

## Potentiostatic Polarization of Immersed Austenitic Stainless Steel in 3.5 wt.% NaCl at Potential Zero Charge ( $E_{PZC}$ )

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**ABSTRACT.** The consumption of potentiostatic polarization current on austenitic type 304 stainless steel in 3.5 wt.% NaCl solution was studied at pH 4 to 7. The H<sub>2</sub>SO<sub>4</sub> droplet was used to control the solution pH. To obtain the  $E_{PZC}$  effect, the sample potential was scanned repeatedly just below  $E_{CORR}$  with magnitude between -3 to -0.3 mV vs  $E_{CORR}$ . The potential scanning was done at the lowest rate 0.01 mV/min. Potentiostatic polarization shows a lower and steadily stable current consumption on lower potential scanning magnitudes as well as at solution pH that nearly to neutral (pH 7). As predicted, the higher current consumption was found at pH 4 and the highest scanning magnitude (-3 mV to  $E_{CORR}$ ) was  $-9.30 \times 10^{-7}$  A/cm<sup>2</sup>, whereas the lowest current consumption occurs at pH 7 at the lowest scanning magnitude (-0.3 mV to  $E_{CORR}$ ) was just  $-0.03 \times 10^{-7}$  A/cm<sup>2</sup>. The pH level displays a predictable finding at all potential scanning magnitude. The averages of current consumption were found to reduce with the increasing of studied pH as a manifestation of the passive film on stainless steel surface in the presence of Cl<sup>-</sup> ions. The current spikes were clearly observed at lower pH (pH 4) resulted by the passivation and the breakdown of the passive film repeatedly. The current spikes gradually disappear as the increasing of the studied pH.

**Keywords:** Corrosion, Stainless steel, Potentiostatic, Polarization, Potential of zero charge;

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### 1. INTRODUCTION

Corrosion is one of the destructive attacks of the metals by electrochemical or chemical reaction with its environment. Cathodic protection is the most popular techniques of corrosion prevention. The selection of stainless steel materials is also one of the methods of corrosion prevention. The high corrosion resistance of stainless steel arises from the formation of complex chromium oxide (Cr<sub>x</sub>O<sub>y</sub>) which is characterized as a passive and protective [1]. The existence of a Cr<sub>x</sub>O<sub>y</sub> layer on the surface acts as a barrier of underneath metal interacting to the solution, hence blocking the ionic charge transfer in the electrode-electrolyte interface. Therefore, the corrosion or oxidation reaction of metal-solutions ( $M \rightarrow M^{2+} + 2e^{-}$ ) does not occur. It is known that, the Cr<sub>x</sub>O<sub>y</sub> layer has an ability to heal itself in a wide variety of environments. Nevertheless, under chloride (Cl<sup>-</sup>) containing environment, the passive behavior may be lost. For that reason, the root cause of failure for most of stainless steel based structure generally resulted by pitting corrosion due to interaction with the Cl<sup>-</sup> ions [2].

Pitting corrosion is the most dangerous form of localized corrosion in aqueous environment. According to Qiao et al. [3], the presence of complex Cr<sub>x</sub>O<sub>y</sub> layers on the stainless steel surface in chloride-containing

solutions results in an increase in charge carrier density when the applied potential was amplified. At large applied potential, the  $\text{Cl}^-$  has sufficient energy to penetrate the particular passive films. On the other hand, in the case of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) solution, sulfate ( $\text{SO}_4^{2-}$ ) ion is extremely corrosive to stainless steel. The dissolution rate of stainless steel was high resulted in the increase of relative solubility of metal cations in pit solution as the increasing of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  ratio occurred [4]. Wang et al. [5] was reported that the ratio of  $\text{Cl}^-/\text{SO}_4^{2-} = 0.75$  produce highest propagation rate of pits in depth and width.

