



## Electrochemical engineering of passive films on AISI 304 stainless steel in $\text{H}_2\text{SO}_4$ : The critical role of polarization slope in optimizing corrosion resistance

### Ingeniería electroquímica de películas pasivas en acero inoxidable AISI 304 en $\text{H}_2\text{SO}_4$ : El papel crítico de la pendiente de polarización en la optimización de la resistencia a la corrosión

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Received: January 21, 2026; Accepted: March 29, 2026

**Abstract** This study investigates an electrochemical strategy to enhance the corrosion resistance of AISI 304 stainless steel in 1 M  $\text{H}_2\text{SO}_4$  through the active growth of a passive film. The performance of samples passivated using fixed potentiostatic potentials (CP) and potentiodynamic polarization (PD) was compared to untreated (control) samples and those treated according to the conventional ASTM A967 standard. Electrochemical Impedance Spectroscopy (EIS) data, fitted to an  $R(Q(RW))$  circuit, revealed that samples polarized at potentials within the negative-slope region of the passive range developed a stable, highly protective film. This was evidenced by a dramatic increase in polarization resistance (e.g., 514 k $\Omega$  for CP03, compared to only 77  $\Omega$  for the control) and a corresponding drop in corrosion current density by several orders of magnitude (e.g., 0.0342  $\mu\text{A}/\text{cm}^2$  vs. 303.1  $\mu\text{A}/\text{cm}^2$ ). XPS analysis identified that the superior passive layer consists primarily of  $\text{Cr}_2\text{O}_3$ . Among all treatments, the potentiodynamic passivation (PD01) yielded the optimal performance ( $I_{\text{corr}} = 0.0183 \mu\text{A}/\text{cm}^2$ ,  $R_p = 1.26 \text{ M}\Omega$ ). This work demonstrates that electrochemical passivation, particularly within the negative-slope region of the passive range, is a highly effective and rapid alternative to traditional chemical methods for achieving exceptional corrosion resistance in aggressive environments.

**Keywords:** AISI 304, Passivation, Corrosion, Tafel, EIS, XPS.

#### Resumen

Este estudio investiga una estrategia electroquímica para mejorar la resistencia a la corrosión del acero inoxidable AISI 304 en  $\text{H}_2\text{SO}_4$  1 M mediante el crecimiento activo de una película pasiva. Se comparó el desempeño de muestras pasivadas utilizando potenciales potencioestáticos fijos (CP) y polarización potenciodinámica (PD) con el de muestras sin tratar (control) y con el de aquellas tratadas según la norma convencional ASTM A967. Los datos de Espectroscopía de Impedancia Electroquímica (EIS), ajustados a un circuito  $R(Q(RW))$ , revelaron que las muestras polarizadas a potenciales dentro de la región de pendiente negativa del intervalo pasivo desarrollaron una película estable y altamente protectora. Esto quedó evidenciado por un aumento drástico en la resistencia a la polarización (por ejemplo, 514 k $\Omega$  para CP03 frente a 77  $\Omega$  para el control) y una disminución correspondiente de la densidad de corriente de corrosión en varios órdenes de magnitud (por ejemplo, 0.0342  $\mu\text{A}/\text{cm}^2$  frente a 303.1  $\mu\text{A}/\text{cm}^2$ ). El análisis por XPS identificó que la capa pasiva superior consiste principalmente en  $\text{Cr}_2\text{O}_3$ . Entre todos los tratamientos, la pasivación potenciodinámica (PD01) proporcionó el desempeño óptimo ( $I_{\text{corr}} = 0.0183 \mu\text{A}/\text{cm}^2$ ,  $R_p = 1.26 \text{ M}\Omega$ ). Este trabajo demuestra que la pasivación electroquímica, particularmente dentro de la región de pendiente negativa del intervalo pasivo, es una alternativa altamente eficaz y rápida a los métodos químicos tradicionales para lograr una resistencia a la corrosión excepcional en entornos agresivos.

**Palabras clave:** AISI 304, Pasivación, Corrosión, Tafel, EIS, XPS.

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<https://doi.org/10.24275/rmiq/Mat26765>

ISSN:1665-2738, issn-e: 2395-8472

## 1 Introduction

The degradation of metallic components through corrosion represents a significant global challenge, impacting their longevity, safety, and economic viability (Cisquini *et al.*, 2019; Loukil *et al.*, 2025). To mitigate this, stainless steels, notably AISI 304, are extensively employed due to their inherent corrosion resistance resulting from the formation of a protective passive film (Rossi *et al.*, 2024). A prevalent and cost-effective method to enhance or restore this passivity is chemical treatment according to established standards, such as ASTM A967. This standard is primarily intended for chemical cleaning and removal of surface contaminants, allowing native oxide reformation under controlled conditions. While effective for many applications, this approach has inherent limitations for components destined for highly aggressive environments, where a deliberately engineered passive film with enhanced protective properties may be required. Therefore, this work investigates an electrochemical methodology that actively promotes the formation of an optimized passive film on AISI 304 stainless steel, with the aim of achieving protective qualities beyond those obtained through conventional chemical passivation.

