

*Creating and analyzing a Tafel plot is a powerful and time-tested electrochemical testing method to understand corrosion behaviors*

A Tafel plot is defined as a plot of the log of current vs. potential. It is named after Julius Tafel who derived the famous Tafel equation in the year 1905. Understanding how to analyze Tafel plots plays a central role in the mechanistic understanding of electrochemical reactions. In the context of corrosion studies, a Tafel plot can be used to calculate corrosion current or the rate of corrosion

**Equation #1**

$$\eta = a + b \log (i)$$

$\eta$  is the overpotential  
 $i$  is the current  
 $a$  and  $b$  are constants

**Equation #1**, the Tafel equation, is empirically-derived and suggests a linear relation between the potential and the log of current. In a Tafel plot, one is looking for a range of potential showing a linear relation with the current. Overpotential is the difference between the equilibrium potential ( $E_{eq}$ ) at the working electrode, given by the Nernst Equation, and the actual electrode potential ( $E$ ). In practice,  $E_{eq}$  can be considered as steady-state potential at the open circuit as the current is zero and the system is at equilibrium. The overall profile of the Tafel plot does not change if plotted against either  $\eta$  or  $E$ .

Although the Tafel equation was empirically derived, the same equation can be deduced using a more systematic approach of the Butler-Volmer equation (**Equation #2**). The Butler-Volmer equation does not consider mass-transfer effects and assumes Arrhenius-type kinetics.

**Equation #2**

$$i = i_0 [e^{-\alpha f \eta} - e^{(1-\alpha) f \eta}]$$

where  $f = F/RT$

$i_0$  is the exchange current density  
 $\alpha$  is the transfer coefficient  
 $F$  is the Faraday constant  
 $R$  is the universal gas constant  
 $T$  is temperature

For large values of  $\eta$ , the Butler-Volmer equation can be simplified. For cases with a large negative  $\eta$ ,

$e^{-\alpha f \eta} \gg e^{(1-\alpha) f \eta}$  and the Butler-Volmer equation becomes:

**Equation #3**

$$i = i_0 e^{-\alpha f \eta}$$

which can be rearranged to...

$$\eta = 2.3 RT [\log i_0 - \log i] / \alpha F$$

Equation #3 is the same as the Tafel equation where  $a = 2.3RT \log i_0 / \alpha F$  and  $b = -2.3RT / \alpha F$ . Similar mathematical operations can be done for a large positive  $\eta$  to simplify the Butler-Volmer equation into Tafel form.

There are two important points about this mathematical treatment. The first is that the Tafel relation holds in the absence of mass-transfer effects. In other words, the rate of reaction should be limited by kinetics, not mass-transfer effects. Second, the overpotential should be large enough such that  $e^{-\alpha f\eta} \gg e^{(1-\alpha)f\eta}$  or  $e^{(1-\alpha)f\eta} \gg e^{-\alpha f\eta}$ . In other words, either the oxidation or reduction process should dominate in the chosen range of the potential to perform the linear regression.

So far, this narrative has discussed the Tafel equation only in the context of a single reaction. However, corrosion involves at least two electrochemical reactions. To apply the Tafel equation to a corrosion reaction, we must make two hypotheses.

- 1) One reaction is shifted from its equilibrium with high positive  $\eta$  where oxidation dominates, and another reaction is shifted from its equilibrium with high negative  $\eta$  where reduction dominates. Since  $|\eta|$  is sufficiently high, the Tafel equation is applicable.
- 2) Since charges should be conserved, oxidation current produced from the reaction with high positive  $\eta$  must be equal in magnitude to the reduction current produced from the reaction with high negative  $\eta$ . This oxidation current is called the **corrosion current** ( $i_{\text{corr}}$ ). The potential, where the oxidation current is equal to the reduction current, is called **corrosion potential** ( $E_{\text{corr}}$ ).

With this in mind, an expression to calculate these corrosion kinetics can be written in the form of the Butler-Volmer equation as:

#### Equation #4

$$i = i_{\text{corr}} [\exp\{2.303(E-E_{\text{corr}})/\beta_a\} - \exp\{-2.303(E-E_{\text{corr}})/\beta_c\}]$$

$\beta_a$  is the anodic Tafel slope  
 $\beta_c$  is the cathodic Tafel slope

The Tafel form of Equation #4 can be obtained when  $E-E_{\text{corr}}$  is large.

When generating a Tafel plot, the essential requirement is that the measurement is taken at a steady state. Equation #4 is a theoretical treatment that assumes steady-state conditions. The experimental parameters to program into a potentiostat depend on the electrochemical system under investigation. The results not only depend on the type of electrodes and electrolytes, but also the configuration of the electrodes and their relative positions. To begin plotting, typically a potential sweep with a very slow scan rate (for example 0.167 mV/s) is performed on a three-electrode cell. The scan can be linear or staircase since there is not much difference between a staircase and a linear scan at such a slow scan rate. But one advantage of a staircase scan is that some potentiostats include stability range settings that can be configured for the measured current during a voltage step.

