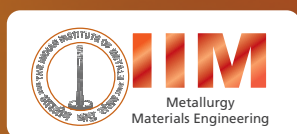


Indian Institute of Metals Series

U. Kamachi Mudali · Toleti Subba Rao ·  
S. Ningshen · Radhakrishna G. Pillai ·  
Rani P. George · T. M. Sridhar *Editors*

# A Treatise on Corrosion Science, Engineering and Technology



 Springer

# Indian Institute of Metals Series

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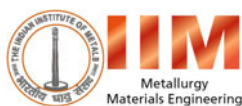
The study of metallurgy and materials science is vital for developing advanced materials for diverse applications. In the last decade, the progress in this field has been rapid and extensive, giving us a new array of materials, with a wide range of applications, and a variety of possibilities for processing and characterizing the materials. In order to make this growing volume of knowledge available, an initiative to publish a series of books in Metallurgy and Materials Science was taken during the Diamond Jubilee year of the Indian Institute of Metals (IIM) in the year 2006. Ten years later the series is now published in partnership with Springer.

This book series publishes different categories of publications: textbooks to satisfy the requirements of students and beginners in the field, monographs on select topics by experts in the field, professional books to cater to the needs of practicing engineers, and proceedings of select international conferences organized by IIM after mandatory peer review. The series publishes across all areas of materials sciences and metallurgy. An eminent panel of international and national experts acts as the advisory body in overseeing the selection of topics, important areas to be covered, and the selection of contributing authors.

More information about this series at <https://link.springer.com/bookseries/15453>

U. Kamachi Mudali · Toleti Subba Rao ·  
S. Ningshen · Radhakrishna G. Pillai ·  
Rani P. George · T. M. Sridhar  
Editors

# A Treatise on Corrosion Science, Engineering and Technology



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*This compendium of articles was released on the occasion of superannuation of Dr. U. Kamachi Mudali, Formerly, Distinguished Scientist, Chairman and Chief Executive of Heavy Water Board, DAE on 30 September 2020. The articles presented in this book are contributed by his associates/colleagues/students in the area of Corrosion Science, Technology and Engineering to honour him.*

# Foreword

The success towards prevention of failures of industrial components lies in the efficient management of corrosion processes through regular inspection, understanding of the corrosion processes and mitigation through effective corrosion prevention technologies. In the present era, corrosion prevention and control is one of the main global challenges irrespective of the industrial sectors where metals and alloys are employed. However, most practising corrosion engineers and material scientists were unable to understand the complex phenomena of corrosion which is interdisciplinary in nature. Many new materials and alloy combinations were produced, fabricated into components and tested for their performance; however, still the problem of corrosion is an enigmatic issue. I had the worthy opportunity to go through the contents of the this book on 'A Treatise in Corrosion Science, Engineering and Technology', which was compiled as 'A Commemorative Volume' to honour and recognize the three decades of yeoman contributions and service to the department and nation in the area of corrosion science and technology by Dr. U. Kamachi Mudali, who is my senior colleague at the Department of Atomic Energy.

This unique volume presents an updated overview of the essential aspects of corrosion science and engineering that underpin the tools and technologies used in understanding the mechanism of corrosion, which enhances reliability, and prevent failures. Although there are many books on corrosion, the basic organization of the book reflects the experiences of the contributing authors in their field of expertise. I am overwhelmed with the response of the authors who have put in their valuable research outcome in this treatise. I am happy to note that most of the authors are colleagues, associates and students of Dr. U. Kamachi Mudali who have worked or interacted with him over the last three decades.

The authors have complemented their subject of discussion with numerous examples to help illustrate important findings in corrosion and prevention and control. This enables the readers clearly to fully understand the science of corrosion and its control and, in turn, help reduce the massive economic and environmental losses. The commemorative volume is a must read for postgraduates and students of materials science and engineering, as well as for practising engineers, technologists and researchers, who need information on this industrially relevant subject. I foresee

this corrosion treatise with information on corrosion prevention and control with coverage of the latest developments in the field, including advances in theory and mechanism, new alloys and materials, industrial experience and practical solutions in response to public demand. I wish being a practising engineer in the design of critical components for nuclear industry that the authors must continue their endeavour and interest in corrosion science and engineering and suggest the practising engineers and technologists to follow the cardinal principle in corrosion prevention and control and save our industrial assets for future generations.

K. N. Vyas  
Chairman, Atomic Energy  
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# Series Editor's Preface

The Indian Institute of Metals Series is an institutional partnership series focusing on metallurgy and materials science and engineering.

## About the Indian Institute of Metals

The Indian Institute of Metals (IIM) is a premier professional body (since 1947) representing an eminent and dynamic group of metallurgists and materials scientists and engineers from R&D institutions, academia, and industry, mostly from India. It is a registered professional institute with the primary objective of promoting and advancing the study and practice of the science and technology of metals, alloys, and novel materials. The institute is actively engaged in promoting academia–research and institute–industry interactions.

## Genesis and History of the Series

The study of metallurgy and materials science and engineering is vital for developing advanced materials for diverse applications. In the last decade, the progress in this field has been rapid and extensive, giving us a new array of materials, with a wide range of applications and a variety of possibilities for processing and characterizing the materials. In order to make this growing volume of knowledge available, an initiative to publish a series of books in metallurgy and materials science and engineering was taken during the Diamond Jubilee year of the Indian Institute of Metals (IIM) in the year 2006. IIM entered into a partnership with Universities Press, Hyderabad, and, as part of the IIM book series, 11 books were published, and a number of these have been co-published by CRC Press, USA. The books were authored by eminent professionals in academia, industry, and R&D with outstanding background in their respective domains, thus generating unique resources of validated expertise

of interest in metallurgy. The international character of the authors' and editors has enabled the books to command national and global readership. This book series includes different categories of publications: textbooks to satisfy the requirements of undergraduates and beginners in the field, monographs on selected topics by experts in the field, and proceedings of selected international conferences organized by IIM, after mandatory peer review. An eminent panel of international and national experts constitutes the advisory body in overseeing the selection of topics, important areas to be covered, in the books and the selection of contributing authors.

