

Journal of ASTM International
Selected Technical Papers



STP 1506

Advances in
Electrochemical
Techniques for
**Corrosion
Monitoring and
Measurement**

JAI Guest Editors

Sankara Papavinasam

Neal S. Berke

Sean Brossia

Journal of ASTM International
Selected Technical Papers STP1506
**Advances in Electrochemical
Techniques for Corrosion Monitoring
and Measurement**

JAI Guest Editors:

Sankara Papavinasam

Neal S. Berke

Sean Brossia



INTERNATIONAL

Standards Worldwide

ASTM International
100 Barr Harbor Drive
PO Box C700
West Conshohocken, PA 19428-2959

Printed in the U.S.A.
ASTM Stock #: STP1506

Library of Congress Cataloging-in-Publication Data

Advances in electrochemical techniques for corrosion monitoring and measurement / guest editors, Sankara Papavinasam, Neal S. Berke, Sean Brossia.

p. cm. -- (Journal of ASTM International special technical publication; STP1506)

Papers from a symposium held May 22-23, 2007 in Norfolk, Virginia.

Includes bibliographical references and index.

ISBN 978-0-8031-5522-0 (alk paper)

1. Corrosion and anti-corrosives--Measurement--Congresses. 2. Nondestructive testing--Congresses. 3. Electrochemical analysis--Congresses. I. Papavinasam, Sankara, 1962-II. Berke, Neal Steven, 1952-III. Brossia, Sean.

TA462.A238 2009

2009042261

620.1'1223--dc22

Copyright © 2009 ASTM INTERNATIONAL, West Conshohocken, PA. All rights reserved. This material may not be reproduced or copied, in whole or in part, in any printed, mechanical, electronic, film, or other distribution and storage media, without the written consent of the publisher.

Journal of ASTM International (JAI) Scope

The JAI is a multi-disciplinary forum to serve the international scientific and engineering community through the timely publication of the results of original research and critical review articles in the physical and life sciences and engineering technologies.

These peer-reviewed papers cover diverse topics relevant to the science and research that establish the foundation for standards development within ASTM International.

Photocopy Rights

Authorization to photocopy items for internal, personal, or educational classroom use, or the internal, personal, or educational classroom use of specific clients, is granted by ASTM International provided that the appropriate fee is paid to ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959, Tel: 610-832-9634; online: <http://www.astm.org/copyright>. The Society is not responsible, as a body, for the statements and opinions expressed in this publication. ASTM International does not endorse any products represented in this publication.

Peer Review Policy

Each paper published in this volume was evaluated by two peer reviewers and at least one editor. The authors addressed all of the reviewers' comments to the satisfaction of both the technical editor(s) and the ASTM International Committee on Publications. The quality of the papers in this publication reflects not only the obvious efforts of the authors and the technical editor(s), but also the work of the peer reviewers. In keeping with long-standing publication practices, ASTM International maintains the anonymity of the peer reviewers. The ASTM International Committee on Publications acknowledges with appreciation their dedication and contribution of time and effort on behalf of ASTM International.

Citation of Papers

When citing papers from this publication, the appropriate citation includes the paper authors, "paper title", J. ASTM Intl., volume and number, Paper doi, ASTM International, West Conshohocken, PA, Paper, year listed in the footnote of the paper. A citation is provided as a footnote on page one of each paper.

Foreword

THIS COMPILATION OF THE *JOURNAL OF ASTM INTERNATIONAL (JAI)* STP 1506, on *Advances in Electrochemical Techniques for Corrosion Monitoring and Measurement*, contains only papers published in JAI that were presented at a symposium in Norfolk, VA, on May 23, 2007 and sponsored by ASTM Committee G01 on Corrosion of Metals.

The JAI Guest Editors are Dr. Sankara Papavinasam, CANMET, Materials Technology Laboratory, OTTAWA, ON, CANADA, Neal S. Berke, W. R. Grace & Company Construction Products, Cambridge, MA, USA, and Sean Brossia, DNV Columbus, Dublin, OH, USA.

