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The Measurement and Correction of Electrolyte Resistance in Electrochemical Tests

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Foreword

The Symposium on Ohmic Electrolyte Resistance Measurement and Compensation was held at Baltimore, MD on 17 May 1988. ASTM Committees G-1 on Corrosion of Metals and G1.11 on Electrochemical Measurements in Testing sponsored the symposium. L. L. Scribner and S. R. Taylor, University of Virginia, served as chairmen of the symposium and are editors of the resulting publication.

Contents

Overview

The measurement of any electrode potential includes an error caused by a voltage drop through the electrolyte. This error is caused by the inherent resistance (IR) of the solution and is proportional to the cell current. It has therefore been referred to as IR drop, ohmic overpotential, IR voltage error, or potential error caused by solution resistance. As the current or solution resistivity increase, or both, the error in electrode potential measurements can become quite large, thus distorting current-potential data and preventing accurate interpretation. Due to the ubiquitous nature of ohmic electrolyte resistance throughout the electrochemical sciences, an understanding of the phenomenon, methods to measure it, and means to correct for its presence are required to obtain precise data.

The purpose of this book is to present, review, and critique new and existing methods for the correction of ohmic electrolyte resistance. Although the 13 papers have been segregated into the areas of Theory, Critical Comparisons, Mathematical Approaches, and Applications, many of the papers are more broadly based, covering more than one of the above areas.

The reader is introduced to the theoretical considerations of ohmic electrolyte resistance measurements by Hack, Scully, and Moran in their review of the impact and methods for correcting IR in electrochemical measurements. This is complemented by Ehrhardt's paper, which includes consideration of cell geometry, current distribution, and the type of experiment on the IR voltage drop.

The next section critically compares several of the commonly available methods for correcting the error associated with IR voltage drop. Nisancioglu compares the current interruption, potential pulse, and electrochemical impedance techniques, and discusses error correction using electrode design, measurement technique, and data analysis. Mansfeld, Chen, and Shih compare correction methods present in commercially available systems and discuss the practical advantages and limitations of the respective techniques and equipment. Ehrhardt also reviews existing correction methods, but compares them experimentally to a new system introduced by the author, which is capable of combining different methods.

Esteban, Lowry, and Orazem introduce a numerical method to adjust current-potential data for the electrolyte resistance. This has provided better agreement between experimental data and mathematical models for the rotating disc electrode. Farozic and Prentice utilize numerical simulation of the potential distribution in more complex systems (for example, multiple electrode, irregular electrode shape) to provide insight into data interpretation and optimization of electrode arrangement.

The last section examines engineering applications of IR voltage drop measurement and correction. Thompson discusses the issues related to potential measurements of buried pipelines under cathodic protection. Abraham, Jones, Whitbeck, and Case use a modified Wheatstone bridge to assess ohmic interference associated with corrosion measurements of nuclear waste containers in desert soil. Another important area in which high-resistivity media complicate electrode potential measurements is that of rebar corrosion in concrete. The paper by Escalante describes the use of current interruption as a means to eliminate the IR error that arises in the measurement of the potential of steel in concrete under galvanostatic conditions. Berke, Shen, and Sundberg look at the same rebar/concrete system, but compare two correction methods, current interruption and electrochemical impedance measurements. Streinz et al. present a number of methods for determining the sources of ohmic resistance in lithium/iodine batteries. The final paper by Shaw focuses on the importance of ohmic potential drop in crevice corrosion measurements, an area of extreme importance when one realizes its relevance to other areas such as environmentally assisted fracture.

The universal nature of the ohmic electrolyte resistance and its bearing on subsequent electrode potential measurements must be recognized and corrected for by those in the electrochemical sciences. We feel that the depth, range, and relevance of the topics presented here will make this STP an excellent reference and source for the electrochemical scientist and engineer.

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Theory

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Influence of Electrolyte Resistance on Electrochemical Measurements and Procedures to Minimize or Compensate for Resistance Errors

REFERENCE: Hack, H. P., Moran, P. J., and Scully, J. R., "**Influence of Electrolyte Resistance on Electrochemical Measurements and Procedures to Minimize or Compensate for Resistance Errors,**" *The Measurement and Correction of Electrolyte Resistance in Electrochemical Tests, ASTM STP 1056,* L. L. Scribner and S. R. Taylor, Eds., American Society for Testing and Materials, Philadelphia, 1990, pp. 5–26.

