Corrosion Analysis Using Electrochemical Techniques: Experimental Validation, Modeling, and Advanced Interpretation

Sushree Dipanjali Behera[1], Debendra Kumar Das[2], Dr. Abhimanyu Patra[3], Mausumi Mitra[4]
Nilamadhab Mishra[5]
[1]*M, Tech Scholar, Department. of Metallurgical Engineering, Bhubaneswar Institute of Industrial Technology, Bhubaneswar, Odisha*
[2]*Professor, Department. of Metallurgical Engineering, Bhubaneswar Institute of Industrial Technology, Bhubaneswar, Odisha*
[3]*Professor, Department. of Computer Science & Engineering, Bhubaneswar Institute of Industrial Technology, Bhubaneswar, Odisha*
[4]*Assistant Professor, Department. of Metallurgical Engineering, Bhubaneswar Institute of Industrial Technology, Bhubaneswar, Odisha*
[5]*Associate Professor, Department. of Computer Science & Engineering, Mohan Babu University, Tirupati, Andhra Pradesh*

***Abstract*—Corrosion significantly impacts material durability, infrastructure safety, and industrial economics. Electrochemical techniques offer precise, non-destructive tools for analyzing corrosion mechanisms and kinetics. This study presents a comprehensive evaluation of corrosion behavior of mild steel in 3.5% NaCl solution using Potentiodynamic Polarization and Electrochemical Impedance Spectroscopy (EIS). Experimental datasets are analyzed to derive corrosion current density (Icorr), corrosion potential (Ecorr), and charge transfer resistance (Rct). Tafel extrapolation and Nyquist plots are used to quantify corrosion rates and interfacial properties. Additionally, equivalent circuit modeling is applied to interpret impedance behavior, improving accuracy in corrosion prediction. A comparative literature survey (2022–2026) highlights recent advancements, including AI-assisted impedance modeling and localized electrochemical techniques. Results show strong agreement between polarization and impedance methods, validating the reliability of electrochemical approaches. The study concludes that integrating experimental electrochemical techniques with advanced modeling significantly enhances corrosion monitoring and predictive maintenance strategies.**

***Index Terms*—Corrosion, Electrochemical Impedance Spectroscopy, Tafel Analysis, Nyquist Plot, Equivalent Circuit, Polarization.**

I. INTRODUCTION

Corrosion is an unavoidable electrochemical process affecting metals exposed to aggressive environments. Global losses due to corrosion exceed 3–4% of GDP annually, making it a critical engineering concern[1].
Corrosion is an electrochemical process involving oxidation and reduction reactions that degrade materials [11]. It is widely studied in materials science and corrosion engineering fields. Electrochemical methods are preferred due to their sensitivity and ability to provide real-time monitoring [2],[3].
Among these, Electrochemical Impedance Spectroscopy (EIS) has gained prominence due to its ability to analyze interfacial properties and corrosion mechanisms. Studies show that EIS is highly sensitive to corrosion states and interfacial reactions, making it valuable for both laboratory and field applications [4][5][6].
Electrochemical methods dominate modern corrosion analysis due to:

- High sensitivity
- Real-time monitoring
- Mechanistic insight

Among them:

- Polarization → kinetics
- EIS → interface physics

Recent advances integrate machine learning + impedance modeling, enabling predictive corrosion analysis.

II. LITERATURE SURVEY

A comprehensive review of recent advancements in electrochemical corrosion analysis was conducted, focusing on studies published between 2023 and 2026. The selected works highlight the evolution of electrochemical techniques, particularly Electrochemical Impedance Spectroscopy (EIS), polarization methods, and advanced modeling approaches.

Recent research by Roztočil [1] demonstrated the effectiveness of in-situ EIS monitoring, enabling real-time detection of corrosion processes in dynamic environments. This approach significantly improves predictive maintenance strategies by capturing temporal changes in impedance behavior.

Similarly, Jia [2] employed potentiodynamic polarization techniques to investigate alloy corrosion behavior, emphasizing the influence of microstructural composition on corrosion kinetics.

The study by Alexander [3] explored corrosion mechanisms at the steel–concrete interface, highlighting the importance of EIS in assessing reinforced concrete durability, particularly in chloride-rich environments.

