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POWER ULTRASOUND IN ELECTROCHEMISTRY

FROM VERSATILE LABORATORY TOOL TO ENGINEERING SOLUTION

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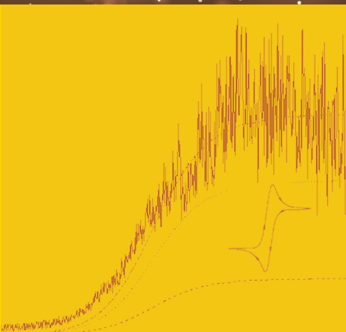

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From Versatile Laboratory Tool to Engineering Solution

Edited by

BRUNO G. POLLET

The University of Birmingham
Edgbaston, United Kingdom

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I dedicate this book to:

A wonderful Man and a brilliant Scientist –
Professor John Phil Lorimer

and

Mes parents et ma petite soeur que j' aime énormément

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Foreword

When I think back to my first excursions into the world of ultrasound and its effects on chemical reactions it takes me back to 1975 when I obtained my first permanent academic post as an organic chemist at an institution that was then called Lanchester Polytechnic but later became Coventry University. The department I joined was Chemistry and Metallurgy, reflecting the applied nature of science courses at that time. One day I was walking through a metallurgy laboratory and saw an ultrasonic bath being used to clean metal samples. The process intrigued me for I could see that the ultrasonic bath was producing a large amount of energy as evidenced by the disturbance of the water with which it was filled. It occurred to me that this was perhaps a form of energy which might be employed to influence chemical reactivity using as an example a simple solvolysis reaction. However, the initial results were puzzling but I was sharing an office with a physical chemist, the late Phil Lorimer, but neither of us had heard of using ultrasound as a source of energy to promote chemical reactivity. Together we pursued this new subject and met many problems in convincing the UK science fraternity that we were 'on to something big'. We produced our first paper in 1980 as a *Chemical Communication*, in which we reported a small (twofold) enhancement in the hydrolysis rate of 2-chloro-2-methylpropane. By 1986 the idea of using ultrasound to influence reactions had greatly expanded worldwide and we were involved in organising the first ever international conference on sonochemistry at Warwick University.

So where does electrochemistry fit into the development of sonochemistry? Phil Lorimer was originally an electrochemist and so had an interest in all things that might influence electrochemical processes. Together with another colleague, David Walton, we began to apply ultrasound to electrochemistry in the late 1980s and discovered that it could, for example, modify the electrochemical oxidation mechanism of cyclohexanecarboxylate. In 1990 we published a review using the term 'Sonoelectrochemistry' for the first time in a peer-reviewed journal. This review forced us to look at the literature surrounding the uses of ultrasound in electrochemistry and brought to light a number of research publications that had not previously been drawn together. Other sources have been unearthed since then, including the pioneering work of Young and Kersten in 1936 on the effects of ultrasonic radiation on electrodeposits. This was perhaps the first observation of improvements in hardness and brightness induced by ultrasound. Walker reinvestigated and advanced the work in the 1970s and in 1993 wrote a comprehensive review of his and other work entitled 'Ultrasonic Agitation in Metal Finishing'. It is surprising to me that the very early work on sonoelectrochemistry has not been cited extensively. This is the case with the 1953 paper of Yeager and Hovorka entitled 'Ultrasonic Waves and Electrochemistry'. It provided a survey of the electrochemical applications of ultrasonic waves that were discussed in terms of (i) the effects of ultrasonic waves on electrode processes, (ii) electrokinetic phenomena involving ultrasonic waves, and (iii) the use of ultrasonic waves as a tool in the study of the structure of electrolytic solutions.

Our own work in sonoelectrochemistry progressed at a pace and in 1995 we took on one of our own young and bright chemistry graduates to study for a PhD. He obtained his doctorate three years later with a thesis entitled 'The Effect of Ultrasound upon Electrochemical Processes' and his name was Bruno G. Pollet – the editor of this book. Bruno became more and more involved in the work on sonoelectrochemistry and looked at a range of topics, including the effect of ultrasonic frequency and power upon electrochemical systems, from the theory and modelling to 'real' industrial applications.

