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Electrochemical Characterization of Corrosion Processes: Techniques, Data Interpretation, and Predictive Modeling

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ABSTRACT

Electrochemical characterization techniques have become indispensable for understanding corrosion phenomena, enabling both fundamental mechanistic insights and practical corrosion monitoring across diverse industrial applications. This comprehensive review systematically examines the principles, applications, and data interpretation strategies for key electrochemical methods used in corrosion research. Cyclic voltammetry (CV) has emerged as a powerful mechanistic probe, capturing real-time redox activity and surface transformations, though historically underutilized due to the irreversible nature of corrosion reactions. Electrochemical impedance spectroscopy (EIS) remains the most versatile technique, providing frequency-dependent information on charge transfer resistance, double-layer capacitance, and diffusion processes, with applications ranging from reinforced concrete diagnosis to nanostructured coating evaluation. Potentiodynamic polarization enables rapid determination of corrosion current density, Tafel slopes, and pitting potentials through the Stern-Geary relationship. Electrochemical noise analysis detects spontaneous current and potential fluctuations sensitive to localized corrosion events such as metastable pit growth. Recent advances in machine learning have revolutionized data interpretation, with hybrid models achieving $R^2>0.99$ prediction accuracy for corrosion rate forecasting through integration of swarm intelligence optimization with deep learning architectures. Four-dimensional impedance analysis has emerged for time-varying systems, enabling instantaneous impedance determination during non-stationary corrosion processes. This review concludes that effective corrosion characterization requires integrated approaches combining complementary techniques with advanced data analytics, bridging laboratory mechanistic understanding with field-applicable monitoring solutions.

Introduction

Corrosion of metallic materials represents one of the most pervasive and economically burdensome challenges confronting modern industry, with annual costs estimated at USD 6 trillion when accounting for both direct and indirect impacts. This persistent threat to infrastructure, transportation, marine assets, and energy systems has motivated substantial multidisciplinary efforts toward developing reliable diagnostic tools to monitor and understand the electrochemical pathways governing corrosion initiation and propagation.

Regular maintenance is a vital strategy to mitigate corrosion's detrimental effects; research indicates that adhering to established, proven practices could reduce corrosion costs by 14-33%, conserving resources while protecting lives and the environment.

Corrosion primarily occurs in aqueous environments through an established electrochemical mechanism

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requiring four essential components: anode, cathode, metallic conductor, and electrolyte.

The anode, cathode, and metallic conductors are inherent to metals or alloys, while the electrolyte is typically an ionically conducting liquid such as an aqueous solution. At the anode, metal ions leave the surface, releasing electrons and causing oxidation (metal loss). These electrons travel through the metallic conductor to the cathode, while metal ions are transported via the electrolyte, where ions are reduced by gaining electrons. The electrolyte's ion concentration and conductivity influence the corrosion rate, with common cathodic reduction reactions including hydrogen evolution in acidic environments and oxygen reduction in neutral or alkaline media.

The electrochemical nature of corrosion necessitates sophisticated characterization techniques capable of probing these dynamic interfacial processes. Over recent decades, a diverse array of electrochemical methods has been developed, each offering unique advantages in sensitivity, temporal resolution, and mechanistic insight. Electrochemical impedance spectroscopy (EIS) has emerged as the most versatile technique, providing frequency-dependent information on charge transfer resistance, double-layer capacitance, and diffusion processes, with applications ranging from reinforced concrete diagnosis to nanostructured coating evaluation. Potentiodynamic polarization enables rapid determination of corrosion current density, Tafel slopes, and pitting potentials through the Stern–Geary relationship. Electrochemical noise analysis detects spontaneous current and potential fluctuations sensitive to localized corrosion events such as metastable pit growth. Cyclic voltammetry has been increasingly recognized as a dynamic, versatile technique providing real-time insights into redox-active processes, enabling investigation of both anodic and cathodic processes across a defined potential range.

The integration of electrochemical characterization with advanced data analytics represents a transformative paradigm shift. Machine learning approaches have demonstrated exceptional capabilities for corrosion rate prediction and corrosion-type identification, with hybrid models achieving $R^2>0.99$ prediction accuracy through integration of swarm intelligence optimization with deep learning architectures. However, challenges persist in data standardization, model interpretability, and field deployment. This comprehensive review aims to synthesize current knowledge on electrochemical characterization techniques for corrosion processes, systematically examining their principles, applications, data interpretation strategies, and emerging trends in predictive modeling.

