

Application Area: Corrosion

Calculation of Corrosion Parameters with NOVA

Keywords

Corrosion; Electrochemical methods; Corrosion rate; Kinetics

Introduction

Electrochemical methods provide an alternative to traditional methods used to determine the rate of corrosion. For example, corrosion rate, the rates at which a specimen corrodes, can be calculated from simple electrochemical measurements like a linear sweep voltammetry (LSV).

Weight loss measurements

The simplest way of measuring the corrosion rate of a metal is to expose the sample to a test medium (e.g., seawater) and measure the loss of weight of the material as a function of time. Although these tests are straightforward, there is no simple way to extrapolate the results to predict the lifetime of the sample under investigation. Moreover, some corrosion processes occur with no significant mass change (e.g., pitting corrosion), making difficult the measurement of corrosion rates by gravimetric methods.

Electrochemical tests

Most corrosion phenomena are of electrochemical nature and consist of oxidation reactions on the surface of the corroding metal. Therefore, electrochemical methods can be used to characterize corrosion mechanisms and predict corrosion rates.

Calculation of corrosion rates

The corrosion rate is the measure of how fast a metal deteriorates under corrosion. It depends on the kinetics of both anodic (oxidation) and cathodic (reduction) reactions. According to Faraday's law, there is a linear relationship between the metal dissolution rate, or corrosion rate, R_M (mm/year) and the corrosion current i_{corr} (A):

$$R_M = 3.17E - 9 \frac{M}{nF\rho A} i_{corr} \quad 1$$

Where $3.17E - 9$ is the conversion factor from $cm s^{-1}$ to $mm year^{-1}$; M ($g mol^{-1}$) is the atomic weight of the sample;

n is the number of electrons exchanged in the reaction; ρ ($g cm^{-3}$) is the density of the sample; F ($96485 C mol^{-1}$) is the Faraday constant; and A (cm^2) is the area of the sample. The ratio M/n is also named equivalent weight.

Corrosion currents

In order to calculate the corrosion rates, the corrosion currents are needed. When the reaction mechanisms for the corrosion reaction are known, the corrosion currents can be calculated using the Tafel slope analysis.

Under charge transfer (kinetic, or activation) control, the relationship between the current i and the overpotential η is given by the Butler-Volmer equation:

$$i = i_{corr} \left(e^{2.303 \frac{\eta}{b_a}} - e^{-2.303 \frac{\eta}{b_c}} \right) \quad 2$$

Where i_{corr} is the corrosion current, the rate of charge transfer at the corrosion potential E_{corr} ; 2.303 is the conversion factor between \log_e and \log_{10} ; η (V) is the overpotential, defined as the difference between applied potential E and the corrosion potential E_{corr} and b_a (V) and b_c (V) are the Tafel slopes of the anodic and cathodic branch, respectively. The corrosion potential E_{corr} is the open circuit potential of a corroding sample. The corrosion current i_{corr} and the Tafel slopes b_a and b_c can be calculated from the experimental data.

For large anodic overpotentials ($\frac{\eta}{b_a} \gg 1$), the Butler-Volmer equation simplifies as the Tafel equation for the anodic reaction, Equation 3:

$$\eta = b_a \cdot \log \left(\frac{i}{i_{corr}} \right) \quad 3$$

Analogously, for large cathodic overpotentials ($\frac{\eta}{b_c} \ll -1$) the Tafel equation for the cathodic reaction is given by:

$$\eta = -b_c \cdot \log \left| \frac{i}{i_{corr}} \right| \quad 4$$

The Tafel Equations 3 and 4 predict a straight line for the variation of the logarithm of the current with the potential. Therefore, currents are often shown in semi logarithmic plots,

known as Tafel plots. This type of analysis is referred to as Tafel slope analysis.

Corrosion Rate Analysis in NOVA

The NOVA software provides a convenient interface for performing corrosion rate analysis, starting from a current, vs. potential plot. In Figure 1 for example, the current potential curve for an iron screw immersed in seawater is shown.

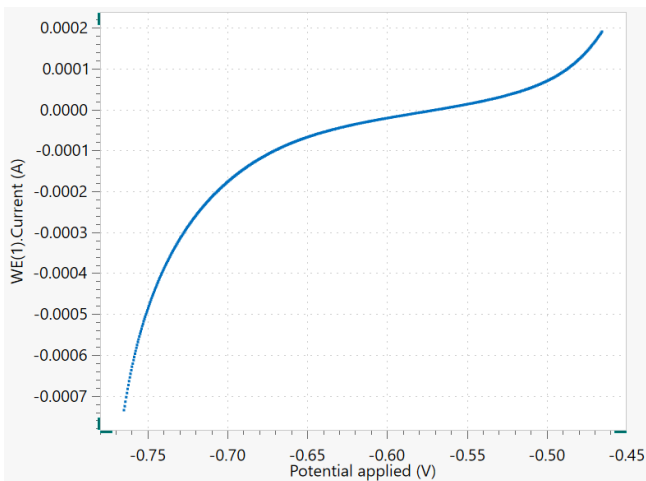


Figure 1 – Current potential curve for iron screw immersed in seawater

Selecting the Corrosion Rate Analysis command, a Tafel plot is added, Figure 2.