Contents

Overview	vii
----------------	-----

Keynote Papers

Electrochemical Techniques in Corrosion: Status, Limitations, and Needs G. S. Frankel	3
Development of Electrochemical Standards for Corrosion Testing S. W. Dean	41

New Experimental Set-up

Use of Coupled Multi-Electrode Arrays to Advance the Understanding of Selected Corrosion Phenomena H. Cong, F. Bocher, N. D. Budiansky, M. F. Hurley, and J. R. Scully	69
A Review of Coupled Multielectrode Array Sensors for Corrosion Monitoring and a Study on the Behaviors of the Anodic and Cathodic Electrodes L. Yang and K. T. Chiang	105
On Using Laboratory Measurements to Predict Corrosion Service Lives for Engineering Applications R. E. Ricker	127

New Methods of Analysis

Study of Corrosion Initiation of a Steel Panel from a Defect in Coating Using Localized Electrochemical Impedance Spectroscopy (LEIS) X. Wu, T. Wang, E. Montalvo, T. Provder, C. Handsy, and W. Shen	143
Electrochemical Impedance Spectroscopy Measurement during Cathodic Disbondment Experiment of Pipeline Coatings S. Papavinasam, M. Attard, and R. W. Revie	160

New Techniques

Measuring the Repassivation Potential of Alloy 22 Using the Potentiodynamic-Galvanostatic-Potentiostatic Method K. J. Evans and R. B. Rebak	189
Comparison of Corrosion Rate Measurement of Copper, Zinc, and C1018 Steel Using Electrochemical Frequency Modulation and Traditional Methods D. Loveday and R. Rodgers	211
Performance of An Enzyme Electrode Designed for a Sulfide Monitoring Biosensor R. Sooknah, S. Papavinasam, M. Attard, R. W. Revie, W. Douglas Gould, and O. Dinardo	226
Electrochemical Quartz Crystal Microbalance Technique to Monitor External Polymeric Pipeline Coatings S. Papavinasam, M. Attard, and R. W. Revie	240

Advances in Field Applications

Comparison of Measurements Provided by Several Corrosion Rate Meters with Modulated Confinement of the Current	
I. Martinez, C. Andrade, E. Marie-Victoire, V. Bouteiller, and N. Rebolledo	259
Corrosion of Phosphoric Irons in Acidic Environments	
G. Sahoo and R. Balasubramaniam	271
Crevice Corrosion of Grade-12 Titanium	
X. He, J. J. Noël, and D. W. Shoesmith	281
Measurement of Corrosion Potentials of the Internal Surface of Operating High-Pressure Oil and Gas Pipelines	
A. Demoz, S. Papavinasam, K. Michaelian, and R. W. Revie	300
Author Index	313
Subject Index	315

Overview

While the foundation of electrochemistry were established in the 17th and 18th century by the work of Galvani, Volta, Davy, Faraday, Ritter, and Daniell, it was during the later part of the 19th century that electrochemical methods of monitoring corrosion rates were established. During this period many advances - in both the theoretical and practical aspects - were made including:

- the development of the relationship between the rate of electrochemical reaction to the overpotential (1905, Tafel Equation),
- the establishment of the linkage between thermodynamics (electrode potential) and kinetics (corrosion current) (1929, Evans diagram),
- the development of local anodes and local cathodes (1938, Wagner and Traud),
- the introduction of the term "potentiostat" (1942, Hickling),
- the development of the potential and pH diagram (1950s, Pourbaix),
- the discovery of correlation between inversion of polarization resistance to the general corrosion rate (1957, Stern and Geary Equation),
- development of electrochemical impedance spectroscopy (1960s, Epelboin), and
- the observation of potential fluctuations (1968, Iverson).

By the latter part of the 19th century, electrochemical techniques for measuring corrosion rates, at least in the laboratory, were firmly established. This was made possible due to the commercial availability of high-impedance electrometers for measuring electrode potentials, electronic potentiostats to conduct potentiodynamic measurements, and zero-resistance ammeters. It was at this juncture that ASTM G01 Corrosion Committee (1964) and ASTM G01.11 (originally as subcommittee XI) Electrochemical Techniques for Corrosion Measurements Sub-Committee (1965) were established.