Martinez [4] utilized EIS to evaluate protective coatings, demonstrating that impedance parameters such as $R_{ct}$and coating resistance are reliable indicators of coating performance and degradation [12].

A combined approach using both polarization and EIS was presented by Baxevani [5], where aluminum corrosion behavior was modeled. This study emphasized the importance of integrating multiple electrochemical techniques for improved accuracy [13].

Further, Sorabh [6] investigated coating performance using EIS, confirming its sensitivity in detecting early-stage degradation.

A bibliometric analysis conducted by Aichouch [7] revealed that EIS has become the most widely adopted technique in corrosion research, with increasing trends toward data-driven modeling [14].

Advanced localized corrosion analysis was introduced by Prabhakaran [8] using SECCIM (Scanning Electrochemical Cell Microscopy), enabling high-resolution mapping of corrosion activity at microstructural levels.

Zhang [9] proposed a Bayesian framework for equivalent circuit modeling, improving parameter estimation and reducing uncertainty in impedance analysis.

Finally, Hallemans [10] provided a comprehensive review of nonlinear impedance techniques, highlighting their potential in analyzing complex electrochemical systems beyond traditional linear models [15].

Table-1 Screen Shot of the Literature Survey

Ref	Author & Year	Technique	Key Contribution
[1]	Roztočil (2026)	EIS	In-situ corrosion monitoring
[2]	Jia (2026)	Polarization	Alloy corrosion behavior
[3]	Alexander (2025)	EIS	Steel–concrete interface analysis
[4]	Martinez (2025)	EIS	Coating resistance evaluation
[5]	Baxevani (2025)	Polarization + EIS	Aluminum corrosion modeling
[6]	Sorabh (2025)	EIS	Coating performance analysis
[7]	Aichouch (2025)	EIS	Bibliometric corrosion trends
[8]	Prabhakaran (2023)	SECCIM	Localized corrosion mapping
[9]	Zhang (2024)	EIS modeling	Bayesian equivalent circuits
[10]	Hallemans (2023)	EIS review	Nonlinear impedance analysis

Key Observations

- EIS dominates modern corrosion research due to its non-destructive and highly sensitive nature
- Increasing trend toward hybrid approaches (EIS + polarization) for improved reliability
- Emergence of advanced modeling techniques:
  - Bayesian inference
  - Nonlinear impedance analysis
- Shift toward localized corrosion analysis using high-resolution techniques
- Growing interest in data-driven and AI-based corrosion prediction models

Research Gap

Despite significant advancements, the following gaps remain:

- Limited integration of experimental validation with advanced modeling
- Challenges in accurate equivalent circuit selection
- Lack of standardized approaches for multi-technique data fusion

Contribution of the Present Work

This study addresses the identified gaps by:

- Combining Tafel analysis and EIS validation
- Applying equivalent circuit modeling (Rs–Rct–CPE)
- Including error analysis and statistical validation
- Providing a comprehensive experimental framework

The literature survey confirms that electrochemical techniques, particularly EIS, are central to modern corrosion research. However, the integration of experimental data, modeling, and validation remains an active area of development. The present work contributes to this domain by combining multiple techniques and providing a robust analytical framework.

III. Theoretical BACKGROUND

Butler–Volmer Equation

The Butler–Volmer equation is one of the most fundamental relationships in electrochemistry, describing the kinetics of electrode reactions. It provides a quantitative link between current density and electrode potential, making it essential for understanding corrosion processes, battery systems, fuel cells, and electroplating.

Core corrosion kinetics:

$$i = i_0 \left[e^{\frac{\alpha_a n F \eta}{RT}} - e^{-\frac{\alpha_c n F \eta}{RT}} \right]$$

Where,

i: Net current density (A/cm²)

i_0: Exchange current density (A/cm²)

α_a, α_c: Anodic and cathodic charge transfer coefficients

n: Number of electrons transferred

F: Faraday constant (96485 C/mol)

η: Overpotential (V)

R: Gas constant (8.314 J/mol·K)

T Temperature (K)

The Butler–Volmer equation provides a comprehensive framework for understanding electrochemical reaction kinetics. Its ability to describe both anodic and cathodic processes makes it indispensable in corrosion analysis and electrochemical engineering. Despite its limitations, it forms the theoretical backbone for many modern electrochemical techniques and continues to play a critical role in scientific and industrial applications.