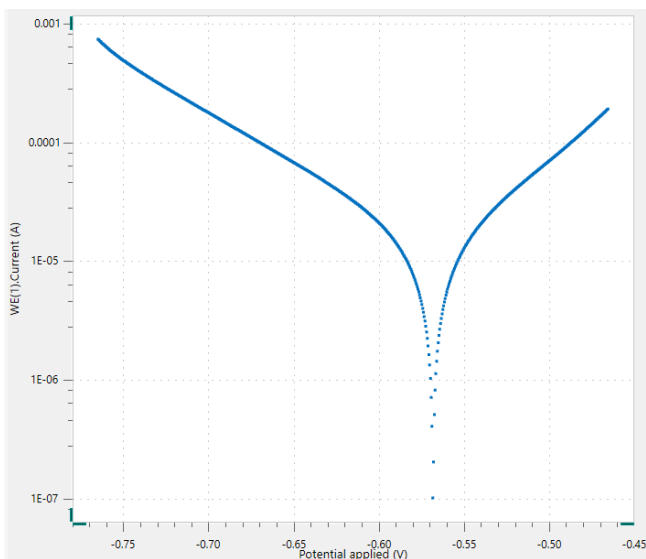


Figure 2 - Tafel plot for an iron screw immersed in seawater.

In the Properties area of the Corrosion Rate analysis command, Figure 3, it is possible to specify the analysis mode

(Tafel analysis or polarization resistance), the density of the sample, its equivalent weight, and the surface area. It is also possible to choose to perform a fit.

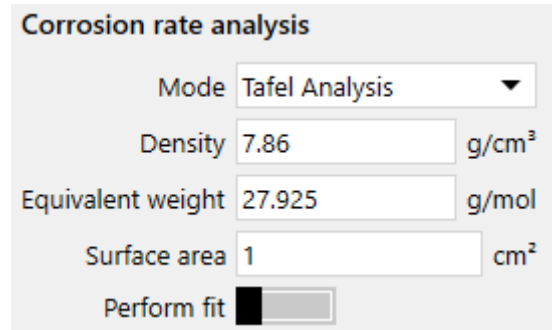


Figure 3 - The parameters used in the corrosion rate analysis

In order to perform a corrosion rate analysis, the linear regions of the anodic and cathodic side of the Tafel plot must be specified. This is accomplished with the help of four markers, two per the anodic side and two for the cathodic side. Such markers define the lines for the linear regressions, according to Equations 3 and 4, respectively. Once the regions are selected, the linear regressions would appear in the plot. Then, the corrosion potential and the corrosion current are calculated, as being the X and Y coordinates, respectively, of the intersection of the two regression lines, Figure 4.

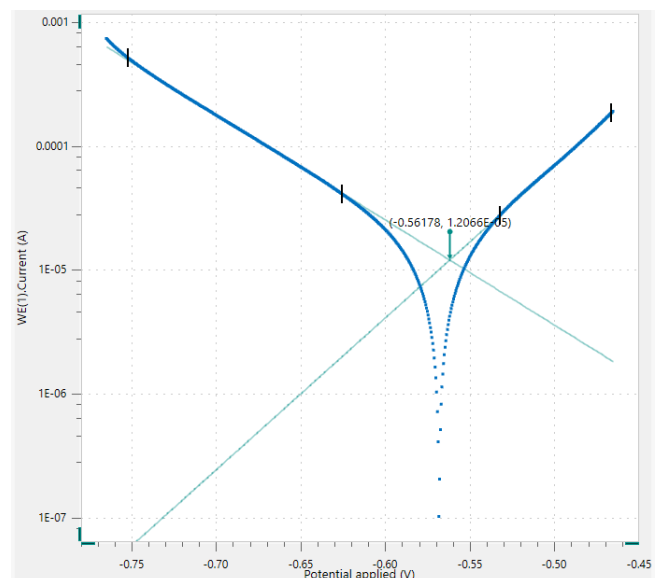


Figure 4 – The linear regions of the Tafel plot are identified by placing markers. The green lines refer to the linear regressions. The corrosion potential and corrosion current are also shown.

Tafel analysis

For a Tafel analysis, the results of the Corrosion Rate Analysis command are listed in Figure 5.

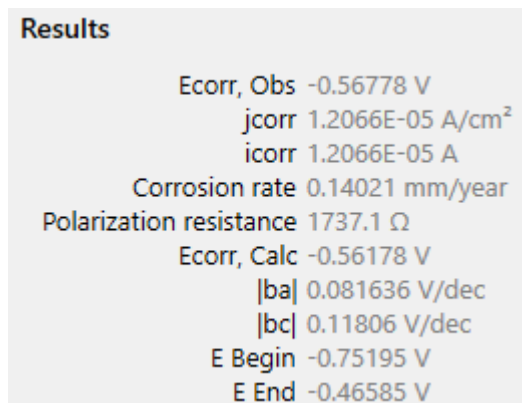


Figure 5 – The results of the Tafel Slope analysis

The Tafel analysis provides a quick estimation of the corrosion rate and the polarization resistance. The corrosion rate is calculated with Equation 1 and the estimated corrosion current i_{corr} .