As a result, significant research efforts have been dedicated to developing highly effective corrosion protection methods for various atmospheric and environmental conditions (Almeraya-Calderón *et al.*, 2025). Stainless steels, particularly the AISI 304 grade used in this study, represent a widely used and versatile group of alloys. Its superior corrosion resistance, combined with economic viability and active-passive behavior in corrosive media, has led to widespread use in industries (Baddoo 2008; Gooch 2000, March). Multiple techniques exist to improve corrosion resistance. However, passivation remains a low-cost and commonly used option. Traditionally, passivation treatment is performed according to the ASTM A967 standard, where stainless steel parts are treated in a specified aqueous solution and kept within a specified temperature range for a specified time. It is important to note that this standard is primarily intended for chemical cleaning and removal of surface contaminants, and it is effective for many general-purpose applications. However, for components exposed to highly aggressive media, such as concentrated sulfuric acid, a more robust passivation method may be required such as the electrochemical method proposed in this work. Although previous studies (Maller 2007; Mani *et al.*, 2025; J. Villegas-Tovar *et al.*, 2023) have attempted to improve the ASTM A967 process by modifying its conditions, it suffers from the disadvantage of slow passive layer formation kinetics. In addition, other

works (Fattah *et al.*, 2011; María Lara-Banda *et al.*, 2020) show that to form a passive oxide film, samples are polarized at a fixed desired potential within the passive range for a set period (e.g., 30 minutes). Consequently, these studies report an improvement in the speed of passive layer formation and an increase in corrosion resistance. Given the limitations of the conventional chemical passivation method, this research is driven by the following question: How can an electrochemical passivation strategy, utilizing controlled potentiostatic (CP) and potentiodynamic (PD) polarization within the passive potential range, be designed to actively grow a passive film on AISI 304 stainless steel that demonstrates significantly superior corrosion resistance in an aggressive 1 M H<sub>2</sub>SO<sub>4</sub> environment compared to traditional methods?

## 2 Experimental

AISI 304 stainless steel square substrates of 20 mm x 20 mm and approximately 2 mm in thickness were used. To minimize the influence of residual stress on the material (Fattah *et al.*, 2011; Saldaña-Robles *et al.*, 2023), the samples were cut to the desired dimensions using a metal laser cutter. The cut samples were subsequently mounted in phenolic resin using a custom-built, low-cost mounting device (Márquez-Herrera 2025) to facilitate handling during the polishing stages. The samples were mechanically polished with SiC paper up to a 1500 grit finish. To clean the surface, the samples were washed with deionized water.

Electrochemical experiments were performed using a custom-built, 3D-printed cell (Creality K1 Max 3d printer) fabricated from polypropylene filament for its high acid resistance (Hossain *et al.*, 2024; Maddah *et al.*, 2016). A 1 M H<sub>2</sub>SO<sub>4</sub> solution was used at room temperature as the electrolyte solution. An Ag/AgCl electrode (saturated KCl) and a platinum mesh were used as the reference electrode and counter electrode, respectively. An area of 1 cm<sup>2</sup> of the steel substrate was used as the working electrode. Prior to experiments and measurements, an open circuit potential (OCP) was monitored for 60 min. Before electrochemical measurements, the working electrode was initially potentiodynamically scanned from -0.15 V to +1.3 V versus the OCP at 0.5 mV/s to determine the passive range. Then, a passive film was formed on AISI 304 stainless steel by polarizing the sample potentiostatically at a potential determined to fall within the passive zone for 30 minutes. The potentiostatically passivated samples were then compared with samples passivated using potentiodynamic polarization within the passive range at a scan rate that ensured the total sweep time



was 30 minutes. For the impedance test (EIS), a sinusoidal AC signal with a 10 mV (RMS) amplitude and a sweep from 1 MHz to 10 mHz was used; simulated impedance curves were generated using the ZSimpWin impedance fitting program. The corrosion evaluation was conducted using the Tafel test. The Tafel plots were recorded by performing scans from -150 to +150 mV versus OCP using VersaStudio corrosion test software, which provided a numerical fit of the data to the Tafel equation. It is worth noting that each treatment and measurement was performed in three independent experimental replicates ( $n=3$ ).

The chemical environment structures of iron, chromium, nickel, and oxygen were analyzed using X-ray Photoelectron Spectroscopy (XPS) (model K alpha, Thermo Scientific). The general survey, as well as the high-resolution spectra in the regions of C 1s, O 1s, Fe 2p, and Cr 2p, were obtained. The binding energy of the C 1s line at 284.8 eV was taken as the reference peak to calibrate the obtained spectra. Background subtraction was performed using the mathematical model derived by Shirley (Shirley 1972). The O 1s, Fe 2p, and Cr 2p were fitted with an asymmetric Gaussian-Lorentzian function using the CasaXPS software (Fairley et al., 2021).

### 3 Results and Discussion

Figure 1 shows the cell designed to hold a 1 M  $\text{H}_2\text{SO}_4$  electrolyte solution at room temperature and accommodate a standard three-electrode configuration: an Ag/AgCl (saturated KCl) reference electrode, a platinum mesh counter electrode, and the AISI 304 working electrode with an exposed area of 1  $\text{cm}^2$ . PTFE gaskets were used to ensure a proper seal and prevent crevice corrosion.

On the other hand, according to the open circuit potential (OCP), the mean current potential obtained for all samples and replicas before treatments was -343.204 mV, with a standard deviation of 1.623 mV. This small standard deviation indicates that the measurements are precise and consistent, and that the experiment has been conducted with good control of the variables, which increases the reliability of the results.

On the other hand, traditionally, ASTM A967 is the widely recognized standard that specifies chemical passivation procedures for stainless steel parts. Figure 2 presents potentiodynamic polarization curves (from -150 mV versus OCP to +1200 mV versus Ref) comparing a control sample (untreated) with two passivated samples treated according to the ASTM A967 standard: a sample passivated in 34 % nitric acid ( $\text{HNO}_3$ ) by volume and another passivated in 10 % citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ) by volume for 30 minutes.

As seen in Figure 2, there are no significant visual differences between the control and the ASTM A967-treated samples. This observation is quantified by the Root Mean Square Error (RMSE).