## **Current Series Information**

To increase the readership and to ensure wide dissemination among global readers, this new chapter of the series has been initiated with Springer in the year 2016. The goal is to continue publishing high-value content on metallurgy and materials science and engineering, focusing on current trends and applications. So far, four important books on state of the art in metallurgy and materials science and engineering have been published and, during this year, three more books are released during IIM-ATM 2021. Readers who are interested in writing books for the Series may contact the Series Editor-in-Chief, Dr. U. Kamachi Mudali, Former President of IIM and Vice Chancellor of VIT Bhopal University at [ukmudali1@gmail.com](mailto:ukmudali1@gmail.com), [vc@vitbhopal.ac.in](mailto:vc@vitbhopal.ac.in) or the Springer Editorial Director, Ms. Swati Meherishi at [swati.meherishi@springer.com](mailto:swati.meherishi@springer.com).

Dr. U. Kamachi Mudali  
Editor-in-Chief

# Preface

Corrosion is a disease to engineering materials and components just like a disease to human beings. Corrosion is defined as a degenerative process, wherein metals or alloys interact with an environment which can be liquid, gas or solid, resulting in chemical/electrochemical reactions that damage and degrade the properties leading to catastrophic failures. Accordingly, materials such as ceramics, plastics or concrete may well be subjected to degradation of their properties with time. Corrosion is described as an electrochemical process mainly due to the fact that the electron transfer reaction occurring during the metal–environment interactions determines the rate of corrosion process. It is entirely in this regard that the term corrosion is used in this book to describe the phenomenon of corrosion which manifests in various forms in different industrial applications. Nowadays than earlier, it is prudent to devote more attention to metallic corrosion, due to the following reasons: (a) a very significant increase in the use of metals and alloys in all fields of industry and technology, (b) the use of specialty and expensive metals/alloys in special applications, such as in atomic energy, aerospace and defence, whose preservation requires specific precautions, (c) a more aggressive environment required in industries for enhancing the efficiency of the processes, and (d) the use of metallic constructions of more thinner dimensions, which do not tolerate corrosive attacks to the same extent as did the heavy constructions used to tolerate. The book elaborates on the various corrosion processes in different applications and their prevention strategies. An interesting contribution that is getting importance in the recent past is the biological fouling and microbiologically induced corrosion, and the book has fair contribution in this interesting topic. This book will serve as a mini encyclopaedia of corrosion science and technology and relevant to everyone in the materials science field. Key features of this book are as follows:

- Comprehensive covering of the principles of corrosion, engineering issues, methods of corrosion protection and defines corrosion processes and control in select aggressive end industrial environments.

- The structure of the book is so designed that it caters to corrosion science and engineering students at master's and doctorate level, and is an ideal reference that readers want to use in their professional work from various types of industries.
- Corrosion issues in automobile, biomaterial, concrete, power plant, aerospace and atomic energy sectors have been covered. A special section on biologically assisted fouling and corrosion processes is also elaborated with the description of antifouling and anti-corrosion methods.

There are six parts in the book containing articles by specialists on varied topics on corrosion manifestation as well as on corrosion prevention strategies such as corrosion evaluation techniques (2 chapters), corrosion in nuclear industry (9 chapters), environmental corrosion (4 chapters), corrosion of special materials (7 chapters), biological fouling, microbial corrosion and biomaterials (6 chapters) and corrosion prevention strategies (12 chapters). The authors have provided lucid presentation of the topics with relevant figures and schematic illustrations.

In Part I on corrosion evaluation techniques, electrochemical impedance spectroscopy technique for corrosion study and analysis was explained in detail. Other article describes test protocols for corrosion testing by gravimetric methods in oil and gas industry.

Coming to Part II, on nuclear materials and corrosion, there are good articles on nitric acid corrosion issues, particularly for spent nuclear fuel reprocessing. Nitric acid corrosion issues of reprocessing plant materials and article on stainless steel materials, describing the limitations of stainless steel 304L and an alternate 304L NAG SS, Ti and Zr alloy materials for an aggressive nitric acid unit in reprocessing plants are included. Article on SS-316LN discusses the influence of metallurgical variables on the stress corrosion cracking phenomenon. The other article is on surface modification of titanium to improve its corrosion resistance in nitric acid medium. Apart from steels and titanium, Stellite is the other hardfacing material, wherein its typical corrosion in the primary system of the nuclear power plant was explained. Molten salt corrosion and material degradation and ageing management of heavy water plants are also provided with many details.

In environmental effects on corrosion studies Part III, mitigating environmentally assisted cracking in copper containing aluminium alloys was described. Besides, environmental effects on short-term and long-term failure analysis of engineering components were also provided. Corrosion and life assessment of concrete structures were dealt in detail, followed by an article on cement-based anticorrosive polymer coating on steel rebar for small-scale applications.

In Part IV on corrosion of special materials, advancement in titanium aluminide and its high-temperature oxidation behaviour and high-temperature oxidation and corrosion studies using thermal spray coatings is discussed. Corrosion as a monitoring tool in the development and airworthiness of select aluminium and magnesium aero grade alloys were elaborated in an interesting article. The other two articles were on corrosion behaviour of magnesium alloys and its mitigation by wet deposition methods and chemical conversion coatings for improved corrosion resistance of magnesium alloys.

Part V is on biological fouling, microbial corrosion and biomaterials. The first article is on microbially influenced corrosion, which was followed by marine biofouling process and corrosion monitoring of long-term marine structures. The other article was on advancements and modifications to polydimethylsiloxane antifouling coatings. This was followed by adhesion and anti-microbial performance of epoxy-based nanocomposite coatings and non-conventional methods for biofilm and biocorrosion control. Finally, in this section graphene oxide hybrid deposits on implant alloys for biomedical applications were described in detail and the recent developments in the inhibitor technology are elaborated.

