Overview

Over the past quarter century electrochemical impedance has blossomed into a major corrosion measurement technology. Its usage has grown to include applications ranging from fundamental studies of corrosion mechanisms and material properties to very applied studies of quality control and routine corrosion engineering. Today, computer controlled "user friendly"systems are available from several manufacturers. This has made data acquisition a routine procedure, whereas only a decade ago users were confronted with the need to develop their own data acquisition systems. However, diagnostic tools for evaluating the validity of the data, procedures for developing a fundamental understanding of the results and their relationship to the process being studied, and knowledge of the limits of practical application to real world systems are still under active investigation. This Special Technical Publication has been published as a result of the 1991 symposium entitled Electrochemical Impedance: Analysis and Interpretation held in San Diego, California. The goal of the symposium was to provide a clear picture of the current state of the art in interpretation and analysis of electrochemical impedance data. The symposium was a natural extension of the efforts within ASTM Subcommittee G.01.11 on Electrochemical Corrosion Testing and Task Group G.01.11.06 on Electrochemical Impedance to provide standardized methodologies for using this technology and reporting the results. Both of these groups are part of ASTM Committee G.01 on Corrosion of Metals.

The collection of twenty-seven papers published in this volume has been grouped into six major categories that very closely characterize the major areas of research and engineering application of Electrochemical Impedance Techniques in corrosion. These areas are: corrosion process characterization and modeling, applications of Kramers-Kronig transformations for evaluating the validity of data, corrosion and its inhibition by either corrosion products or specially added inhibitors, corrosion of aluminum and aluminum alloys, corrosion of steel in soils and concrete, and evaluation of coatings on metal substrates. The papers range from theoretical modeling to practical applications. The effort has been made to include many of the recognized contributors in this field. A careful reading of the papers should provide a broad overview of the plethora of information available and the important questions being asked about this technology.

Modeling and Corrosion Processes

Corrosion characterization and modeling impacts virtually all applications of this technology. The papers in this section should provide methodologies that would be useful in a number of areas. Modeling has tended to encompass use of electrical equivalent circuit models, the elements of which are used to represent physical processes. Bertocci and Ricker take the opposite approach and attempt to calculate polarization scans and impedance spectra from basic kinetic equations including the metal reaction, oxygen reduction, and hydrogen evolution as a function of pH. This approach, while a long way from being generally implemented, would circumvent the ambiguities that can occur when using passive linear circuit analogues. Low-conductivity fluids are difficult media in which to conduct electrochemical studies. Chechirlian, Keddam, and Takenouti discuss an equivalent circuit which might be used to help to eliminate artificial relaxation processes that occur when generating impedance spectra in low-conductivity media. Mansfeld, Shih, Greene, and Tsai attempt to tailor software packages to specific corrosion phenomena. Their paper presents a number of results that show that such tailoring can lead to good fits with the data and interesting insights into the corrosion phenomena. Roberge presents an alternative to modeling by a number of equivalent circuits. His method in which he projects the center of a semicircle from a series of permutations of three points on the spectra is suggested to provide a rich source of information concerning the corrosion processes. High-frequency artifacts are often present when generating impedance spectra. Stewart, Kolman, and Taylor discuss the factors that may contribute to the occurrence of such artifacts and propose a model that can reproduce spectra for a set of measuring resistors using a particular make of potentiostat. New applications of electrochemical impedance techniques are continually being reported. The paper by Kelly, Young, and Newman reports an application of the impedance technique to study the development of porosity due to dealloying of silver as well as gold surface diffusion in solid solution silver-gold alloys.