Literature Review

Historical Foundations and Evolution of Electrochemical Corrosion Characterization:

The application of electrochemical methods to corrosion science traces its origins to the early work of Faraday, who established the fundamental principles governing electrode reactions and charge transfer. The recognition that corrosion proceeds through electrochemical half-reactions anodic oxidation and cathodic reduction provided the foundation for developing quantitative characterization techniques. The introduction of the Nernst equation and the establishment of potential-pH diagrams by Pourbaix enabled thermodynamic prediction of corrosion susceptibility, while kinetic studies led to the development of polarization techniques for measuring corrosion rates.

The late 20th century witnessed significant advances in electrochemical instrumentation, enabling sophisticated characterization techniques. Electrochemical impedance spectroscopy (EIS) was first applied to reinforced concrete corrosion diagnosis in the late 1970s, with the impedance response known to be sensitive to the corrosion state of reinforcement. Theoretical and empirical studies established appropriate measurement configurations and the ability to detect localized corrosion, improving analysis accuracy. Concurrently, linear polarization resistance (LPR) emerged as a widely adopted method for corrosion rate estimation, relying on the Stern-Geary relationship to convert polarization resistance to corrosion current density.

The development of electrochemical noise (EN) analysis represented a significant advance, enabling investigation of spontaneous current and voltage fluctuations in a three-electrode setup. Different types of corrosion processes can be recognized through EN analysis: uniform corrosion rate can be evaluated by estimating polarization resistance between the metal and electrolyte, while local corrosion events such as passive layer breakdown produce characteristic transients observable in noise. Cyclic voltammetry, historically underutilized in corrosion science due to the irreversible nature of corrosion reactions, has gained renewed attention as a mechanistic probe capable of capturing real-time redox activity and surface transformations.

The past decade has seen transformative advances through integration of electrochemical characterization with computational and data-driven approaches. Four-dimensional impedance analysis has emerged for time-varying systems, enabling instantaneous impedance determination during non-stationary corrosion processes. Machine learning applications have expanded dramatically, with algorithms including artificial neural networks, support vector regression, and ensemble learning applied to predict corrosion rates from multivariate electrochemical and environmental datasets. Data-driven models can reproduce current density evolution, mass loss behavior, and other electrochemical indicators with improved accuracy compared to traditional empirical relations while revealing mechanistic patterns.

Fundamental Principles of Electrochemical Corrosion Characterization:

Electrochemical characterization techniques are grounded in the fundamental principles governing electrode reactions, charge transfer kinetics, and mass transport. In aqueous corrosion systems, four essential components anode, cathode, metallic conductor, and electrolyte are required for corrosion to occur. The anodic reaction involves metal dissolution ($M \rightarrow M^{n+} + ne^-$), releasing electrons that travel through the metallic conductor to the cathode, where reduction reactions such as hydrogen evolution ($2H^+ + 2e^- \rightarrow H_2$) or oxygen reduction ($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$) consume electrons. The electrochemical double layer at the metal electrolyte interface governs charge transfer processes and is influenced by ion concentration, pH, and surface heterogeneity.

The thermodynamic framework for corrosion characterization is established through the Nernst equation and Pourbaix diagrams, enabling prediction of corrosion spontaneity and identification of passivation, immunity, and corrosion regions. Kinetic analysis of electrochemical reactions is governed by activation polarization, concentration polarization, and ohmic resistance. The Butler-Volmer equation relates current density to overpotential, while Tafel analysis provides kinetic parameters essential for corrosion rate estimation. The Stern–Geary relationship (icorr=β_aβ_c/ [2.303 Rp (β_a+β_c)]) enables conversion of polarization resistance (Rp) to corrosion current density (icorr), though this relationship assumes quasi-linear behavior near the corrosion potential and well-defined Tafel slopes.

The concept of passivity spontaneous formation of thin oxide films (1-10 nm) that dramatically reduce corrosion rates has attracted substantial research attention. Passive films act as physical barriers to ion transport and electron transfer, reducing corrosion rates by orders of magnitude compared to active dissolution. However, passive films are susceptible to localized breakdown in aggressive environments containing chloride ions, leading to pitting, crevice corrosion, and stress corrosion cracking. Electrochemical characterization techniques are essential for probing passive film stability, breakdown mechanisms, and protective performance of coatings and inhibitors.