Part VI is on corrosion prevention strategies, wherein many articles provide practical solutions for various corrosion issues. Corrosion protection of metals by electrodeposition of composition modulated multilayer coatings and erosion corrosion resistant coatings for seawater piping components is discussed. Polymer composite coatings and graphene oxide coatings to achieve remarkable corrosion resistance are interesting areas of research with promising applications. Corrosion protection of metals/alloys through multifunctional sol-gel nanocomposite coatings and the new generation self-healing coatings for active corrosion prevention is detailed.

Corrosion protection of 316L SS bipolar plates in proton exchange membrane fuel cells and assessment of dual-plating alloy composite coating for corrosion protection and metal surfaces with plasma-sprayed thermal barrier coating articles are worthy contributions. Corrosion prevention and surface engineering practices in automotive component industries were described lucidly. A holistic approach for export-oriented automotive component supply chain corrosion protection is an interesting article of industrial relevance. As an example of recent developments, an interesting article on bio-inspired multifunctional super-hydrophobic coatings for corrosion protection was also presented for the benefit of readers.

The present book is published by IIM-Springer Book Series in order to disseminate the extensive knowledge on corrosion and its prevention strategies to the metallurgical and corrosion community at large.

Bhopal, India  
Kalpakkam, India  
Kalpakkam, India  
Chennai, India  
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U. Kamachi Mudali  
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Radhakrishna G. Pillai  
Rani P. George  
T. M. Sridhar

# Contents

## Corrosion Evaluation Techniques

<b>EIS Technique for Corrosion Study and Analysis</b> .....	3
Ramanathan Srinivasan and Ranjith Punathil Meethal	

<b>Laboratory Test Protocols for Corrosion Testing in Upstream Oil Industry: Some Experiences in Using Gravimetric Methods</b> .....	21
Parvatalu Damaraju	

## Corrosion in Nuclear Industry

<b>Nitric Acid Corrosion Issues of Spent Fuel Nuclear Fuel Reprocessing Plants Materials</b> .....	43
S. Ningshen, R. Priya, and U. Kamachi Mudali	

<b>Limitations of 304L Stainless Steel and Exploring Alternate Materials for Aggressive Nitric Acid Service in Reprocessing Plants</b> ....	67
K. Chandra, Amrita Mahanti, Prafful Sinha, and Vivekanand Kain	

<b>Comparative Study on Surface Modification of Titanium for Improving Resistance to Corrosion in Nitric Acid Medium</b> .....	87
A. Ravi Shankar, N. S. Karthiselva, and U. Kamachi Mudali	

<b>Effect of Metallurgical Variables on the Stress Corrosion Cracking Behavior of AISI-Type 316LN Stainless Steel</b> .....	99
Anita Toppo	

<b>Electrochemical Impedance Studies on Corrosion of Stellite#6 in Permanganate-Based Decontamination Formulations</b> .....	113
Veena Subramanian, Sinu Chandran, and S. V. Narasimhan	

<b>Material Degradation and Ageing Management of Heavy Water Plants</b> .....	125
Niraj Kumar and U. Kamachi Mudali	

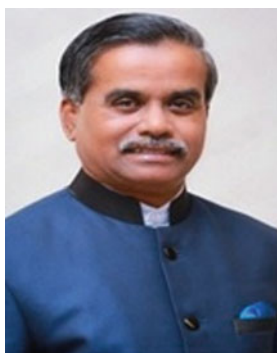
<b>Molten Salt Corrosion Behaviour of Graphite Materials</b> .....	143
Jagadeesh Sure and U. Kamachi Mudali	
<b>Structural Materials for Molten Salt Reactors</b> .....	169
Y. V. Harinath, T. V. Krishna Mohan, S. Rangarajan, and Shaju K. Albert	
<b>Electrochemical Corrosion Evaluation of Materials for Use in Chemical Treatment of Radioactive Liquid Effluent</b> .....	193
Sumathi Suresh, S. Rangarajan, A. G. Shanmugamani, Chitra Sengadhir, and Biplob Paul	
<b>Molten Salt Corrosion and Its Mitigation for Pyrochemical Reprocessing Applications</b> .....	205
Ch. Jagadeeswara Rao, S. Ningshen, and U. Kamachi Mudali	
<b>Environmental Corrosion</b>	
<b>Mitigating Environmentally Assisted Cracking in 7xxx Cu Containing Aluminum Alloys</b> .....	223
M. Ajay Krishnan and V. S. Raja	
<b>Environmental Effects on Short-Term and Long-Term Failures of Engineering Components</b> .....	237
P. Parameswaran, N. Sivai Bharasi, V. Thomas Paul, S. Chandra Mouli, M. Shanmugavel, and U. Kamachi Mudali	
<b>Corrosion and Service Life Assessment of Concrete Structures</b> .....	259
Deepak Kamde, Dyana Joseline, Sripriya Rengaraju, Jayachandran Karuppanasamy, and Radhakrishna G. Pillai	
<b>Cement Polymer Anticorrosive Coating on Steel Rebars: A Feasible Solution for Corrosion Prevention in Small Scale Projects</b> ...	277
M. S. Haji Sheik Mohammed and V. Roopa	
<b>Corrosion of Special Materials</b>	
<b>Advancement in Titanium Aluminide and its High Temperature Oxidation Behaviour</b> .....	295
Anupama Dutta, Andreas Weisheit, and Jyotsna Dutta Majumdar	
<b>Corrosion Behaviour of Magnesium Alloys and Chemical Conversion Coatings for their Improved Corrosion Resistance</b> .....	315
S. Arun Kumar, Jithu Jayaraj, and A. Srinivasan	
<b>Corrosion in the Development and Airworthiness Certification of Select Al and Mg Aerograde Alloys</b> .....	331
T. Ram Prabhu, Shirish S. Kale, and N. Eswara Prasad	

