Application Note AN-COR-003

化阻量

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

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

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 × $b_{a/c}$ (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).

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.

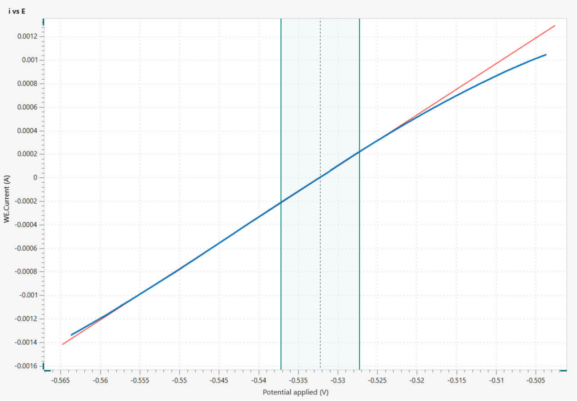

Figure 1. LSV sweep (blue) and tangent line (red) for a sample of Type 430 stainless steel in 0.5 mol/L sulfuric acid.

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.

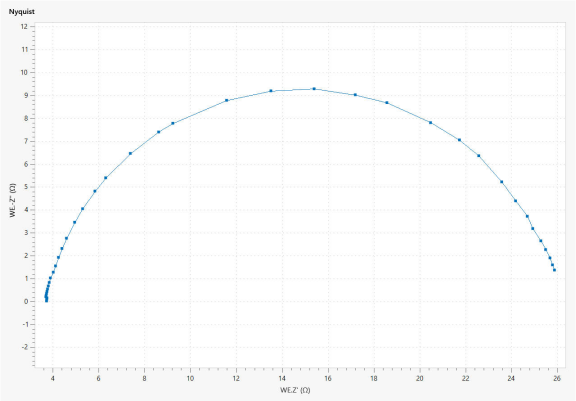

Figure 2. EIS of a sample of Type 430 stainless steel in 0.5 mol/L sulfuric acid measured at OCP.

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.

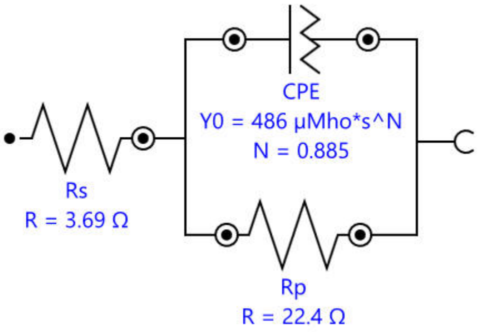

Figure 3. Equivalent circuit used to fit the data in Figure 2.

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.

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CONFIGURATION

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- 准流 ± 6 A
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- 化学阻抗 (EIS)
- 可浮配件
- 第二量 (S2)
- 模描

Autolab PGSTAT204

PGSTAT204 合了小巧格和模化。器包括基本恒位/恒流,其从 20 V,最大流 400 mA 或 10 A,与 BOOSTER10A 合使用。此恒位可随用附加模行展,例如 FRA32M 化学阻抗(EIS)模。

PGSTAT204 是一款惠的器,可置于室的任何位置。具有模和数字入/出,可控制 Autolab 附件和外部。

PGSTAT204 包括内置模分器。与高性能的 NOVA 件用,可用于大多数准化学技。

Autolab PGSTAT302N

恒位/恒流,具有 30 V 从, 1 MHz,可与我的 FRA32M 模用,化学阻抗而。

PGSTAT302N 是流行的 PGSTAT30 的后款型。最大流 2 A,借助 BOOSTER20A 流范可展至 20 A,当流范 10 nA 流分辨率 30 fA。

1 L

Autolab 1 L 腐池用于按照 ASTM 准行的腐量。腐池有一个用于温度控制的恒温套和一些用于、pH 感器、温度、Luggin-Haber 毛管和气体排气的孔。

1 L 的腐池用于量直径 14.7 至 16 mm 厚度 0.5 至 4 mm 的品腐情况。裸露的表面 1 cm2。用天然橡密封。

0.250 L

完整的腐量池,250 mL。

Autolab 400 ml 腐池用于腐量。池具有一个恒温外用于温度控制,和一系列口可用于相、pH 感器、温度、金-哈伯毛管以及气体化。

400 ml 的腐池用于量直径 14 mm 厚度 1 mm 的扁形品浸入解中的腐情况。裸露的表面 0.785 cm2。支架由 Delrin 聚甲脂制成,用 Viton 橡密封。

用于大型扁平品的完整平面品平台。

字:腐池,性化,塔菲,腐速度,扁平品,