The Root Mean Square Error (RMSE), Eq. 1, is a measure that indicates, on average, how much one curve or a set of predicted points ( $y_1$ ) deviates from another curve or observed points ( $y_2$ ) (Hodson 2022).

$$\text{RMSE} = \sqrt{\frac{1}{n} \sum_{i=1}^n (y_{1,i} - y_{2,i})^2} \quad (1)$$

In this sense, the RMSE was calculated to quantify the deviation of the treatment curves from the control, as shown in Figure 2. The analysis was conducted using the current density values within the passive potential range of the curves. The curves obtained from the treatments with nitric acid and citric acid showed excellent agreement with the control curve, with RMSE values lower than 1  $\mu\text{A}$  (0.993  $\mu\text{A}$  and 0.626  $\mu\text{A}$ , respectively). This indicates that the error is orders of magnitude smaller than the measured signal, suggesting that the difference lacks practical relevance; that is, the curves from the nitric and citric acid treatments can be considered functionally equivalent to the control curve.

The root cause of this performance gap lies in the fundamental mechanism of traditional passivation. Standards like ASTM A967 primarily act as a chemical cleaning process, effectively removing exogenous iron and other contaminants from the surface. The subsequent formation of the protective chromium oxide ( $\text{Cr}_2\text{O}_3$ ) layer occurs naturally. This passive approach has two direct consequences: (1) it results in slow formation kinetics, which are inefficient for industrial processing, and (2) it yields a passive film whose protective properties are not optimized, as the process does not actively control the electrochemical parameters critical for film growth, such as potential. The ultimate effect is that components treated with the conventional method may remain vulnerable to premature failure in highly aggressive environments like concentrated sulfuric acid, leading to increased maintenance costs, unplanned downtime, and potential safety hazards. The implications of inadequate passivation extend beyond industrial settings. For instance, in the case of metallic orthopedic implants, if they are not passivated prior to implantation, the passive layer would form inside the body. This process can lead to the release of metal ions, which may trigger adverse biological reactions and pose serious health risks to the patient (Matusiewicz and Richter 2022). Nevertheless, it is important to recognize that ASTM A967 is not designed to produce an optimized passive film for extreme environments, but rather to restore the native oxide under standard conditions. Consequently, ASTM A967 does not specify a

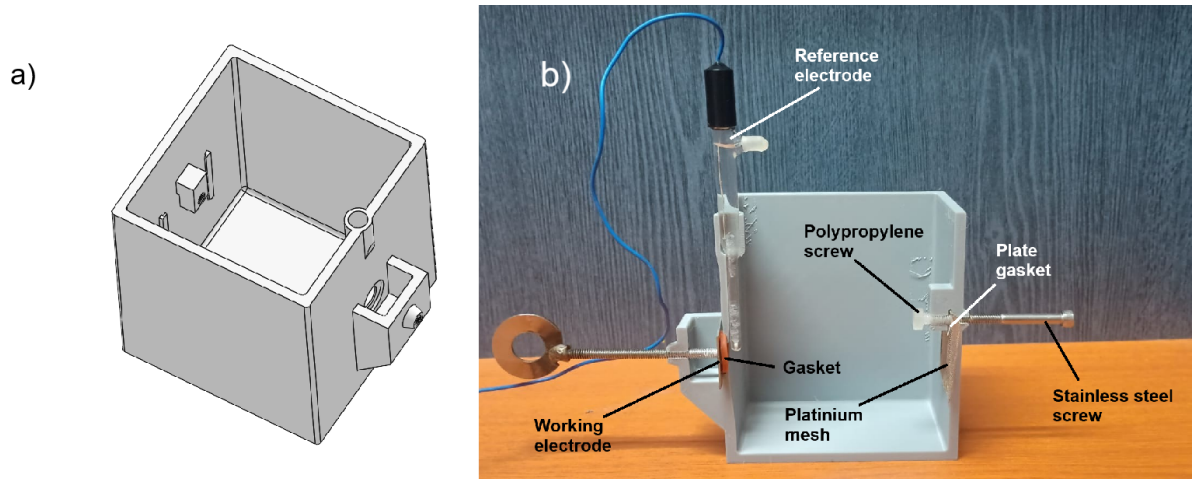


Fig. 1: (a) CAD model of the 3D-printed electrochemical cell; (b) cross-sectional view showing the electrode arrangement.

