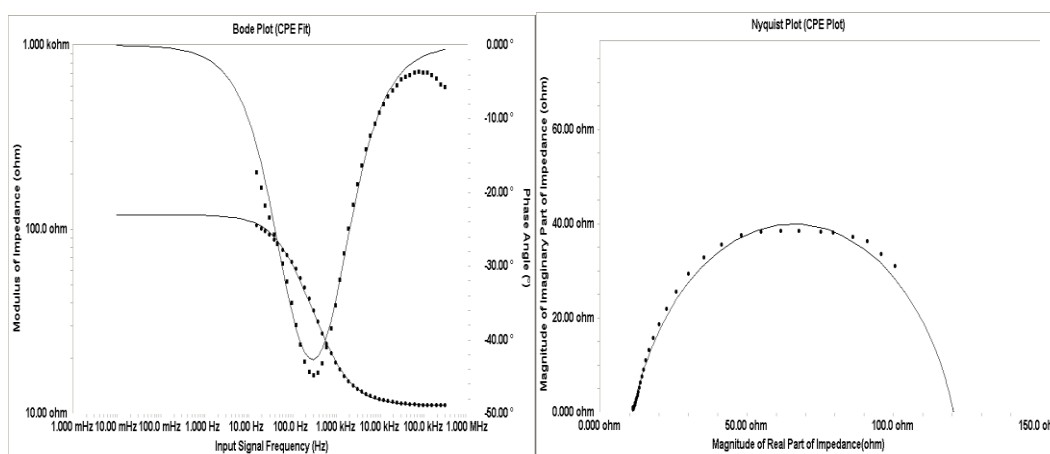

Figure 12: EIS plots of passivated (by potentiostatic passivation method in 1.0 N sulfuric acid at 350mV vs SCE passivating potential and holding for 30 minutes) 304 stainless steel in NACE solution.

Figure 13: EIS plots of passivated (by potentiostatic passivation method in 1.0 N sulfuric acid at 550mV vs SCE passivating potential and holding for 10 minutes) 304 stainless steel in NACE solution.
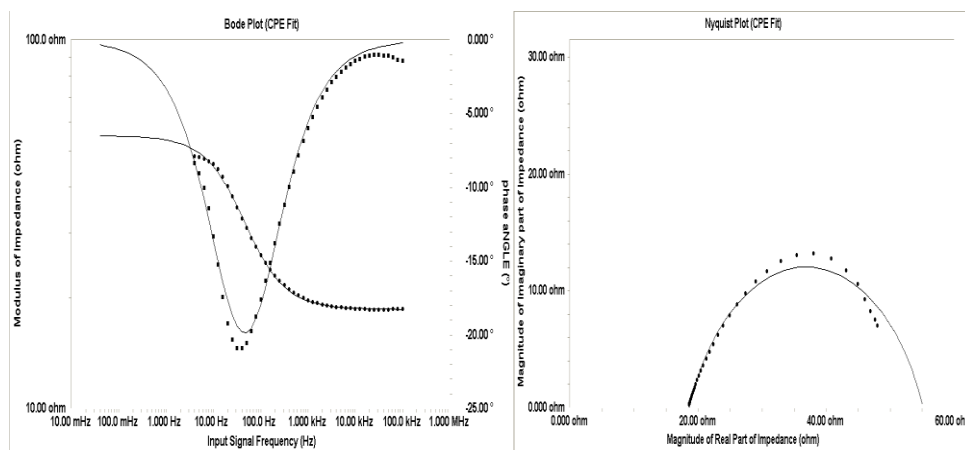