ABSTRACT: Electrolyte resistance is receiving increasing attention as a source of error in electrochemical measurements when not properly managed. This paper is designed as an introduction to, and summary of, this topic. A discussion of electrolyte resistance and its effect on the results of electrochemical measurements is presented. A broad spectrum of methods for minimizing or correcting the errors caused by electrolyte resistance is described. Several advanced ideas are also introduced. References are given to lead the reader to additional information.

KEY WORDS: corrosion testing, electrochemical testing, electrolyte resistance, IR drop, IR compensation, current distribution, current interruption, electrochemical impedance spectroscopy, AC impedance, potentiostatic testing

Introduction

Electrolyte resistance and resistances of other components in the electrochemical circuit can have significant effects on the measurements being performed. The IR error in any electrochemical measurement in which there is an applied current, such as in corrosion testing, causes the applied potential (in potentiostatic or potentiodynamic control) or the measured potential (in current control) to deviate from that of the actual potential across the electrode/electrolyte interface being studied. This error can be large for the cases of high currents and/or low electrolyte conductivity. Alternatively, the error may be small enough to be ignored, but it cannot be completely eliminated. This paper is designed to be an introduction to, and summary of, the topic of electrolyte resistance as a source of error in electrochemical measurements.

What Effect Does Electrolyte Resistance Have?

In Figs. 1 and 2, two identical electrodes are electrically connected by external wires of zero resistance, and a battery is used to force a potential difference, E_A, between them. The

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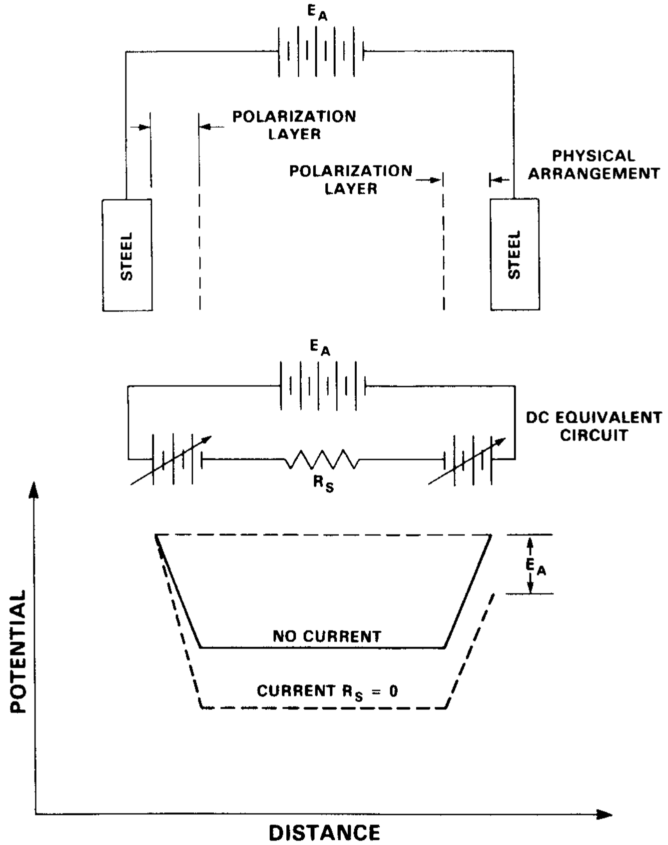

FIG. 1—*Potential distribution in a cell with no electrolyte resistance.*

resultant current flow will change the magnitude of the initial potential step across each double layer so that these steps sum to E_A. In the case of zero electrolyte resistance, as in Fig. 1, the potential will be uniform throughout the electrolyte.

Figure 2 illustrates the same situation when the electrolyte resistance is significant. Imposing a potential will cause a current to flow through the resistive electrolyte that generates a potential drop in the electrolyte of I times the solution resistance R_S. In a one-dimensional cell, such as a tube of electrolyte with electrodes at both ends, this results in a linear potential gradient through the electrolyte. In more complex three-dimensional geometries, the profile will not be linear. The total imposed cell potential in the case of a significant electrolyte resistance now includes I times R_S in the electrolyte as well as the sum of the potential steps at the two electrodes.

Figures 1 and 2 also contain the DC equivalent circuits for the situations described. The applied potential, E_A, is represented by a battery, potential steps in the polarization layers by variable batteries, and solution resistance by a resistor.