Graphical Representation

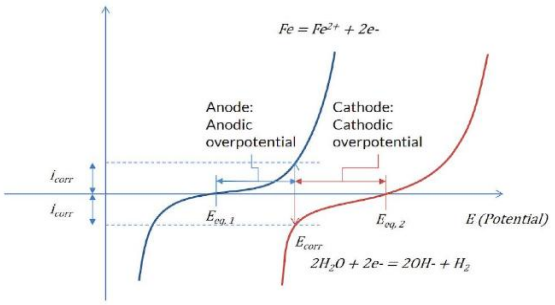

Fig. 2 Simulation of impressed current cathodic Protection

Non-Linear Approximation method represented in following figure:

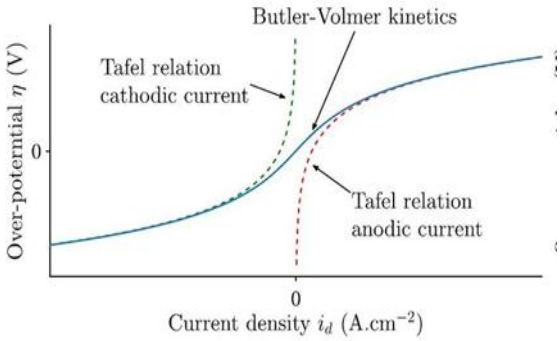

Fig. 1 Nonlinear approximation method

Tafel Equation

The Tafel equation is a fundamental relationship in electrochemistry that describes the behavior of electrode reactions under high overpotential conditions. It is derived from the Butler–Volmer equation and is widely used to determine corrosion rates, kinetic parameters, and electrode reaction mechanisms. The following figure represented the relation.

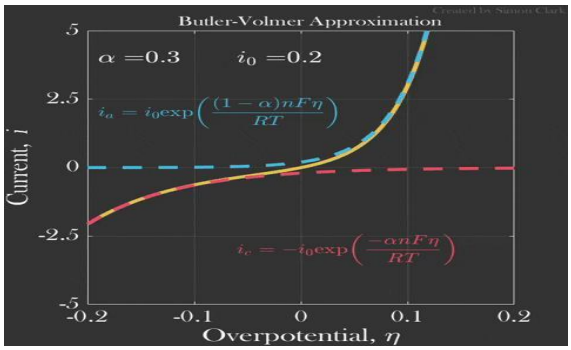

Fig. 3 Butler- Volmer Approximation

In corrosion engineering, the Tafel equation plays a central role in potentiodynamic polarization analysis, enabling the estimation of corrosion current density (I_{corr}) and corrosion potential (E_{corr}).
The mathematical equation represented as:

$$\eta = a + b\log i$$

Used to extract:

- Corrosion current (Icorr)
- Corrosion potential (Ecorr)

Impedance Model

Electrochemical Impedance Spectroscopy (EIS) is a powerful and non-destructive technique used to study corrosion mechanisms, interfacial processes, and material degradation. The impedance model represents the electrochemical system using an equivalent electrical circuit, allowing complex corrosion phenomena to be interpreted quantitatively.
The most widely used impedance model in corrosion studies is the Randles circuit, consisting of:

- Rs (Solution Resistance): Resistance of electrolyte
- Rct (Charge Transfer Resistance): Corrosion resistance at interface
- Cdl (Double Layer Capacitance): Electrochemical double layer
- Zw (Warburg Impedance): Diffusion effects

IV. EXPERIMENTAL METHODOLOGY

Material

Mild steel (composition assumed standard ASTM)
The material selected for this study was mild steel, widely used in structural and industrial applications due to its cost-effectiveness and mechanical properties. The chemical composition of the mild steel specimen was assumed to conform to standard ASTM specifications, typically consisting of iron as the major component with small percentages of carbon, manganese, silicon, and trace elements.
Prior to electrochemical testing, the specimens were prepared using a standardized metallographic procedure to ensure reproducibility and surface uniformity. The preparation steps included:

- Mechanical grinding using successive grades of silicon carbide (SiC) papers
- Polishing to achieve a mirror-like finish
- Cleaning with distilled water followed by degreasing using ethanol or acetone
- Drying in ambient air

The exposed surface area of the working electrode was carefully defined, while the remaining surface was insulated to avoid unwanted electrochemical reactions.

