

## Calculating Corrosion Rates from a Tafel Plot

*Analyzing a Tafel plot is a powerful and time-tested method to obtain corrosion data using electrochemical methods*

A Tafel plot is a plot of log of current vs. potential. It is named after Julius Tafel who derived the famous Tafel equation in the year 1905:

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

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

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 steady-state potential at open circuit as the current is zero and the system is at steady-state, or in other words equilibrium, at such a condition. The overall profile of the Tafel plot does not change if plotted against either  $\eta$  or  $E$ .

The equation above 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 linear relation with the current. Tafel analysis plays a central role in mechanistic understanding of electrochemical reactions. It is used in many other areas of electrochemistry. However, in this note, its use in corrosion studies are discussed as a method to obtain corrosion current or the rate of corrosion.

The Tafel equation was empirically derived. A relatively more theoretical approach can be taken using the Butler-Volmer equation to arrive at the same equation. The Butler-Volmer equation does not consider mass-transfer effects and assumes Arrhenius-type kinetics.

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

$i_0$  is the exchange current density,  $\alpha$  is the transfer coefficient,  $f = F/RT$ , where  $F$  is Faraday constant,  $R$  is universal gas constant and  $T$  is temperature.

For large values of  $\eta$ , the Butler-Volmer (BV) equation can be simplified. For cases with large negative  $\eta$ ,  $e^{-\alpha f \eta} \gg e^{(1-\alpha) f \eta}$  and the BV equation becomes:

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

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

which is the Tafel equation where  $a = 2.3 RT \log i_0 / \alpha F$  and  $b = -2.3 RT / \alpha F$ . Similar mathematical operations can be done for large positive  $\eta$  and simplify the BV equation into Tafel form.

From the above mathematical treatment, two important points should be noted. The first is that the Tafel relation holds in absence of mass-transfer effects. Second, the overpotential should be large enough such that  $e^{-\alpha f \eta} \gg e^{(1-\alpha) f \eta}$  or  $e^{(1-\alpha) f \eta} \gg e^{-\alpha f \eta}$ . So, the log  $i$  vs.  $\eta$  data should be taken in the absence of mass-transfer effects and to perform the linear regression, data should be chosen far from equilibrium potential.

In corrosion, at least two reactions are taking place simultaneously. One reaction is shifted from its equilibrium towards oxidation and another is shifted from its equilibrium towards reduction. Hence both

reactions are not their respective equilibrium. However due to conservation of total charge, their absolute rates are equal i.e. rate of the oxidation reaction is equal to the rate of the reduction reaction. The potential at which the rates of these opposing reactions are equal is called corrosion potential ( $E_{\text{corr}}$ ) and the rates that are equal are called the corrosion current ( $i_{\text{corr}}$ ). This is the mixed potential theory (MPT). Now an expression for the corrosion kinetics can be written in the form of BV equation as:

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

$\beta_a$  is the anodic tafel slope and  $\beta_c$  is the cathodic Tafel slope.

The Tafel form of the above equation can be obtained when  $E-E_{\text{corr}}$  is large.

There are several ways to acquire data to generate a Tafel plot. The essential requirement is that the measurement be at steady-state, as in the above theoretical treatment steady state is assumed. As far as the experimental parameters are concerned, they 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 position. Hence the results might differ from one lab to another and one user to another.

To obtain a Tafel plot, a potential sweep with a very slow scan rate (eg. 0.167 mV/s) is performed on a three-electrode cell. As with other electrochemical experiments, the cell should be properly configured. The scan can be linear or staircase. Because of a very slow scan rate, there is not much difference between a staircase and a linear scan. The advantage with a staircase scan is that with some potentiostats the criteria for stability can be set for the measured current during a voltage step.

Before starting the potential scan, the system should be allowed to come to a steady state. Whether the system has reached a steady state can be monitored by tracking the rate of change of open circuit potential (OCP). If the change in OCP is within the accuracy of the potentiostat, the system can be said to be at a steady state.

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

It is also advised that during the measurement, uncompensated resistance ( $R_u$ ) be corrected.  $R_u$  can be measured from a high frequency electrochemical impedance scan, a current interrupt measurement, or a positive-feedback measurement before the experiment. It might be argued that this one-time correction for  $R_u$  is not reliable as it can change during the experiment. In some potentiostats, dynamic correction for  $R_u$  is available during a scan using fast current-interrupt techniques. Since the scan rate is very slow and the system is at steady-state, such interruption should not create errors in the measurement.

After having taken care of these things, whether one obtains a reliable Tafel plot depends on the system itself. As discussed above, the current vs. potential curve should be from kinetic polarization only; however, in practice, other polarization effects such as concentration, migration, diffusion and convection

affects the data. To ensure that the data is from kinetic polarization only, the kinetic rate should be many times slower than the 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.

After accomplishing the above-mentioned tasks, hopefully, potential ranges exist on both the anodic slope and the cathodic slope in the Tafel plot where the log of current varies linearly with the potential. If the regions exist, they should be fitted with linear fits. These fitted linear lines should be extrapolated to where they intersect 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.

If the scan was anodic starting from OCP, only anodic region should be fitted with a 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 ( $i_{corr}$ ). From  $i_{corr}$ , corrosion rate can be calculated using Faraday's law of electrolysis:

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

M is the molar mass, n is the number of electrons involved in reaction per ion and F is Faraday constant.

For metals with one or more composition, M/n is replaced by EW (equivalent weight) in the above equation. 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 taken.

The corrosion rate obtained is true if the rate of corrosion is uniform over the entire surface during the lifetime of the sample. Therefore, at best, the value is good for initial estimation and comparison among similar samples.

Therefore, measuring the corrosion current from a Tafel slope is not so straightforward. It is highly recommended that a researcher follows strict experimental protocol and repeat their experiment many times to obtain a statistically significant result.

Below is an example of a Tafel analysis carried out in the Admiral Instruments wetlab at room temperature using 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 potentiodynamic sweep at the scan rate of 2 mV/s.