<b>Corrosion Behavior of Magnesium and Its Alloys and Mitigation by Wet Deposition Methods</b> .....	355
Charu Singh and Raghuvir Singh	
<b>Corrosion Prevention and Surface Engineering Practices in Auto-Components Industries</b> .....	369
E. Vignesh and T. Sundararajan	
<b>High-Temperature Oxidation and Hot Corrosion of Thermal Spray Coatings</b> .....	407
S. Milan Shahana, Srinivasa Rao Bakshi, and M. Kamaraj	
<b>Biological Fouling, Microbial Corrosion and Biomaterials</b>	
<b>A Review on Corrosion, Adhesion, and Anti-Microbial Performance of Epoxy-Based Nanocomposite Coatings</b> .....	423
S. S. Ananthapadmanabhan, Geetanjali Mishra, and Smrutiranjana Parida	
<b>Marine Biofouling and Corrosion on Long-Term Behavior of Marine Structures</b> .....	447
L. Vedaprakash, P. Senthilkumar, D. Inbakandan, and R. Venkatesan	
<b>Advancements and Modifications to Polydimethylsiloxane Foul Release Antifouling Coatings</b> .....	467
P. Sriyutha Murthy, V. P. Venugopalan, T. V. Krishna Mohan, Y. V. Nanchariah, Arindam Das, S. Venkatnarayanan, S. Sathya, and T. Subba Rao	
<b>Non-Conventional Methods for Biofilm and Biocorrosion Control</b> .....	513
B. Anandkumar, Rani P. George, and T. Subba Rao	
<b>Graphene Oxide Hybrid Coatings on Implant Alloys for Biomedical Applications</b> .....	537
J. Manovasuki, K. Aruna, Rani P. George, T. M. Sridhar, and U. Kamachi Mudali	
<b>Bio-Inspired Multifunctional Superhydrophobic Coatings for Corrosion Resistance</b> .....	559
Shalini Halan Joghee, Navami Sunil, Gokul Selvaraj, Kamachi Mudali Uthandi, and Biji Pullithadathil	
<b>Corrosion Prevention Strategies</b>	
<b>Corrosion Protection of Metals by Electrodeposition of Composition Modulated Multilayer Coatings</b> .....	579
Liju Elias and A. C. Hegde	
<b>Erosion–Corrosion-Resistant Coatings for Seawater Piping Components—A Review</b> .....	591
K. Sridhar and V. Balasubramanian	



<b>Polymer/Polymer Composite Coatings for the Corrosion Protection of Steel Substrates</b> .....	611
Suryakanta Nayak and Tapan Kumar Rout	
<b>Anti-Corrosion Studies of Polyindole and Copper Oxide–Polyindole Composites Prepared from Water–Methanol Binary Solvents in Highly Acidic and Saline Environments</b> .....	627
N. Aravindan, Subrata Mondal, S. Preethi, and M. V. Sangaranarayanan	
<b>Corrosion Protection of Metals/Alloys Through Multifunctional Sol–Gel Nanocomposite Coatings</b> .....	641
Swapnil H. Adsul, K. Pradeep Prem Kumar, S. Manasa, Aarti Gautam, K. V. Gobi, Shirish H. Sonawane, and R. Subasri	
<b>Self-Healing Coatings for Active Corrosion Protection: The Concept, Design, Evaluation and Challenges</b> .....	663
C. Arunchandran	
<b>Corrosion Protection of 316L SS Bipolar Plates in Proton-Exchange Membrane Fuel Cells: A Polyparaphenylenediamine Conducting Polymer Approach</b> .....	695
C. Shanmugham and N. Rajendran	
<b>Assessment of Corrosion Protection Behavior of Composite Coatings Developed Through Electro and Electroless Approach—A Review</b> .....	715
H. Usharani, T. S. N. Sankaranarayanan, K. M. Veerabadrn, and T. M. Sridhar	
<b>An Overview of Plasma-Sprayed Thermal Barrier Coating Activities in India</b> .....	733
P. G. Lashmi and S. T. Aruna	
<b>A Holistic Approach on Export Supply Chain Corrosion Protection of Auto-Components</b> .....	755
Venkatesh Kumar	
<b>Electrophoretically Deposited Al<sub>2</sub>O<sub>3</sub>-siloxane Nanocomposite Coating Stable up to 750 °C on Mild Steel for Improved Corrosion Resistance</b> .....	765
Sanjukta Dey, Bimal P. Singh, Shubhra Bajpai, Bikash K. Jena, Tapan K. Rout, Dilip K. Sengupta, and Laxmidhar Besra	
<b>Recent Trends in the Development of Corrosion Inhibitors</b> .....	783
M. A. Quraishi and Dheeraj Singh Chauhan	

## About the Editors



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# **Corrosion Evaluation Techniques**

# EIS Technique for Corrosion Study and Analysis



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## 1 Introduction

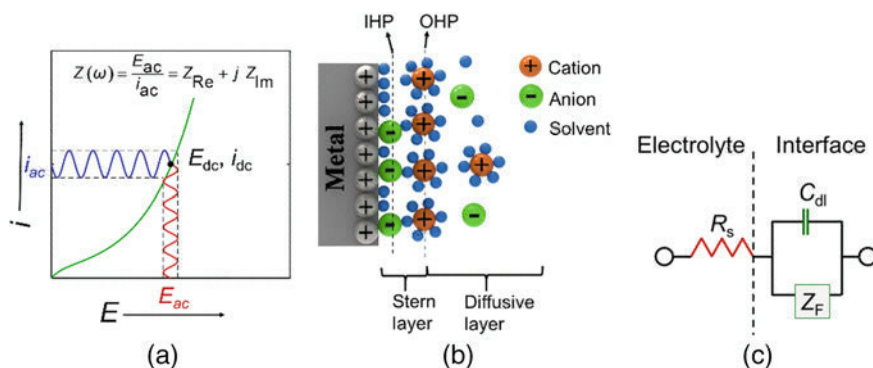
### 1.1 Electrochemical Impedance Spectroscopy (EIS)

