THE CHARACTERISTICS OF A TRUE TAFEL SLOPE

Gareth Kear [a,*] and Frank C. Walsh [b]

INTRODUCTION

2005 is the 100th anniversary of the two original publications of the Tafel equation [1,2]. The international corrosion community is currently celebrating [3] the use of the corresponding Tafel slope (β), which is one of the most frequently used parameters in electrochemical corrosion. Even now, with the use of modern research and testing techniques, both electrochemists and corrosion engineers are frequently encountering this 'Tafel constant' in the technical literature and in instrumentation manuals (you can't use an LPR meter without assuming beta values). Unfortunately, Tafel slopes are commonly misused and measured completely out of context. So, what is a Tafel slope? Perhaps most importantly, when is an apparent 'Tafel' slope a *true* Tafel slope?

KEYWORDS

Tafel, electrochemistry, copper, reduction, stainless steel

CHARGE TRANSFER

Charge transfer across an interface makes a chemical reaction, an electrochemical reaction. The addition of electrons to an oxidized reactant is termed reduction and oxidation is a process involving the removal of electrons:

Oxidised Species + ze^- $\Leftrightarrow$ Reduced Species   (1)

Both processes involve charge transfer. During polarization, measured currents produced by oxidation or reduction of electro-active species will be limited by one of the following rate determining steps [4-9]:

1. the transfer of electrons at the electrode/electrolyte interface (charge transfer controlled current),

2. the movement of reactants or products at distances close to the electrode (mass transport controlled current), or

3. a combination of both points 1 and 2 (mixed control current).

[a] BRANZ, Materials Section, Science and Engineering Services, Private Bag 50908, Porirua City, New Zealand
[b] Surface & Electrochemical Engineering Groups, University of Southampton, School of Engineering Sciences, Highfield, Southampton, SO17 1BJ, United Kingdom.

[*] Corresponding author: GarethKear@branz.co.nz; Tel: +64 (0) 4 237 1170; Fax: +64 (0) 4 237 1171

All of these cases will influence the shape of the experimental polarization curve and, therefore, will give clues to whether Tafel analysis can be used. Such analysis methods can include the measurement of slope values, derivation of mechanistic details and Tafel slope extrapolation to derive corrosion rates. It should be remembered, however, that only pure charge transfer controlled current can be accepted as true Tafel data.

The rate of charge transfer between an electrode material and the electroactive species is related to how fast the substrate material can accept or give up electrons. This kinetic behavior of an electrode will depend on its surface 'activity' [4,7,10]. When dealing with the movement of charge, a simple way to improve the rate of reaction is to increase the potential difference (the applied energy). Where, 1 Volt ($kg\ m^2\ A^{-1}\ s^{-3}$) is the equivalent of 1 joule ($kg\ m^2\ s^{-2}$) per coulomb (A s). Catalytic activities accelerate charge transfer without the required addition of extra energy [11]. Here the reaction can be made relatively easy with the introduction of catalytically favorable electrode materials. In this case, a lower energy is required to drive the exchange of charge and higher currents will be measured at lower potential differences. Metallic materials will have different levels of catalytic ability for a particular reaction and it is possible that the activity of a given material may be altered with surface conditioning.

Figure I [12] shows a series of linear sweep voltammetric (potentiodynamic) curves for aqueous cupric ion reduction as a function of Cu^{2+} concentration in acid sulphate solution. This is a very common electroplating reaction in metal finishing. Similar curves can also be produced for important corrosion reactions involving species such as oxygen. The reaction of interest involves the negative polarisation of the equilibrium [13-15]:

$$Cu^{2+}_{(aq)} + 2e^- \Leftrightarrow Cu_{(s)}$$ (2)

Application of a negative potential (initiated at the right hand side of Figure I) will encourage the forward process shown in reaction (1). This will plate copper at the working electrode (reduction of Cu^{2+}).

