



Tafel analysis in practice

Danlei Li, Chuhong Lin, Christopher Batchelor-McAuley, Lifu Chen, Richard G. Compton*

Department of Chemistry, Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, United Kingdom



ARTICLE INFO

Keywords:

Tafel analysis
Mass transport
Voltammetry
Microelectrode
Computational electrochemistry

ABSTRACT

Voltammetric waves under five different mass-transport regimes (macroelectrode, microdisc, micro-hemisphere, micro-hemicylinder and single microband) for an irreversible one-electron transfer process were simulated and analysed to find the appropriate Tafel region for accurate analysis. The transfer coefficient was found to deviate significantly from its true value as a function of potential in all cases due to the influence of mass-transport. If and how a simple analytical mass-transport correction in which the current is corrected for the change in the reactant concentration at the surface can be used to improve the measurement of transfer coefficient was investigated. It is shown that this correction is only rigorously valid for a uniformly accessible microelectrode under a true steady-state condition. This translates to hemispherical electrodes only of the set of five considered. The fraction of the current used in Tafel analysis (Tafel region) can be increased to around 50% for quasi-steady state regimes (hemicylindrical and single band electrodes) with this analytical correction but it completely failed in linear diffusion regimes (macroelectrodes). In the latter case an improved empirical correction is suggested.

1. Introduction

Voltammetric experiments can yield significant thermodynamic and kinetic information [1,2]. However, due to the convolution of the time and energy domains extraction of this data is often non-facile. In many cases measurement of the related physico-chemical parameters may only be fully achieved through simulation of the system. Notwithstanding this, due in part for ease and expediency, it is very common for voltammetric experiments to be analysed using mathematically analytical procedures. Of these analytical methods, Tafel analysis is a cornerstone of the electrochemist's tool box. Tafel analysis of a voltammogram yields a measure of the electrochemical system's transfer coefficient [3,4]. First, under appropriate conditions, the transfer coefficient can provide information regarding the electrochemical mechanism [5]. Classically, Tafel analysis has been used to great effect in the analysis and elucidation of the catalytic activity of various metal surfaces towards the hydrogen evolution reaction [6,7]. Second, for irreversible voltammetry at a macroelectrode (linear diffusion regime) the transfer coefficient needs to be known in order for the species diffusion coefficient to be accurately determined [8].

The transfer coefficient is a dimensionless parameter and describes how the rate of an interfacial oxidation or reduction reaction varies as a function of the applied potential, under the caveat that the concentration of the reactant at the electrode surface is unaltered from its value in bulk solution. The physical interpretation of the transfer coefficient is

often dependent upon the assumption of an underlying electrochemical mechanism. Moreover, for electrochemical processes involving the transfer of multiple electrons and/or the formation and breaking of chemical bonds (i.e. processes comprised of multiple sequential elementary steps) the interpretation of the transfer coefficient is not straightforward [9]. However, for a simple and single electron transfer process the transfer coefficient is commonly qualitatively interpreted as a being a measure of the 'position' of the transition state [8], where a transfer coefficient close to unity implies the transition state is 'reactant-like' and similarly a value close to zero implies a 'product-like' transition state for an oxidative process.

The Butler-Volmer equation is a phenomenological description of the rate of an interfacial redox reaction where the reaction rate increases exponentially as a function of the applied potential. In this framework it is commonly assumed that the transfer coefficient is a constant and independent of the applied potential. In contrast Marcus-Hush theory [10–12] provides a microscopic model of an interfacial electron transfer process, here the rate of the reaction is rationalised in terms of the reaction Gibbs energy and a reorganisation energy [13]. The reorganisation energy is related to the energy required to distort the reactant molecule and its solvation shell to those of the product. Commonly, the force constants for the reduced and oxidised species are assumed to be equal (symmetric): this is equivalent to assuming that at low overpotentials that the transfer coefficient has a value of 0.5. However, even for many apparently outer-sphere redox processes the

* Corresponding author.

E-mail address: Richard.compton@chem.ox.ac.uk (R.G. Compton).

<https://doi.org/10.1016/j.jelechem.2018.08.018>

Received 3 July 2018; Received in revised form 6 August 2018; Accepted 16 August 2018

Available online 17 August 2018

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transfer coefficient is found to deviate from 0.5 [14]. Relaxation of the assumption of equal force constants, allows (asymmetric) Marcus-Hush theory to be reconciled with the Butler-Volmer equation [15,16]. The latter can be viewed as a good approximation of the former at low overpotentials and the transfer coefficient can be quantitatively interpreted as reflecting the asymmetry in the force constants for the reduced and oxidised species.

For both the symmetric and asymmetric forms of Marcus-Hush theory, these microscopic theories predict a deviation of the reaction rate from exponentially increase at high overpotentials; ultimately the rate becomes independent of the applied potential, becoming mass-transport controlled. The predicted deviation away from exponentially increasing reaction rate may be expressed as a potential dependent transfer coefficient (or equivalently as a ‘curved’ Tafel slope). The experimental reporting of such curved Tafel slopes and potential dependent transfer coefficients have historically [17,18] played an important role in validating and advancing our physical insight into this class of heterogeneous reactions. However, during the course of a voltammogram the reactant rapidly becomes depleted at the electrode surface and the rate determining step becomes the mass-transport of material to the electrode surface. Consequently, before interpreting an experimental Tafel plot and the associated transfer coefficient it is important to quantify over what range of voltammetric currents can the voltammogram be directly analysed within the Butler-Volmer approach to yield an accurate measure of the transfer coefficient? A further issue is to what extent can the depletion of the reactant be corrected for using analytical approximations? The present paper addresses and answers these two questions.