Over the past half century, the G01 Committee sponsored over 50 symposia. Almost all symposia sponsored by G01 Committee have had at least one or two papers dealing with electrochemical techniques for measuring or monitoring corrosion rates. Two Special Technical Publications (STPs) that dealt exclusively on electrochemical techniques are:

- STP 1188: Electrochemical impedance: Analysis and Interpretation
- STP 1277: Electrochemical noise measurement for corrosion applications

ASTM Committee G01 on Corrosion of Metals and its Subcommittee G01.11: Electrochemical Techniques for Corrosion Monitoring, organized a symposium on "Advances in Electrochemical Techniques for Corrosion Monitoring and Measurement" May 22-23, 2007 in Norfolk, Virginia. The main objective of the symposium was to discuss advances in electrochemical

techniques for corrosion monitoring and measurement, modeling, life prediction, and to identify potential areas for developing new standards. At the symposium, 27 papers were presented. Fifteen peer-reviewed papers from the symposium are collected in this STP. The papers are arranged in five sections:

- Keynote Papers,
- New Experimental Set Up
- New Methods of Analysis
- New Techniques
- Advances in Field Applications

Keynote Papers

In his keynote paper, Dr. Frankel describes available electrochemical and non-electrochemical test methods and highlights the importance of proper design of experimental tests. He identifies four possible combinations in which electrochemical techniques can be used and points out unfilled needs for each one of the four categories.

- For metals in solution, electrochemical techniques have been used successfully to monitor uniform corrosion and to characterize passive metals, but application of electrochemical techniques for localized corrosion, especially for measuring the kinetics, requires further development.
- For metals in atmosphere, there is no good electrochemical technique available at present. Standardized procedures for electrochemical monitoring should be pursued.
- For coated metals in solution, the electrochemical impedance spectroscopy (EIS) technique is well suited. Even though several equivalent circuits (ECs) have been developed, it is yet to be determined which EC should be used under what conditions.
- The life-time prediction of coated metals in atmosphere is difficult due to the absence of useful electrochemical techniques.

In the second keynote paper, Dean reviews the historical evolution of electrochemical techniques for corrosion testing. Advances made during the 1950s and 1960s resulted in the widespread usage of electrochemical techniques. During the 1960s, ASTM Committee G-1 on the Corrosion of Metals and Alloys established Subcommittee G01.11 (originally Subcommittee XI) to address three problems that had been inhibiting the development of electrochemical tests:

- Lack of reproducibility of electrochemical tests and the lack of understanding of the variation in results,
- Absence of standardized procedures for carrying out the tests, and
- Use of several conventions to present electrochemical data that made interpreting the test results difficult.

Between the 1960s and 1990s, this subcommittee developed the following standards to address these three issues.

- ASTM G3 to address conventions for use in presenting results of elec-

trochemical tests.

- ASTM G102 to provide guidance on interpreting data from electrochemical tests.
- ASTM G5 as a reference test method to provide an understanding of the reproducibility of polarization curves.
- ASTM G59 to provide a reference test method for running potentiodynamic polarization resistance measurements.
- ASTM G61 as a reference test method to demonstrate the tendency of passive metals to resist localized corrosion in chloride containing environments.
- ASTM G100 to evaluate the behavior of aluminum alloys in chloride environments where pitting corrosion can cause serious damage.
- ASTM G106 as a reference method to use the EIS technique to evaluate corrosion mechanism.
- ASTM G69 to determine the degree to which copper and zinc are in solid solution in aluminum alloys.
- ASTM G108 to detect sensitization of UNS S30403 stainless steel in nuclear power plants.
- ASTM G150 to determine the critical pitting temperature for stainless steel alloys.