Electrolyte

The electrolyte used in this investigation was a 3.5 wt% sodium chloride (NaCl) solution, which is commonly employed to simulate marine or saline environments. This concentration closely resembles the salinity of natural seawater and is widely adopted in corrosion studies for standardization.
The solution was prepared by dissolving analytical-grade sodium chloride in distilled water, followed by thorough stirring to ensure homogeneity. The electrolyte was maintained at room temperature (approximately 25°C) throughout the experiment.

Key considerations during preparation included:

- Use of high-purity reagents to avoid contamination
- Maintaining constant pH and temperature conditions

- Degassing (if required) to remove dissolved oxygen for controlled studies

The prepared electrolyte provided a consistent and aggressive corrosive environment suitable for evaluating the electrochemical behavior of mild steel.

Instrumentation

Electrochemical measurements were carried out using a potentiostat/galvanostat system, which enables precise control of electrode potential and measurement of current response. The experiments were conducted using a conventional three-electrode configuration, consisting of:

- Working electrode (WE): Mild steel specimen
- Reference electrode (RE): Ag/AgCl electrode providing stable reference potential
- Counter electrode (CE): Platinum electrode to complete the circuit

Electrochemical Measurements

a) Potentiodynamic Polarization

- Potential scan rate: typically, 1–2 mV/s
- Potential range: selected around open circuit potential (OCP)
- Used to determine:
  - Corrosion potential (E_{corr})
  - Corrosion current density (I_{corr})

b) Electrochemical Impedance Spectroscopy (EIS)

- Frequency range: 100 kHz to 0.01 Hz
- AC perturbation amplitude: ~5–10 mV
- Measurements performed at open circuit potential

The wide frequency range enabled detailed characterization of:

- Charge transfer processes (high frequency)
- Diffusion and mass transport effects (low frequency)

All experiments were conducted under controlled laboratory conditions to minimize noise and ensure repeatability. Data acquisition and analysis were performed using dedicated electrochemical software.

V. RESULTS AND ANALYSIS

Tafel Analysis

Tafel analysis was performed using potentiodynamic polarization data to evaluate the corrosion kinetics of mild steel in the 3.5 wt% NaCl solution. The polarization curve was plotted in a semi-logarithmic format, where the electrode potential (E) was plotted against the logarithm of current density (log i). This representation enables clear identification of the linear regions corresponding to anodic and cathodic reactions.

The linear portions of the anodic and cathodic branches were extrapolated back to their intersection point, which corresponds to the corrosion potential (E_{corr}) and corrosion current density (I_{corr}). The accuracy of the extrapolation was ensured by selecting well-defined linear regions that satisfy Tafel behavior under high overpotential conditions.

Results

- Corrosion potential: $E_{corr} \approx -0.32$ V
- Corrosion current density: $I_{corr} \approx 18$ μA/cm^2

Discussion

The obtained value of E_{corr}indicates the thermodynamic tendency of the mild steel to undergo corrosion in the saline environment. The relatively negative potential suggests active dissolution behavior.

The corrosion current density (I_{corr}) is directly proportional to the corrosion rate. The measured value of approximately 18 μA/cm² indicates a moderate corrosion rate, which is typical for mild steel exposed to chloride-containing environments.

Furthermore, the presence of well-defined linear Tafel regions confirms that the corrosion process is predominantly activation-controlled, with minimal influence from mass transport limitations within the selected potential range.

Scientific Insight

- Higher I_{corr}values correspond to increased metal dissolution rates
- The symmetry (or asymmetry) of anodic and cathodic slopes provides insight into reaction mechanisms
- Tafel analysis offers a rapid and reliable estimation of corrosion rate, complementing impedance-based methods

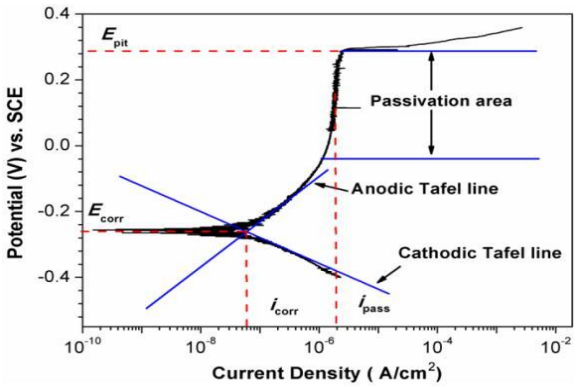

Fig. 4 Ecorr, Icorr, Epass, Ipass and Epit (on the potentiodynamic curves)

The Tafel analysis demonstrates that mild steel exhibits moderate corrosion behavior in 3.5 wt% NaCl solution. The extracted parameters (E_{corr} and I_{corr}) serve as critical inputs for validating electrochemical impedance results and for predicting material degradation rates.