Potential of zero charge ( $E_{pzc}$ ) is the potential of the electrodes for any metal surface which has no electrical charge when in contact with electrolyte. It was initially emphasized by Frumkin and Gorodetzka in 1928. Trasatti and Lust [6] stated that the  $E_{pzc}$  is the potential (against a reference electrode) which removes all electronic charges from metal surfaces. The absence of charges on electrode surface lead the loss attraction force of water bipolar and the charge orientation in Helmholtz plane does not occur. At  $E_{pzc}$ , the negative ( $\text{OH}^-$ ) as well as positive charge ( $\text{H}^+$ ) not be able not to touch the metal surfaces resulted by the sort of electric resistance layer as depicted in Fig. 1.

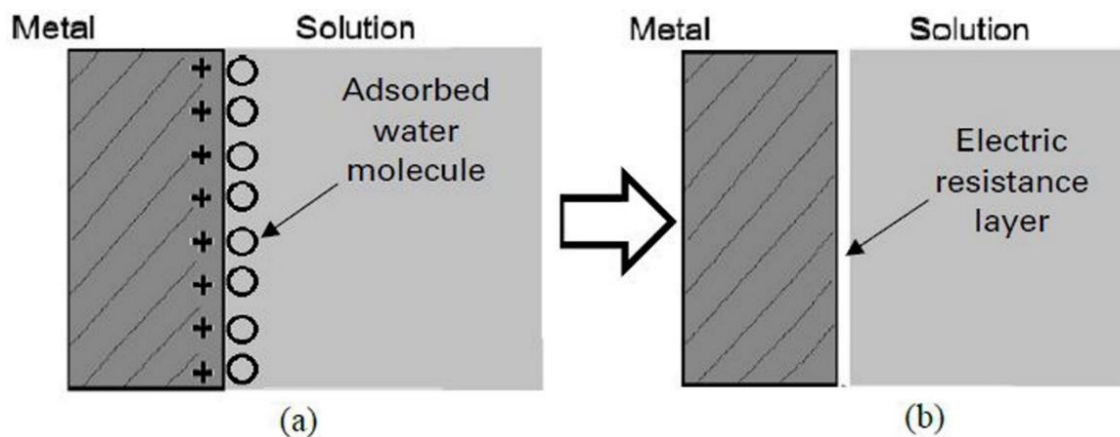


Fig. 1 Metal-solution interface (a) before  $E_{pzc}$  and (b) at  $E_{pzc}$  state [7]

Although the corrosion behavior of austenitic stainless steel has been well documented, the systematic studies into the kinetics of the various complex process involved in the studied solutions is rarely reported. Therefore, it is worth to study from the fundamental and practical standpoint of acidity, chloride and sulfate ions. The aim of this paper is to probe the current density consumption on immersed austenitic stainless steel in 3.5 wt.% of sodium chloride ( $\text{NaCl}$ ) in the presence of  $\text{SO}_4^{2-}$  at various potential scanning magnitudes.

## 2. MATERIALS AND METHODS

The raw material used in this study is 304 types austenitic stainless steel (304SS) which was supplied by STG Stainless Steel Sdn. Bhd. The specimens were cut from a rod to desired size. The working surface of specimens exposed to the test solution was  $1.23 \text{ cm}^2$  and all other unexposed areas were coated with epoxy-resin mixture. Both chemicals used in this investigation, namely  $\text{NaCl}$  and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) were reagent grade supplied by HmbG Chemicals. The test electrolyte was 3.5 wt.%  $\text{NaCl}$  with different pH (4, 5, 6 and 7) which controlled by addition of diluted  $\text{H}_2\text{SO}_4$ . Electrochemical studies were carried out in a three-electrode single container cell (K0047, PAR). The potential of the working electrode was measured against saturated calomel electrode (SCE). In order to minimize the solution resistance between the steel and the reference electrode, the tip of SCE was placed as close as possible to the surface of the working electrode. The counter electrode was a  $1 \text{ cm}^2$  platinum sheet.