Based on the experience gained from the widespread usage of these standards, Dean identifies the following areas on which ASTM G01.11 Subcommittee should focus:

- Expansion of ASTM G102 to cover calculations from EIS data, to provide guidelines to analyze impedance data from coated specimens (reiterating the views of Frankel), and to handle polarization resistance information when both cathodic and anodic reactions have significant diffusion limitation components.
- Expansion of ASTM G108 by standardizing the double-loop method and by including other stainless steel alloys.
- Development of a reference test method for the electrochemical-noise technique.

New Experimental Set Up

Because localized corrosion is one of the predominant mechanisms for metal failure in many industries, several techniques are being developed to investigate this phenomenon. Among these techniques, the coupled multi-electrode array (MEA) technique shows the most promise. MEAs are arrays of electrically isolated electrodes, connected by zero-resistance ammeters. The array electrodes may be made up of either the same material or different materials.

Cong *et al.* demonstrate the ability of MEAs to determine the current for individual electrodes allowing simultaneous spatial and temporal measurements. By interrogating each electrode under open-circuit conditions, they established that persistent anodes on copper surfaces that will develop into sites for pits to initiate and propagate can be identified by MEA. They also

demonstrate the influence of solution chemistry in the development of the anodes.

The work of Cong *et al.*, also indicates that MEAs can be used to differentiate the localized corrosion behaviour of metals in different environments. For instance, pits that initiate on a limited number of sites on carbon steel in a simulated concrete pore solution trigger global depassivation of the entire electrode surface under open-circuit potentials, but pits that initiate on 316L stainless steel do not trigger global depassivation even under aggressive conditions. This study shows the advantage of replacing carbon steel rebar in concrete with more corrosion-resistant stainless steel materials.

Cong *et al.* further demonstrate the application of MEAs to investigate crevice corrosion and intergranular corrosion. MEAs can be used to monitor the regions of electrode surfaces that are located both within and outside the crevice and to determine the influence of the potentials at the crevice mouth on the propagation of corrosion within the crevice. Using MEAs, Cong *et al.* also establish that the spreading of intergranular corrosion of sensitized stainless steel is due to depletion of chromium in the grain boundaries.

A paper by Yang *et al.* compliments that of Cong *et al.* in terms of advancing the knowledge of MEAs. After providing the historical developments, theoretical background of this technique, and typical experimental set up, Yang *et al.*, illustrate the application of MEAs in a number of practical systems for real-time corrosion monitoring. MEAs have been used successfully in several environments including: cooling water, simulated seawater, salt-saturated aqueous solution, concentrated chloride solution, concrete, soil, low-conductivity drinking water, process streams of chemical plants at elevated temperature, coatings, deposits of sulphate-reducing bacteria, deposits of salt in air, high-pressure simulated natural gas systems, H₂S systems, oil/water mixture, and high-temperature acidic solution. MEAs have also been successfully used to optimize corrosion control strategies including optimization of both corrosion inhibitors and cathodic protection.

Ricker proposes an approach to estimate field performance based on laboratory measurements. Using his approach, the corrosion performance of different materials exposed to a range of different environmental conditions can be predicted from a single database of corrosion damage rate functions. The advantage of this approach is that, once the variation of corrosion rates with environmental conditions is known, it can be combined with any number of distributions of environmental conditions to make predictions. To illustrate his approach Ricker describes a three-electrode sample design for simulating crevice corrosion. In this design, a nonconductive film separates electrodes 1 and 2, and a porous electrode separates these two electrodes from the third. From the electrochemical noise and electrochemical impedance spectra recorded using the three-electrode design, Ricker demonstrates that a database can be used for setting inspection intervals, life-cycle cost estimates and other design and operation decisions.

New Methods of Analysis

Electrochemical impedance spectroscopy is a useful technique for monitoring coating deterioration, however it measures the impedance of a relatively larger area. Corrosion of metals covered by protective coatings originates from smaller defects, e.g., pinhole, voids. Localized electrochemical impedance spectroscopy (LEIS) can be used for this purpose; it measures the distribution of impedance on the surface of a sample by scanning with a probe placed above the surface. Using a cold-rolled steel panel containing a protective coating with a pinhole, Wu et al. demonstrate that LEIS can be used to study the corrosion processes occurring in the initial stages. Though the signals obtained are noisy, and some features of the spectra are not fully understood, Wu predicts that, with improvements in the lateral resolution, LEIS will play an important role in understanding localized corrosion.