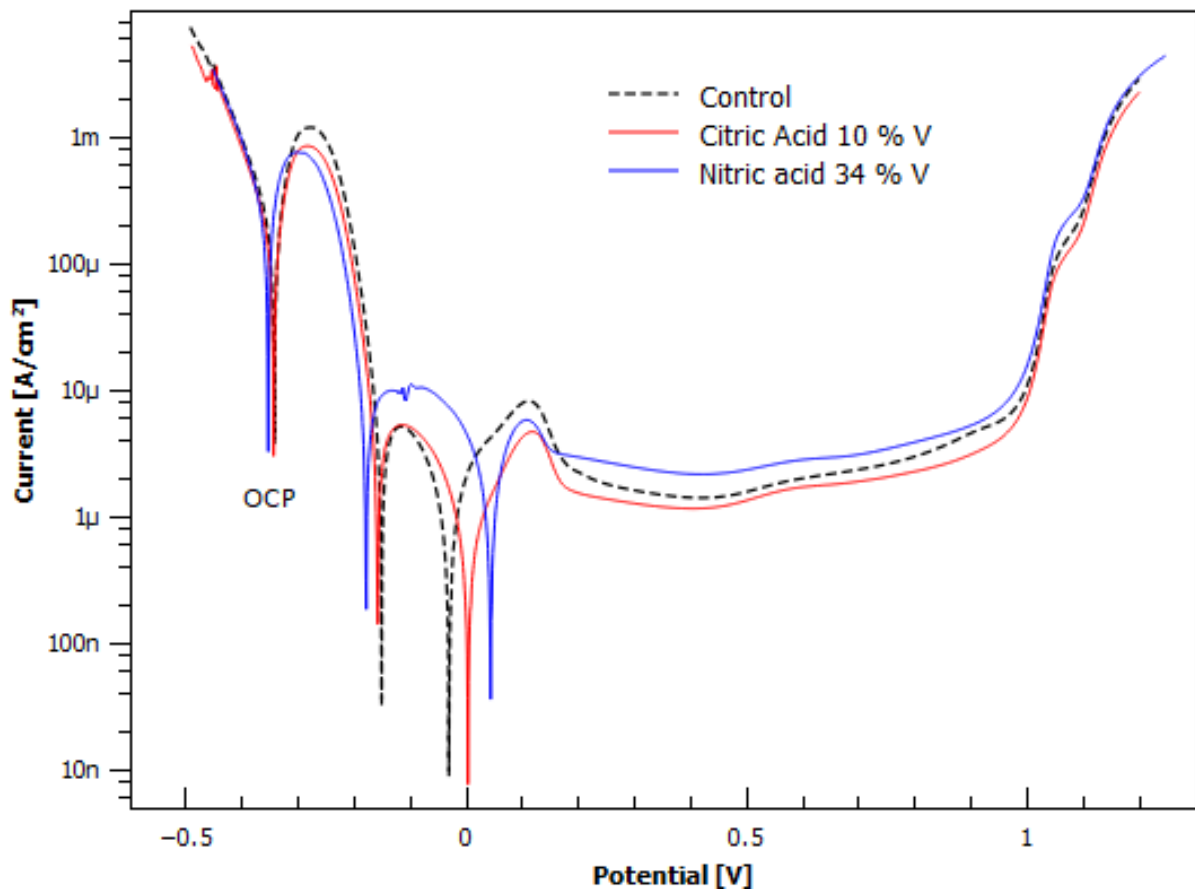


Fig. 2: Potentiodynamic polarization curves in 1M H<sub>2</sub>SO<sub>4</sub> solution of control sample, treated sample in 34 % nitric acid (HNO<sub>3</sub>) and a treated sample in 10 % citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>) by volume.

dedicated methodology to actively induce passivation, a limitation that directly motivates this research.

Furthermore, Figure 3 shows the scanned potentiodynamic sweep to determine the passive range. The control sample (Control) exhibits a passive zone of about +482 mV vs OCP to +1282 mV vs OCP, where chromium (18 wt%) (Ha *et al.*, 2018; Rodríguez-Martínez *et al.*, 2013) could be the main alloying element that forms a resistant passive oxide layer (Iglesias and Díaz 2025) on the surface, as the material has the highest percentage by weight after iron.

Table 1 shows the potentiostatic polarization applied to samples in a solution of 1 M H<sub>2</sub>SO<sub>4</sub> for 30 minutes, which are marked in Figure 3 as CP01, CP02, and CP03. Additionally, the potentiodynamic polarization applied to samples is marked as PD01, PD02, and PD03.

Table 1. Potentiostatic and potentiodynamic polarization were applied to samples.

| Sample | Potential<br>(mV vs OCP) |
|--------|--------------------------|
| CP01   | 482                      |
| CP02   | 591                      |
| CP03   | 700                      |
| CP04   | 991                      |
| CP05   | 1228                     |
| PD01   | 482 to 700               |
| PD02   | 700 to 1228              |
| PD03   | 482 to 1228              |

Samples CP01 and CP02 correspond to points in the passive range (Figure 2) with a negative tangent slope (instantaneous derivative (dI/dV) at a specific point) on the curve, while samples CP04 and CP05 correspond to points with positive slopes; sample CP03 exhibits a zero slope. CP02 corresponds to the midpoint between CP01 and CP03, while CP04 corresponds to the midpoint between CP03 and CP05.

Furthermore, Table 1 shows the potentiodynamic polarization range applied to samples in 1 M H<sub>2</sub>SO<sub>4</sub> solution for 30 minutes: from +482 to +1228 mV, +700 to +1228 mV, and +482 to +1228 mV versus OC, which are marked in Figure 3 as PD01, PD02, and PD03, respectively.

On the other hand, Figure 4 shows the EIS spectra obtained during the test of all samples in 1 M H<sub>2</sub>SO<sub>4</sub> solution.

The EIS data were fitted to the equivalent electrical circuit R(Q(RW)) (inset, Figure 4a) with a low Relative Standard Error (RSE < 10%), and the parameters are presented in Table 2.

Table 2. Parameters of the proposed equivalent electric circuit for all samples. Main values are presented as mean  $\pm$  standard deviation (n=3).