Applications of Kramers-Kronig Transformations

"Are my spectra valid?" is a question continually asked. Kramers-Kronig Transformations provide a way of assuring that the impedance spectra truly reflect the corrosion process and are not affected by phenomena such as too large of an amplitude or the system not being at steady state. In their paper, Agarwal, Orazem, and Garcia-Rubio introduce the concept of a measurement model as a tool for identifying possible frequency-dependent errors in the data. They show that the measurement model can be used to determine that the spectra are consistent with the Kramers-Kronig transformations without having to explicitly integrate the transforms. Impedance spectra are sometimes generated in a potential region in which a small increase in potential results in a decrease in current, a negative resistance. Gabrielli, Keddam, and Takenouti provide evidence and suggest how Kramers-Kronig transforms can be used to check validity under these circumstances. Lastly, Dougherty and Smedley provide an application of the use of Kramers-Kronig transformations to show the validity of impedance spectra generated in aluminum-methanol-water systems. Their results show an ability to discern when the requirements of linearity, stability, and causality are violated.

Corrosion and Inhibition

Corrosion of metals can be affected by corrosion products, corrosion inhibitors, or other constituents in the fluid that are either adsorbed onto the surface or become incorporated in the three-dimensional surface region. Electrochemical impedance has been an important tool for studying the electrochemistry of this interaction. However, relating the spectra to actual physical phenomena can be difficult. Turgoose and Cottis start from first principles to construct the impedance spectra. They create a generalized equivalent circuit in which all elements are defined and constrained by physical, chemical, or electrochemical processes. They show that this generalized circuit can account for many of the features observed in the spectra from film-covered electrodes. However, such an approach cannot be implemented on a routine basis in poorly characterized systems. Silverman takes an alternative approach of using simple circuits to extract corrosion-related parameters on a routine basis from the spectra of steel in near neutral uninhibited and inhibited water. He shows that by careful use of the circuit models, practical estimates of corrosion rates and practical insights into the corrosion mechanism can be obtained. Also under the category of inhibitors, Hirozawa and Turcotte show that electrochemical noise and electrochemical impedance techniques can be combined to give interesting insights into corrosion inhibition of aluminum. They show that elimination or reduction of electrochemical noise may indicate improvement in the protectiveness of the oxide film. Product films can also affect corrosion as in the case of helping to protect copper-nickel alloys in seawater. Hack and Pickering use electrochemical impedance to shed light on the reason that such films are protective. They report that oxygen reduction which affects corrosion of these alloys is itself controlled by diffusion through the outer product layer. Lastly, steel corrosion in aqueous systems can be a function of whether the steel is base metal, weld metal, or lies in the heat-affected zone. Rothwell, Dawson, Eden, and Palmer discuss an electrode and instrumentation that is proposed to allow the generation of impedance measurements on single electrodes while they are effectively galvanically coupled as in the real situation. In this way, base and weld metal can be studied separately under coupled conditions.

Corrosion of Aluminum

Corrosion and protection of aluminum alloys is an area of tremendous technological interest given the increased application of this material over the last 30 years. Electrochemical impedance has expanded both the depth and breadth of corrosion and protection information that can be acquired. Dawson, Thompson, and Ahmadun survey the literature on electrical equivalent circuit models useful for interpreting the impedance behavior of anodized aluminum. Circuit parameters are then used to monitor detailed changes in anodized film hydration and barrier properties. Mansfeld, Wang, Lin, Xiao, and Shih describe electrical equivalent circuit models and experimental data fitting procedures for detecting and monitoring pitting corrosion. They emphasize the utility of the technique for studying stable pitting phenomena under freely corroding conditions at open circuit potentials that are above the pitting potential. Scully extends the application of impedance techniques to aluminum thin films of one micrometer thicknesses or less. The nondestructive nature of the method is one of the key advantages of the technique in these applications. Passivity, salt film formation, and localized corrosion of aluminum in hydrofluoric acid solutions are characterized. Roberge, Halliop, and Yousri discuss EIS and polarization techniques as replacements for the long-term salt spray exposure method. They seek to advance electrochemical impedance as a tool for routinely monitoring anodized film quality or anodizing baths, or both. Schueller and Taylor discuss a novel application of EIS. The aim of their paper is the detection of delamination between an aluminum alloy/polymer laminate. The approach is technologically significant as a possible nondestructive tool for characterizing damage in adhesively bonded components. An equivalent circuit model was proposed using transmission line circuitry which describes the impedance spectra of edge exposed laminates. Model laminates with known rectangular defects were analyzed and compared with the circuit model.

