

The Potentiodynamic Polarization Scan

Technical Report 33



The Potentiodynamic Polarization Scan

Technical Report 33

*David G Enos
Center for Electrochemical Science & Engineering
Department of Materials Science & Engineering
University of Virginia
Charlottesville, VA*

*Louie L Scribner
Scribner Associates Inc.
Charlottesville, VA*

Solartron Instruments
a division of Solartron Group Ltd
Victoria Road, Farnborough
Hampshire, GU14 7PW, UK

Issue 2.0 - January 1997

©1997

Solartron

Victoria Road, Farnborough
Hampshire GU14 7PW England
Tel: +44 (0)1252 376666
Fax: +44 (0)1252 544981
Fax: +44 (0)1252 547384 (Transducers)

Solartron Transducers

19408 Park Row, Suite 320
Houston, Texas, 77084 USA
Tel: +1 281 398 7890
Fax: +1 281 398 7891

Solartron

964 Marcon Blvd, Suite 200
91882 MASSY, Cedex
France
Tel: +33 (0)1 69 53 63 53
Fax: +33 (0)1 60 13 37 06

**Solartron Overseas Sales Ltd
Instruments Division**

Block 5012 TECHplace II
Ang Mo Kio Ave. 5, #04-11
Ang Mo Kio Industrial Park
Singapore 2056
Republic of Singapore
Tel: +65 482 3500
Fax: +65 482 4645

Solartron**Beijing Liaison Office**

Room 327. Ya Mao Building
No. 16 Bei Tu Chen Xi Road
Beijing 100101, PR China
Tel: +86 10 2381199 ext 2327
Fax: +86 10 2028617

Email: solartron@solartron.com

Web: <http://www.solartron.com>

For details of our agents in other countries, please contact our Farnborough, UK office.

Solartron Instruments pursue a policy of continuous development and product improvement. The specification in this document may therefore be changed without notice.

Contents

1.	Introduction	1
2.	Theory	1
2.1	General	1
2.2	The Potential (Thermodynamic Information)	2
2.3	Current (Kinetic Information)	3
2.4	Theoretical Polarization Scans	3
2.4.1	The Anodic Scan	3
2.4.2	The Cathodic Scan	4
3.	Experimental Set-up	5
3.1	The Electrochemical Cell	6
3.1.1	Cell Design - electrodes and cell materials	6
3.1.2	Solution Preparation	7
3.1.3	Reference Electrodes	7
3.2	Sample Preparation	8
3.3	Instrumentation	9
3.3.1	Electrochemical Interface (Potentiostat/Galvanostat)	9
3.3.2	Computer Controlled Experimentation and Data Acquisition System	9
4.	Experimental Procedures	9
4.1	General parameters	9
4.1.1	Boundaries of the Potential Scan	9
4.1.2	Scan Rate	10
5.	Data Interpretation	
5.1	Corrosion Rate	10
5.2	Other Kinetic Information	12
5.3	Specific Techniques Involving Potentiodynamic Polarization Scans	12
5.3.1	Degree of Sensitization - Single and Double Loop EPR	12
5.3.2	Corrosion Rate - Linear Polarization Resistance	13

1. Introduction

DC electrochemistry, and in particular, the potentiodynamic polarization scan, allows considerable information on electrode processes to be acquired. Through the DC polarization technique, information on the corrosion rate, pitting susceptibility, passivity, as well as the cathodic behavior of an electrochemical system may be obtained. This application note provides a brief overview of the theory behind this technique, as well as how to extract useful information from a polarization scan. A description of the system components (hardware and software) required to perform these measurements, as well as a description of each component and its function is provided. In addition, this note details how to perform a DC polarization experiment utilizing CorrWare in combination with electrochemical equipment from Solartron, Inc., such as the Model 1287 electrochemical interface.

2. Theory

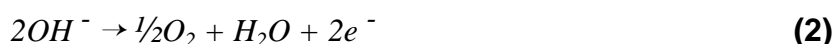
2.1 General

In order for an electrochemical process to take place, there must be an anode, a cathode, as well as both an ionic and electrical conduction path between the two. When performing a DC polarization scan, as will be discussed in this application note, the ionic conduction path is provided through the solution separating the working and counter electrodes, while the electrical conduction path is provided through the potentiostat. This potentiostat is then used to control the driving force for electrochemical reactions taking place on the working electrode. The magnitude of this driving force in turn dictates which electrochemical processes actually take place at the anode and cathode, as well as their rate. Electrons flow from the *anode* to the *cathode* through the electrical path described above. As such, the anode is typically thought of as the negative electrode, and the cathode as the positive.

At the *anode*, oxidation takes place. In the case of metal oxidation, this may be represented by a reaction such as;



where M represents the pure metal or alloy, M^{x+} represents the ion of the metal, and xe^{-} represents the number of electrons transferred in the process. It should be noted that oxidation of the metal being investigated is not the only oxidation process which may take place - other chemical species present within the environment may be oxidized (e.g., in iron containing solutions, ferrous ions may be oxidized to ferric ions, $Fe^{2+} \rightarrow Fe^{3+}$) or at sufficiently positive potentials, oxygen production may occur in aqueous environments;



At the *cathode*, reduction takes place. Reactions such as the reduction of an oxide or hydroxide present on the cathode surface may take place;



As with the anode, the reduction reactions which take place on the surface of the cathode are not limited to reduction of the oxide present on that electrode. For example, at sufficiently negative potentials, water reduction may take place in aqueous environments.