The effect of the potential gradient in the electrolyte on a potentiostatic test, such as that in ASTM Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements (G 5), is illustrated in Fig. 3. Between the working electrode surface and the reference electrode position is a portion of the electrolyte resistance,

$R_{S(Uncomp)}$. Between the working electrode and the counter electrode position is the electrolyte resistance, R_S. The potentiostat will hold the potential difference between the specimen and the reference electrode position at a constant value, E_{SET}. If the electrolyte resistance is significant, then the electrolyte potential gradient will cause an error in the measured working electrode potential of magnitude I times $R_{S(Uncomp)}$. The specimen will not be at the potential set by the potentiostat, but at a potential, E_{ACTUAL}, that depends on the location of the reference electrode, the electrolyte resistivity, and the total current flow.

Other Sources of Error

Any component of the electrical circuit of the electrochemical cell which gives rise to a resistance other than that at the double layers can also introduce similar errors. The most common of these is lead resistance, caused by a significant lead wire resistance that creates a voltage drop that makes the potential at the specimen terminal of the potentiostat different from that actually at the sample. In this case, the potential at the specimen terminal has an error, whereas with electrolyte resistance, the potential at the reference electrode position is in error. The effect, however, is the same.

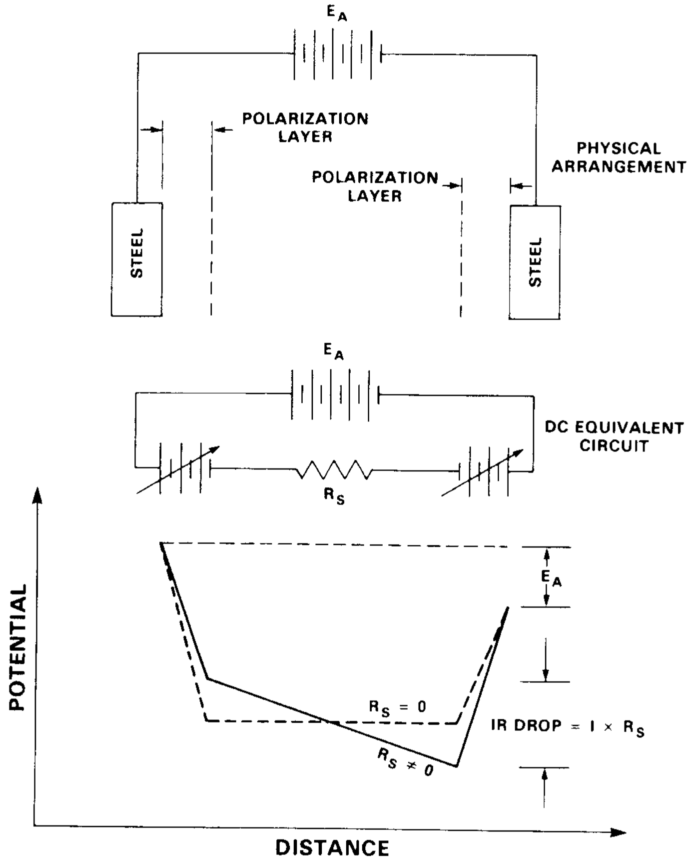

FIG. 2—*Potential distribution in a cell with electrolyte resistance.*

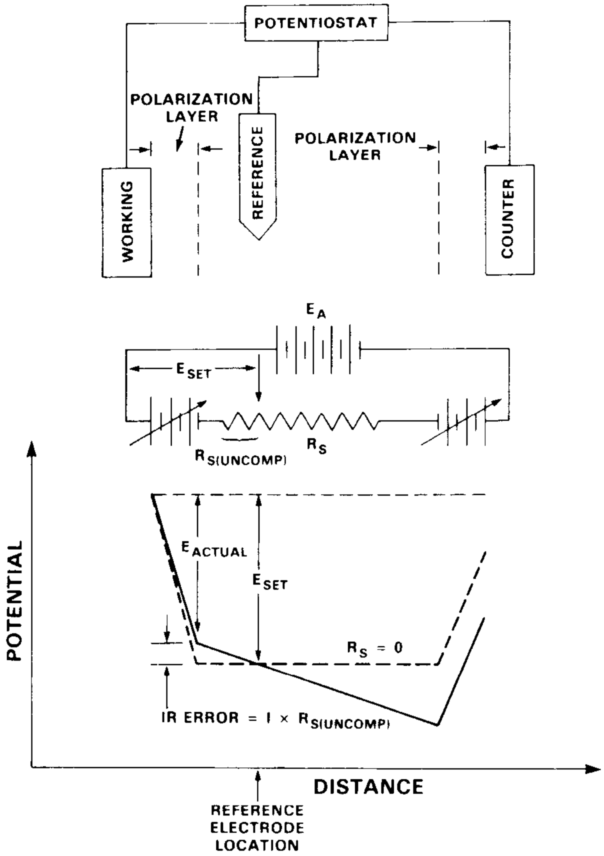

FIG. 3—*Potential distribution in a cell with a potentiostat.*

If the electrical connection to the working electrode is poor, it adds a high resistance which will result in measurement errors in the working-reference voltage. This can be the result of a cold solder joint, improper cleaning of a threaded connection, insufficient pressure or cleaning of a pressure connection, etc. The current flowing through the resistance at the poor joint creates a potential difference between the metal specimen and the wire connected to it. A long working electrode lead may itself have a significant resistance. Although the reference circuit carries almost no current, a sufficiently high resistance there will still cause a reference potential error. If the glass sheath of a glass-encased reference electrode drys out, a high resistance may be created in the electrolyte path of the reference electrode. These factors can contribute errors to the measurement and are easily avoided by proper experimental technique.

If the specimen material itself is extremely thin or is not a good conductor of electricity, a potential difference may be generated between the wire connection point and the specimen surface at the electrolyte due to the resistance of the bulk specimen material. This is a particularly difficult problem to handle since the resistance between the connection point and a given point on the specimen surface may vary with location, giving a potential error which is not the same everywhere on the specimen surface. This might occur, for example, on a composite specimen where conductive graphite fibers are in a nonconductive matrix like epoxy.