| Sample  | R <sub>sol</sub><br>( $\Omega$ ) | Q, Yo<br>(S-sec <sup>n</sup> ) | n     | R<br>( $\Omega$ )                | W, Yo<br>(S-sec <sup>0.5</sup> ) | R <sub>p</sub><br>( $\Omega$ )   |
|---------|----------------------------------|--------------------------------|-------|----------------------------------|----------------------------------|----------------------------------|
| Control | 3.10 $\pm$ 0.15                  | 2.00 $\times 10^{-4}$          | 0.876 | 73.47 $\pm$ 5.2                  | —                                | 77 $\pm$ 5                       |
| CP01    | 2.52 $\pm$ 0.12                  | 4.37 $\times 10^{-5}$          | 0.919 | (2.275 $\pm$ 0.18) $\times 10^5$ | 1.56 $\times 10^{-5}$            | (2.275 $\pm$ 0.18) $\times 10^5$ |
| CP02    | 3.40 $\pm$ 0.16                  | 3.53 $\times 10^{-5}$          | 0.881 | (3.022 $\pm$ 0.24) $\times 10^5$ | 1.32 $\times 10^{-5}$            | (3.022 $\pm$ 0.24) $\times 10^5$ |
| CP03    | 3.41 $\pm$ 0.16                  | 4.16 $\times 10^{-5}$          | 0.895 | (5.144 $\pm$ 0.41) $\times 10^5$ | 3.75 $\times 10^{-5}$            | (5.144 $\pm$ 0.41) $\times 10^5$ |
| CP04    | 2.91 $\pm$ 0.14                  | 1.00 $\times 10^{-4}$          | 0.875 | 130 $\pm$ 9                      | —                                | 133 $\pm$ 9                      |
| CP05    | 3.17 $\pm$ 0.15                  | 2.36 $\times 10^{-5}$          | 0.921 | 1645 $\pm$ 115                   | —                                | 1645 $\pm$ 115                   |
| PD01    | 3.32 $\pm$ 0.16                  | 3.20 $\times 10^{-5}$          | 0.886 | (1.262 $\pm$ 0.10) $\times 10^6$ | 7.07 $\times 10^{-6}$            | (1.262 $\pm$ 0.10) $\times 10^6$ |
| PD02    | 4.33 $\pm$ 0.21                  | 3.62 $\times 10^{-5}$          | 0.903 | (5.414 $\pm$ 0.43) $\times 10^5$ | 9.31 $\times 10^{-6}$            | (5.414 $\pm$ 0.43) $\times 10^5$ |
| PD03    | 2.32 $\pm$ 0.11                  | 2.88 $\times 10^{-5}$          | 0.939 | (1.333 $\pm$ 0.11) $\times 10^5$ | 8.53 $\times 10^{-5}$            | (1.333 $\pm$ 0.11) $\times 10^5$ |

The solution resistance (R<sub>sol</sub>) was consistent across all samples. The polarization resistance (R<sub>p</sub>), which represents the core charge-transfer resistance and is a direct indicator of the corrosion protection capability of the passive layer, revealed stark contrasts between the treatments.

The impedance was significantly higher for samples CP01, CP02, and CP03 than for the control, CP04, and CP05 samples (Figure 4). This was quantitatively confirmed by the R<sub>p</sub> values, which were

orders of magnitude greater for samples passivated at potentials with a negative or zero slope (CP01-CP03), reaching up to 514 k $\Omega$  for CP03, compared to merely 77  $\Omega$  for the control (Table 2). The need for a Warburg (W) diffusion element in the equivalent circuit for these high-performance samples (CP01-CP03, PD01-PD03) indicates that the mass transport of ions through a thick, protective film became the rate-limiting step. Conversely, its absence for the control and CP04/CP05 samples suggests that the

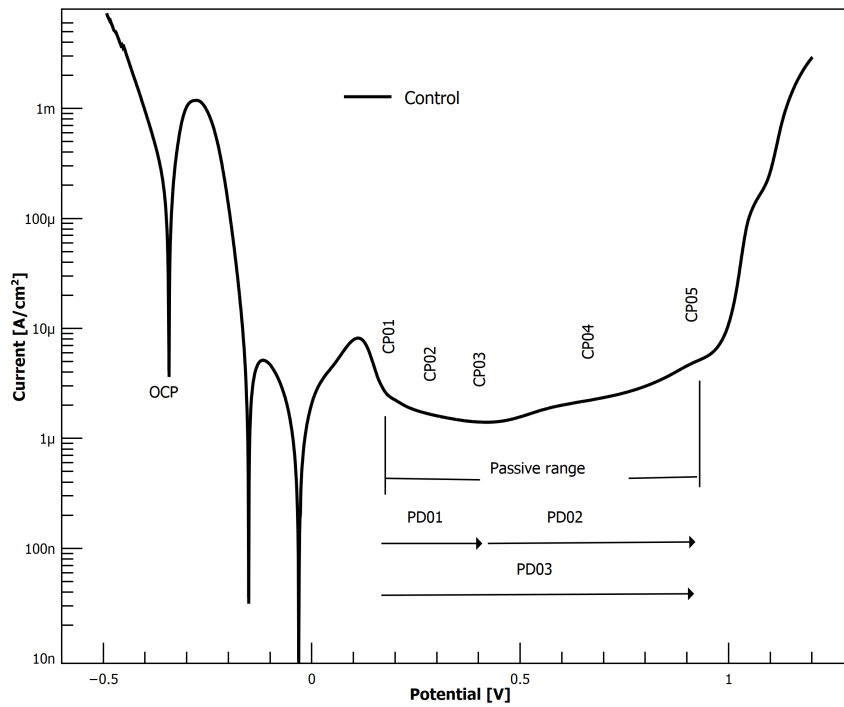


Fig. 3: Potentiodynamic polarization curve of control sample in 1M  $\text{H}_2\text{SO}_4$  solution.