EIS is a versatile AC technique used to characterize electrochemical processes [1–5]. Impedance ( $Z$ ) can be thought of as a generalized resistance and is the vector ratio of potential to current. Here, a sinusoidal potential of a given frequency is applied. When the amplitude of the applied potential is small, the response current is also sinusoidal (Fig. 1a). The ratio of the magnitude of potential to current is recorded as impedance magnitude, and the phase difference between the potential and current is recorded as the impedance phase. At a given frequency, for small amplitude perturbations, impedance is independent of the perturbation amplitude, and hence, linear system theory can be employed to analyze EIS data. The impedance has a magnitude that is always positive and a phase that is between 0 and 360°. For convenience, impedance is often expressed as a complex number in Cartesian coordinates. The impedance of a given system may vary with the frequency of the applied sine wave. This measurement can be repeated at several frequencies to obtain the impedance spectrum. A detailed introduction to the EIS technique is available in the literature [6, 7].

EIS is a very general technique that has a wide variety of applications and is particularly useful in understanding the detailed mechanism of electrochemical reactions [8]. A frequency range of several decades, usually spanning from a hundred kHz to a few milli-Hz, is used. EIS can help distinguish the contribution of each process to the overall response [3]. In any electrochemical system, several processes can contribute to the signal. A simplified schematic of an electrode–electrolyte interface is given in Fig. 1b. An electrode is polarized, with ions aligned to the electrode. If there is no

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**Fig. 1** a Current potential diagram, with AC perturbation superimposed over DC. b Pictorial of an electrified interface. c Equivalent electrical circuit

electrochemical reaction, such as corrosion, at the interface, then the interface can be modeled by a simple capacitor.

On the other hand, if a reaction occurs, an additional element, called faradaic impedance ( $Z_F$ ), is in parallel with the capacitor, as shown in Fig. 1c. If the electrode has a porous film, additional elements need to be included in the model. In some cases, the reaction may depend on the concentration of a chemical species that diffuses from (to) the bulk electrolyte to (from) the interface. Then, another element, known as Warburg impedance ( $W$ ), is required to model the diffusion process. In short, a circuit comprising electrical elements can be employed to model electrochemical systems, and this type of analysis is known as equivalent electrical circuit (EEC) analysis.

## 1.2 Graphical Representation of EIS Data

EIS data can be presented in Nyquist format, where the negative of the imaginary component ( $-Z_{Im}$ ) is plotted against the real component ( $Z_{Re}$ ), as shown in Fig. 2a, or in Bode format where the magnitude and phase are plotted against the frequency in logarithmic scale, as shown in Fig. 2b. The high-frequency limit represents the solution resistance ( $R_s$ ), and the low-frequency limit is denoted by ( $R_s + R_p$ ) where  $R_p$  is the polarization resistance. In the figure,  $R_t$  denotes the charge transfer resistance. These parameters are defined in the following sections.

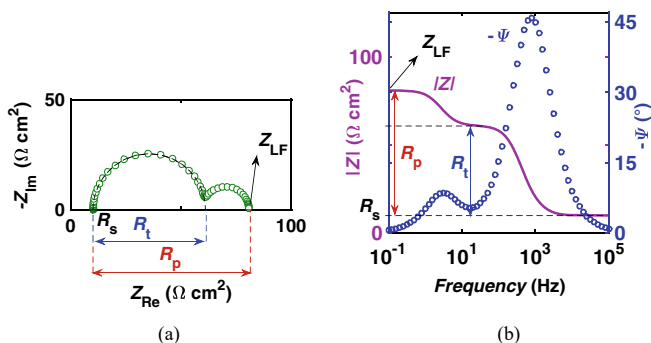


Fig. 2 a Nyquist and b Bode representation of impedance data. From [9], licensed under CC BY

## 2 Corrosion

In the context of a metal exposed to an aqueous environment, corrosion is essentially an electrochemical reaction [10–12]. Here, the metal is oxidized, and simultaneously, dissolved oxygen or hydrogen ion is reduced. Thus, electrochemical techniques are very appropriate to investigate corrosion processes [13, 14]. Various electrochemical techniques are available to deal with corrosion of metals, either to measure the corrosion rate or to understand the reaction mechanism involved in the corrosion process [15]. Traditional electrochemical techniques such as EIS, linear polarization (LP), and potentiodynamic polarization (PDP) can be used to understand the corrosion behavior of metals, alloys, and coatings. Among these traditional techniques, EIS and LP have the advantage of being nondestructive in nature but have the limitation that the corrosion parameters cannot be evaluated from these techniques. These two techniques can be used to evaluate  $R_p$ , which is a qualitative measure of the resistance of a material to corrosion. A few selected electrochemical techniques are used to estimate the corrosion rate of a particular metal or alloy in a given environment, and to evaluate the efficiency of corrosion inhibitors. Knowledge of the oxidation state of the metal after corrosion enables one to relate the corrosion rate, i.e., the loss in mass per unit exposed area per unit time, to a term called corrosion current density ( $i_{\text{corr}}$ ).