Figure 14: EIS plots of passivated (by potentiostatic passivation method in 1.0 N sulfuric acid at 550mV vs SCE passivating potential and holding for 20 minutes) 304 stainless steel in NACE solution.
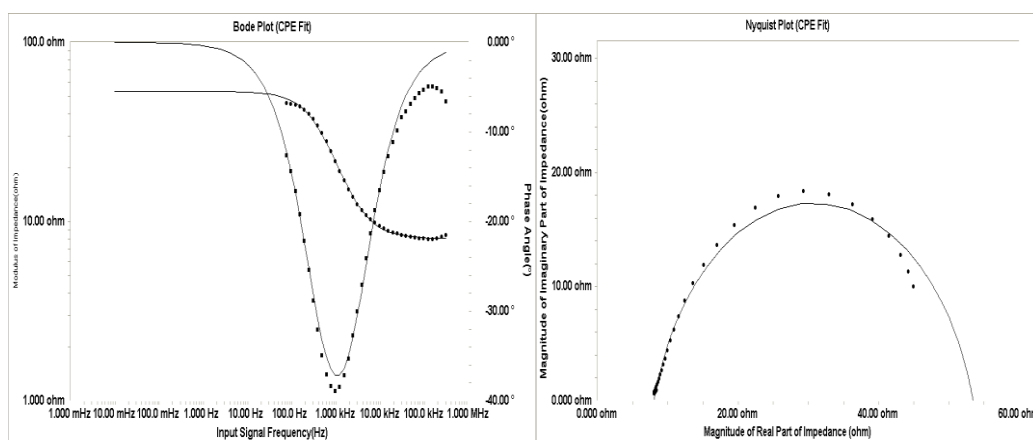

Figure 15: EIS plots of passivated (by potentiostatic passivation method in 1.0 N sulfuric acid at 550mV vs SCE passivating potential and holding for 30 minutes) 304 stainless steel in NACE solution.
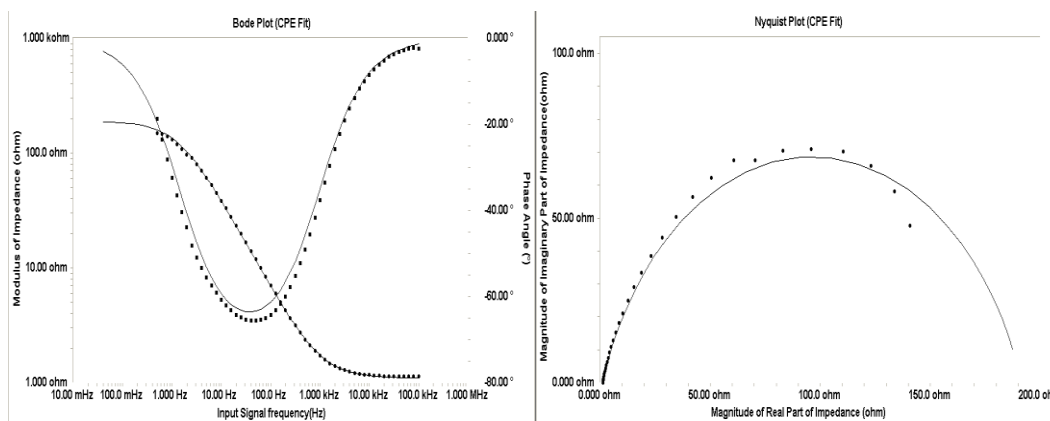
Figure 16: EIS plots of passivated (by potentiostatic passivation method in 1.0 N sulfuric acid at 750mV vs SCE passivating potential and holding for 10 minutes) 304 stainless steel in NACE solution.
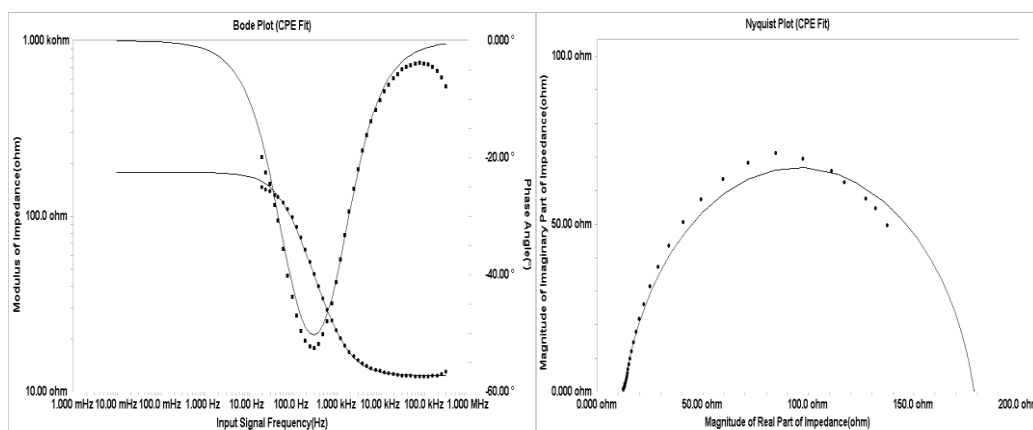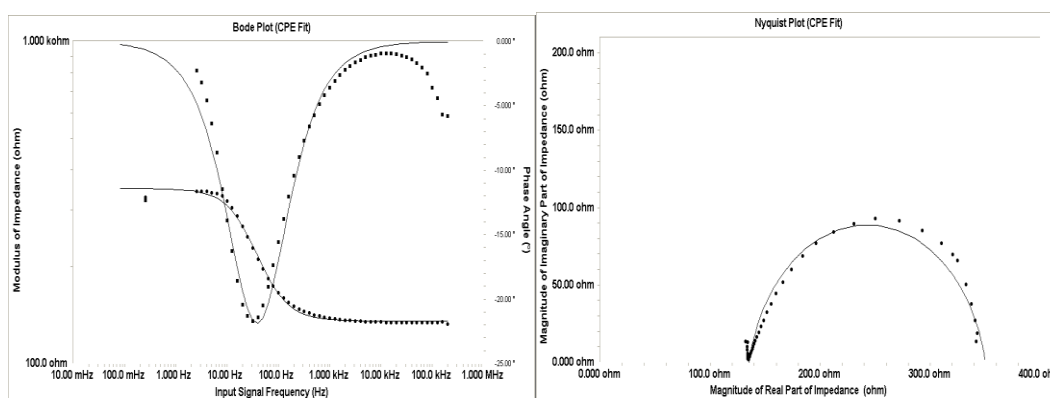