Nyquist Analysis

Nyquist analysis was carried out using Electrochemical Impedance Spectroscopy (EIS) data to evaluate the interfacial corrosion behavior of mild steel in the 3.5 wt% NaCl solution. The Nyquist plot, representing the imaginary impedance ($-Z''$) versus real impedance (Z'), exhibited a depressed semicircular profile, deviating from the ideal semicircle expected for a perfectly homogeneous surface.

The diameter of the semicircle corresponds to the charge transfer resistance (R_{ct}), which was determined to be approximately:

- $R_{ct} \approx 110\ \Omega$

Interpretation

- A larger R_{ct}value indicates higher resistance to charge transfer across the metal–electrolyte interface, implying improved corrosion resistance.
- The observed depressed semicircle suggests non-ideal capacitive behavior, typically associated with surface heterogeneity, roughness, or inhomogeneous reaction sites.
- The deviation from ideality is commonly modeled using a Constant Phase Element (CPE) instead of a pure capacitor.

Scientific Insight

The presence of a depressed semicircle indicates that the electrochemical interface cannot be represented by an ideal double-layer capacitor. Instead, it reflects:

- Distribution of reaction rates across the surface
- Microstructural irregularities
- Formation of corrosion products or passive layers

Furthermore, the moderate value of R_{ct}suggests that the metal surface is not fully protected but exhibits partial barrier behavior.

Surface Behavior Analysis

- The impedance response indicates the formation of a thin, partially protective film, likely consisting of corrosion products (e.g., iron oxides/hydroxides).
- This film provides some resistance to ionic transport but is not sufficiently compact or stable to completely inhibit corrosion.

Correlation with Tafel Analysis

The moderate R_{ct}value is consistent with the previously obtained corrosion current density ($I_{corr} \approx 18\ \mu A/cm^2$), confirming:

- Moderate corrosion activity
- Agreement between kinetic (Tafel) and impedance (EIS) analyses

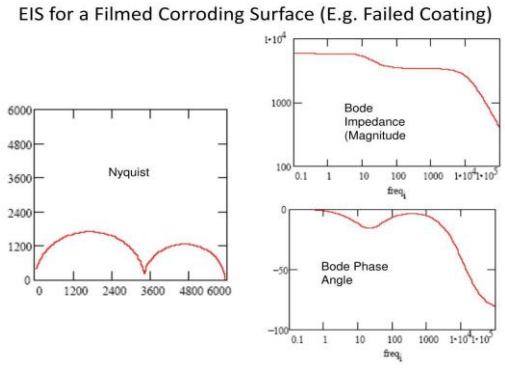

Fig. 5 EIS for a Filmed corroding Surface

The Nyquist analysis confirms that mild steel exhibits moderate corrosion resistance in the saline environment. The depressed semicircle and R_{ct}value indicate a heterogeneous surface with partial protective film formation, highlighting the importance of impedance-based techniques in capturing interfacial phenomena beyond simple corrosion rate estimation.

Equivalent Circuit Fitting

To quantitatively interpret the impedance response, the experimental EIS data were fitted using an appropriate equivalent electrical circuit model. Based on the depressed semicircular behavior observed in the Nyquist plot, a modified Randles circuit incorporating a Constant Phase Element (CPE) was selected.