The electrochemical measurement was carried out by a potentiostatic polarization method using a computerized potentiostat (ACM, Gill AC). Potentiostatic polarization was performed at 4 different potential

scanning magnitudes ranging from -3 to -0.3 mV with respect to the corrosion potential ( $E_{\text{corr}}$ ) at very slow scanning potential (0.01 mV/min). All experimental works were conducted at room temperature (25 °C).

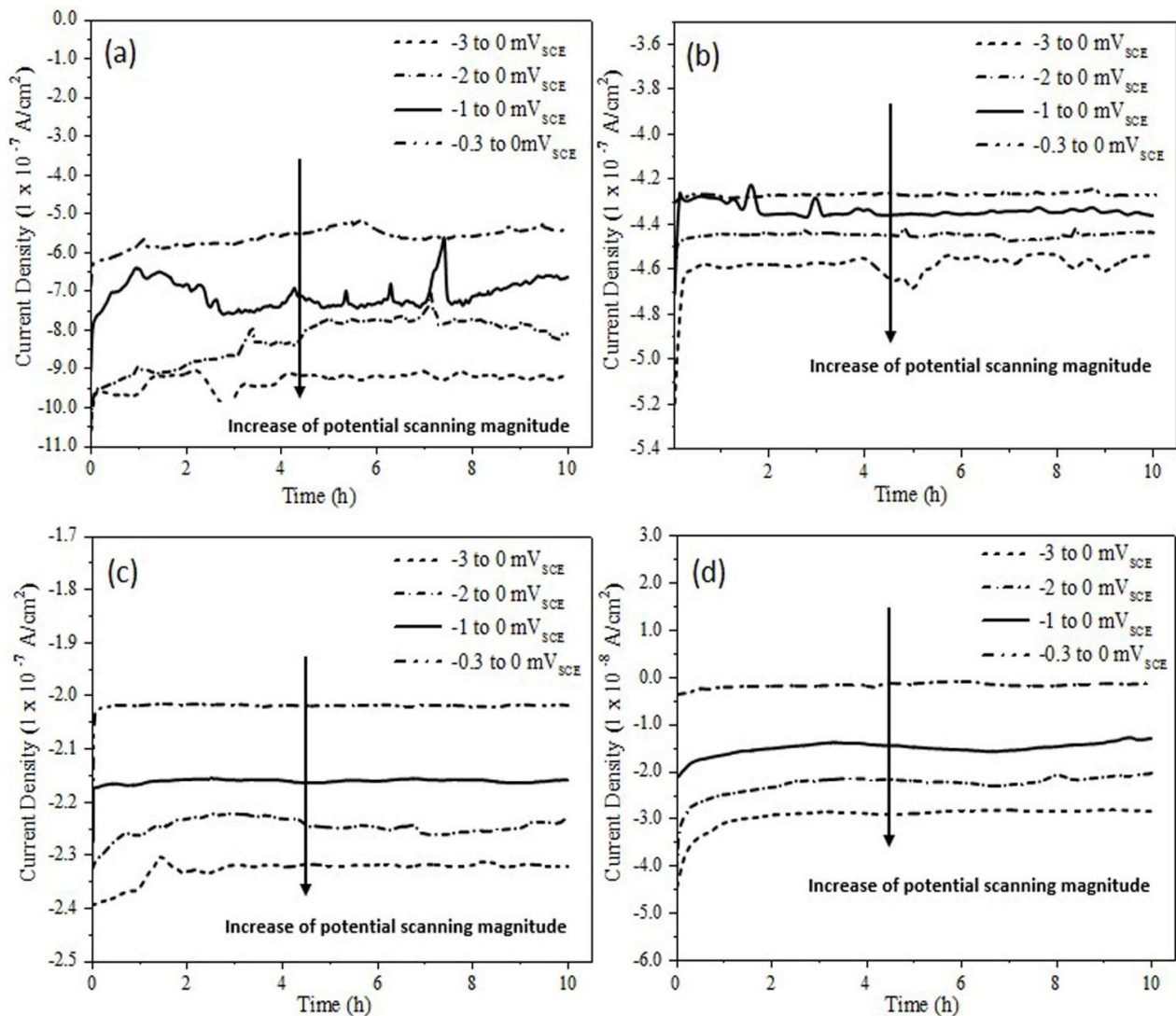
### 3. RESULTS AND DISCUSSION

The curves of potentiostatic polarization for 10 hours of immersed 304SS in 3.5 wt.% NaCl solution at different pH (4, 5, 6 and 7) were shown in Fig. 2. Overall, the curves for all pH variations show a quite similar trend as predicted. It can be observed that the current density curves at all pH starts from higher and rapidly decreases just in a few minutes at all potential scanning magnitudes. This phenomenon describes the rapid nucleation and growth of the passive film compared to the material dissolution rate [8]. At all pH levels, within the applied potential ranging -0.3 to -3 mV against  $E_{\text{corr}}$ , there were relatively steady state current consumption as a function of time. This occurrence shows the longer the immersed period in the studied solution, the formation of the passive layer on the 304SS surface became steadily stable without film breakdown.

The curve at pH 4 exhibits the noise or instability of the current density against time (Fig. 2a). It exists, particularly at high potential scanning magnitudes. The current instability is associated with the current spikes. Some opinion of the previous researchers stated that these current spikes were either nucleation or metastable pitting events [9]. The formation of metastable pitting, in fact, does not significantly appeared because it occurs in an extremely small scale and in a short period it back to form a passive film [10]. The metastable pits only growth in the early stage of all stable pits before stabilizing. It microscopically difficult to access on the stainless steel surfaces and only can be detected by the high-resolution current sensor of the potentiostat at the slowest scanning rate.