Coatings are the first line of defense against corrosion of many types of infrastructure including oil and gas pipelines. If they fail, the infrastructure is protected by cathodic protection (CP). To evaluate the compatibility between coatings and CP, cathodic disbondment (CD) tests are commonly conducted. Several CD test standards have been developed. Papavinasam et al. compare the EIS measurement obtained during CD experiments with the cathodic disbonded area determined after the completion of the test. The EIS technique can be used to qualitatively predict coating performance. Papavinasam et al. also caution that such prediction depends strongly on the type of coating.

New Techniques

ASTM G61 provides a method to evaluate the susceptibility of alloys to crevice corrosion using a Cyclic Potentiodynamic Polarization (CPP) technique. This CPP technique is only reproducible when the alloy is susceptible to crevice corrosion. A new method, known as the Tsujikawa-Hisamatsu-Electrochemical, or THE, method, that combines sequentially potentiodynamic, galvanostatic, and potentiostatic treatments has recently been developed. Evans *et al.* compare the applicability of the CPP technique and THE method to evaluate the crevice corrosion of Alloy 22. Based on round-robin experiments they report that:

- The THE method complements the CPP technique; and
- When the system is aggressive (e.g., high chloride or high temperature) both techniques produce similar results, but when the system is not aggressive (e.g., low chloride or low temperature) the reproducibility of the THE method is better than that of CPP method.

Based on the results obtained, they recommend development of a new ASTM standard for the THE method.

Electrochemical Frequency Modulation (EFM) is a nondestructive technique that can be used to measure corrosion rate without prior knowledge of the Tafel constants. During EFM, a potential perturbation in the form of two

sine waves at different frequencies is applied to the sample, and the current response of the sample is recorded. From the frequency domain analysis of the data, corrosion rates and Tafel constants are determined. Loveday *et al.* compared the corrosion rates of iron, copper, and zinc, as determined by the EFM technique, with those determined by polarization resistance and EIS techniques. The results obtained by all techniques agree with one another within the experimental variation. They also present the frequency range in which reliable EFM measurements can be performed.

Corrosion resulting from the attachment and activities of microorganisms on metal surfaces is referred to as microbiologically influenced corrosion (MIC) or biocorrosion. MIC is a concern to many industrial sectors, including oil and gas, food processing, aircraft, construction, water treatment and distribution, and nuclear. It is difficult to assess the economic impact of MIC, primarily due to a lack of online techniques to simultaneously monitor microbial activities and corrosion rates. Sooknah *et al.*, present a sulfide oxidase enzyme electrode for monitoring of biogenic sulfide resulting from the activities of sulfate-reducing bacteria (SRB). SRB is one of the predominant organisms causing MIC. This probe responds linearly in a wider range of sulphide ion concentrations making it a promising candidate for monitoring SRB activity. However further studies need to be carried out to characterize this biosensor in terms of the influence of pH, temperature, and biocides on its performance.

Electrochemical Quartz Crystal Microbalance (EQCM) can be used to monitor changes in several material properties including mass, electrochemistry, viscosity, adsorption, and deposition. By placing the crystals at the metal-coating interface, Papavinasam *et al.* evaluate the EQCM technique to monitor changes to the metal-coating interface well before any visible/physical changes to the coating. Based on the monitoring of over 100 samples with thirteen different coatings, they demonstrate that the EQCM correctly predicts the performance of coatings. In order for the technique to be used routinely, the placement of crystals and analysis methods should be standardized.

Advances in Field Applications

Electrochemical techniques for measuring corrosion rates in the laboratory have been well established, in fact several have also been successfully used in the field. There has not, however, been a systematic study to evaluate the repeatability and reproducibility of the electrochemical techniques in many industrial systems and in the evaluation of various materials for a particular industry.