In addition, other chemical species present within the environment may be reduced as well. It is important to note that a number of different reactions may be taking place on the electrode surface, and at best the only information which may be obtained is the *total current* resulting from all of those reactions.

In a DC potentiodynamic polarization scan, the nature of the interface being interrogated, in terms of its behavior as an anode or a cathode, is controlled, as will be discussed below.

2.2 The Potential (Thermodynamic Information)

The thermodynamic tendency for an electrochemical reaction to occur, such as metal oxidation, is determined by the free energy change associated with that reaction. Take the following symbolic reaction as an example;



The free energy change associated with the above reaction can be expressed in terms of the energy of formation of each specie within the reaction;

$$\Delta G = (lG_L + mG_M + \dots) - (jG_J + kG_K + \dots) = \sum v_i G_i \quad (6)$$

Where G_X represents the energy of formation of specie X, and ΔG is the free energy change associated with the reaction. The change in free energy associated with any reaction may also be expressed as $\Delta G = -nFE$ where E is the thermodynamic potential, n is the number of electrons transferred in the reaction, and F is Faraday's constant (96,500 Coul/eq). At equilibrium, $\Delta G = 0$. Combining these two expressions, we see that deviations from equilibrium may be accounted for by utilizing the chemical activity of each specie. Thus, if E^0 is used to represent the equilibrium value, the following expression is readily obtained:

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_L^l \cdot a_M^m \cdot \dots}{a_J^j \cdot a_K^k \cdot \dots} \quad (7)$$

Through this relationship, known as the Nernst equation, the half cell potential associated with a given reaction may be calculated.

It is important to note that the free energy change associated with a reaction, and hence the potential, is a thermodynamic property. In addition, it is a state function - in other words, the free energy change for a reaction is independent of the path which the reaction takes - it depends only on the initial and final states. More importantly, while the magnitude of the energy change associated with a reaction provides information on whether or not a reaction can occur (i.e., there exists a driving force), it *can not be used to predict the rate* at which the reaction will take place (i.e., the kinetics of the reaction).

2.3 Current (Kinetic Information)

In a potentiodynamic experiment, the current represents the rate with which the anodic or cathodic reactions are taking place on the working electrode. Typically, the current is expressed in terms of the current per unit area of the working electrode, or the current density. Numerous variables will influence the rate of a given electrochemical reaction, including the temperature, the surface condition of the surface being interrogated, as well as the chemical environment in which the experiment is performed. In general, cathodic currents are considered to be negative, and anodic currents to be positive. It should be noted that in an Evans diagram (a plot of E vs $\log(I)$) the absolute value of the current density is plotted (i.e., both anodic and cathodic currents are plotted as positive values).

The reaction rate may be controlled by two different kinetic phenomena. The first is charge transfer or activation control. In this case, the reaction rate is controlled by the size of the driving force available (e.g., hydrogen evolution reaction or water reduction reaction). As the driving force increases, so does the reaction rate. The other mechanism which may control the reaction rate is mass transfer. In this case, the reaction rate is controlled by mass transfer through the electrolyte to the electrode surface (e.g., oxygen reduction reaction). Since the reaction rate is controlled by diffusion, it can not increase indefinitely as the driving force increases. Instead, the current reaches a maximum, or limiting, current density which is itself a function of the concentration of the specie of interest in the solution as well as its diffusivity. Once the rate for a particular reaction has reached its limiting value, further increases in driving force will not result in any additional increase of the reaction rate.

2.4 Theoretical Polarization Scans

The following two subsections detail the features found on a typical anodic or cathodic potentiodynamic scan. It should be stressed that these figures are idealized representations of features typically observed in practice. A given polarization scan may have some, but not necessarily all, of the features described below. In addition, other features may also be present not detailed here. In order to completely understand a system, knowledge of the potential anodic and cathodic reactions which may take place is essential.

Before observing the theoretical polarization scans, it is important that the user understand what they display. In a potentiodynamic experiment, the driving force (i.e., the potential) for anodic or cathodic reactions (depending on the nature of the scan) is controlled, and the net change in the reaction rate (i.e., current) is observed. The potentiostat measures the current which must be applied to the system in order to achieve the desired increase in driving force, known as the applied current. As a result, at the open circuit potential (potential at which the total anodic current is equivalent to the total cathodic current) the measured or applied current will be zero.