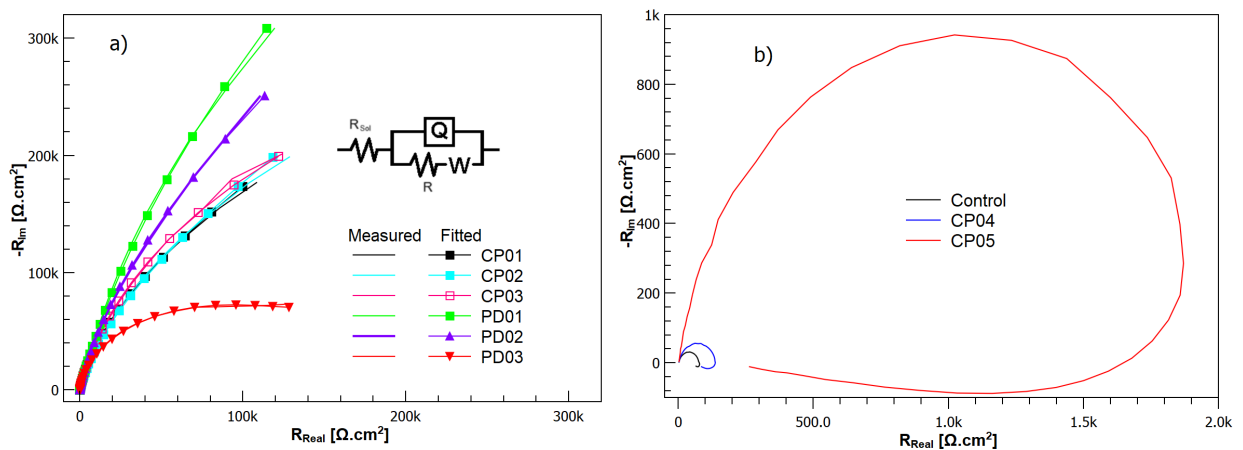


Fig. 4: EIS plots for samples in 1 M  $\text{H}_2\text{SO}_4$  solution for (a) CP01, CP02, CP03, PD01, PD02 and PD03 samples where the inset represents the suggested equivalent circuit,  $R_{sol}(Q(RW))$ , used in samples; (b) CP04, CP05 and control sample.



reaction was under charge-transfer control at a largely exposed metal surface (Singh *et al.*, 2022), consistent with their poor performance.

While this study demonstrates the superior short-term corrosion resistance of electrochemically grown passive films, it is important to acknowledge that no long-term immersion tests were conducted. The durability of these films under continuous exposure to an aggressive 1 M H<sub>2</sub>SO<sub>4</sub> environment remains to be verified. However, Based on the significantly higher polarization resistance ( $R_p$ ), which indicates that mass transport through a thick film is the rate-limiting step (Abildina *et al.*, 2020), it is reasonable to infer that these films would offer enhanced long-term protection compared to conventionally treated surfaces. Future work should focus on extended immersion tests and electrochemical monitoring to confirm the sustained stability and self-healing capabilities of these optimized passive layers.

To analyze the influence of the applied potential on the samples, according to Table 1, the Tafel curves are presented in Figure 5.

The values of corrosion potential ( $E_{corr}$ ) and corrosion current ( $I_{corr}$ ) obtained from the Tafel polarization curves are shown in Table 3.

Table 3. The values of corrosion current ( $I_{corr}$ ) and corrosion potential ( $E_{corr}$ ) for the samples. Values are presented as the mean  $\pm$  standard deviation (n=3).

| Sample  | $E_{corr}$<br>(mV) | $I_{corr}$<br>( $\mu\text{A}/\text{cm}^2$ ) |
|---------|--------------------|---------------------------------------------|
| Control | $-343.8 \pm 4.1$   | $303.1 \pm 28.3$                            |
| CP01    | $64.4 \pm 2.8$     | $0.0367 \pm 0.0042$                         |
| CP02    | $19.5 \pm 1.7$     | $0.0404 \pm 0.0046$                         |
| CP03    | $-127.5 \pm 3.5$   | $0.0342 \pm 0.0039$                         |
| CP04    | $-344.1 \pm 4.2$   | $275.7 \pm 24.1$                            |
| CP05    | $-344.4 \pm 4.3$   | $283.1 \pm 25.6$                            |
| PD01    | $19.5 \pm 1.6$     | $0.0183 \pm 0.0021$                         |
| PD02    | $73.9 \pm 2.9$     | $0.0300 \pm 0.0035$                         |
| PD03    | $-17.2 \pm 1.4$    | $0.212 \pm 0.019$                           |

This remarkable improvement in barrier properties was directly correlated with the corrosion kinetics. Tafel analysis (Figure 5, Table 3 showed a drastic reduction in corrosion current density ( $I_{corr}$ ) for samples CP01-CP03, with values falling below  $0.04 \mu\text{A}/\text{cm}^2$  compared to  $303.1 \mu\text{A}/\text{cm}^2$  for the control. Note that the corrosion current density for the control sample is on the order of hundreds of  $\mu\text{A}/\text{cm}^2$ , characteristic of an actively corroding surface.

In contrast, samples treated at potentials with a positive slope (CP04, CP05) exhibited  $R_p$  and  $I_{corr}$  values virtually indistinguishable from the control (e.g.,  $R_p = 133 \Omega$  and  $1645 \Omega$ , respectively), demonstrating that passivation in this region fails to enhance corrosion resistance. This collective electrochemical data underscores that the critical factor is not merely being within the passive range

but the specific applied potential's characteristic slope. A negative or zero slope promotes dominant film formation kinetics, leading to the suppression of active dissolution and the formation of a superior passive layer. This observed dependence of passive film quality on the slope of the polarization curve ( $dI/dV$ ) can be rationalized within the framework of the Point Defect Model (PDM) and high-field oxide growth theory. According to the PDM (Macdonald 1999), passive film growth is controlled by the generation and annihilation of cation vacancies at the metal/film and film/solution interfaces. A negative  $dI/dV$  indicates a regime where the rate of cation vacancy annihilation at the metal/film interface exceeds their generation rate, resulting in a net decrease in defect density and the formation of a more stoichiometric and compact oxide layer. In contrast, a positive  $dI/dV$  suggests an increase in the generation rate of cation vacancies, leading to a more defective film and enhanced dissolution. The high-field model further explains that the ionic current density through the film is exponentially dependent on the electric field strength. As the film thickness, the field decreases, but in the negative-slope region, the net current decreases due to reduced defect density, promoting dominant film growth kinetics. Thermodynamically, the stability of Cr<sub>2</sub>O<sub>3</sub> is favored in this potential region, as indicated by Pourbaix diagrams (Beverskog and Puigdomenech 1997), where Cr(III) oxides are stable and soluble Cr(VI) species are not yet formed. Thus, the negative-slope region corresponds to optimal conditions for the formation of a highly protective Cr<sub>2</sub>O<sub>3</sub>-rich layer.