Classification and Applications of Electrochemical Characterization Techniques:

The diversity of electrochemical characterization techniques reflects the complexity of corrosion phenomena and the need for complementary approaches. Potentiodynamic polarization (PDP) is one of the most commonly used direct current (DC) methods in corrosion measurements, involving scanning the potential of the working electrode while measuring the corresponding current density. The polarization curve provides corrosion potential (Ecorr), corrosion current density (icorr), and Tafel anodic/cathodic slopes through Tafel extrapolation. The advantage of PDP is evident in the ability to detect localized corrosion, rapid determination of corrosion rate, and assessment of corrosion protection effectiveness. However, the technique is quite damaging and cannot be used for online corrosion monitoring, especially in field studies.

Electrochemical impedance spectroscopy (EIS) is widely regarded as the most versatile technique for corrosion characterization, providing frequency-dependent information on interfacial processes. EIS measurements are performed over a range of frequencies, typically from 100 kHz to 10 mHz, and the impedance response is represented as Nyquist and Bode plots. Key parameters extracted include charge transfer resistance (Rct), double-layer capacitance (Cdl), film resistance (Rf), and diffusion-related elements. EIS has been successfully applied to reinforced concrete corrosion diagnosis, where the impedance response is sensitive to the corrosion state of the reinforcement. However, challenges persist in accurate relation of impedance response to physical characteristics of the system, with factors such as nonuniform current distribution and measurement configuration affecting data interpretation.

Cyclic voltammetry (CV) has emerged as a powerful mechanistic probe for corrosion research, capturing real-time redox activity and surface transformations. Unlike static methods, CV enables investigation of both anodic and cathodic processes across a defined potential range, revealing reaction reversibility, surface passivation, intermediate formation, and kinetic parameters through characteristic current potential profiles. The shape, symmetry, and current magnitude of voltammograms encode critical information about the coating–electrolyte interface and underlying metal activity. CV has been used to study oxidation of steel in chloride-containing environments, inhibition behavior of organic molecules on copper, and evaluation of self-healing coatings. However, CV interpretation can be complex and sensitive to scan rate, potential window, and electrolyte composition, and historically saw limited use among corrosion scientists because most corrosion reactions are not readily reversible.

Electrochemical noise (EN) analysis involves observation of spontaneous current and voltage fluctuations in a three-electrode setup. Uniform corrosion rate can be evaluated by estimating polarization resistance between the metal and electrolyte, while local corrosion events (e.g., passive layer breakdown) that produce characteristic transients can be detected. EN analysis is particularly valuable for non-stationary systems and field applications where controlled polarization is impractical. Advances in signal processing algorithms have enhanced EN analysis capability for corrosion-type identification.

Data Interpretation and Modeling Approaches:

Data interpretation remains one of the most challenging aspects of electrochemical corrosion characterization, requiring integration of theoretical models, empirical observations, and computational approaches. Equivalent circuit models are widely used to interpret EIS data, representing the electrochemical system as an electrical circuit composed of resistors, capacitors, and other elements corresponding to physical processes. However, equivalent circuit selection is not unique, and distinct models can reproduce the same impedance response, creating identifiability and interpretation ambiguities. Advanced physical models including point defect models (PDM), electrochemical kinetic models, and power-law models (PLM) have been developed to relate impedance parameters to physical properties such as oxide film thickness, defect density, and resistivity distribution.

Machine learning has emerged as a transformative approach for electrochemical data interpretation, enabling quantitative interpretation of complex electrochemical responses involving interactions among environmental variables, alloy composition, and surface chemistry. ML applications in corrosion include corrosion rate prediction from multivariate electrochemical and environmental datasets, and corrosion-type identification through analysis of electrochemical noise data, in situ images, and microscopy-based measurements. The SSA-CNN-BiGRU hybrid framework, combining swarm intelligence optimization (SSA) with convolutional neural networks (CNN) for feature extraction and bidirectional gated recurrent units (BiGRU) for temporal dependency capture, has achieved $R^2=0.99165$ for corrosion rate forecasting. However, a central debate persists regarding whether models trained on limited electrochemical conditions can generalize to new regimes, addressed through hybrid approaches incorporating physics-informed parameters that enhance interpretability and improve extrapolation.

Advanced data-driven approaches include integration of density functional theory (DFT), molecular dynamics (MD), and machine learning for smart corrosion inhibitor design. DFT provides quantum-level insight into electronic structure and adsorption energetics, MD captures time-dependent interfacial behavior, and ML enables data-driven prediction and high-throughput screening. Four-dimensional impedance analysis enables instantaneous impedance determination during non-stationary corrosion processes, with the impedance plotted on a three-dimensional complex impedance plot composed of real, imaginary, and time axes. The 3D impedance plots enable identification of time-dependent variations in oxide film resistance and charge transfer resistance, providing insights into dissolution and oxide film formation dynamics.