2.4.1 The Anodic Scan

A schematic anodic polarization curve is illustrated in Figure 2.1. As can be seen in the figure, the scan starts from point 1 and progresses in the positive (potential) direction until termination at point 2. There are a number of notable features on the curve. The *open circuit or rest potential* is located at point A. At this potential the sum of the anodic and cathodic reaction rates on the electrode surface is zero. As a result, the measured current will be close to zero. This is due to the fact that the potentiostat only measures the current which it must apply to achieve the desired level of polarization. As the potential increases, we move into region B, which is the *active region*. In this region, metal oxidation is the dominant reaction taking place. Point C is known as the *passivation potential*, and as the applied potential increases above this value the current density is seen to decrease with increasing potential (region D) until a low, passive current density is achieved (*Passive region* - Region E).

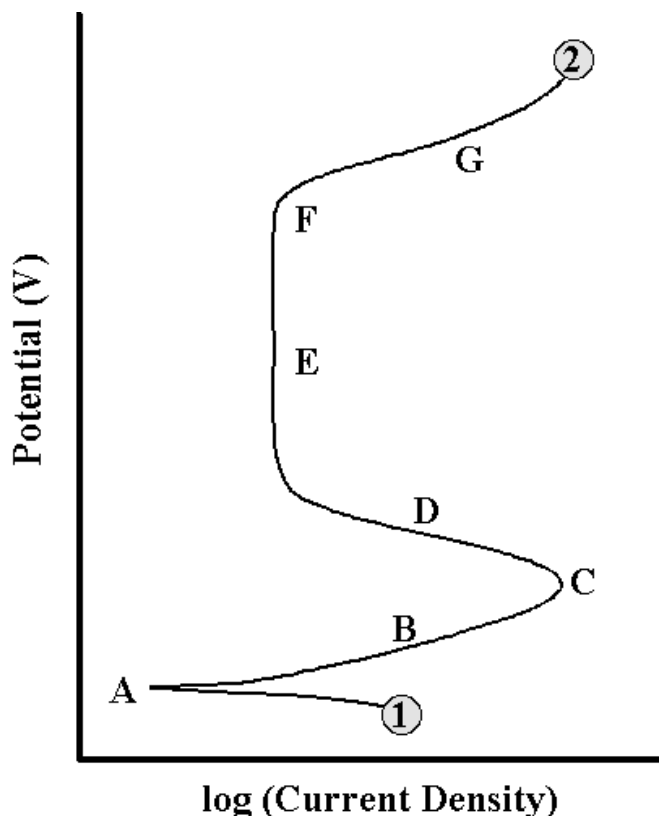


Figure 2.1 - Theoretical anodic polarization scan

Once the potential reached a sufficiently positive value (Point F, sometimes termed the *breakaway potential*) the applied current rapidly increases (region G). This increase may be due to a number of phenomena, depending on the alloy/environment combination. For some systems (e.g., aluminum alloys in salt water) this sudden increase in current may be pitting (localized breakdown of passivity), while for others it may be transpassive dissolution. For some alloys, typically those with a very protective oxide, such as cobalt, the sudden increase in current is due to oxygen evolution.

Again, it should be stressed that this is a schematic diagram illustrating some of the possible regions present on an anodic polarization scan. Depending on the nature of a particular system, some or all of these features may be present.

2.4.2 The Cathodic Scan

A schematic cathodic polarization scan is illustrated in Figure 2.2. In a cathodic potentiodynamic scan, the potential is varied from point 1 in the negative direction to point 2. The open circuit potential is located at point A. As with the anodic scan, the open circuit potential represents the potential at which the sum of the anodic and cathodic reactions occurring on the electrode surface is zero. Depending on the pH and dissolved oxygen concentration in the solution, region B may represent the oxygen reduction reaction. Since this reaction is limited by how fast oxygen may diffuse in solution (mass transport controlled) there will be an upper limit on the rate of this reaction, known as the limiting current density (as discussed above in Section 2.3).