Figure 17: EIS plots of passivated (by potentiostatic passivation method in 1.0 N sulfuric acid at 750mV vs SCE passivating potential and holding for 20 minutes) 304 stainless steel in NACE solution.

Figure 18: EIS plots of passivated (by potentiostatic passivation method in 1.0 N sulfuric acid at 750mV vs SCE passivating potential and holding for 30 minutes) 304 stainless steel in NACE solution.
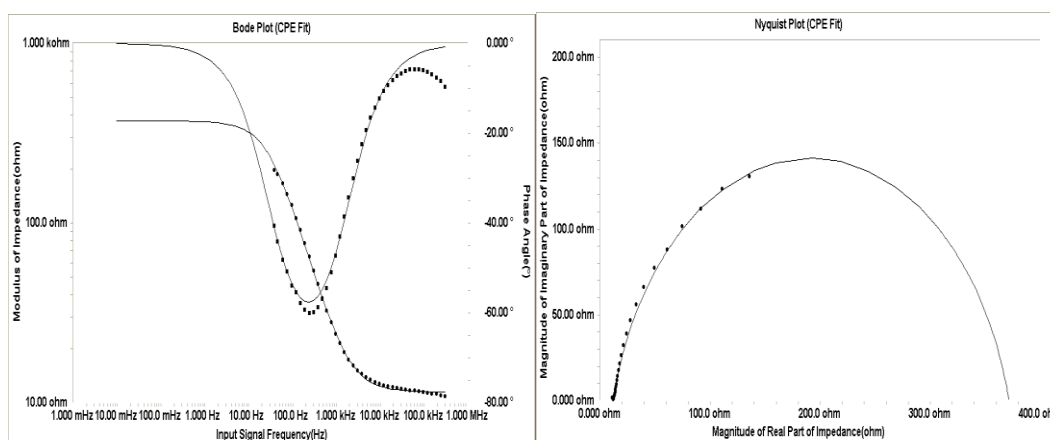
Electrolyte	Rp (ohm-cm^2)	Ru (ohm-cm^2)	Fitting model	Goodness of Fit (×10^{-3})
1.0 N Sulfuric Acid	5633	11.14	CPE	0.783
NACE Solution	4.15	0.0000025	CPE	1.49

Table 3: Electrochemical Impedance Spectroscopy data of as received sample.