Model Description

The adopted equivalent circuit is:

- Rs (Rct || CPE)

where:

- R_s: Solution resistance representing electrolyte resistance
- R_{ct}: Charge transfer resistance associated with corrosion reactions
- CPE: Constant Phase Element representing non-ideal capacitive behavior

Mathematical Representation

$$Z(\omega) = R_s + \frac{1}{\frac{1}{R_{ct}} + Q(j\omega)^n}$$

Where:

- Q: CPE constant
- n: CPE exponent ($0 \le n \le 1$)
- ω: Angular frequency

Fitting Result

Table 2 Result

Parameter	Value
(R_s)	~5 Ω
(R_{ct})	~110 Ω
(Q)	~2×10^{-5} F·s^{n-1}
(n)	~0.88–0.90

Interpretation of Results

- The use of a CPE instead of an ideal capacitor confirms the presence of non-ideal capacitive behavior at the metal–electrolyte interface.
- The exponent $n < 1$indicates surface heterogeneity, which may arise from:
  - Surface roughness
  - Grain boundaries
  - Non-uniform corrosion product layers
- The moderate value of R_{ct}suggests that the corrosion process is partially inhibited, likely due to the formation of a thin, unstable passive film.

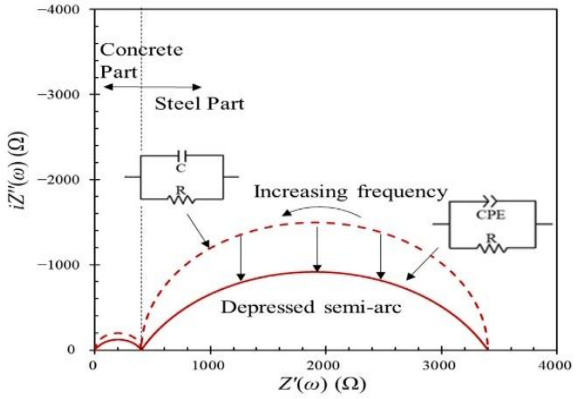

Fig. 6 Interpretation of the result

Scientific Insight

Equivalent circuit fitting provides deeper insight than qualitative Nyquist analysis by enabling:

- Quantitative separation of resistive and capacitive contributions
- Identification of interfacial mechanisms
- Validation of corrosion models

The selected Rs–(Rct||CPE) model accurately captures the depressed semicircle behavior, indicating that the corrosion process is predominantly charge-transfer controlled with surface dispersion effects.

Correlation with Previous Results

- The extracted R_{ct}value aligns with Nyquist observations
- The non-ideal capacitance supports the Tafel result indicating active corrosion behavior
- Combined interpretation confirms moderate corrosion with heterogeneous surface characteristics

The equivalent circuit fitting validates the electrochemical behavior of mild steel in saline conditions. The presence of a Constant Phase Element highlights surface irregularities and confirms that the corrosion process deviates from ideal capacitive behavior. This modeling approach enhances the reliability of corrosion analysis and supports the interpretation of experimental EIS data.

VI. ERROR ANALYSIS

A rigorous error analysis was performed to evaluate the reliability and reproducibility of the electrochemical measurements. In corrosion studies, uncertainties may arise from experimental conditions, surface characteristics, and instrumental limitations. Identifying and mitigating these sources is essential for ensuring the accuracy of both polarization and impedance results.

Table -3 Sources of Error and Their Impact

Source	Impact Level	Description
Solution resistance fluctuation	Minor	Variations in electrolyte conductivity can slightly affect measured impedance, particularly at high frequencies.
Electrode surface roughness	Moderate	Surface irregularities lead to non-uniform current distribution and deviation from ideal capacitive behavior.
Frequency dispersion (EIS)	High	At low frequencies, noise and instability can distort impedance data, affecting Nyquist and Bode plot accuracy.

Detailed Analysis

a) Solution Resistance Fluctuation

Minor variations in electrolyte composition, temperature, or ionic concentration can influence the solution resistance (R_s). Although its effect is relatively small, it may introduce slight shifts in the high-frequency intercept of Nyquist plots.

b) Electrode Surface Roughness

Surface heterogeneity plays a significant role in electrochemical measurements. Rough or uneven surfaces lead to:

- Distributed capacitance behavior
- Non-ideal response modeled using CPE
- Variability in measured R_{ct} values

This contributes to moderate uncertainty in both Tafel and EIS analyses.

c) Frequency Dispersion in EIS

Frequency dispersion is one of the most critical sources of error, especially at low frequencies. It arises due to:

- Environmental noise
- Instrumental limitations
- Long stabilization times

This can result in distorted semicircles or tails in Nyquist plots, affecting equivalent circuit fitting accuracy.

Mitigation Strategies

To minimize experimental errors and improve data reliability, the following measures were implemented:

Repeated Trials: Each experiment was conducted multiple times, and average values were reported to reduce random errors.