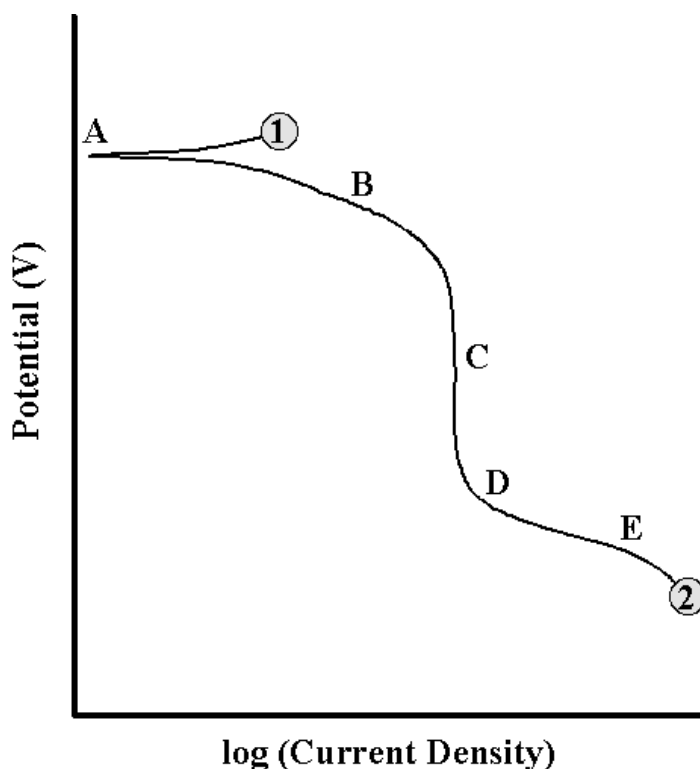


Figure 2.2 - Theoretical cathodic polarization scan

Further decreases in the applied potential result in no change in the reaction rate, and hence the measured current (Region C). Eventually, the applied potential becomes sufficiently negative for another cathodic reaction to become operative (i.e., there is a sufficient thermodynamic driving force for an additional cathodic reaction to begin taking place), such as illustrated at Point D. As the potential, and hence driving force, becomes increasingly large, this reaction may become dominant, as illustrated in Region E. This additional reaction is typically the reduction of other species in the environment (such as the hydrogen evolution reaction, also known as the water reduction reaction). An increase in current may also be observed if sufficient driving force exists to reduce the oxide present on the electrode surface.

3. Experimental Set Up

In order to perform a polarization scan on a particular metal/solution system, a number of components must be assembled and appropriately prepared. First, an electrochemical cell which contains both the metal to be investigated, the environment in which the polarization scan is to be performed, as well as all of the implements required to conduct the measurement, must be acquired. Prior to performing the experiment, the sample surface must be prepared such that the initial condition, or starting point, of the measurement is well defined and does not vary from test to test. Finally, equipment capable of performing the measurement and acquiring data is required.

3.1 *The Electrochemical Cell*

The electrochemical cell serves a number of purposes. First, it provides a means to establish the environmental conditions under which the measurement is to be performed. Variables controlled often include the solution chemistry, temperature, and the surface condition (e.g., roughness, surface film/oxide, etc.) of the metal/solution interface being interrogated. In addition, the cell must provide a convenient means with which to electrochemically alter the conditions at the surface, without introducing large errors due to iR drop, etc. Finally, a stable reference electrode with a known reference potential is used to aid in the control and measurement of the surface potential throughout the polarization scan.

3.1.1 Cell Design - electrodes and cell materials

There are three primary components to the typical electrochemical cell. They include the cell body, the electrodes, and the implements used to monitor and control the environment. The following section is intended to give some general guidelines for cell design and construction, after which a number of general use, commercially available cell designs will be presented.

Cell Body

The body of the cell is required to contain the test environment, which may or may not be aggressive. The material chosen to construct the cell from should take into consideration the requirements of the experimentation which will be conducted within, such as the operating temperature range, pH, need for aeration/deaeration, etc. Typical materials include glass (can be used in most temperatures; resistant to many environments, with the exception of HF containing solutions, very high pH solutions, etc. which will gradually etch the glass; can be difficult to produce custom cell designs), acrylic (easy to machine; wide range of useful temperatures; not a good choice for very aggressive environments or solvents which will attack the acrylic), and polytetrafluoroethylene (PTFE or teflon) (extremely chemical resistant; can be challenging to machine in complex shapes; flows at elevated temperatures).

Electrodes

There are typically three electrodes - the working electrode, the counter electrode, and the reference electrode. The working electrode is the sample being interrogated, and will vary. The reference electrode provides a stable "reference" against which the applied potential may be accurately measured, as will be illustrated below. The counter electrode is used to provide the applied current, and as such should be composed of a highly corrosion resistant material, such as platinum. As with the cell body, the actual choice of a counter electrode material may vary with the environment under consideration, but platinum, or a platinized substrate material is typically a good choice. Counter electrodes which corrode over the course of an experiment may significantly alter the solution chemistry, complicating and potentially invalidating the measurement. The size of the counter electrode should scale with the amount of current which it is to provide, typically being equal to or larger than the working electrode in size.

Environmental Control:

Variables which often require a method with which the user can accurately control them over the course of an experiment include the temperature, the dissolved oxygen concentration, the environmental chemistry, and the pH. Temperature control is often achieved with either an external (to the cell body) heater or an internal heating coil in combination with a thermometer or thermocouple. The dissolved oxygen concentration may be controlled via a gas inlet connected to a gas dispersion frit or tube within the solution and a gas outlet. Inert gases (N₂, Ar) are typically used to reduce the dissolved oxygen concentration, while air is often bubbled through to maintain a high concentration. Similarly, a solution inlet (and possibly and outlet) may be used to monitor and control the environmental chemistry and pH throughout the test.

Cell designs may vary, depending on the needs of the experiment. Below are descriptions for two commercially available examples.

Coating Cell

Figure 3.1 illustrates a flat cell. The sample is clamped onto the base of the cell. Above the base is the counter electrode (platinized niobium mesh) and the reference electrode. The top of the cell is exposed to the atmosphere, so the environment cannot be deaerated. Similarly, without an external heater and thermometer, temperature may not be controlled either.

Greene Cell

Figure 3.2 illustrates the Greene cell. This cell is composed of glass and has ports through which the working, counter, and reference electrodes are inserted. An external heater may be used to maintain the temperature. As the cell is readily sealed, experiments in either aerated or deaerated environments may be performed. Preparation of the working electrode requires somewhat more effort than for the coating cell. Flag shaped specimens or specimens which fit into a small holder are often used.