Martinez *et al.* address this issue by comparing the performance of five commercial instruments used to monitor the corrosion of steel reinforcement in concrete. All five instruments produced reproducible measurements with respect to corrosion potential and resistivity, but there were differences with respect to corrosion rates (using the polarization resistance method).

Based on the analysis of the results, Martinez *et al.* propose several best practices to minimize errors including: keeping the sweep rate to 10 mV/min, ensuring that corrosion potential is stabilized between consecutive measurements, repeating the measurements at least three times, and recognizing that some errors can result from the assumption of Tafel constant (26 mV), variation of temperature during measurement, and sensor and reference electrode maintenance.

The iron pillar in Delhi, India has attracted the attention of engineers, especially corrosion technologists, because it has withstood corrosion for more than 1600 years. The relatively high phosphorus content (0.25 wt %) in the forge-welded Pillar plays a major role in its corrosion resistance. Balasubramaniam *et al.* compare the corrosion resistance of phosphoric irons (i.e., Fe-P alloys containing phosphorus in the range 0.1 to 0.5 wt %) prepared using the ingot metallurgy route with plain carbon steel and low alloy (Cu-Cr) steel, in acidic and in neutral (chloride containing) environments using electrochemical techniques. They report similar corrosion rates of all alloys in neutral environments, but higher corrosion rates of phosphoric irons (when compared to Cu-Cr carbon steel) in acidic environments.

Several groups have been studying the properties of materials aimed at developing containers for long-term storage (i.e., thousands of years) for the disposal of high-level nuclear waste. Noel *et al.* illustrate the benefit of combining the electrochemical and non-electrochemical techniques. They elucidate the mechanism of crevice corrosion of titanium alloys (a candidate material for the nuclear waste containers) using a combination of electrochemical (galvanic coupling) and non-electrochemical (metallography, image analysis, and microscopy) techniques. While secondary ion mass spectrometry (SIMS) enables them to determine the location of absorbed hydrogen, and metallographic and image analysis techniques help them to determine the penetration depths, the electrochemical techniques enable them to deduce that 97% of total crevice propagation is driven by proton reduction inside the crevice area rather than by oxygen reduction outside the crevice. The presence of particles (i.e., Ti_2Ni) increases the internal cathodic areas relative to anodic areas resulting in the repassivation of the corroded site before extensive damage occurs.

Corrosion potential is a fundamental electrochemical parameter critical to understanding the thermodynamic aspects of corrosion. Many corrosion theories are based on corrosion potentials which are routinely and easily measured in the laboratory. In order to transfer this scientific knowledge from the laboratory to the field, it is necessary to determine the corrosion potential under operating field conditions. Demoz *et al.* describe unique challenges in measuring the corrosion potentials of an industrial environment using measurement of the corrosion potential of the internal surface of pipelines as an example. They present methods to overcome these challenges, and to measure the corrosion potentials in operating oil and gas pipelines.

Summary

It is hoped that the papers in the STP will provide the state-of-the-art of electrochemical techniques for measuring and monitoring corrosion both in the laboratory and in the field, and that some of the techniques described will eventually lead to the development of new ASTM standards. It is encouraging to note that, between the time of the symposium and the publication of the STP, ASTM published two standards on techniques discussed in the symposium and described in this STP:

- ASTM G192: Test Method for Determining the Crevice Repassivation Potential of Corrosion Resistant Alloys Using A Potentiodynamic-Galvanostatic-Potentiostatic Technique
- ASTM G199: Standard Guide for Electrochemical Noise Measurement

It is hoped that the trend of developing new ASTM standards on other advanced electrochemical techniques will continue!

Sankara Papavinasam
CANMET Materials Technology Laboratory
Ottawa, Ontario, Canada

Neal S. Berke
W. R. Grace & Co. Conn. Products
Cambridge, MA

Sean Brossia
DNV Columbus
Dublin, OH



www.astm.org

ISBN: 978-0-8031-5522-0
Stock #: STP1506