The group of authors that Bruno has assembled for this book have been able to cover many of the main areas of sonoelectrochemistry with contributions on fundamentals, analysis, organic synthesis, nanoparticles, polymerisation and much more. I recommend this book to you as a compendium of current thoughts and approaches to sonoelectrochemistry written by experts in the field.

Tim Mason
May 2011

About the Editor

Bruno recently joined The University of Birmingham from Industry. He is an expert in the area of Proton Exchange Membrane Fuel Cell (PEMFC), Electrochemical Engineering and Sonoelectrochemistry (www.sonoelectrochemistry.com). He is currently responsible for the Hydrogen Fuel Cell Vehicle projects and PEMFC and Membrane Electrode Assembly (MEA) activities at the university. He is CEO of West Midlands Fuel Cells Ltd, CTO of H2Tech (Hawaii), Head of the Birmingham PEM Fuel Cell Research Group, Associate Director of The Centre for Hydrogen and Fuel Cell Research, Visiting Professor Fuel Cell Nanomaterials Center at The University of Yamanashi (Japan), Operations and Delivery Director of the UKRC Doctoral Training Centre in Hydrogen, Fuel Cells and their Applications and Programme Director of the MRes and PhD with Integrated Studies in Hydrogen, Fuel Cells and their Applications. He has worked for Samuel Banner Ltd (Banner Chemicals Group) and Albion Chemicals Ltd (now Brenntag (UK) Ltd) in Sales and Marketing, Johnson Matthey Fuel Cells Ltd (Johnson Matthey Plc) as Test Facility Scientist, Membrane Electrode Assembly (MEA) Design Scientist and Programme Leader, SmartWater Europe Ltd as Research Manager, and Coventry University as Head of Sonoelectrochemistry, Project Development Manager and Lecturer in Environmental and Physical Sciences. He has also worked as an EPSRC and EU Research Fellow in the field of Fuel Cells and Electrochemiluminescence at the Liverpool Electrochemistry Group. Bruno was awarded an Engineering Diploma in Chemistry and Material Sciences from the Université Joseph Fourier (Grenoble, France), a BSc (Hons) in Applied Chemistry from Coventry University and an MSc in Analytical Chemistry from The University of Aberdeen. He also gained his PhD in Physical Chemistry in the field of Electrochemistry (Sonochemistry and Sonoelectrochemistry) under the supervision of Professor J. Phil Lorimer at Coventry University. Bruno has published several publications and chapters in the field of Fuel Cells, Sonoelectochemistry and Sonochemistry.

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- International Society of Electrochemistry (ISE)
- Electrochemical Society (ECS)
- International Journal of Hydrogen Energy (IJHE) Editorial Board
- Journal of Nano Energy and Power Research (JNEPR) Editorial Board
- Member of The Society of Chemical Industry (SCI) – Electrochemistry Technology Group
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Introduction to Electrochemistry

Bruno G. Pollet and Oliver J. Curnick

I.1 Introduction

This summary introduces some fundamental aspects of electrochemistry, explaining the various electrochemical phenomena occurring at the electrode surface when a potential is applied across it. For this purpose, electrode kinetic and mass-transport parameters will be defined in detail.

I.2 Principles of Electrochemistry

All chemical interactions involve the interaction of electrons at the atomic or molecular level, so that, in a sense, all chemistry is electrochemistry. The fundamental process in electrochemistry is the transfer of electrons between the surface of the electrode and the molecules of a chemical species in the region adjacent to this surface. The nature of this region has a significant effect on the current response, thus it is very important to have some idea about its structure.

Several models have been proposed for the interfacial region. In the simplest model, the charge on the electrode is balanced by a layer of solvated ions of opposite charge held at the electrode surface by coulombic attraction. This region is called the 'electric double layer' [1]. A consequence of this arrangement is that the potential drop between the electrode and the solution occurs across an interfacial region which is a few nanometers thick, leading to a high electric field.