3.1.2 Solution Preparation

The most important aspects of the solution are the reagents used to produce it. They should be of high purity and quality, and weighed as accurately as possible. When purchasing readily hydrated materials, such as calcium chloride, etc., for use in aqueous environments, they should be purchased in the hydrated state. By doing so, errors caused by the gradual absorption of water by the stock container will be avoided. Solution concentrations are commonly expressed in term of the molarity of specific species within the solution (i.e., the number of moles of a given component per liter of solution), although molality (moles of each component per liter of solvent) and normality (moles of each component divided by their hydrogen equivalent per liter of solution) are also used.

The purity of the bulk environment (i.e., water, etc.) is also very important. Water may be purified in a number of ways. Possibly the most commonly applied purification technique is distillation. A deionization system will result in further purification. Finally, in many cases the solution is electrolyzed using two platinum electrodes to remove impurities which may deposit on the working electrode during the course of an experiment. In any event, all constituents and their purity should be documented to aid in the diagnosis of any unexpected results.

3.1.3 Reference Electrodes

A reference electrode provides a means to accurately measure the potential applied to the working electrode. In general, the reference electrode is based upon a reaction which is more or less at equilibrium and is not influenced by changes occurring at the working electrode which is being monitored. This reaction must be reversible and non-polarizable (high exchange current density and low polarization resistance - i.e., a large change in current will result in a very small change in potential).

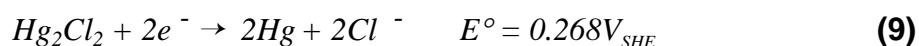
The appropriate reference electrode for a particular application will depend on the environment and temperatures anticipated. As an example, in environments which are chloride free, and must be maintained that way, the saturated calomel electrode, which contains potassium chloride, would be a poor choice as Cl^- will leak through the glass frit separating the reference electrode from the solution, contaminating the bulk environment. A better choice would be the copper/copper sulfate electrode or a similar reference electrode. Alternatively, care could be taken to separate a chloride containing reference electrode from the bulk electrolyte through some sort of salt bridge.

The standard reference electrode which is often referred to is the standard hydrogen electrode (SHE). All other reference electrodes can be expressed in terms of some constant deviation from the SHE. The SHE is based upon the reaction;

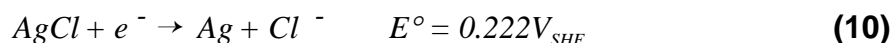


where E° is the reference state at standard temperature and pressure. It should be noted that this potential is independent of temperature (not true for many other electrodes, as will be illustrated below) and a function only of the reference electrolyte pH ($E^\circ = -0.059 \cdot \text{pH}$).

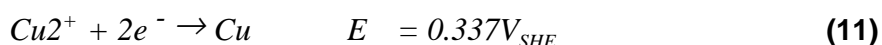
Some of the more commonly utilized reference electrodes include the saturated calomel electrode (SCE), the silver-silver chloride reference electrode, and the copper-copper sulfate reference electrode (least accurate, but most durable of the three). The saturated calomel electrode consists of pure mercury covering a platinum wire which passes through a sealed glass tube. The mercury is covered with mercurous chloride and immersed in saturated potassium chloride. The temperature coefficient is $-6.6 \times 10^{-4} \text{ V/}^\circ\text{C}$ and the reference reaction is;



The silver-silver chloride reference electrode consists of a silver or silver plated wire, the surface of which has been chloridized (transformed to silver chloride), typically in dilute hydrochloric acid. The temperature coefficient is $-4.3 \times 10^{-4} \text{ V/}^\circ\text{C}$ and the reference reaction is;



Finally, the copper - copper sulfate reference electrode consists of a piece of reasonably pure copper immersed in saturated copper sulfate. The temperature coefficient is $-7 \times 10^{-4} \text{ V/}^\circ\text{C}$ and the reference reaction is;



3.2 Sample Preparation

The sample preparation procedures required for a particular test depend on the nature of the information to be gathered. The most important point is that the sample preparation procedure be documented to ease the performance of replicate tests. In some cases, the as-received or initial surface condition may be required. For such experiments, care should be taken to preserve that surface while performing any cutting or other machining required to place the sample into the electrochemical cell.

If a clean, polished metal surface is desired, there are a number of steps which should be taken, as outlined below;

1. Section the sample (cut with saw, EDM, etc.) to the desired shape.
2. Clean the sample to remove any cutting oils, etc. This may be done using soapy water, or an appropriate solvent (e.g., acetone, methanol, etc...).
3. If necessary, mount the sample in epoxy or a phenolic resin.

4. Polish the sample using increasingly fine polishing paper. Typically, progressing from 180 grit to 240 to 320 to 400 and then finally 600 grit is adequate. Polishing may be accomplished either wet or dry, depending on the application. While polishing, care should be taken to change the orientation of the sample frequently. In addition, all scratches from the previous grit paper should be removed by the current paper and the sample cleaned of polishing media before progressing to a finer grit. Although a 600 grit finish is fine for most applications, the sample may be further polished to 800 grit followed by 1 μm or smaller alumina or diamond paste.
5. Surface should be cleaned thoroughly with an appropriate cleanser (soapy water, solvent, etc.) after which it should be rinsed in distilled or deionized water to remove any traces of the cleanser.

