Application Note AN-COR-003

Measurement of polarization resistance

ASTM G59 and more

The use of Tafel analysis to obtain the corrosion rate of various metals and alloys in different environments is covered in Application Note AN-COR-019. However, in some cases the reaction mechanism is not always known, or it is not possible to extract meaningful Tafel slopes from the polarization curve due to side reactions or other electrochemical phenomena. In such cases, Tafel analysis becomes impossible. Polarization resistance (R_p) provides a convenient way to quantify the corrosion resistance of metals in this scenario. R_p has become an important parameter for corrosion analysis because it is rapid, easy to measure, and is also considered nondestructive.

ASTM G59 describes how to undertake a polarization resistance measurement but was originally developed to calibrate and verify that the instrument and test cell are responding properly. This Application Note provides an overview of the methodology and practical applications of polarization resistance measurements in corrosion studies.

INTRODUCTION

Remember that an electrode is considered polarized when its potential is forced away from its value at open circuit or the corrosion potential (E_{corr}). Polarization of the electrode causes current to flow due to electrochemical reactions at its surface. A polarization curve (i vs E) monitors the changing current as the potential at the electrode is swept. The polarization resistance (R_p) is defined as the gradient of the polarization where i = 0:

$$R_p = \left(\frac{d\Delta E}{di}\right)_{i=0,\Delta E \to 0}$$

In this equation, ΔE is the variation of the applied potential around the corrosion potential ($\Delta E = E - E_{corr}$) and i is the resulting polarization current. Therefore, the polarization resistance can be calculated from the inverse of the slope of polarization curve at the corrosion potential.

During the polarization, the magnitude of the current is determined by the reaction kinetics and diffusion to and from the electrode surface. The Butler-Volmer equation relates the current with the overpotential.

$$i = i_{corr}\left(e^{2.303\frac{\eta}{b_a}} - e^{2.303\frac{\eta}{b_c}}\right)$$

The overpotential η (V) is defined as the difference between applied potential E and the corrosion potential E_{corr} (i.e., η (V) = $E - E_{corr}$).

The corrosion potential E_{corr} is the open circuit potential (OCP) of a corroding metal. The corrosion current i_{corr} and the Tafel constants b_a and b_c can be measured from the experimental data. Refer to AN-COR-019 for more information.

For small overpotentials η, i.e., for potentials close to corrosion potential, the previous equation can be reduced to:

$$i_{corr} = \frac{B}{R_p}$$

B is known as the Stern-Geary constant and is related to the anodic and cathodic Tafel slopes

$$B = \left[\frac{b_a b_c}{2.303(b_a + b_c)}\right]$$

INTRODUCTION

If the Tafel slopes are known, the corrosion currents can be calculated from the polarization resistance using the above equations, which in turn can be related to the corrosion rate by the following:

$$CR = 3.27 * 10^{-3}\,\frac{i_{corr} E_w}{\rho}$$

where E_w is the equivalent weight and ρ is the density.

If the Tafel slopes are not known (e.g., when the corrosion mechanism is not known), R_p can still be used as a quantitative parameter to compare the corrosion resistance of metals under various conditions. A specimen with low R_p will corrode more easily than a specimen with a high R_p.

An example polarization resistance measurement is described in ASTM G59 and can also be used as a way to calibrate and verify that the instrument and cell are set correctly.

SAMPLE AND EXPERIMENTAL

a, ASTM G59: For this experiment, the sample was immersed in a 1 N (0.5 mol/L) aqueous sulfuric acid solution. Two stainless steel rod counter electrodes were used as the counter electrode. As a reference electrode, an Ag/AgCl 3 mol/L KCl Metrohm reference electrode was chosen. The cell was the ASTM-compliant 1 L Metrohm Autolab corrosion cell.

The solution of sulfuric acid was deaerated by bubbling nitrogen gas through it for one hour in order to minimize dissolved oxygen. The disk was immersed in the solution for a total of 55 minutes before the experiment, during the nitrogen bubbling step. A nitrogen blanket was maintained above the solution throughout the experiment in order to obstruct any oxygen diffusion from the atmosphere into the solution.

b, Tafel analysis: In this experiment, the stainless steel sample was immersed in artificial sea water (3% NaCl). Two stainless steel rods were chosen as the counter electrode. As the reference electrode, an Ag/AgCl 3 mol/L KCl Metrohm reference electrode was chosen. The cell was the 250 mL Metrohm Autolab corrosion cell.