Finally, surface films on the specimen may also cause an unwanted resistance in the current path. These may be due to air-formed oxides, calcareous deposits, biological layers, etc., and can introduce measurement error. Unlike the previous resistances discussed, a surface film may not generate a potential drop strictly by Ohm's Law, but may have a current-dependent resistance, or may even rectify the current like a diode such that the resistance of the film is different depending on the direction of current flow.

What Is a Significant Resistance?

The significance level for resistance depends on the total current flowing in the cell and the level of potential error (produced by the product of current times resistance) that can be tolerated. This depends on the type of experiment being performed as well as the system being studied. If in doubt, procedures for minimization or correction of these errors should be performed.

What Is This Type of Error Called?

A number of terms have been coined for the above described type of error, but none is perfectly descriptive. "IR drop" error implies that measurement errors are usually due to a current, I, flowing through a resistance, R, creating a potential drop via Ohm's Law. The term "uncompensated ohmic resistance" implies that the impedance causing the error is ohmic, with no capacitive or inductive components (unlike most impedances across double layers), and is not compensated for by simple measurement techniques. Since there are many ways used to compensate for this type of error, as described below, this term cannot be applied for a well-conducted test. The term "uncompensated electrolyte resistance" also implies that the test was not conducted with proper compensation, and refers only to electrolyte resistance, thereby ignoring the other causes such as lead resistance. "Ohmic resistance" error implies that impedances leading to these errors have no capacitive or inductive components. This can be confusing since there are ohmic components of polarization resistance that are not part of this error. The term "solution resistance" is vague and unspecific. For the purposes of the remainder of this paper, the term "IR error" will be used.

Why Is It Bad?

IR error is bad for electrochemical measurements because it causes incorrect measurements to be made. Several specific errors associated with specific types of tests are described below:

Overestimation of Polarization Resistance—The polarization resistance test, such as in ASTM Practice for Conducting Potentiodynamic Polarization Resistance Measurements (G 59), is designed to measure R_P. The resistance of the electrolyte between the specimen and the reference electrode position, the resistance of any lead or connection, and the bulk specimen resistance are all in series with the resistance of the double layer being measured. These various resistances cannot be distinguished by the potentiostat in a DC measurement, and therefore the measured resistance will include the sum of all of these terms. If these resistances are not accounted for, they will give a polarization resistance which is higher than the true value [*1*]. This can be seen in Fig. 4. Even small electrolyte resistances can lead to significant errors in polarization resistance for rapidly corroding materials that have low polarization resistances. If IR errors associated with this type of test are not con-