3.3 Instrumentation

3.3.1 Electrochemical Interface (Potentiostat/Galvanostat)

An electrochemical interface, such as the Solartron Models 1280, 1286 or 1287, in this case functioning as a potentiostat, is used to control the rate of the reactions occurring at the electrode surface. In the case of a potentiodynamic scan this is done indirectly by controlling the potential, and hence the driving force, available for reactions which might occur. The rate of the available reactions will vary based on the size of the driving force and the nature of the reaction itself (i.e., mass or charge transfer controlled).

The second function of the potentiostat is to measure the current applied by the potentiostat to achieve the desired degree of polarization. As such, it is important that the instrument be sufficiently sensitive to measure the currents which are anticipated.

3.3.2 Computer Controlled Experimentation and Data Acquisition System

The role of the data acquisition system is to acquire the current and potential information from the electrochemical interface described above. Such a system must be able to accurately acquire information at a sufficiently high rate. Ideally, the system should enable data to be readily archived for future use or data analysis. An example of such a system is a personal computer equipped with a communication device, such as a GPIB board (IEEE-488), to exchange information with the electrochemical interface, in combination with software capable of controlling the electrochemical interface and acquiring data.

Such a software package is the combination of CorrWare (for hardware control and data acquisition) and CorrView (for data comparison and analysis) from Scribner Associates, Inc. The use of this system to perform and analyze a potentiodynamic polarization scan will be detailed below.

4. Experimental Procedures

4.1 General parameters

4.1.1 Boundaries of the Potential Scan

When configuring your instrumentation to perform a potentiodynamic scan, there are a number of parameters which must be specified. The first is the initial and final potentials which define the "path" which the scan will take. The starting point will depend on the type of information which is desired. Ideally, both anodic and cathodic scans should be initiated from the open circuit potential. Often times scans will be initiated at a potential slightly anodic of the open circuit potential for a cathodic scan and slightly cathodic of the open circuit potential for an anodic scan. While these deviations from open circuit do not alter the experiment in many cases, it should be realized that you are altering the metal surface.

This alteration may be in the form of an increased or decreased oxide thickness, or the plating of components of the solution onto the metal surface - in any event, the interface will have been changed. In general, the larger the deviation from the open circuit potential, the larger the effect.

The location of the final potential also depends on the type of information you wish to obtain. Often times, the scan is run until a particular current density is achieved, then the scan is halted. For example, for a passive metal in a chloride containing electrolyte, once pitting has initiated, further increasing the potential and hence the current will not yield any useful information. Similarly, in a cathodic scan, once the potential is sufficiently negative for hydrogen evolution to occur, increasing the potential much more will not yield any additional information. On the other hand, the scan may be reversed once a particular current or potential has been reached after which the scan will progress to another endpoint. In the case of the passive metal system discussed above, reversing the scan will allow the establishment of the repassivation potential (potential at which active pits repassivate).

Another factor which may influence the placement of the final potential is the IR drop which results from the uncompensated solution resistance. When the currents are small, the measured potential is essentially equal to the applied potential. However, once the product of the current and the solution resistance becomes significant, it will shift the measured potential. In other words, the measured potential is equal to the sum of the applied potential and that due to IR through the electrolyte.

4.1.2 Scan Rate

The scan rate refers to the rate with which the potential is changed while the potentiodynamic scan is being performed (typically expressed in mV/s). The speed of the scan rate will largely influence the type of information obtained. In general, higher scan rates do not allow sufficient time for the system to stabilize at each potential. As a result, parameters such as the location and size of the active nose, the passivation potential, and the pitting potential are often shifted to more positive values. The ASTM standard scan rate is 0.1667 mV/s.

5. Data Interpretation

5.1 Corrosion Rate

One of the pieces of information often extracted from potentiodynamic polarization scans is the corrosion rate. For reactions which are essentially activation controlled (i.e., charge transfer controlled reactions, or mass transfer controlled reactions occurring at a rate much less than the limiting rate), the current density can be expressed as a function of the overpotential, η , where $\eta = E_{\text{applied}} - E_{\text{open circuit}}$ as follows;

$$\eta = \beta \log \frac{i}{i_0} \quad (12)$$

This expression is known as the Tafel equation, where β is the Tafel slope, i the applied current density, and i_0 the exchange current density (the reaction rate at the reversible potential for that particular reaction). Thus, the Tafel slope for the anodic and cathodic reactions occurring at open circuit may be obtained from the linear regions of the polarization curve, as illustrated in Figure 5.1. Once these slopes have been established, it is possible to extrapolate back from both the anodic and cathodic regions to the point where the anodic and cathodic reaction rates (i.e., currents) are equivalent. The current density at that point is the corrosion current density (i_{corr}) and the potential at which it falls is the corrosion potential (E_{corr}).