Other models have also shown that the interfacial region can be viewed as two layers of equal and opposite charge separated by a dielectric material (Figure I.1). The first region consists of adsorbed solvent molecules and anions and is defined as the inner Helmholtz plane (IHP). The next layer is defined as the outer Helmholtz plane (OHP) and consists of solvated cations held in this plane by coulombic attraction extending into the diffusion layer where there is competition between the ordering effect of coulombic attraction and disordering of thermal motion. In other words, any electrode immersed in an electrolyte can be modelled as a resistor and capacitor connected in series (an rC system) (by analogy with electrical circuits) where the double layer act as a capacitor C and the ionic medium as a

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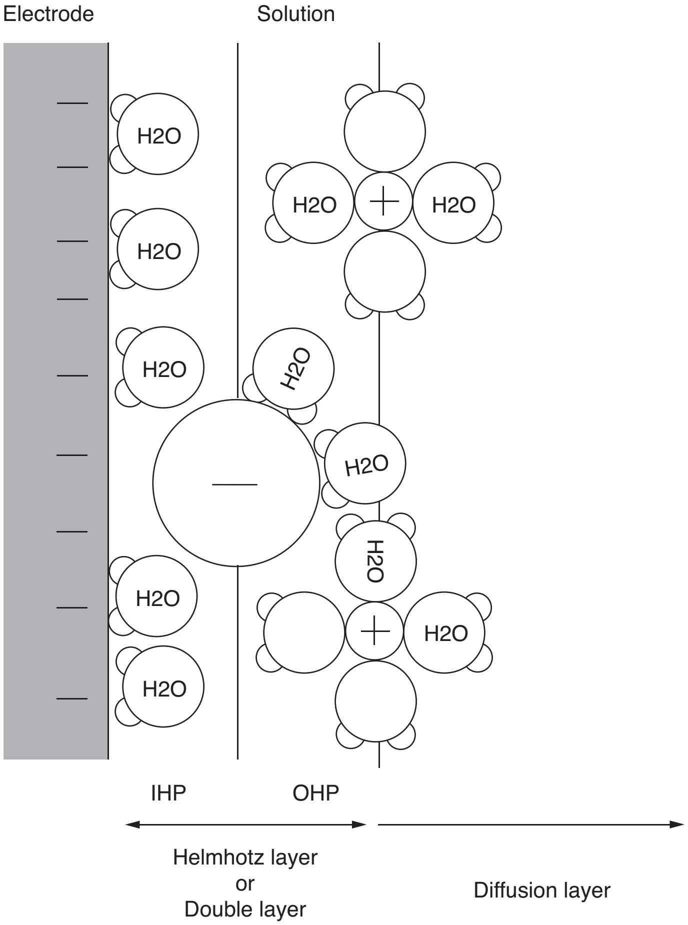

Figure I.1 *Relative positions of the inner and outer Helmholtz planes of electrode double layer.*

resistor r. The product rC is very important in electrochemistry since it determines the rate at which the current flowing to or from the electrode responds to a change in the applied potential, in the absence of any electrochemical reactions taking place at the surface [1].

The next section discusses electrochemical reactions occurring in the interfacial region, that is, the electron-transfer kinetics and the mass-transport of the electroactive species within the double layer.

I.3 Electron-Transfer Kinetics

When a metal (R) is dipped into a solution of its ions (O) an equilibrium such as

$$M^{n+} + ne^{-} \leftrightarrow M \tag{I.1}$$

or

$$\mathrm{O} + n\mathrm{e}^- \; {<}{=}{=}{=} \; \overset{k_\mathrm{f}}{\underset{k_\mathrm{r}}{}} \; {=}{=}{=}{>} \; \mathrm{R}$$

is established at its surface. Such an electrode will adopt a potential difference with respect to the solution, whose value is a measure of the position of the equilibrium, which in turn depends on the concentrations of the O and R species at the electrode surface.