In all cases, a VIONIC potentiostat/galvanostat was used for the measurement. The procedure and data treatment were done with the INTELLO software. Fitting of the EIS data was done with the NOVA software.

RESULTS AND DISCUSSION

ASTM G59

The procedure described in ASTM G59 and reproduced here is to first measure the OCP after 5 minutes of immersing the sample in the electrolyte, and once more after 55 minutes of immersion time. An LSV (linear sweep voltammetry) is then initiated -30 mV from the OCP measured after 55 minutes of immersion and ended at +30 mV vs the OCP. Here, the scan rate was 0.6 V per hour.

The OCP measured after 5 minutes of insertion was -0.54 V, and -0.52 V after 55 minutes. **Figure 1** shows the resulting polarization curve, plus the linear regression tangent to the data from -10 mV to +10 mV vs E_{corr}. The polarization curve must be linear in the range used for the analysis. Therefore, the potential range used is usually smaller than $0.1 \times b_{a/c}$ (typically around 10 mV or less). For accurate results, care should be taken to ensure that the measured current is only due to the corrosion. This can be achieved by minimizing the contribution of the ohmic drop (iR drop correction, increased electrolyte conductivity, and/or reduced electrode size) and also by minimizing the capacitive current (using staircase LSV with very low scan rates, e.g., around 0.1 mV/s).

RESULTS AND DISCUSSION

The regression analysis gives a polarization resistance of 22 ohm/cm^2. This value is slightly higher than that reported in the ASTM standard, possibly because the temperature was not set to 30 °C in this example case.

This system, cell included, is ASTM G59-compliant and can be used for other polarization resistance measurements.

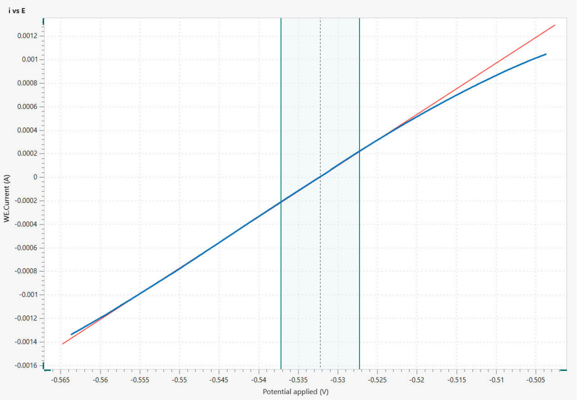

Figure 1. LSV sweep (blue) and tangent line (red) for a sample of Type 430 stainless steel in 0.5 mol/L sulfuric acid.

Although not discussed in ASTM G59, it is also possible to calculate polarization resistance through the use of electrochemical impedance spectroscopy (EIS) and then fit to an appropriate equivalent circuit. In **Figure 2**, the Nyquist plot of the stainless steel sample used in the previous experiment is shown.

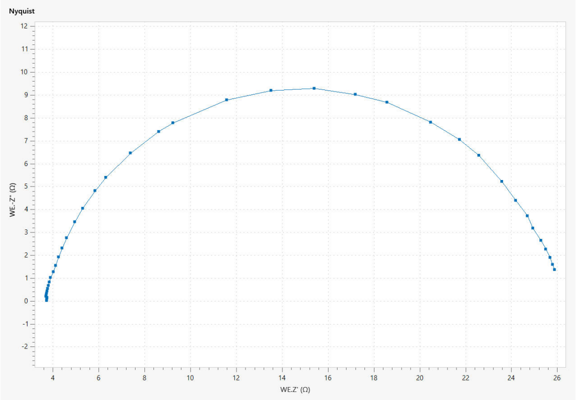

Figure 2. EIS of a sample of Type 430 stainless steel in 0.5 mol/L sulfuric acid measured at OCP.

The semicircle can be fitted with the simple equivalent circuit (shown in **Figure 3**) to obtain a comparable value of 22.4 ohm/cm^2.