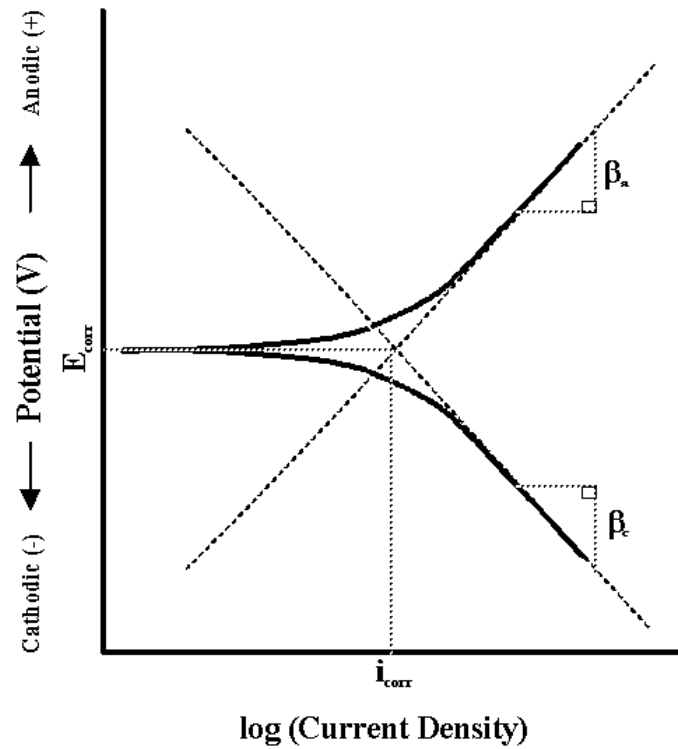


Figure 5.1 - Tafel slope calculation

The corrosion current density may then be combined with Faraday's law;

$$W = \frac{A \cdot W \cdot Q}{zF} \quad (13)$$

where W is the mass of material removed, AW the atomic weight of the sample, Q the total charge passed (i.e., $i_{\text{corr}} \cdot \text{time}$), z the number of electrons transferred in the reaction, and F is Faraday's constant. However, since experiments are rarely performed on pure metals, but alloys instead, this must be taken into account. The equivalent weight, or the mass of material per unit charge, is equal to the atomic weight of the element in question divided by its valence. For an alloy, the equivalent weight may be expressed as a weighted average of its constituents. The calculation of the equivalent weight for an alloy requires knowledge of the oxidation state of each constituent as well as its molecular fraction of the alloy. This is combined in the following expression to calculate the equivalent weight;

$$\text{Equivalent Weight (EW)} = \left(\sum \frac{f_i z_i}{AW_i} \right)^{-1} \quad (14)$$

where f_i is the atomic fraction and z_i the valence of each component. Once the weight of material has been calculated, the volume of material, and hence the rate of corrosion in terms of depth per unit time, may be established through the density (ρ) and exposed surface area (SA);

$$\text{Corrosion Rate} = \frac{W \cdot SA}{\rho} \quad (15)$$

It should be noted that, in the case of pitting or some other type of localized corrosion, this expression is not valid. It is valid only for the case of general corrosion.

5.2 Other Kinetic Information

In addition to general information on the kinetics of the various anodic and/or cathodic reactions taking place on the working electrode surface, the potentiodynamic polarization scan may also be used to acquire information on a number of other processes. The following subsections briefly outline some of the other types of information which may be obtained, and how one goes about obtaining it.

5.3 Specific Techniques Involving Potentiodynamic Polarization Scans

5.3.1 Degree of Sensitization - Single and Double Loop EPR

Many stainless steels, such as 304, are prone to a phenomenon known as sensitization. This phenomenon is the result of chromium depletion along grain boundaries due to the precipitation of chromium carbides. This detrimental carbide precipitation is often the result of thermal cycling due to processes such as welding. The resulting chromium depleted zones are not as corrosion resistant as the bulk alloy, resulting in preferential corrosion along grain boundaries.

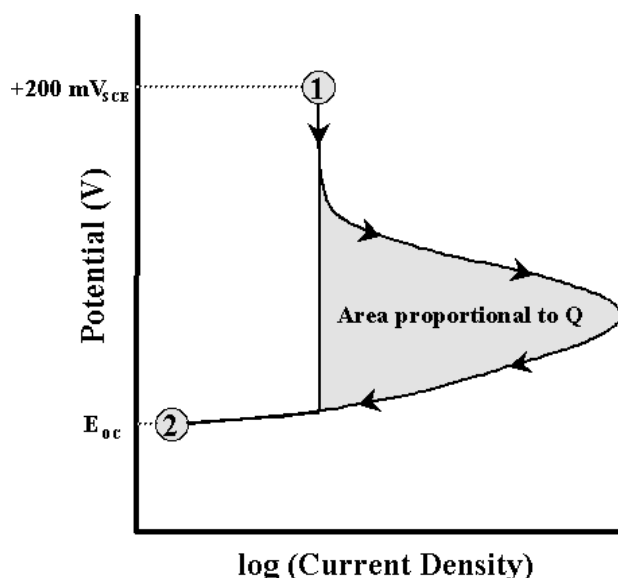


Figure 5.1 - Single loop EPR

The single and double loop electrochemical potentiokinetic reactivation techniques (SL-EPR and DL-EPR, respectively) are techniques which employ potentiodynamic scans to assess the degree of sensitization. Both tests are performed in an 0.5 M H₂SO₄ + 0.01 M KSCN solution at room temperature. In the single loop technique (See Figure 5.1), the sample is first allowed to stabilize in the solution, arriving at an open circuit potential typically around -400 mV_{SCE} (Point 2 in the Figure).