Stainless steel has a large repassivation tendency for metastable pits and transformation to stable pits which can be achieved at higher potential [11]. Additionally, the activation and passivation alternation during pit metastable growth produces a current fluctuation or overlapped peaks as reported by Tian et al. [10]. However, in the case of potential of zero charge, the presence of the pitting can be ruled out. This is because, the potential scanning was carried out slightly below  $E_{\text{corr}}$ . Therefore, it is quite impossible that pitting can be formed at extremely low applied potential at potential just below  $E_{\text{corr}}$ . Here, the  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  ions ingress to the passive film by occupying anion vacancies. When the cation vacancies start accumulating at the metal interfaces, a breakdown of the films will start to take place as reported by Szklarska-Smialowska [12]. Theoretically, as the potential scanning magnitude increased, the  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  ions were forced to penetrate the film and causes the formation of complex metal chloride,  $\text{MCl}_x$  and metal sulfate,  $\text{MSO}_x$  at the metal-solution interface particularly intermingled in between the oxide atoms of metal surface as described by Galvele et al. [13].

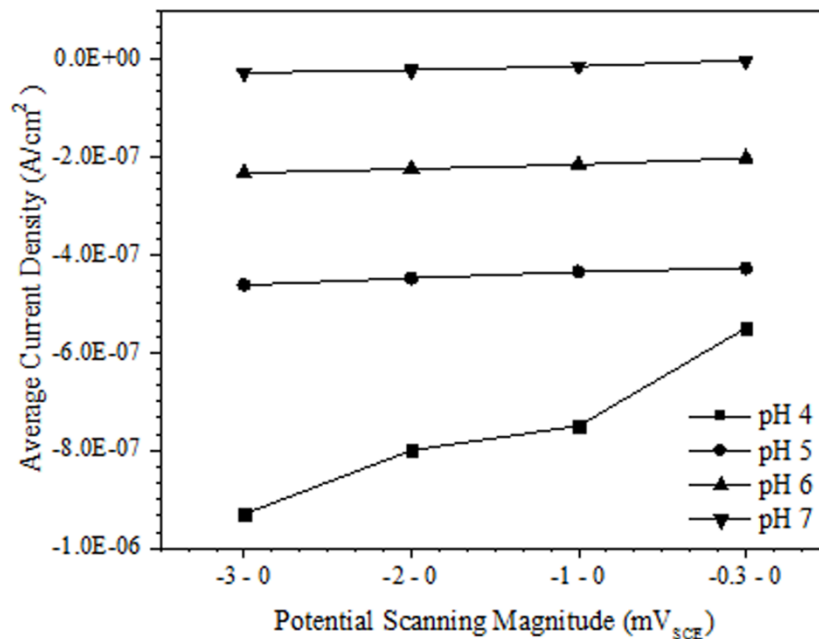
The formation of  $\text{MCl}_x$  and  $\text{MSO}_x$  at a larger molar volume compared to the expansion of metal oxide will cause the abrupt mechanical breakdown of the 304SS passive film. It was easier to understand that the current spikes in the current studies were a fluctuation that generally denotes to the formation and breakdown of passive layers alternately on the 304SS surface. The formation of passive layers causes the consumption of negative currents to be lower while the breakdown of passive layer results in the excessive negative current consumed in order to eliminate the positive charges resulting from the reactions of exposed metal with the solutions. The instability or the current spikes were decreased when the experiments were performed on the solution having pH 5 (Fig. 2b) and the current begin to show the stability at pH 6 (Fig. 2c) and finally displays the steady state at pH 7 (Fig. 2d).