Methodology

This comprehensive review was developed through systematic analysis of peer-reviewed literature indexed in major scientific databases including Scopus, Web of Science, ScienceDirect, PubMed, and Google Scholar. The search strategy employed combinations of keywords including "electrochemical characterization," "corrosion," "electrochemical impedance spectroscopy," "cyclic voltammetry," "potentiodynamic polarization," "electrochemical noise," "machine learning corrosion," "corrosion monitoring," "data interpretation," and related terms. Particular emphasis was placed on studies published between 2015 and 2026, while seminal earlier works were included were mechanistically or historically significant.

The literature screening process involved identification of peer-reviewed research articles, review papers, and industry reports. Studies were selected based on relevance to the review scope, methodological rigor, completeness of reported experimental conditions, mechanistic significance, and applicability to industrial contexts. Representative studies for comparative analysis were chosen based on clear presentation of experimental methodology, characterization results, and performance metrics. Publications lacking sufficient methodological detail or quantitative performance data were excluded. Priority was given to studies examining fundamental electrochemical mechanisms, technique applications across diverse systems, and emerging computational approaches for data interpretation.

Quantitative data synthesis focused on electrochemical parameters including corrosion current density (icorr), polarization resistance (Rp), charge transfer resistance (Rct), double-layer capacitance (Cdl), Tafel slopes (β_a, β_c), and prediction accuracy metrics (R^2values). Performance metrics were extracted and analyzed where available. For machine learning applications, specific attention was given to reported prediction accuracy, model architectures, and validation approaches. For advanced impedance techniques, 4D analysis capabilities and parameter extraction methodologies were evaluated.

Electrochemical principles and analysis drew upon established frameworks including the Stern-Geary relationship, Butler-Volmer kinetics, and equivalent circuit modeling approaches. Thermodynamic considerations incorporated Nernst equation and Pourbaix diagram principles. Data interpretation strategies were evaluated based on their theoretical foundations, practical applicability, and limitations for different corrosion systems. Environmental and industrial context considerations were examined through analysis of application case studies across oil and gas, marine, infrastructure, and coating sectors.

Results

Table 1. Comparative Performance of Electrochemical Characterization Techniques for Corrosion Studies

Technique	Principle	Key Parameters	Advantages	Limitations	Development Status
Potentiodynamic Polarization (PDP)	Potential scan; current measurement	Ecorr, icorr, β_a, β_c	Rapid corrosion rate determination; localized corrosion detection	Destructive; cannot be used for online monitoring	Mature
Linear Polarization Resistance (LPR)	Small potential perturbation near Ecorr	Rp, icorr	Rapid, non-destructive	Stern–Geary assumptions; under-represents localized corrosion	Mature
Electrochemical Impedance Spectroscopy (EIS)	Frequency-domain AC response	Rct, Cdl, Rf, diffusion elements	Mechanistic insights; non-destructive	Interpretation challenges; non-unique equivalent circuits	Mature
Cyclic Voltammetry (CV)	Potential cycling; redox probing	Peak currents/potentials; reversibility	Real-time redox activity; surface transformations	Complex interpretation; irreversible systems	Emerging
Electrochemical Noise (EN)	Spontaneous potential/current fluctuations	Noise resistance; localization index	Non-perturbing; localized event detection	Interpretation complexity; data analysis requirements	Commercial
AC/DC/AC Method	Accelerated cyclic electrochemical testing	Coating impedance degradation	Rapid degradation simulation; predictive capability	Protocol standardization challenges	Emerging Commercial
4D Impedance Analysis	Time-varying impedance measurement	Instantaneous impedance; parameter evolution	Non-stationary system analysis	Complex data analysis; specialized instrumentation	Research

Data compiled from references.

Analysis of Table 1: The comparative analysis reveals that each electrochemical technique offers distinct advantages and limitations for corrosion characterization, necessitating complementary approaches for comprehensive assessment. Potentiodynamic polarization and LPR are mature techniques widely adopted for rapid corrosion rate determination, though their limitations destructive nature for PDP and Stern-Geary assumptions for LPR constrain applicability for field monitoring. EIS is the most versatile technique, providing frequency-dependent mechanistic insights through charge transfer resistance, double-layer capacitance, and diffusion elements, though interpretation challenges persist due to non-unique equivalent circuit selection and extrinsic effects mistaken for physical features.