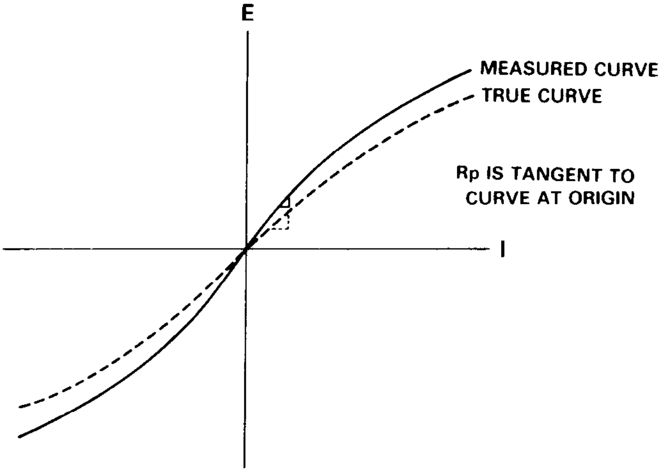

FIG. 4—*Effect of IR error on polarization resistance.*

sidered, polarization resistance overestimation that will occur will result in an underestimation of corrosion rate due to the reciprocal relationship between these two properties. This will provide measured corrosion rates that are too low.

Incorrect Polarization Curves—In the generation of polarization curves, such as the testing described in ASTM G 5 and ASTM Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys (G 61), IR error will shift the potential by an amount proportional to the current being measured. As shown in Fig. 5, if the specimen is being anodically polarized, the actual potential will be more negative than that set on the potentiostat. If the specimen is being cathodically polarized, the actual potential will be more positive than the set potential. The measured polarization curve will deviate from the true curve by an amount proportional to the current. For tests run to a fixed maximum potential, this will lead to termination of the test at a true potential less than that desired, with resulting loss of data. The remainder of the data can be corrected for as described later. The effect of solution resistance may limit the actual potential that can be applied to an electrode, as additional cell voltage will partially go into additional IR error, and not entirely into electrode polarization.

When an active-passive polarization curve is measured, some data may be lost, that is, not recoverable or correctable [*2*]. This is illustrated in Fig. 6. The measured curve (dashed line) is shifted away from the true curve (solid line) by a potential proportional to the measured current. The effect of the IR error is to tilt the curve over slightly. By itself, this effect is correctable as described later, but if the shift becomes too pronounced, the measured curve could be forced to double back on itself as shown by the short dashes between points A and B in the figure. A potentiostat will not measure such a curve shape, but will instead jump directly from point A to point B as shown on the long-dashed curve. All information on the real curve between these two points will not be measurable. Only by reducing the sources of the IR error will this portion of the curve be able to be measured.

Variable "Constant" Potential—A potentiostat controls the potential between the reference electrode and working electrode by varying the potential applied to the counter electrode, and thus the cell current. The IR error between the reference location and the surface