**Fig. 2** Current-time transient for immersed 304SS in (a) pH 4, (b) pH 5, (c) pH 6 and (d) pH 7 in 3.5 wt.% NaCl solution (Note: 0 mV referred to  $E_{corr}$ )

Fig. 3 shows the effects of current consumption against potential scanning magnitudes. The overall current consumption is depicted occur in the steadily stable at pH 5, 6 and 7. However, at pH 4, it was observed the current consumption was increased ( $-9.30 \times 10^{-7}$  A/cm<sup>2</sup>) especially on high potential scanning magnitude (-3 mV to  $E_{corr}$ ). Nevertheless, the current consumption was found to decrease ( $-5.50 \times 10^{-7}$  A/cm<sup>2</sup>) at the lower magnitude of the potential scanning (-0.3 mV to  $E_{corr}$ ). NaCl solution at lower pH, contains high hydrogen ions ( $H^+$ ). At high magnitude potential scanning,  $H^+$  ions were aggressively to cause a breakdown of the passive film on the 304SS surface. The aggressiveness of  $H^+$  ion was gradually decreased as lowering the magnitude of potential scanning until it was no longer active when the potential approaching  $E_{corr}$ . The high scanning potential magnitude, particularly -3 to  $E_{corr}$  causes the movement of the anions and/or cations through the passive film become aggressive, which results in the high current consumption in order to repel the positive charges of metal due to the metal-solution reaction. The repellent of positive charges was done by the electrons or negative current supplied by the potentiostat. The damaged passive film causes the adsorption of aggressive anions (such as  $Cl^-$  and  $SO_4^{2-}$ ) of the passive film on 304SS surfaces. The presence of  $Cl^-$  and  $SO_4^{2-}$  anions together at lower pH of NaCl solution results the increase of the current density during

the potential scanning due to the high conductivity of these anions towards the double layer to destroy the passive layer as reported by Roy et al. [14] and Gadala et al. [15] were agreed.



**Fig. 3** Average current density for immersed 304SS in (a) pH 4, (b) pH 5, (c) pH 6 and (d) pH 7 of 3.5 wt. % NaCl solution (0 mV referred to  $E_{corr}$ )

#### 4. SUMMARY

From the experimental studies, it can be concluded that the pH variations with the presence of  $Cl^-$  ions affect the current consumption in order to maintain the effect of zero charge potential on the metal-solution interface. If a passive layer exists, the current consumption to maintain the  $E_{pzc}$  was significantly small and steadily stable. On the contrary, the negative current consumption becomes larger and unstable at low pH. These phenomena occur due to the large metal exposes to the solution that requires a high electron to repel or eliminate the positive charges present on the metal surface as a result of the metal-solution reactions. With  $E_{pzc}$ , the current density consumption can be reduced and more economical.

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