Among all treatments, the potentiodynamic passivation within the 482–700 mV range (PD01) yielded the optimal performance, with the highest  $R_p$  ( $1.26 \text{ M}\Omega$ ) and the lowest  $I_{corr}$  ( $0.0183 \mu\text{A}/\text{cm}^2$ ). The PD03 sample (sweeping the entire passive range) showed good but not exceptional performance ( $R_p = 133 \text{ k}\Omega$ ,  $I_{corr} = 0.21 \mu\text{A}/\text{cm}^2$ ), indicating that sweeping into the less optimal positive-slope region diminishes the overall effectiveness of the treatment.

Additionally, Figure 6 shows the XPS spectra obtained from the control and PD01 samples.

The first row (a) in Figure 6 shows the XPS spectra of Fe 2p, Cr 2p, and O 1s for the control sample, while the second row (b) corresponds to the PD01 sample. XPS analysis confirms that the passive layer consists primarily of oxides such as Cr<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, but it also contains hydroxides like Cr(OH)<sub>3</sub> and Fe(OH)<sub>3</sub>, consistent with other reports (Cardenas *et al.*, 2014; Jung *et al.*, 2012; Liu *et al.*, 2024). For example, the deconvolution of the Cr 2p spectrum of the control sample revealed that the chromium ion species in the layer are composed of 47.77 % of Cr<sup>3+</sup> (hyd), 37.46 % of Cr<sup>3+</sup> (ox), with the remaining 14.77 % contributing to Cr<sup>0</sup> metallic chromium. In contrast, the quantitative analysis for the PD01 sample shows

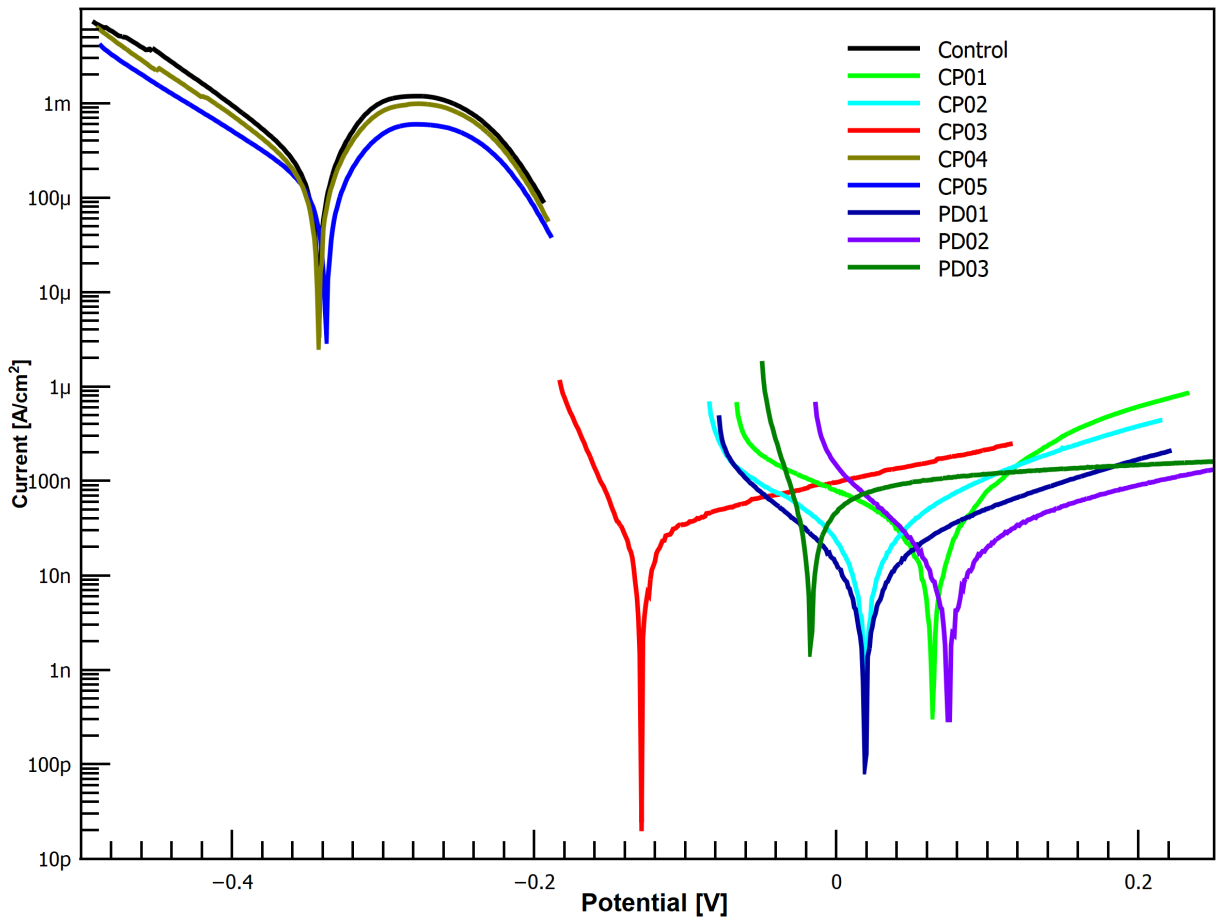


Fig. 5: Polarization plots for control and passivated samples in 1 M  $\text{H}_2\text{SO}_4$  solution.