Cyclic voltammetry has transitioned from an underutilized technique to an emerging mechanistic probe, with the shape, symmetry, and current magnitude of voltammograms encoding critical information about coating-electrolyte interfaces and underlying metal activity. Its ability to capture real-time redox activity and surface transformations complements conventional methods, though complex interpretation and sensitivity to experimental parameters present challenges. Electrochemical noise analysis offers unique non-perturbing detection of localized corrosion events through spontaneous current and voltage fluctuations, with advanced signal processing algorithms enhancing corrosion-type identification capability. The AC/DC/AC method represents an emerging accelerated testing approach, enabling rapid coating degradation simulation and performance prediction, though protocol standardization remains challenging. Four-dimensional impedance analysis represents the forefront of research development, enabling time-varying impedance characterization for non-stationary systems, though specialized instrumentation and complex data analysis constrain widespread adoption.

Table 2. Data Interpretation Approaches and Modeling Frameworks

Interpretation Method	Theoretical Basis	Application	Key Parameters	Advantages	Limitations
Equivalent Circuit Modeling	Electrical analog representation	EIS data fitting	R_s, Rct, Cdl, W	Intuitive; standardized	Non-unique solutions; physical ambiguity
Tafel Extrapolation	Butler-Volmer kinetics	Polarization data	β_a, β_c, i_corr	Standardized; rapid	Large overpotential required; surface alteration
Point Defect Model (PDM)	Defect transport in oxide films	Passive film characterization	Film thickness; defect density	Mechanistic insight	Complex; system-specific
Power-Law Model (PLM)	Transmission-line analogy	Coating/oxide film analysis	Resistivity distribution	Physical interpretation	Model assumptions
4D Impedance Analysis	Time-dependent impedance	Non-stationary systems	Instantaneous impedance; parameter evolution	Time-varying analysis	Specialized instrumentation
Machine Learning (ML)	Data-driven pattern recognition	Corrosion rate prediction; type classification	Multiple features; R^2 accuracy > 0.99	Nonlinear capture; high-throughput	Data dependency; generalization challenges
Hybrid ML-Physics	Combined data mechanistic models	Corrosion prediction	Physics-informed parameters	Improved generalization	Model complexity

Data compiled from references.

Analysis of Table 2: The diversity of data interpretation approaches reflects the complexity of electrochemical corrosion data and the need for multi-faceted analysis. Equivalent circuit modeling remains the most widely used EIS interpretation method, providing intuitive electrical analog representation of interfacial processes, though non-unique solutions create identifiability ambiguities. Tafel extrapolation enables rapid corrosion current determination through Stern-Geary relationship application, though large overpotential requirements and surface alteration effects limit applicability for passive systems. Advanced physical models point defect model, power-law model provide mechanistic insights into oxide film properties, including thickness, defect density, and resistivity distribution, though complexity and system-specific assumptions constrain widespread adoption.

Four-dimensional impedance analysis enables time-varying characterization for non-stationary systems, with 3D complex impedance plots composed of real, imaginary, and time axes enabling determination of instantaneous impedance at arbitrary times. This approach provides unique insights into dissolution and oxide film formation dynamics, though specialized instrumentation and complex data analysis limit current adoption to research applications. Machine learning has emerged as a transformative approach, with data-driven models capable of capturing nonlinear interactions among environmental variables, alloy composition, and surface chemistry. Hybrid ML-physics approaches integrating data-driven and mechanistic models offer improved generalization beyond the original training domain through physics-informed parameters and structural constraints, addressing the central debate regarding model generalization.

Table 3. Applications of Electrochemical Characterization in Corrosion Research

Application Area	Primary Techniques	Key Findings	Performance Metrics	Challenges	Development Status
Reinforced Concrete Corrosion	EIS, LPR	Impedance response sensitive to corrosion state	Rct, Cdl variation	Nonuniform current distribution; field deployment	Commercial/Research
Organic Coatings Evaluation	EIS, AC/DC/AC	Coating degradation and self-healing capability	Coating impedance; low-frequency impedance	Long-term performance prediction	Commercial/Emerging
Corrosion Inhibitor Assessment	PDP, EIS, CV	Inhibition efficiency; adsorption mechanisms	icorr reduction; Rct increase; peak analysis	Temperature/ flow effects; performance variability	Research/Commercial
Nanostructured Coatings	EIS, PDP, local probes	Nanomaterial barrier enhancement; self-healing	Charge transfer resistance; coating capacitance	Durability; scalability	Research
Microbiologically Influenced Corrosion	EIS, EN	Biofilm effects on corrosion	Localized corrosion detection; impedance variation	Detection; field application	Research
Marine/Offshore Corrosion	EIS, PDP, EN	Chloride effects; pitting susceptibility	Pitting potential; passive film resistance	Environmental variability	Commercial/Research
Additive Manufacturing	EIS, 4D Impedance	Unique microstructures; oxide film dynamics	Instantaneous impedance; parameter evolution	Non-stationary analysis	Research
Smart Corrosion Monitoring	ML-Integrated EIS/EN/Imaging	Predictive modeling; pattern recognition	$R^2 > 0.99$ prediction accuracy	Data quality; model validation	Emerging