Ideally, a redox process is governed by the Nernst equation (Equation I.2) [2], which describes the relationship between the electrode potential, $E_{\mathrm{O/R}}$, and the concentrations at the electrode surface of the electroactive species O and R (assuming that the activity coefficients of O and R are unity). The Nernst equation is then [2]

$$E_{\mathrm{O/R}} = E^{\mathrm{o}}_{\mathrm{O/R}} + \frac{RT}{nF} \ln \frac{C^{\mathrm{S}}_{\mathrm{O}}}{C^{\mathrm{S}}_{\mathrm{R}}} \tag{I.2}$$

where

R is the gas constant in J K^{-1} mol^{-1} ($R = 8.3184$ J K^{-1} mol^{-1} at 298 K),
T is the temperature in K,
F is the Faraday constant in C mol^{-1} ($F = 96\,484.6$ C mol^{-1}),
$E_{\mathrm{O/R}}$ is the working electrode potential in V,
$E^{\mathrm{o}}_{\mathrm{O/R}}$ is the *formal* redox couple (or standard reduction potential – SRP) in V,
n is the number of electrons transferred per ion or molecule,
$C^{\mathrm{S}}_{\mathrm{O}}$ is the electrode surface concentration of O, M (electrode) in mol cm^{-3}, and
$C^{\mathrm{S}}_{\mathrm{R}}$ is the electrode surface concentration of R, M (electrode) in mol cm^{-3}.

[*Formal* implies that the activity coefficients are assumed to be unity.]

Experimentally, the electrode potential ($E_{\mathrm{O/R}}$) cannot be measured directly. However, it can be inferred from a measurement of the potential difference between the electrode and some second electrode placed into the same solution (cell potential, E_{cell}), provided the potential on the second electrode is well known. This requires a reference electrode, for example, a saturated calomel electrode (SCE) or a standard hydrogen electrode (SHE) [2–4].

Thus, by convention, one may write that the cell potential is

$$E_{\mathrm{cell}} = E_{\mathrm{O/R}} - E_{\mathrm{reference}} \tag{I.3}$$

If $E_{\mathrm{reference}} = 0$ V (as for the SHE), then,

$$E_{\mathrm{cell}} = E_{\mathrm{O/R}} \tag{I.4}$$

If no current flows through the electrochemical cell, that is, no electrochemical changes have occurred, the electrochemical cell is said to be at equilibrium. In other words, the electrode will adopt an equilibrium or reversible potential (E_{rev}).

Thus one may write that

$$E_{\mathrm{O/R}} = E_{\mathrm{rev}} \tag{I.5}$$

or

$$E_{\mathrm{rev}} = E^{\mathrm{o}}_{\mathrm{O/R}} + \frac{RT}{nF} \ln \frac{C^{\mathrm{S}}_{\mathrm{O}}}{C^{\mathrm{S}}_{\mathrm{R}}} \tag{I.6}$$

Equation (I.6) implies that there is a dynamic equilibrium at the electrode surface, that is, the oxidation of R and the reduction of O occur at the same rate. Experimentally, it is observed that, at the reversible potential, no net current flows in the cell, that is, the forward and the reverse currents are equal in magnitude [3]. Thus one may write

$$I_f = I_r = I_o \tag{I.7}$$

where I_f and I_r are the partial currents for the forward and reverse electrochemical reactions respectively and I_o is an important kinetic parameter of an electron-transfer reaction known as the exchange current at E_{rev}. I_o is a measure of the intrinsic ability of O and R to take part in electron-transfer reactions at the electrode surface; for example, large values indicate that electron transfer is facile.

In 'real' situations, information on the electron-transfer processes cannot be obtained using a two-electrode system at equilibrium. Electrode kinetic parameters such as I_o can only be determined if the equilibrium $O + ne^- \leftrightarrow R$ is 'disturbed', that is, a potential difference is applied to the electrochemical cell. In order to quantify relationships between current and potential, it is necessary to employ a three-electrode system in which the potential difference is varied between a working electrode (W.E.) [on which the electrode reaction occurs] and a reference electrode (R.E.) and the current, developed by one or several electrode reactions at the working electrode, is measured between a counter electrode (C.E.) and the working electrode. These three electrodes are linked to a potentiostat (Figure I.2).