The initial section of the measured cathodic polarization curves (region [a]) shows an exponential rise in the rate of copper deposition. This is indicative of pure charge transfer control. The negative current, which is proportional to reaction
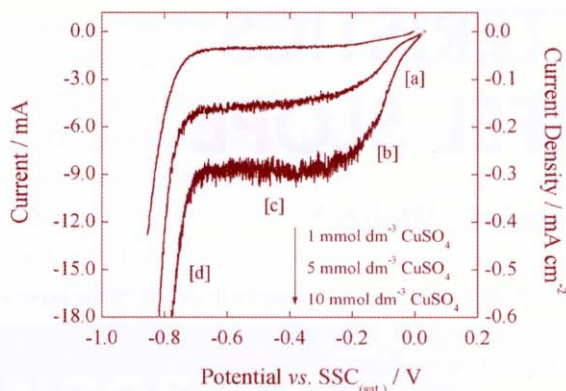
Figure I. Steady-state cupric ion reduction on a brass rotating cylinder electrode (diameter 12 mm; area 302.0 mm²) in 0.5 mol dm⁻³ sodium sulphate at pH 2 and 25°C

rate, rises in response to a negative increase in the applied potential. The driving force (applied energy per coulomb) is represented by the potential difference relative to a saturated silver/silver chloride electrode (SSC$_{[sat.]}$). In this region of the curve, the cathodic charge transfer controlled current density (i) is directly related to the bulk solution electro-active species concentration (c$_b$) via:

$$\vec{i} = -zF\,\vec{k}\,c_b \tag{3}$$

In the case of our copper plating example, the electroactive species is the cupric ion. The Faraday constant (F) gives the quantity of charge associated with the exchange of 1 mole of electrons. The potential dependent rate constant ($\vec{k}$) will be described in more detail later.

Within region [c] the current is independent of applied potential as the reaction rate is no longer limited by charge transfer. Here, the cupric ion is being used up so fast at the surface that the plating reaction is limited by its transport from the bulk of the solution. Thus, for a reaction under pure mass transport control, the current density will be generally independent of the nature of electrode material (assuming 100% current efficiency and the same set of reaction and environmental conditions). In this case, it is only the rate of transfer of the species within the fluid which will directly control the rate determining step of the overall electrochemical reaction. The rate of reaction is directly related to the transport of cupric ions from the bulk of the fluid to the surface of the electrode [4,7]. Thus, increasing the energy applied to each unit of charge in this potential region of mass transport control will not increase the reaction rate.

Somewhere between these two idealized conditions of pure charge transfer or pure mass transport control lies a middle ground of mixed charge and mass transport (region [b]) [7]. Moving from regions [a] to [b], the exponential rise the rate of copper deposition will continue until the quantity of available cupric ions at the surface begins to decrease relative to the demand and the exponential rise will become limited.

REACTION EQUILIBRIUM PRIOR TO POLARISATION

The initial investigations of charge transfer behaviour were of a rather empirical nature, although the current response can now be approximated using electrochemical theory. For a simple electron transfer reaction, illustrated by the copper electro-deposition reaction shown in reaction (2), the equilibrium potential (E$_e$), which is the potential when no net current flows, can be calculated for a given set of conditions from the Nernst relationship as shown in equation (4).

$$E_e = E_e^o + \frac{2.3RT}{zF}\log\frac{[\text{Oxidized}]^n}{[\text{Reduced}]^n} \tag{4}$$

R is the molar gas constant and T is the absolute temperature. E$_e^o$ is the standard electrode potential, where the activity of the cupric ions in solution equals 1.0 and the temperature, T, is 298 K at atmospheric pressure (1 atm or 101.325 kPa). Here, the Nernst equation is written in terms of concentrations rather than activity (this assumes a large excess of inert background solute/electrolyte). The equilibrium between the oxidized and reduced species (see equation [1]) at the electrode surface is dynamic, where the overall current density (j) will be zero and equal to the sum of the cathodic and anodic parts:

$$i = -\vec{i} + \overset{\leftarrow}{i} = 0 \tag{5}$$

$\overset{\leftarrow}{i}$ is the partial current density due to the oxidation reaction. At equilibrium, the magnitude of each partial current density at equilibrium is identical and equal to the exchange current density (i$_o$) for the reaction.

$$i_o = -\vec{i} = \overset{\leftarrow}{i} \tag{6}$$

i$_o$ is another widely used kinetic parameter in electrochemical corrosion. It describes how fast a reaction is occurring at the equilibrium (or, rest) potential and, for specific reactant concentrations; the exchange current is proportional to the rate of electron transfer (i.e., how easily the charge transfer process can occur).