2. Background theory

2.1. Butler-Volmer (BV) theory

We consider the following one electron transfer oxidative process under different mass-transport geometries:



where the reactant and product in the process are assumed to have equal diffusion coefficients with only reactant present in bulk solution.

Butler-Volmer (BV) theory is experimentally the most commonly used kinetic model [19,20]. According to BV theory, the oxidative and reductive rate constants (k_a , k_c) are functions of the transfer coefficients, the standard rate constant k^0 and the formal potential E_f^0 [8]:

$$k_a = k^0 \exp[\alpha_{a,BV} \theta] \quad (2)$$

$$k_c = k^0 \exp[-\alpha_{c,BV} \theta] \quad (3)$$

where the anodic transfer coefficient $\alpha_{a,BV}$ and the cathodic transfer coefficient $\alpha_{c,BV}$ are between 0 and 1, $\alpha_{a,BV} + \alpha_{c,BV} = 1$, and θ is the dimensionless potential given by:

$$\theta = \frac{F}{RT}(E - E_f^0) \quad (4)$$

where E is the potential of the working electrode, F is the Faraday constant (96,485 C mol⁻¹), R is the gas constant (8.314 J mol⁻¹ K⁻¹) and T is the temperature in K. $\alpha_{a,BV}$ and $\alpha_{c,BV}$ are commonly assumed to be independent of potential.

2.2. Tafel analysis

The International Union of Pure and Applied Chemistry (IUPAC) formally defines the anodic and cathodic transfer coefficients as being experimentally determined values and given by [3,4]:

$$\alpha_a = \frac{RT}{F} \left(\frac{d \ln j_{a,corr}}{dE} \right) \quad (5)$$

$$\alpha_c = -\frac{RT}{F} \left(\frac{d \ln |j_{c,corr}|}{dE} \right) \quad (6)$$

where $j_{a,corr}$ and $j_{c,corr}$ are the anodic and cathodic current densities corrected for any changes in the reactant concentration at the electrode surface with respect to its bulk value. The definitions avoid the need for any knowledge of the overall number of electrons transferred.

If a process is considered to be fully irreversible, for an oxidative process, when the applied potential is sufficiently far from the equilibrium potential E_{eq} , it is possible to neglect the flux contribution from the reduction. Hence, the electrochemical flux can be expressed as:

$$j_a = k_a [A]_0 = k^0 \exp \left[\frac{\alpha_a F (E - E_f)}{RT} \right] [A]_0 \quad (7)$$

where j_a is the experimentally measured anodic flux density and $[A]_0$ is the concentration of the reactant at the electrode surface, which is typically different from that in bulk solution except close to the ‘foot’ of the voltammetric wave. Due to the sensitivity of j_a to $[A]_0$, surface depletion of the reactant can and often does lead to a mass-transport limitation of the measured current.

This electrochemical flux can be directly related to the measured current by:

$$I_a = \int F j_a dA \quad (8)$$

where I_a is the anodic current.

By combining Eqs. (7) and (8), rearranging and assuming the flux is uniform across the electrode surface, we get the expression:

$$\ln |I_a| = \frac{\alpha_a F (E - E_f^0)}{RT} + \ln (FAk^0 [A]_0) \quad (9)$$

Consequently, if $[A]_0$ does not deviate significantly from its bulk value, a plot of $\ln |I_a|$ versus E yields a straight line with a gradient proportional to α_a . Hence plots of $\ln |I|$ versus E are commonly used to extract the transfer coefficient from voltammetric data and are referred to as ‘Tafel plots’. The resulting line of best fit will yield a measure of the transfer coefficient averaged over a range of potentials. However, mirroring the IUPAC recommendations, if the plot is curved, the transfer coefficient can be defined as a function of potential.

Problematically, implementation of Eqs. (5) and (6) requires precise knowledge of the mass-transport regime to allow the flux to be suitably corrected for deviations in the surface concentration of the reactant. Consequently, for expediency and/or due to the lack of knowledge regarding the nature of the mass-transport regime (in contrast to Eqs. (5) and (6)), the experimentally accessible parameters are:

$$\frac{RT}{F} \frac{d \ln I_a}{dE} = \alpha_{a,nc} \quad (10)$$

$$-\frac{RT}{F} \frac{d \ln |I_c|}{dE} = \alpha_{c,nc} \quad (11)$$

where I_c is the cathodic current, $\alpha_{a,nc}$ and $\alpha_{c,nc}$ are the non-mass-transport corrected or ‘apparent’ transfer coefficients. The transfer coefficient α_{nc} may deviate from its true value α_a due to the local depletion of reagents at the electrochemical interface. However, at low current densities (i.e. $I \rightarrow 0$), $\alpha_{nc} \rightarrow \alpha$.

It is useful to comment that Tafel plots ($\ln |I|$ versus E) as used in this paper differ from its historical form (overpotential η versus $\log_{10} I$) as measured from galvanostatic experiments. The classically defined Tafel slope with the unit as mV per decade of current is directly related to the transfer coefficient (Tafel slope = $2.3RT/\alpha_a F$). For example, $\alpha_a = 0.5$ is equivalent to the Tafel slope of ca. 118 mV per decade. In this paper, potentiostatic control is assumed, and consequently it is appropriate to define the Tafel plot as $\ln |I|$ versus E , the slope of which is proportional to the transfer coefficient.

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