After the sample has been allowed to stabilize, a potential of +200 mV_{SCE} is applied in order to passivate the steel (Point 1 in the Figure). Next, the potential is scanned from +200 mV_{SCE} down to the previously established open circuit potential (Point 2). As the potential is decreased, the grain boundaries will preferentially activate. As such, the total anodic current (or charge, Q) passed as the potential is decreased at a fixed rate will be proportional to the grain boundary area activated, and hence be indicative of the degree of sensitization.

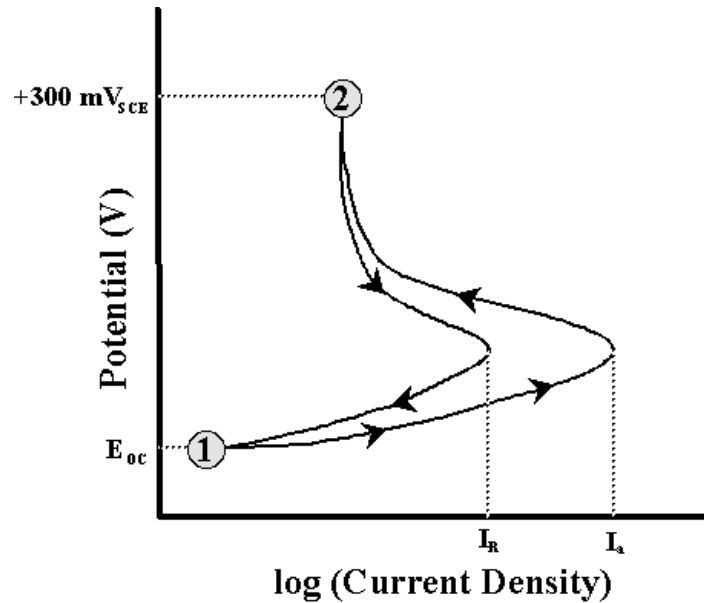


Figure 5.2 - Double loop EPR

The double loop EPS technique is similar in many ways to the single loop technique (see Figure 5.2). Again, the sample is allowed to stabilize at open circuit (Point 1). Next, rather than passivating the sample potentiostatically, the potential is scanned dynamically from open circuit (typically $\sim 400 \text{ mV}_{SCE}$) up to $+300 \text{ mV}_{SCE}$ (Point 2), after which it is scanned back down to the original open circuit potential. At this point, the peak current of the anodic nose from the first anodic polarization (I_a) is compared to the peak current on the return scan (I_r). The current on the return scan is assumed to be due primarily due to the reactivation of the chromium depleted grain boundaries. As a result, the ratio of $I_r:I_a$ is used to establish the degree of sensitization.

5.3.2 Corrosion Rate - Linear Polarization Resistance

Linear polarization resistance (LPR) is a technique through which the corrosion rate is assessed more or less non-destructively (as the magnitude of the potential applied is small). In this technique, the potential is slowly scanned through a potential range of approximately 25 mV about the open circuit potential (see Figure 5.3).

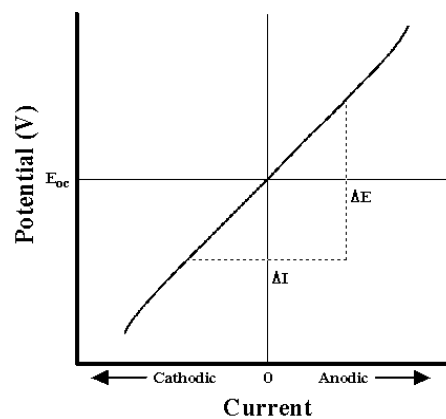


Figure 5.3 - Linear Polarization Resistance

The Potentiodynamic Polarization Scan

For such small deviations from the open circuit potential, the current response is linear. The ratio of the applied potential to the applied current ($\Delta E/\Delta I$) is defined as the polarization resistance, R_p (remember Ohm's law: $V=IR$).

From this polarization resistance, the corrosion current, i_{corr} , may be calculated through the Stern-Geary equation, which is as follows;

$$R_p = \frac{\beta_A \beta_C}{2.3(i_{corr}) (\beta_A + \beta_C)} \quad (16)$$

where β_A and β_C are the Tafel slopes discussed above in Section 5.1. This corrosion current may then be converted into an actual corrosion rate through Equation 15. It should be noted that a potentiodynamic scan as discussed in this application note must be performed in addition in order to determine these slopes.