Passivation Potential (mV)	Time (mins)	Rp (ohm-cm^2)	Ru (ohm-cm^2)	Fitting Model	Good ness of Fit (×10^{-3})
350	10	10.75	19.08	CPE	0.194
	20	39.73	10.15	CPE	2.161
	30	109.4	11.08	CPE	0.865
550	10	36.58	18.57	CPE	0.169
	20	45.42	8.02	CPE	0.646
	30	166.3	12.32	CPE	1.254
750	10	190.5	1.09	CPE	1.694
	20	214.7	135.4	CPE	1.649
	30	360.1	11.46	CPE	1.672

Table 4: Electrochemical Impedance Spectroscopy data of passivated sample.

The microstructures of the as received sample after the corrosion tests in 1.0 N sulfuric acid and in NACE solution are shown in the Figure 19. A thin passive oxide layer on the sample surface of the sample tested in 1.0 N sulfuric acid could be observed, which is however not very uniform. Pits are clearly seen on the sample surface in the later case.
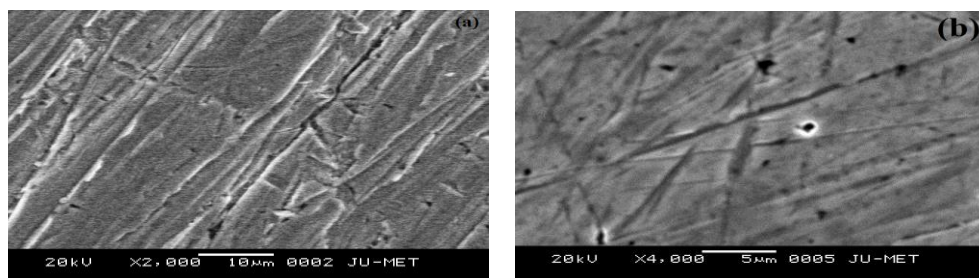

Figure 19: SEM images of as received 304 stainless steel (SS) surface after corrosion test in (a) 1.0 N sulfuric acid and in (b) NACE solution respectively.
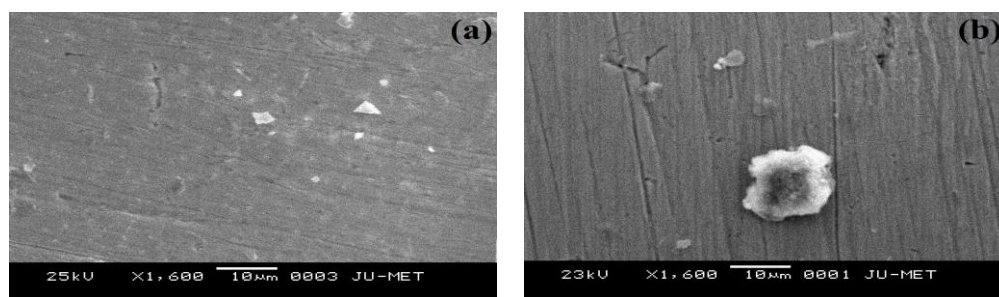

Figure 20: SEM images after corrosion of passivated samples in NACE solution, (a) passivation in 1.0 N sulfuric acid at 350 V for 30 minutes and (b) 750 mV for 30 minutes respectively

Figure 20 depicts the surface morphologies of the passivated sample after the corrosion test in NACE solution following the passivation in 1.0 N SA at the passivation potentials 350 mV for 30 minutes and at 750 mV for 30 minutes respectively. Purposely two almost extreme passivation treatments were chosen. As has been discussed earlier the first one gives poorest passive layer whereas the later one gives the best passivation. It is evident from these SEM images that isolated 'islands' of passive oxides that formed due to passivation can still be noticed after the corrosion test in NACE solution. The remains of the passive layer are more for the sample passivated at higher passivation potential and for longer time.

Conclusion

1. 1.0 N sulfuric acid served as a well behaved passivation medium for the 304 stainless steel in to provide with excellent corrosion resistant property in NACE solution.

2. In case of potentiostatic passivation method, better result is obtained with the combination of high passivation potential and long duration of holding.

3. From the point of view of the stability of the passive layer, the best electrochemical impedance spectroscopy model was the CPE and the goodness of fit was better with better passivation.

4. According to the scanning electron microscope images of the passive layer, the morphology and the thickness of the passive layer was found to be depend on different passivation condition

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