### 2.1 Electrochemical Techniques Used in Corrosion Studies

**Tafel extrapolation.** The classical electrochemical method used to estimate  $i_{\text{corr}}$  is potentiodynamic polarization (PDP) measurement, although new methods such as harmonic analysis [16–18] or electrochemical frequency modulation (EFM) [19] have also been proposed. When a metal dissolves in the aqueous medium, the cathodic



and anodic currents are equal, and hence the net current is zero. In PDP, the electrode is polarized with respect to the equilibrium conditions, and the current is recorded when stable results ensue. When the metal is held at cathodic potential, the cathodic processes are enhanced, the anodic processes are suppressed, and the cathodic processes dominate the total current. Likewise, under anodic conditions, anodic processes contribute substantially to the total current. The electrode potential is varied from cathodic to anodic values. From an analysis of the cathodic and anodic branch of the polarization results,  $i_{\text{corr}}$  is estimated using Tafel extrapolation or Tafel analysis.

Tafel extrapolation assumes that the cathodic and anodic processes are elementary steps and that the cathodic and anodic currents are exponentially related to the potential. These assumptions lead to the following model equation for the polarization curve.

$$i = i_{\text{corr}} \left( 10^{\frac{\eta}{\beta_a}} - 10^{\frac{-\eta}{\beta_c}} \right) = i_{\text{corr}} \left( e^{\frac{2.303 \times \eta}{\beta_a}} - e^{\frac{-2.303 \times \eta}{\beta_c}} \right) \quad (1)$$

Here,  $\beta_a$  and  $\beta_c$  are the anodic and cathodic Tafel slopes in units of V decade<sup>-1</sup> and  $\eta$  is the overpotential measured with respect to the open-circuit potential (OCP). Lower corrosion current densities imply less corrosion rate. Typically, a potential range of  $\pm 250$  mV versus OCP is employed, and typical run time ranges from 10 to 20 min.

From the above equation, we can calculate  $R_p$ , which is the ratio of a small change in overpotential to the corresponding change in the current response, when the overpotential is changed slowly.

$$R_p = [2.303 \times i_{\text{corr}} \times (\beta_a^{-1} + \beta_c^{-1})]^{-1} \quad (2)$$

The polarization resistance is essentially the resistance offered by the system to polarization, i.e., change the metal potential from the open-circuit potential. In an analysis of EIS data,  $R_p$  is written as [20]

$$R_p = \lim_{\omega \rightarrow 0} (Z_F) \quad (3)$$

That is, it is the faradaic impedance at the limit of zero frequency, as shown in Fig. 2. It may be noted that the expression in Eq. (3) is general and is applicable for any reaction, whereas the expression in Eq. (2) is valid only for elementary electrochemical reactions. Tafel extrapolation requires fitting the model equation to the data and is a well-established analysis for which several commercial and free software are available.

*Challenges in Tafel extrapolation.* Although Tafel extrapolation is the direct method to estimate  $i_{\text{corr}}$ , it is fraught with certain difficulties. Firstly, when the sample is polarized in the anodic direction, it is oxidized, and thus it is a destructive method. As such, it can be used only in the laboratory and not in the field. Secondly, the measured current profile may not be modeled adequately by Eq. (1). Often the

cathodic and anodic reactions are not elementary. Mass transport may play a role in the overall reaction rate. In those cases, Eq. (1) will not accurately describe the current potential relationship, and the estimated  $i_{\text{corr}}$  value may not predict the corrosion rate. Thirdly, Tafel extrapolation assumes that the solution resistance is negligible. When the solution is poorly conducting, neglecting  $R_s$  will lead to an incorrect estimation of  $i_{\text{corr}}$ ,  $\beta_a$ , and  $\beta_c$  [13]. Besides, the  $R_p$  obtained from Tafel extrapolation is actually the sum of  $R_s$  and  $R_p$  [21]. Finally, the analysis does not provide any insight into the corrosion process [13]. Thus, alternate techniques are sought to estimate the corrosion rate and to understand the corrosion process mechanism.

Techniques such as harmonic analysis [16–18] or EFM [19] are nondestructive and have been proposed to estimate  $i_{\text{corr}}$ . However, they also suffer from some of the shortcomings mentioned above, viz. the actual reactions may not be elementary,  $R_s$  may not be negligible, and detailed insight into the corrosion process is not obtained. If  $R_p$  and Tafel slopes are obtained by other means, then the corrosion current can be estimated. Often, the Tafel slope values are assumed [13] to be  $120 \text{ mV decade}^{-1}$ , and  $i_{\text{corr}}$  is estimated. Even without these assumptions, the  $R_p$  values of a corroding system with and without a corrosion inhibitor can be used to evaluate the efficacy of the inhibitor [22], since a higher  $R_p$  value corresponds to higher corrosion resistance.

**Linear Polarization (LP).** LP is a classical electrochemical technique used to measure the polarization resistance [23]. The electrode potential is scanned at a very slow rate ( $\sim 0.5 \text{ mV s}^{-1}$ ) around the open-circuit potential. Usually, a range of  $\pm 10$  or  $20 \text{ mV}$  is employed. The current vs. overpotential results are fitted to a straight line, and the inverse of the slope of the line is  $R_p$  (more precisely, it is the sum of  $R_p$  and  $R_s$ ). LP is a nondestructive technique, and it does not assume that the anodic and cathodic reactions are simple electron transfer reactions [21]. While the exact duration of the experiment depends on the potential range and the scan rate employed, a typical run takes a few minutes. LP is a simple technique and does not require sophisticated analysis. However, since LP measures only  $R_s + R_p$ , the solution resistance should be measured using EIS to estimate  $R_p$  accurately. In addition, if the scan rate is not sufficiently low, the  $R_p$  values estimated from LP will be incorrect, as illustrated in Sect. 4. LP does not provide any information regarding the structure of the surface or the mechanism of corrosion. EIS is the third and the most reliable method to calculate  $R_p$ .

### 3 EIS Analysis

EIS is the only method available to directly and accurately measure the solution resistance, which is required to calculate the  $R_p$  values correctly by any method, including Tafel extrapolation and LP. In addition, EIS can provide detailed information on the structure of the electrode–electrolyte interface, formation of porous or non-porous films on the surface, and the mechanism of corrosion reaction as well as protection offered by inhibitors.