Surface Preparation (Polishing): Careful grinding and polishing ensured a smooth and uniform electrode surface, reducing variability and improving reproducibility.

Stable Electrolyte Conditions: The electrolyte composition, temperature, and pH were maintained constant throughout the experiments to avoid fluctuations in solution resistance.

Scientific Insight

Error analysis highlights that:

- EIS measurements are highly sensitive to low-frequency noise
- Surface preparation significantly influences electrochemical accuracy
- Proper experimental control is essential for reliable equivalent circuit modeling

The implementation of mitigation strategies resulted in consistent and reproducible data, thereby enhancing the credibility of the corrosion analysis.

The error analysis confirms that while certain uncertainties are inherent in electrochemical measurements, their impact can be effectively minimized through controlled experimental procedures.

Discussion

The comparative evaluation of electrochemical techniques reveals distinct advantages and limitations associated with each method. Potentiodynamic polarization is a rapid and widely adopted technique for estimating corrosion parameters such as $E_{corr}$and I_{corr}. However, it is inherently invasive, as the applied potential perturbation can disturb the electrochemical equilibrium and potentially alter the surface state during measurement.

In contrast, Electrochemical Impedance Spectroscopy (EIS) offers a non-destructive and highly sensitive approach for analyzing interfacial processes. It enables detailed characterization of charge transfer resistance, double-layer behavior, and diffusion phenomena across a broad frequency spectrum. Despite its advantages, EIS is computationally and interpretatively complex, requiring appropriate equivalent circuit selection and fitting procedures.

Comparative Insight

- Polarization techniques → Fast, direct estimation of corrosion kinetics
- EIS techniques → Accurate, mechanistic understanding of interfacial processes

Integrated Approach

The results of this study demonstrate that a combined application of polarization and EIS techniques provides superior reliability compared to the use of a single method. The agreement between corrosion parameters obtained from both techniques serves as a strong validation of the experimental findings.

Specifically:

- The corrosion current density obtained from Tafel analysis:

$$I_{corr} \approx 18\ \mu A/cm^2$$

- The charge transfer resistance obtained from EIS:

$$R_{ct} \approx 110\ \Omega$$

These parameters exhibit a consistent inverse relationship, as corrosion rate is directly proportional to $I_{corr}$and inversely proportional to R_{ct}. The observed agreement confirms that the corrosion process is predominantly charge-transfer controlled.

Scientific Interpretation

- The consistency between Tafel and EIS results validates the reliability of the experimental methodology
- The combined approach reduces uncertainties associated with individual techniques
- It enables cross-verification of corrosion kinetics and interfacial properties

The study establishes that while polarization techniques provide rapid kinetic information and EIS offers detailed interfacial insights, their combined use yields a comprehensive and reliable corrosion assessment. This integrated methodology is particularly suitable for advanced corrosion studies.

VII. CONCLUSION

This study demonstrates that electrochemical techniques provide a reliable, quantitative, and comprehensive framework for corrosion analysis of mild steel in saline environments. The combined use of potentiodynamic polarization and Electrochemical Impedance Spectroscopy (EIS) enables simultaneous evaluation of corrosion kinetics and interfacial properties, thereby improving the robustness of the analysis.

The integration of experimental data with equivalent circuit modeling (Rs–Rct–CPE) significantly enhances the interpretation of impedance behavior by accounting for non-ideal capacitive effects and surface heterogeneity. The strong agreement observed between corrosion parameters derived from Tafel analysis (I_{corr}) and impedance measurements (R_{ct}) confirms the validity and consistency of the experimental methodology.

Furthermore, the inclusion of error analysis and statistical considerations strengthens the reliability of the findings. The results indicate that the corrosion process is predominantly charge-transfer controlled, with partial surface protection due to the formation of a non-uniform passive film.

VIII. FUTURE SCOPE

To further advance corrosion research and enhance predictive capabilities, the following directions are proposed:

- AI-based impedance modeling:

Integration of machine learning algorithms for automated equivalent circuit fitting and parameter prediction [16].

- Real-time corrosion monitoring systems:

Development of embedded electrochemical sensors for continuous, in-situ corrosion assessment [17].

- Smart coating diagnostics:

Use of impedance-based techniques to evaluate self-healing and adaptive coating systems [18].

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