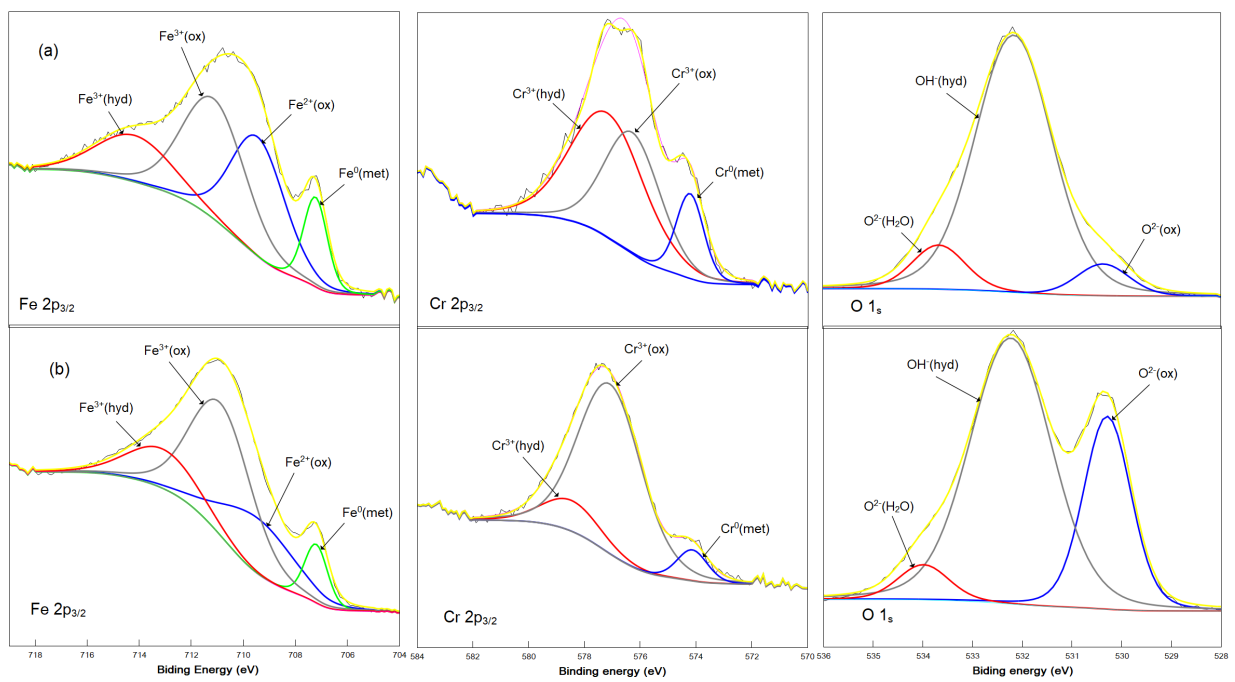


Fig. 6: XPS spectra for surface on AISI 304 stainless steel for (a) control sample and (b) sample subjected to potentiodynamic passivation (PD01 sample).

that the passive layer is composed of 78.75 % of  $\text{Cr}^{3+}$  (ox), 18.51 % of  $\text{Cr}^{3+}$  (hyd), with the remainder being  $\text{Cr}^0$  metallic chromium. This indicates that the XPS spectra reveal a higher concentration of Cr oxide ( $\text{Cr}_2\text{O}_3$ ) in the passive layer formed on the PD01 sample compared to the control sample, accompanied by a decrease in hydroxide content. The increased chromium oxide content (Cruz *et al.*, 2022) and decreased hydroxide content are likely responsible for the superior corrosion resistance observed in the potentiodynamically passivated sample (PD01) compared to the control sample, and this is corroborated by the spectra of O 1s. These results may be due to the fact that, in potentiodynamic passivation, oxidation kinetics are accelerated by progressive anodic polarization, increasing the formation of  $\text{Cr}_2\text{O}_3$  and decreasing the hydroxide content due to  $\text{Cr}(\text{OH})_3$ , which is not thermodynamically stable (Beverskog and Puigdomenech 1997).

While the electrochemical results demonstrate a remarkable improvement in corrosion resistance immediately after passivation, the long-term stability of these films under continuous exposure to 1 M  $\text{H}_2\text{SO}_4$  has not been evaluated in this study. Extended immersion tests or exposure to aggressive environments over prolonged periods would be necessary to assess the durability and potential degradation mechanisms of the electrochemically formed passive layers, such as localized corrosion or film thinning. Nevertheless, based on the high polarization resistance and low corrosion current densities observed, it is reasonable to expect that the optimized films would exhibit superior longevity compared to those formed by conventional methods. Future work should include long-term immersion tests and post-exposure surface analysis to confirm the stability of the passive layer over time.

## 4 Conclusions

This study demonstrates that the electrochemical passivation of AISI 304 stainless steel in 1 M  $\text{H}_2\text{SO}_4$ , particularly when conducted within the negative-slope region of the passive potential range, produces a passive film with significantly enhanced corrosion resistance compared to untreated samples and those treated by conventional chemical methods. EIS analysis revealed that samples polarized in this region exhibited polarization resistance values of up to 1.26 M $\Omega$  (PD01), several orders of magnitude higher than the control (77  $\Omega$ ). Tafel analysis confirmed correspondingly low corrosion current densities (0.0183  $\mu\text{A}/\text{cm}^2$  for PD01 vs. 303.1  $\mu\text{A}/\text{cm}^2$  for control). XPS analysis identified that the superior protective layer consists primarily of  $\text{Cr}_2\text{O}_3$ . The critical role of the polarization slope (negative

dI/dV) can be understood through the Point Defect Model, where the applied potential promotes film formation kinetics over dissolution processes. Among all treatments, potentiodynamic passivation within the 482-700 mV range (PD01) yielded optimal performance. These findings establish electrochemical passivation as a rapid, controllable, and effective alternative to traditional chemical methods for achieving exceptional corrosion resistance in aggressive acidic environments. Future work should focus on evaluating the long-term stability of these engineered passive films through extended immersion testing and exploring their performance in other aggressive media.

## 5 Acknowledgments

The authors appreciate the financial support of the Secretaría de Ciencia, Humanidades, Tecnología e Innovación (SECIHTI), México, under its SNII program.

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