### 3.1 EIS Data Validation

One of the key advantages of EIS over other types of electrochemical measurements is that the data could be validated independently [24]. If a system is linear, causal, and stable, then the EIS data satisfy a relationship known as Kramers–Kronig transform (KKT) [25, 26]. KKT requires EIS data from 0 to infinite frequency, and practically data are available only in a limited frequency range. An alternative method, described as *measurement model approach* [27–31], can be used to verify the KK compliance of the data. If the system changes significantly during EIS measurement, then the data will not be KK compliant and hence should not be used to extract  $R_p$ . EIS data should be analyzed only after validating them with KKT.

### 3.2 Mechanistic Analysis

EIS can also be acquired when an anodic DC bias is applied to the system [32–34]. The bias would essentially enhance the anodic dissolution reaction and suppress the cathodic reaction. The impedance acquired at multiple bias values can be analyzed along with the PDP data to identify the detailed reaction mechanism [32–35]. While this is very informative, it also requires solving very complex problems and hence is not widely used yet. The majority of the published work employs the circuit analogy method, described below.

### 3.3 Circuit Analogy

Equivalent electrical circuits can be used to model EIS data [2], and the individual elements can be assigned to represent physical components or processes. Since EIS data at high frequencies can be acquired quickly, several sine waves can be applied at a given frequency, and high-frequency measurements usually have a good signal-to-noise ratio. On the other hand, measurements at low frequencies require long experiment duration, and the signal-to-noise ratio tends to be poor. Nevertheless, there is a distinct advantage to using EIS for  $R_p$  estimation. When a circuit with several elements is used to model an entire spectrum, all the data points are used, and the noise in low-frequency data has a limited impact on the element values estimated. Thus, the confidence in the  $R_p$  value estimated by EIS is better than those estimated by Tafel extrapolation [15].

Besides, the features in EIS plots can indicate the complexity of the system under investigation. If the electrode is a planar surface and the corrosion is indeed described by simple electron transfer reactions under kinetic control, then EIS data would be a semicircle in the Nyquist plot. The data can be modeled adequately by a simple circuit with a capacitor and two resistors [4]. If there is a film present on the surface, or if the

anodic and cathodic processes are multi-step reactions, then a more complex circuit would be necessary to model the EIS data [33]. Besides resistors and capacitors, other passive elements such as inductors and Warburg impedance may also need to be incorporated in the circuits. Several circuits have been employed to model EIS data in corrosion studies, and a few are described in this work.

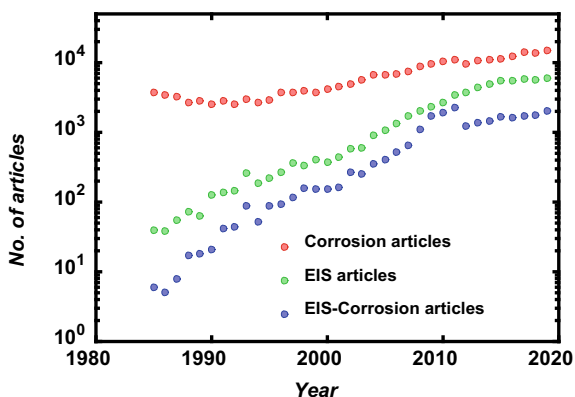
## 4 Applications

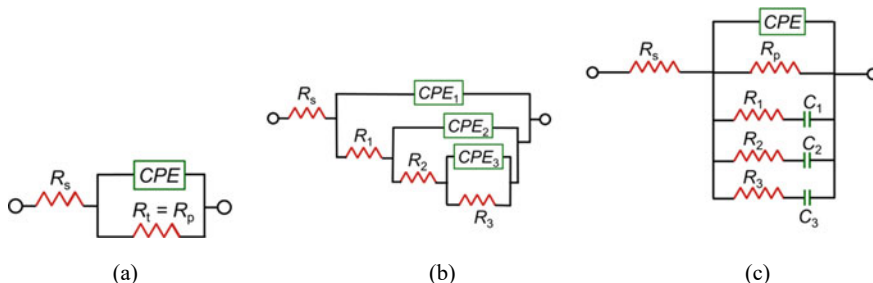
There are thousands of published articles that employ EIS to characterize corrosion processes. A search in Scopus® shows that the number of articles containing corrosion and EIS (or electrochemical impedance spectroscopy) in the title or abstract or keywords is increasing significantly over time (Fig. 3), demonstrating the importance of both corrosion and EIS. It is impractical to compile all the literature reports on the applications of EIS on corrosion in a compact form, and only a few select reports in the last decade are described here.

### 4.1 Metal Corrosion

In the reprocessing of nuclear fuels, highly concentrated acids are used to dissolve the nuclear fuel, and the attack of the dissolver vessels by the acid is a serious concern. The corrosion of a variety of austenitic stainless steels in 6 N and 11.5 N  $\text{HNO}_3$  was investigated by Ningshen et al. [36]. The corrosion process was studied using electrochemical techniques, and the samples were analyzed using optical micrography. The impedance data were fitted using the circuit shown in Fig. 4a. Here,  $R_t$  is the charge transfer resistance, which is defined as

**Fig. 3** Number of publications with *corrosion* or *EIS* or both, in the title, abstract, or keywords, as a function of time. Data from Scopus®





**Fig. 4** Equivalent circuits used to model impedance data of **a** SS corrosion, **b** nanoporous titania-coated Ti in Hank's solution, and **c** Zr in nitric acid with fluoride ions

$$R_t = \lim_{\omega \rightarrow \infty} (Z_F) \quad (4)$$

CPE is a constant phase element that can be used to describe a double layer that exhibits capacitance dispersion [3]. Figure 4b uses a ladder representation, with CPE, to describe the faradaic impedance.