POLARISATION UNDER CHARGE TRANSFER CONTROL

If the concentrations of the oxidized and reduced species are made to differ from those at equilibrium, a net, measurable current density will flow as the rates of the partial reactions will not be equal in magnitude as described in equation (5). For example, from equation (4), if the equilibrium potential is polarized in a negative direction relative negative to E$_e$, the cathodic reaction will increase at the expense of the anodic reaction. In this manner, the electrode will attempt to lower the value of [Cu²⁺], the concentration of the species in the oxidized state. Now, the character of the net current will be predicted by:

$$-\vec{i} > \overset{\leftarrow}{i} = -i \tag{7}$$

and a net cathodic current density will flow as copper is plated at the electrode. From classical kinetics (from which equation 3 is also derived) the rate of each of these partial currents can be further explored through exponential relationships describing the potential dependent rate constants, $\overrightarrow{k}$ (cathodic) and $\overleftarrow{k}$ (anodic).

$$\overrightarrow{k} = \overrightarrow{k}_o \exp \frac{(-\alpha_c zFE)}{RT} \tag{8}$$

$$\overleftarrow{k} = \overleftarrow{k}_o \exp \frac{(\alpha_A zFE)}{RT} \tag{9}$$

where α_c and α_A are the cathodic and anodic transfer coefficients. Commonly, $\alpha_c = \alpha_A = 0.5$. As can be seen from equations (8) and (9), the electrochemical rate constants ($\overrightarrow{k}_o$ and $\overleftarrow{k}_o$) are independent of potential (E). At low overpotentials for generally slow electrode processes (where the concentration of the electro-active species at the electrode wall is the same as that in the bulk of the solution) equation (5) can be adopted to produce:

$$i = \left[zF \overleftarrow{k}_o [Reduced] \exp \frac{(-\alpha_A zFE)}{RT} \right] - \left[zF \overrightarrow{k}_o [Oxidized] \exp \frac{(-\alpha_c zFE)}{RT} \right] \tag{10}$$

and, from equation (5) i_o will be equal to:

$$i_o = zF \overleftarrow{k}_o [Reduced] \exp \frac{(\alpha_A zFE_e)}{RT} = - zF \overrightarrow{k}_o [Oxidized] \exp \frac{(-\alpha_c zFE_e)}{RT} \tag{11}$$

The incorporation of the concept of overpotential (η),

$$\eta = E - E_e \tag{12}$$

into equation (11) leads to the famous Butler-Volmer relationship, equation (13).

$$i = i_o \left[\exp \frac{(\alpha_A zF\eta)}{RT} - \exp \frac{(-\alpha_c zF\eta)}{RT} \right] \tag{13}$$

For a given reaction mechanism, the magnitude of the observed current density under charge transfer controlled polarisation will be dependent on the exchange current density, the number of electrons exchanged in the reaction and, as noted earlier, the applied electrode potential. At values of positive or negative overpotential typically greater than ±10 mV, one term from the Butler-Volmer equation is usually more significant than the other and the lower contributing term can be removed from equation (13). The resulting forms are known as the cathodic and anodic Tafel equations. Tafel plots are characterized by linear $\log|i|$ *vs.* η slopes in each case:

$$\log -i = \log i_o - \frac{\alpha_c zF}{2.3RT} \eta \quad , or \quad \log -i = \log i_o - \frac{1}{\beta_c} \eta \tag{14}$$

$$\log i = \log i_o \frac{\alpha_A zF}{2.3RT} \eta \quad , or \quad \log i = \log i_o \frac{1}{\beta_A} \eta \tag{15}$$

Alternatively, the Tafel slope can be presented in its original format:

$$\eta = a + b \log i \tag{16}$$

From Equations (14) and (15), Tafel plots of logarithmic current density *vs.* overpotential will have log j axis intercepts equal to $\log|i_o|$ and slopes of $1/\beta_A$ (anodic) and $-1/\beta_c$

(cathodic). In Equation (16), constants 'a' and 'b' relate to a y-axis intercept and the measured slope (β) of a plot of current density *vs.* overpotential. Note that in most corrosion texts current density is still presented as the independent, or x-axis due to a corrosion convention dating back to the days of galvanistatic control of the reaction rate (where current was controlled and the potential change was measured). This convention is still observed by many practicing corrosion engineers even with the introduction of advanced computer controlled instrumentation (where most measurements operate in the opposite, potentiostatic mode). Another convention in corrosion science is the use of 'i' to denote current density. On the other hand, electrochemists will insist on using 'j' and they will always place independent data on the x-axis.