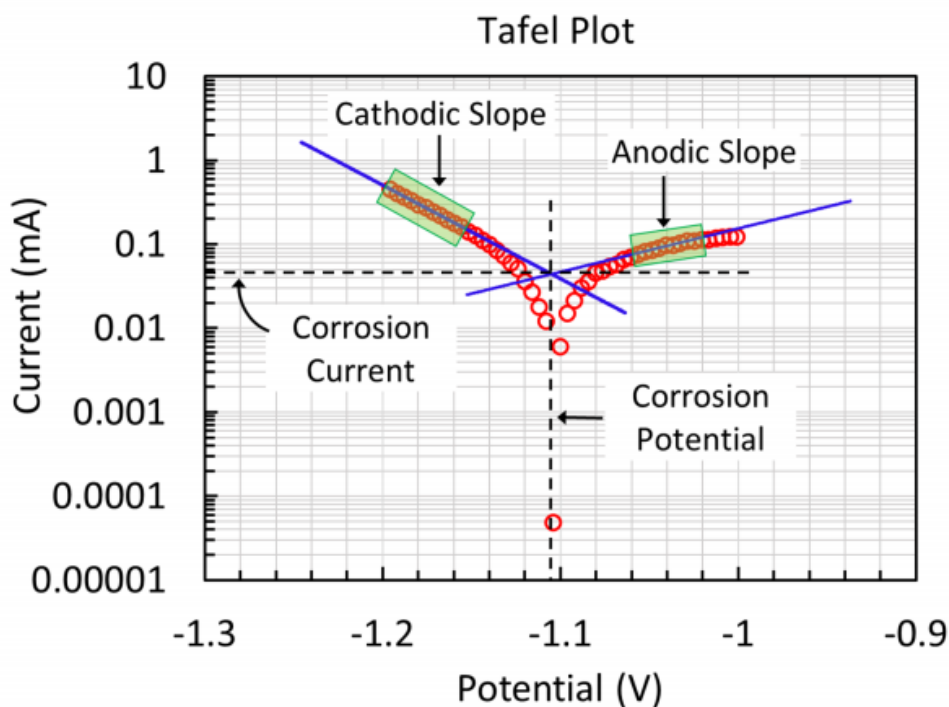
Before starting the potential scan, the sample system under test should be allowed to come to a steady state. Whether the system has reached steady-state conditions can be monitored by tracking the rate of change of

open circuit potential (OCP). If the change in OCP is within the measurement accuracy of the potentiostat, meaning there is negligible change in the reported measured value, the system can be said to be at steady-state.

The potential scan is carried out within a few hundred milli-volts of the OCP. If the system is truly at steady-state, the scan direction should not matter. The starting and ending potential should be far enough away from the OCP such that significant polarization can be achieved. Current vs. potential data shows a linear regression within a few millivolts from the OCP. Therefore, the voltage range should be such that nonlinear deviation from this linear relation can be observed during the scan. Alternatively, the potential scan can be started right from OCP towards a more oxidizing potential or in an anodic direction.

**Uncompensated Resistance** ( $R_u$ ) should be corrected for during a potential scan.  $R_u$  can be measured in advance by using a high-frequency electrochemical impedance scan, a current interrupt measurement, or a positive-feedback measurement. Measuring  $R_u$  before starting the potential scan and making a one-time correction for  $R_u$  is reasonably accurate, but not as accurate as a dynamic  $R_u$  correction that updates in real-time as the potential scan runs. Dynamic, real-time  $R_u$  correction is available on some potentiostats by using fast current interrupt techniques.

Once the potential scan is complete, plotting current on a log scale on the y-axis and potential on the x-axis gives you a Tafel plot ready for analysis! Below is an example of a Tafel plot and subsequent analysis carried out with a [Squidstat Plus](#) potentiostat. The working electrode was a zinc metal coupon immersed in a potassium chloride solution and surrounded by two carbon plates. The zinc metal coupon was subjected to a potentiodynamic sweep at a 2 mV/s scan rate.



There should be regions on both the anodic slope and the cathodic slope in the Tafel plot where the log of current varies linearly with the potential. When a linear fit is applied to both of these regions, as shown by the green squares in the example plot, these fitted linear lines should be extrapolated to where they intersect with each other. **The potential value (x-axis reading) of this intersection gives the corrosion potential and the current value (y-axis reading) gives the corrosion current.** In the example, the corrosion potential is -1.104 V and the corrosion current is 46  $\mu$ A.

If the scan were anodic starting from OCP, only the anodic region should be fitted with linear regression. The fitted line should be extrapolated such that it intersects the x-axis (potential) at OCP. The current reading at this intersection gives the corrosion current ( $i_{\text{corr}}$ ). From  $i_{\text{corr}}$ , the corrosion rate can be calculated using Faraday's law of electrolysis (**Equation #5**):

### Equation #5

$$\text{Corrosion rate (mass loss/time)} = i_{\text{corr}}M/nF$$

**M** is the molar mass  
**n** is # of electrons in reaction per ion  
**F** is the Faraday constant

For metals with one or more material composition,  $M/n$  is replaced by **equivalent weight (EW)** in **Equation #5**. Determining EW for alloys may not be easy if the different metals present in the alloys are oxidizing at different rates. In such a case, an experimental approach might be a better approach. The current vs. potential curve should be from kinetic polarization only. However, other polarization effects such as concentration, migration, diffusion, and convection can sometimes affect the raw data. To ensure that the data is from kinetic polarization only, the kinetic rate should be many times slower than these other processes. If not, the data should be corrected for these effects (which is easier said than done). Only very few experimental configurations allow for such correction. For example, in a rotating disk or cylinder electrode experiment, the mass-transfer currents could be theoretically calculated and corrected from the data.

The corrosion rate obtained with the Tafel plot is true if the rate of corrosion is uniform over the entire surface during the lifetime of the sample. Therefore, Tafel analysis is useful for initial estimation and comparison among similar samples but is simply one of many recommended tools to fully understand the corrosion characteristics of any given system. Admiral Instruments is happy to provide guidance about corrosion characterization methods to ensure your data is reliable and meaningful!