Corrosion of Steel in Concrete or Soil

Advancement in the understanding of corrosion of metals in soils and concrete has been frustrated, in part, because traditional electrochemical polarization methods fail to compensate for the high resistance of the soil or concrete. Impedance methods are able to overcome this obstacle as well as provide a nondestructive tool and, hence, represent an opportunity to advance current understandings. Sudo and Haruyama model the impedance spectra of a two-electrode cell consisting of a buried metallic structure and a small nonpolarizable disk counter electrode at the soil surface. Their results show that care is required in assuming that the low-frequency complex plane impedance intercept with the real axis is always inversely proportional to the corrosion rate. Kranc and Sagüés investigate surface counter electrode placement and current distribution effects for a model reinforced concrete geometry containing both corroding and passive reinforcing steel. Predicted impedance spectra yield apparent polarization resistances which underestimated the corrosion current mainly due to current distribution effects. Finally, Jafar, Dawson, and John discuss the application of harmonic analysis for evaluation of corrosion rates as well as Tafel parameters in the case of laboratory concrete samples containing reinforcing steel. Their paper highlights the advantages of harmonic analysis as an extension of impedance techniques for rapid assessment of corrosion rates.

Coatings on Metals

Impedance techniques continue to develop as a tool for rapidly assessing the performance of organic coatings on metals. The papers presented in this section demonstrate that while the applicability of the technique to various coatings continues to expand, its versatility is not without bounds. Kendig, Jeanjaquet, and Lumsden discuss the theoretical limits of various impedance parameters including the "breakpoint frequency" for estimation of coating delamination. The application described includes adhesion loss adjacent to a macroscopic defect on a fusion bonded epoxy coated pipe steel. Their analysis shows that the low-frequency impedance of such macroscopic delaminations may become insensitive to the depth of the delaminated zone for certain combinations of solution resistance and interfacial impedance associated with the delaminated region. The paper points to possible limitations of certain impedance parameters in detecting coating delaminations. Tait, Handrich, Tait, and Martin apply the impedance technique to internally coated steel aerosol containers. One theme of their paper concerns estimation of the fraction of containers from a total population that will ultimately experience failure. This estimation is based on the statistical treatment of a range of impedance results (due to a range of defects) obtained from a subset of the total population of containers. Feliu, Jr., Barajas, Bastidas, Morcillo, and Feliu report on the use of impedance methods to characterize zinc-rich organic paints. Both the impedance spectra and the protection mechanisms of these coatings differ from those of barrier coatings. The paper focuses on analysis of impedance data for the case of cathodically protected steel substrates resulting from the interconnected zinc particles. This phenomenon is distinguished from the barrier properties of the organic coating by exploiting the differences in the frequency range over which each is effectively probed. Granata and Kovaleski report on their efforts to use impedance as well as chronoamperometry techniques as coating evaluation tools for high-performance fusion-bonded coatings, marine service epoxy, and polyimide used in electronics. Kamarchik applies the impedance approach to automotive and electrodeposited coatings and to container interior coatings for beverage and food end-uses. Impedance provides indication of changes in coating performance long before visual changes were observed using more traditional exposure tests such as continuous salt fog.

Summary

The papers presented in this book should provide the reader with a broad overview of the present state of the art concerning analysis and interpretation of electrochemical impedance spectra. Armed with the information provided in this book, the reader should be better equipped to explore the frontiers of this technology as well as apply it to corrosion science and engineering. The symposium chairmen gratefully acknowledge the efforts of the authors and ASTM personnel in the preparation of this book.

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