Perform fit

The Perform Fit toggle allows the system to fit the data with Equation 2, which allows for an accurate determination of the corrosion current, polarization resistance and corrosion rate.

The Corrosion Rate Fit tool works in the same way of the Corrosion Rate Tafel Slope tool. The linear Tafel region is identified by the use of markers. After the markers have been placed on the plot, the software performs the curve fit and calculates the characteristic corrosion values using the specified density; equivalent weight and surface area (see Figure 6).

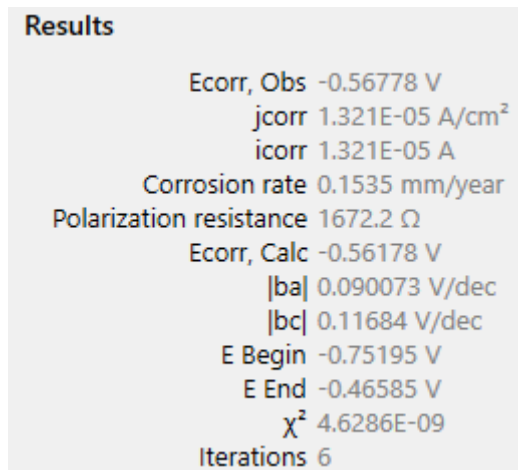


Figure 6 – The results of the Corrosion rate fit analysis

In choosing the regions for Tafel slope analysis, care must be taken. A correct estimate of the Tafel slopes is possible only if the linear Tafel region (region between markers in Figure 3) covers at least one decade in current.

In certain cases, the Tafel slope analysis is not possible.

For example, under the diffusion control, the reactants are hampered in reaching the sample surface (e.g., in stagnant solutions). As consequence, the cathodic reaction does not occur, resulting in $b_c = \infty$.

Similarly, under passivation, the surface of the sample is coated with a protective layer, which prevents the anodic reaction to occur, resulting in $b_a = \infty$.

Polarization resistance

An alternative method to retrieve corrosion data is to use the Polarization Resistance mode, Figure 7.

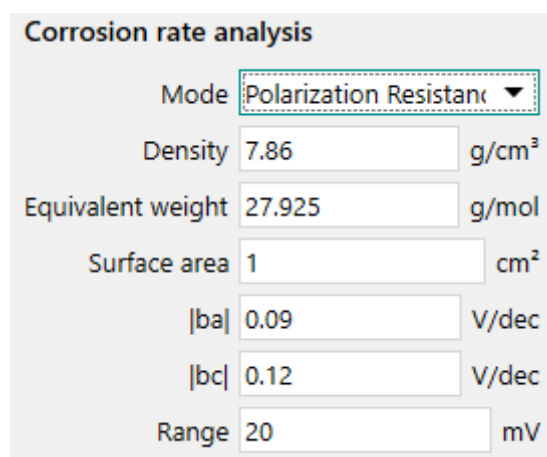


Figure 7 - The polarization resistance mode.

In this mode, Equation 2 is applied for small overpotential values, to have a linear relationship between i_{corr} and η , resulting in Equation 5.

$$i_{corr} \approx \frac{1}{R_p} \left[\frac{b_a b_c}{2.303(b_a + b_c)} \right] \quad 5$$

Being $R_p = \eta/i$.

Here, the Tafel slopes b_a and b_c must be specified. In this example, the same slopes calculated from the fit have been used.

The results of the polarization resistance mode, Figure 8, are the corrosion resistance, the corrosion current and current density, the corrosion rate and the polarization resistance.

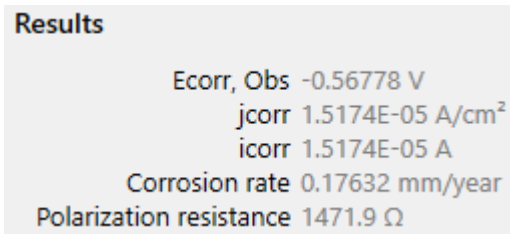


Figure 8 - the results of the polarization resistance mode

Conclusions

In this application note, an overview of different methods to calculate the corrosion parameters by NOVA has been given. As an example, the data from a linear polarization of an iron screw in seawater have been used. A Tafel analysis, a fit and a polarization resistance methods have been embedded in NOVA to retrieve, among all, the corrosion current, the polarization resistance and the corrosion rate.

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For more information

Additional information about this application note and the associated NOVA software procedure is available from your local Metrohm distributor. Additional instrument specification information can be found at www.metrohm.com/en/products/electrochemistry.