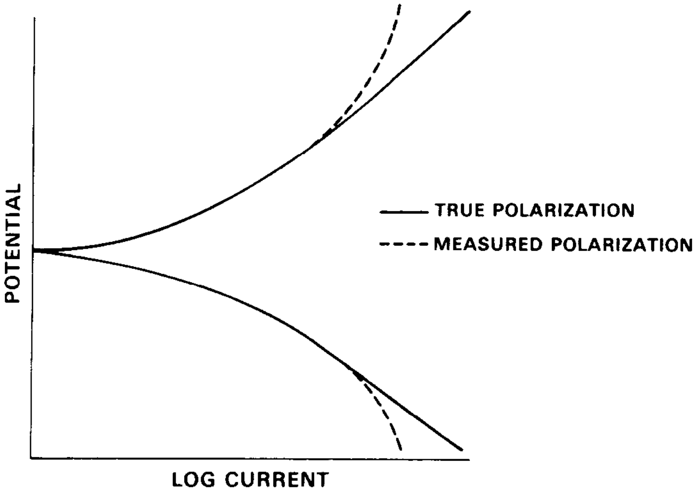

FIG. 5—*Effect of IR Error on polarization curves.*

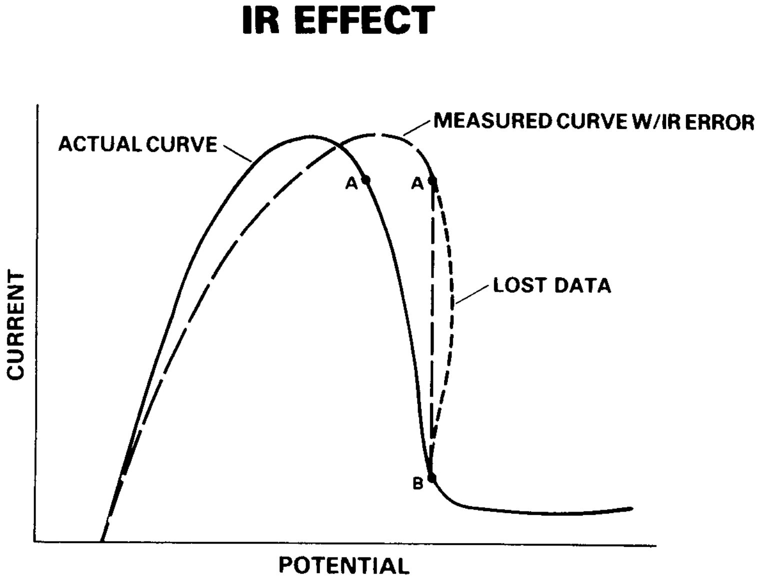

FIG. 6—*Loss of data on active nose due to IR error.*

of the working electrode is a function of this current, and thus a variable IR error will occur, leading to an uncertain working electrode potential, even though the potentiostat is functioning properly. This is particularly important when monitoring the performance of an electrode material over time, or when trying to hold a constant overpotential during stress corrosion testing.

Incorrect Sweep Rate—IR error will cause the potential sweep rate to be different from that expected in a potentiodynamic test [*2-4*]. In areas of the polarization curve where current increases as potential is swept away from the freely-corroding potential, the IR error will increase with time, causing the sweep rate to be lower than anticipated. This can lead to a proportionately large amount of time being spent in the high current area of the active nose of an active-passive curve, leading to excessive corrosion before the onset of passivation in an anodic polarization test. In the sections of active-passive curves where current decreases as potential is swept away from the freely-corroding value, the IR error will decrease with time, causing a larger sweep rate than anticipated. The actual sweep rate when IR errors are present will therefore be variable over the course of the test. Although the data itself can be corrected to remove the IR error, additional difficulties may be introduced if the material is highly sweep-rate sensitive. In practice, there are few corrosion systems that are so sweep-rate sensitive that this effect becomes important if proper IR error minimization measures are used during the test.

Potential and Current Distribution Effects

IR error is affected by the distribution of the total current flowing between the working and counter electrodes. If the current flow concentrates in the area between the working and reference electrodes, the potential gradient and resultant IR error will be higher than if the current concentrates outside of this area. This can be seen in Fig. 7. Since both cur-

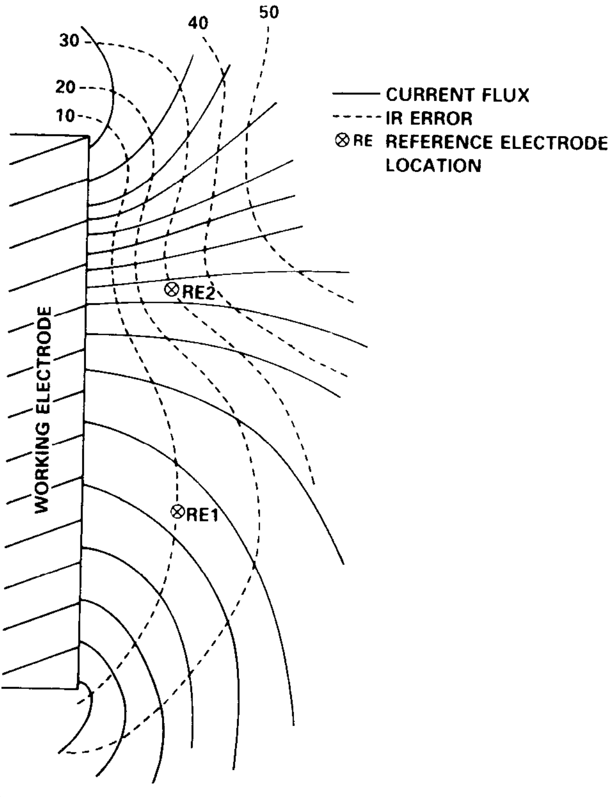

FIG. 7—*IR error variation with reference cell placement and current density variations.*