In Fig. 4a, both  $R_p$  and  $R_t$  are identical, and the results showed that  $R_p$  values correlate inversely with the corrosion current densities. One of the steels, named Uranus 16, exhibited low  $R_p$  and high corrosion rates. SS304L material, implanted with  $N_2$  to enhance the corrosion resistance, was evaluated in 1 N  $HNO_3$ , and electrochemical measurements showed that the corrosion current densities decreased with the extent of  $N_2$  doping [37]. EIS data were fitted to the circuit in Fig. 4a and  $R_p$  values increased with the extent of  $N_2$  doping. XPS analyses revealed that chromium nitride formation enhanced the corrosion resistance.

Nuclear fuel reprocessing fluid is expected to contain oxidizing ions, and it is imperative to evaluate the corrosion resistance of the dissolver vessel material in the presence of these ions. Hence, the corrosion of AISI type SS304L in various concentrations of nitric acid, in the presence of Ce(IV), Ru(III), Fe(III), and Cr(VI) ions, was assessed [38]. Here too, the simple Randles circuit depicted in Fig. 4a was employed to model the impedance data. The corrosion current estimated from Tafel analyses exhibited a negative correlation with  $R_p$  values obtained from EIS analysis. Corrosion of Zr-702 in 11.5 M nitric acid with and without 0.05 NaF was studied using PDP and EIS [39]. In nitric acid without fluoride, the corrosion rate was low, and the impedance data were modeled using the circuit in Fig. 4a. Upon the addition of fluoride ions, the dissolution rate increased dramatically, and the impedance spectrum exhibited inductive loops at mid and low frequencies. The impedance spectrum fitted using the *Maxwell* circuit shown in Fig. 4c, with negative values for two *RC* pairs, so that the inductive loop can be modeled. The decrease in  $R_p$  value with the addition of fluoride ion correlated well with the enhanced dissolution rate.

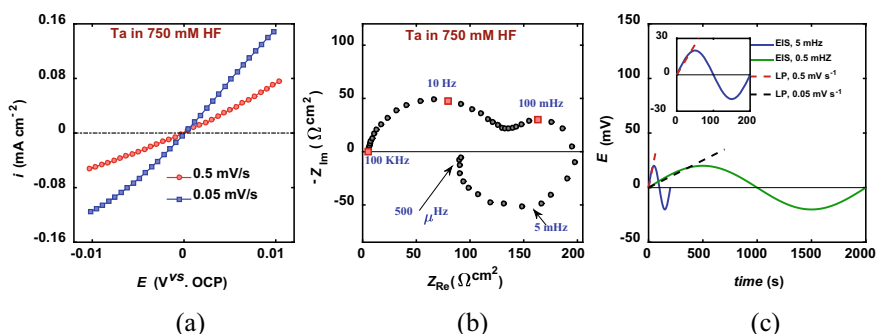
Metal waste form is a type of nuclear waste stored in a geological repository as a form of permanent disposal, and its major constituents are SS and Zr. The corrosion of SS-Zr alloy in simulated geological repository water, whose composition was tuned

to mimic two real locations, was investigated [40]. Although the alloy is resistant to corrosion by groundwater, bacteria can cause microbial induced corrosion. In particular, attack by two types of bacteria, viz. *Bacillus* sp. and *Pseudomonas* sp., was studied using PDP, EIS, and surface characterization techniques. The impedance was fitted using the circuit in Fig. 4a. The results showed that when biofilms formed on the surface,  $R_p$  values decreased. The biofilms facilitated crevice creation and active metal dissolution.

Ti is used as condenser material in cooling systems, and the effect of biofilm formation on corrosion resistance of Ti was evaluated in another study [41]. Experiments were conducted in seawater, using fresh, polished Ti and Ti with biofilms. The EIS data of polished Ti were fitted using the circuit in Fig. 4a. The EIS of Ti covered with biofilm was fitted using the circuit in Fig. 4b but without  $CPE_3$  and  $R_3$ . Ideal capacitors were used in place of  $CPE$ . The pair ( $R_1$  and  $C_1$ ) was used to model the biofilm;  $C_2$  modeled the double layer, and  $R_2$  was equated to  $R_t$ . The formation of a biofilm led to a decrease in  $R_t$  and enhanced corrosion.

The corrosion resistance of Ta in 750 mM HF and 100 M  $Na_2SO_4$  was investigated using LP and EIS [21]. Initially, LP was conducted at a potential scan rate of  $0.5 \text{ mV s}^{-1}$ , and an analysis of the results (Fig. 5a) indicated that ( $R_s + R_p$ ) is  $161 \Omega \text{ cm}^2$ . EIS data were also acquired under the same conditions (Fig. 5b), and the results were fitted using the circuit shown in Fig. 4c, without  $R_3$  and  $C_3$ . The estimated  $R_s$  and  $R_p$  values are 5 and  $84 \Omega \text{ cm}^2$ , respectively. The difference between the  $R_p$  values estimated from EIS and LP is substantial. It could not be explained by run-to-run variations, leading to an apparent inconsistency between LP and EIS results.

An LP scan can be visualized as an approximation to the first quarter of a sine wave, as shown in Fig. 5c. Given an  $E_{ac0}$  and frequency  $f$ , an equivalent LP potential scan rate can be related as scan rate  $\simeq 5 \times E_{ac0} \times f$ . The application of a sine wave of 20 mV amplitude at five milli-Hz frequency is comparable to performing LP at a potential scan rate of  $0.5 \text{ mV s}^{-1}$ . Likewise, the application of a sine wave 0.5 milli-Hz is comparable to LP performed at  $0.05 \text{ mV/s}$ . A careful examination of the



**Fig. 5** a LP of Ta in 750 mM HF and 100 M  $Na_2SO_4$  at OCP. b Nyquist plot of EIS of Ta in the same solution. c Potential versus time of a sine wave at two frequencies, and potential ramp at two scan rates. Adapted from [21]