The application landscape reveals that electrochemical characterization techniques are deployed across diverse corrosion contexts, each presenting unique challenges and performance requirements. Reinforced concrete corrosion diagnosis has advanced substantially since EIS introduction in the 1970s, with the impedance response known to be sensitive to reinforcement corrosion state, though challenges persist in nonuniform current distribution and field deployment. Organic coatings evaluation benefits from EIS and the accelerated AC/DC/AC method, enabling rapid degradation simulation and self-healing capability assessment. Corrosion inhibitor assessment employs multiple techniques PDP, EIS, CV with each providing complementary insights into inhibitor efficiency and adsorption mechanisms. Nanostructured coatings evaluation through EIS and PDP reveals barrier enhancement and self-healing capabilities, though durability and scalability challenges persist. Microbiologically influenced corrosion detection employs EIS and electrochemical noise for biofilm effect characterization, with localized corrosion detection capability essential for oil and gas applications. Marine and offshore corrosion characterization addresses chloride effects and pitting susceptibility through EIS, PDP, and EN, with environmental variability presenting substantial challenges. Additive manufacturing corrosion studies leverage EIS and emerging 4D impedance analysis, enabling investigation of unique microstructures and oxide film formation dynamics. Smart corrosion monitoring integrating machine learning with electrochemical data achieves exceptional prediction accuracy ($R^2>0.99$), though data quality and model validation remain critical challenges.

Table 4. Machine Learning Applications for Corrosion Prediction and Classification

ML Approach	Data Type	Prediction Target	Performance Metric	Key Advantages	Limitations
Random Forest	Environmental + electrochemical	Corrosion rate	$R^2=0.89$	Feature importance; interpretable	Requires labeled data
Support Vector Regression	Multivariate corrosion data	Corrosion current density	Strong predictive performance	High-dimensional performance	Parameter selection
Artificial Neural Networks	Electrochemical + environmental	Corrosion behavior	Good experimental trend agreement	Complex pattern capture	High data requirements
CNN-BiGRU Hybrid	Time-series electrochemical	Corrosion rate forecasting	$R^2=0.99165$; RMSE=0.01283	Temporal + spatial features	Complex architecture
Supervised/Unsupervised Learning	Electrochemical noise; images	Corrosion type identification	>98% detection accuracy	Automated classification	Data quality dependency
Physics-Informed ML	Hybrid (data + mechanistic)	Corrosion rate prediction	Improved generalization	Physical interpretability	Model complexity
Generative Design Framework	DFT + MD + ML	Corrosion inhibitor discovery	Predictive screening	Accelerated discovery	Data scarcity

Machine learning applications in corrosion electrochemistry have demonstrated transformative capabilities for prediction, classification, and discovery. Random forest models trained on long-term exposure data achieve $R^2\approx0.89$ in predicting atmospheric corrosion rates, with built-in feature selection identifying dominant environmental factors consistent with classical corrosion science. Support vector regression and artificial neural networks have demonstrated strong predictive performance for forecasting steel corrosion in seawater and other environments, with early successes opening the door for extensive ML exploration. The CNN-BiGRU hybrid framework, combining swarm intelligence optimization with convolutional neural networks and bidirectional gated recurrent units, achieves exceptional $R^2=0.99165$ with RMSE=0.01283, effectively capturing nonlinear feature interactions and temporal dependencies.

Corrosion type identification through supervised and unsupervised learning analysis of electrochemical noise data, in situ images, and microscopy-based measurements enables automated recognition of uniform attack, pitting initiation, and deposit-controlled localized degradation with >98% detection accuracy. Physics-informed ML approaches incorporating electrochemical rate expressions and structural constraints address the central debate regarding model generalization, enhancing interpretability and improving extrapolation beyond original training domains. Integrated ML-DFT-MD frameworks for smart corrosion inhibitor design combine quantum-level electronic structure analysis, time-dependent interfacial dynamics, and data-driven prediction, though data scarcity, nonstandardized descriptor selection, and insufficient physical interpretability remain challenges. Future developments emphasize standardized open datasets, uncertainty-aware and physics-informed ML architectures, and generative design frameworks capable of coherently linking quantum chemistry, interfacial dynamics, and data-driven prediction.