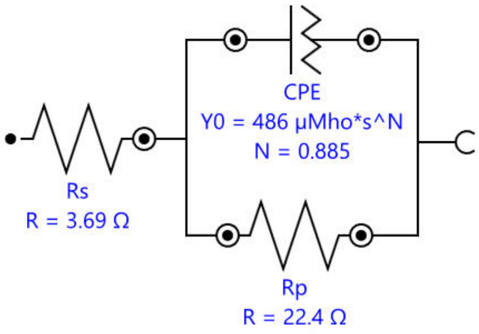

Figure 3. Equivalent circuit used to fit the data in Figure 2.

RESULTS AND DISCUSSION

Tafel analysis and polarization resistance

As discussed above, it is possible to combine Tafel and polarization resistance analysis to obtain the corrosion rate from two different methods and compare them. In this case, an OCP measurement was done, and an LSV measurement was initiated at -0.2 V vs the OCP and ended at +0.2 V vs the OCP.

The corrosion rate from the Tafel analysis was calculated as 0.0013 mm/year and the Tafel slopes were 173 mV/dec and 132 mV/dec. Copying the slopes into the polarization resistance command results in a calculated corrosion rate of 0.0014 mm/year. As both methods give very similar corrosion rates, this is a good indication that the corrosion rate is accurate.

CONTACT

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CONFIGURATION

VIONIC

VIONIC is our new-generation potentiostat/galvanostat that is powered by Autolab's new **INTELLO** software.

VIONIC offers the **most versatile combined specifications of any single instrument** currently on the market.

- Compliance voltage: ± 50 V
- Standard current ± 6 A
- EIS frequency: up to 10 MHz
- Sampling interval: down to 1 µs

Also included in **VIONIC's** price are features that would usually carry an additional cost with most other instruments such as:

- Electrochemical Impedance Spectroscopy (EIS)
- Selectable Floating
- Second Sense (S2)
- Analog Scan

Autolab PGSTAT204

The PGSTAT204 combines the small footprint with a modular design. The instrument includes a base potentiostat/galvanostat with a compliance voltage of 20 V and a maximum current of 400 mA or 10 A in combination with the BOOSTER10A. The potentiostat can be expanded at any time with one additional module, for example the FRA32M electrochemical impedance spectroscopy (EIS) module.

The PGSTAT204 is an affordable instrument which can be located anywhere in the lab. Analog and digital inputs/outputs are available to control Autolab accessories and external devices are available. The PGSTAT204 includes a built-in analog integrator. In combination with the powerful NOVA software it can be used for most of the standard electrochemical techniques.

Autolab PGSTAT302N

This high end, high current potentiostat/galvanostat, with a compliance voltage of 30 V and a bandwidth of 1 MHz, combined with our FRA32M module, is specially designed for electrochemical impedance spectroscopy.

The PGSTAT302N is the successor of the popular PGSTAT30. The maximum current is 2 A, the current range can be extended to 20 A with the BOOSTER20A, the current resolution is 30 fA at a current range of 10 nA.

1 L corrosion cell

The Autolab 1 L corrosion cell is suitable for corrosion measurements according to ASTM standards. The cell has a thermostatic jacket for temperature control and a series of openings for counter electrodes, pH sensor, thermometer, Luggin-Haber capillary and gas purging.

The 1 ll corrosion cell has been designed to measure the corrosion properties samples with a diameter ranging from 14.7 mm to 16 mm and a thickness from 0.5 mm up to 4 mm. The exposed surface is 1 cm2 and the seals are made out of natural rubber.

0.250 L Corrosion Cell

Complete cell for corrosion measurements, 250 mL.

Corrosion cell

The Autolab 400 ml corrosion cell is suitable for corrosion measurements. The cell has a thermostatic jacket for temperature control and a series of openings for counter electrodes, pH sensor, thermometer, Luggin-Haber capillary and gas purging.

The 400 ml corrosion cell has been designed to measure the corrosion properties of 14 mm diameter and 1 mm thick flat circular samples immersed in an electrolyte. The exposed surface area is 0.785 cm2. The holder is made of Delrin with a Viton seal.

Flat Sample Platform

Complete Flat sample platform for large, flat samples.

Keywords: Corrosion cell, linear polarization, Tafel, corrosion rate, flat samples, salt spray