For a reaction, where the number of electrons exchanged equals 1 and the transfer coefficient is 0.5, the theoretical slope for the charge transfer controlled reaction at 25ºC will be equal to -8.5 V (-118 mV decade^{-1}). Thus, Tafel slopes can give valuable information regarding the mechanism of a reaction and indications as to the identity of a rate determining step of the overall reaction scheme. The Tafel equations can also be used to extract i_o values to give relative rates of reaction at equilibrium. It is important to appreciate, however, that only extrapolation to the true equilibrium potential (E_e) will yield i_o. Tafel extrapolation to corrosion potentials, which are usually a mixture of both cathodic and anodic reactions, will not allow isolation of i_o.

An acceptable derivation of a Tafel gradient from experimental data is shown in Figure II for the copper plating reaction discussed earlier. In this figure, a clearly defined linear region (with a high linear correlation coefficient) can be observed for which a Tafel slope of approximately -120 mV decade^{-1} was measured. This indicates that, in this case, a single electron exchange is involved in the rate determining step (if a charge transfer coefficient equal to 0.5 is assumed).

Non-linear $\log|i|$ *vs.* potential curves are not true Tafel slopes. An example [16] of such behavior is given in Figure III, curve [i], where the anodic polarization of a pre-reduced, duplex stainless steel cannot, by any stretch of the imagination, be fitted to the linear response dictated by the anodic Tafel equation. It is important to appreciate that mechanistic details of a reaction can only be extracted via a Tafel analysis if an interfacial charge transfer process controls the electrochemical reaction rate. Moreover, the currents used in the analysis procedure must be fully isolated from the charge passed due to significant side reactions, such as hydrogen evolution during cathodic polarisation.

Very high values of linear slopes can also result where high film resistances are encountered at the electrolyte/electrode interface (*e.g.*, at passive stainless steel, Figure III, Curve [ii]). Incorrect inferences can result if the simple Tafel equation ap-
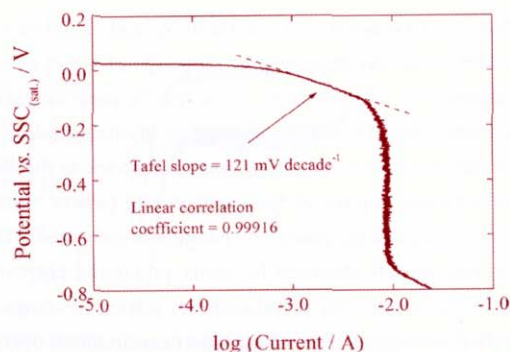
Figure II. Plot of logarithmic current vs. potential for copper deposition from 10 mmol dm^{-3} CuSO$_4$. True Tafel slope behavior is represented (data taken from the original polarization curves presented in Figure I)

proach is applied in these cases. In other systems, the charge transfer coefficient may also be considered to equal unity (or zero) [17]. For the anodic dissolution of copper and a selected copper alloys in chloride solution, an experimental anodic Tafel slope, which would appear to indicate a two-electron exchange, has been shown to only represent a single electron transfer [17-19]. Moreover, highly reversible (fast) reactions, such as ferricyanide reduction on platinum [20], may never produce Tafel slopes because the system will come under the influence of mass transport control at very low overpotentials. In this latter case, region [a], Figure I, will not be observed as the potential-window of charge transfer control will be exceptionally small and impossible to measure directly.

Useful kinetic and diagnostic data, however, can be accurately extracted from relatively complicated systems if the electrochemical response is recognized and correctly characterized. There are standard electrochemical techniques for the extraction of charge transfer data from mixed control data, using controlled flow systems [7].

The humble Tafel slope is certainly open to misuse and striking a straight line through, or at a tangent to, a non-linear curve may not be the best option. The understanding of non-linearities may lead to more useful conclusions.
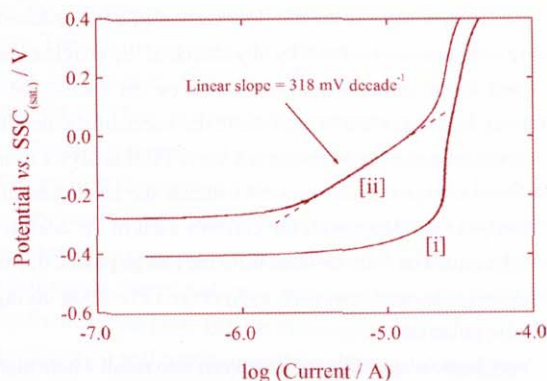

Figure III. Anodic dissolution of S32550 super duplex stainless steel (active area 1004.8 mm^2) in seawater at 25°C; [i] pre-reduced and [ii] mechanically polished surfaces.

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See also Corrosion Science No. 47, issue 12 (2005)