Discussion

Fundamental Insights from Electrochemical Characterization:

The electrochemical framework for understanding corrosion provides robust foundations for characterization and prediction, with techniques enabling direct probing of anodic dissolution and cathodic reduction reactions governing material degradation. Thermodynamic approaches through Nernst equation and Pourbaix diagrams enable assessment of corrosion spontaneity and identification of passivation, immunity, and corrosion regions, while kinetic analysis reveals rate-determining processes. However, significant gaps persist in understanding corrosion under extreme conditions high temperature, high pressure, complex multiphase flow where conventional assumptions regarding electrode kinetics and diffusion processes may be violated.

Cyclic voltammetry has emerged as a powerful mechanistic probe, with its ability to capture real-time redox activity and surface transformations providing insights inaccessible to static methods. The shape, symmetry, and current magnitude of voltammograms encode critical information about coating-electrolyte interfaces and underlying metal activity, with careful interpretation enabling discrimination between capacitive and Faradaic behaviors. However, historical limitations due to corrosion irreversibility and complex interpretation have constrained adoption, with scan rate, potential window, and electrolyte composition effects requiring careful experimental design. Recent advances in electrode fabrication, data modeling, and integration with surface-sensitive methods (XPS, AFM, in situ spectroscopies) have amplified CV's role in identifying reaction intermediates and elucidating complex corrosion pathways.

Electrochemical impedance spectroscopy remains the most versatile technique, with frequency-dependent responses providing mechanistic insights into charge transfer, diffusion, and film formation processes. EIS analysis of passive metals and organic coatings through equivalent circuit models, point defect models, and power-law models enables extraction of oxide film thickness, defect density, and resistivity distribution. However, interpretation challenges persist, with factors influencing impedance response including nonuniform current distribution, measurement configuration, and system nonstationarity complicating accurate analysis. Four-dimensional impedance analysis represents a significant advance for time-varying systems, with 3D complex impedance plots enabling instantaneous impedance determination during non-stationary processes. Application to additively manufactured aluminum alloys reveal variations in oxide film resistance and charge transfer resistance attributed to dissolution and oxide film formation, providing unique insights into unique microstructure effects on corrosion resistance.

Performance and Limitations of Current Characterization Approaches:

The comparative analysis reveals that while electrochemical characterization techniques offer substantial capabilities for corrosion assessment, each faces significant limitations requiring continued methodological development. Potentiodynamic polarization provides rapid corrosion rate determination and localized corrosion detection capability, but the destructive nature and large overpotential requirements constrain application for online monitoring. LPR-based corrosion current estimation relies on Stern-Geary assumptions that may be violated in real service environments, and primarily reflects average uniform corrosion response, under-representing localized processes where active area is uncertain.

EIS interpretation challenges arise from non-unique equivalent circuit selection, where distinct models can reproduce the same impedance response, creating identifiability ambiguities. These difficulties are amplified under dynamic service conditions (wet-dry cycling, intermittent loading, coating degradation), where non-stationarity undermines the linear time-invariant assumptions underlying conventional small-signal EIS. The AC/DC/AC method addresses accelerated testing needs, enabling rapid coating degradation simulation and performance prediction, though gaps remain regarding optimal polarization potential and duration, leading to inconsistent data representation across studies.

Machine learning applications demonstrate exceptional potential yet face significant challenges in data quality, model validation, and generalization. A central debate persists regarding whether models trained on limited electrochemical conditions can generalize to new regimes, addressed through hybrid approaches incorporating physics-informed parameters. Many reported ML-based corrosion models remain fundamentally limited by data scarcity, nonstandardized descriptor selection, insufficient physical interpretability, and poor generalization across chemically diverse systems. Early ML applications show impressive in-sample accuracy but suffer from generalization failure, overfitting, and lack of mechanistic validation, significantly restricting utility for rational design.

Integration and Synergy: Toward Comprehensive Characterization:

The integration of complementary electrochemical techniques with advanced data analytics represents a transformative paradigm for corrosion characterization. Combined EIS and PDP enable correlation of steady-state kinetics with frequency-dependent processes, while CV provides dynamic redox insights. Four-dimensional impedance analysis integrated with conventional EIS enables time-varying characterization during non-stationary processes, with instantaneous impedance determination supporting mechanistic understanding of oxide film formation. Integration of electrochemical techniques with surface-sensitive methods SEM, XPS, AFM, in situ spectroscopies provides structural and chemical context for electrochemical observations.

Machine learning integration with electrochemical characterization offers particular promise for predictive monitoring and accelerated discovery. Physics-informed ML architectures incorporating electrochemical rate expressions and structural constraints enhance interpretability and improve generalization beyond original training domains. Integrated ML–DFT–MD frameworks combine quantum-level electronic structure analysis, time-dependent interfacial dynamics, and data-driven prediction for smart corrosion inhibitor design, though data standardization and model validation remain critical challenges. Generative design frameworks capable of coherently linking quantum chemistry, interfacial dynamics, and data-driven prediction represent the frontier of corrosion characterization and design.

Digital twin technologies, combining physical modeling with real-time electrochemical monitoring and predictive analytics, offer transformative potential for infrastructure integrity management. However, development of robust digital twins requires validation across diverse operational conditions, integration of multiple data streams, and calibration with field performance. The evolution toward predictive, data-driven corrosion management offers potential for significant cost reduction, improved safety, and extended asset life through condition-based maintenance frameworks.

Future Directions and Recommendations:

Future corrosion characterization research and practice should prioritize several interconnected areas. First, standardized testing protocols and data curation standards must be developed to enable meaningful comparison across studies and materials, incorporating field-relevant conditions including temperature cycling, flow effects, and multicomponent electrolytes. Second, fundamental understanding of corrosion under extreme conditions high temperature/pressure, multiphase flow, mixed corrosive species requires advancement through combined experimental and modeling approaches, with 4D impedance analysis offering a pathway for time-varying characterization.

Third, machine learning integration should advance toward physics-informed, interpretable architectures that combine data-driven prediction with mechanistic understanding. Standardized open datasets, explicit solvation and interfacial modeling, uncertainty-aware ML, and generative design frameworks capable of coherently linking quantum chemistry, interfacial dynamics, and data-driven prediction are essential requirements. Fourth, advancement of monitoring technologies toward real-time, predictive systems, integrated with AI and digital twins, enables proactive maintenance and optimization.

Fifth, development of circular-economy-compatible characterization approaches emphasizing non-destructive, environmentally benign, and sustainable monitoring should be prioritized. Sixth, interdisciplinary collaboration across materials science, electrochemistry, data science, and industrial engineering is essential to address complex, multifaceted challenges of corrosion characterization in modern infrastructure. The integration of magnetic and electrochemical monitoring techniques as complementary non-destructive evaluation methods offers particular promise for more robust condition-based maintenance frameworks.

Conclusion

This comprehensive review has systematically examined electrochemical characterization techniques for corrosion processes, spanning fundamental principles to predictive modeling. Corrosion imposes annual global costs estimated at USD 6 trillion, driving urgent need for reliable diagnostic tools to monitor and understand electrochemical pathways governing material degradation. Electrochemical characterization techniques potentiodynamic polarization, linear polarization resistance, electrochemical impedance spectroscopy, cyclic voltammetry, and electrochemical noise provide complementary insights into corrosion thermodynamics, kinetics, and mechanisms.

EIS has emerged as the most versatile technique, providing frequency-dependent information on charge transfer resistance, double-layer capacitance, and diffusion processes, with applications from reinforced concrete diagnosis to nanostructured coating evaluation. CV has gained recognition as a powerful mechanistic probe, capturing real-time redox activity and surface transformations through characteristic current-potential profiles. EN analysis enables non-perturbing detection of localized corrosion events, with advanced signal processing enhancing classification capability.

Machine learning integration has revolutionized data interpretation, with hybrid models achieving $R^2>0.99$ prediction accuracy for corrosion rate forecasting through integration of swarm intelligence optimization with deep learning architectures. Data-driven models can reproduce current density evolution, mass loss behavior, and other electrochemical indicators with improved accuracy compared to traditional empirical relations while revealing mechanistic patterns. Physics-informed ML approaches incorporating electrochemical rate expressions and structural constraints address generalization challenges.

Four-dimensional impedance analysis enables time-varying characterization for non-stationary systems, with 3D complex impedance plots enabling instantaneous impedance determination during dissolution and oxide film formation. Application to additively manufactured aluminum alloys reveal unique microstructure effects on corrosion resistance, advancing understanding of corrosion mechanisms in emerging materials.

Despite substantial progress, challenges persist in data standardization, model validation, field deployment, and interdisciplinary integration. Future research should prioritize standardized testing protocols, fundamental understanding under extreme conditions, advancement of physics-informed ML architectures, real-time predictive monitoring, and interdisciplinary collaboration. With continued innovation, electrochemical characterization techniques offer transformative potential for corrosion management, reducing infrastructure costs and environmental impacts while extending asset service life.

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Authors' Contributions

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