The steady potential resulting from the rapid establishment of the equilibrium in Equation (I.6) can be explained as follows: no net current is flowing when the forward and reverse rates of the reaction are equal. The further such an equilibrium lies to the right, the more negative is the electrode potential. If the working electrode potential is made more negative than the equilibrium potential, the equilibrium may re-assert itself in order to satisfy the Nernst equation, that is, the surface concentration of O and R have to take up new values [see Equation (I.6)]. In this case, C_R^S increases and C_o^S decreases. Thus, a decrease in the ratio C_o^S/C_R^S is observed and a cathodic current will be noted.

It should be emphasized that these predictions are based on thermodynamic parameters. It is important to note that the partial currents flowing in the electrochemical cell at any

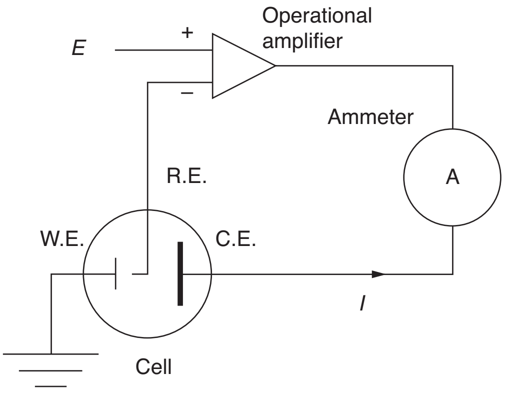

Figure I.2 Potentiostatic assembly for electrode potential measurements.

potential depend on the electron-transfer kinetics. Thus, at any potential the measured current, I_{net}, is related to the forward and reverse partial currents and is given by

$$I_{\text{net}} = I_{\text{r}} - I_{\text{f}} \tag{I.8}$$

For simplicity, it is assumed in the following discussion that the rate of heterogeneous electron transfer is the rate-limiting step, that is, other factors such as mass-transfer effect are not considered.

Since I represents the number of electrons reacting with O per second, or the number of coulombs of electric charge flowing per second, the question 'What is I?' is essentially the same as 'What is the rate, v, of the reaction $\text{O} + n\text{e}^- \leftrightarrow \text{R}$?' The following equations demonstrate the direct proportionality between the Faradaic current and electrolysis rate (Faraday's law) [1]:

$$I = \frac{\text{d}Q}{\text{d}t} \tag{I.9}$$

and

$$\frac{Q}{nF} = \frac{w}{M_{\text{r}}} = N \tag{I.10}$$

where

I is the current flowing in A,
Q is the quantity of electricity passed in C,
t is the time in s,
n is the valence of the element deposited,
F is the Faraday constant in C mol^{-1} ($F = 96\,484.6$ C mol^{-1}),
w is the mass of substance deposited in g,
M_{r} is the relative atomic mass of the element deposited in g mol^{-1}, and
N is the number of moles electrolysed in mol.

Thus if the reaction rate, v, is given by

$$v = \frac{\text{d}N}{\text{d}t} \tag{I.11}$$

then, from Equations (I.9) and (I.10)

$$v = \frac{I}{nF} \tag{I.12}$$

Since electrode reactions are heterogeneous, their reaction rates are described in units of moles per unit area per second; that is,

$$v = \frac{I}{nF\text{A}} \tag{I.13}$$

or

$$v = \frac{i}{nF} \tag{I.13a}$$

where i is the current density ($i = I/A$) in A cm^{-2}, A is the electrode surface area (cm^2) and v is in mol cm^{-2} s^{-1}.

If one assumes, for dilute solutions, that the activity approximates to concentration, one may write

$$v = kC^{\mathrm{S}} \tag{I.14}$$

Employing Equations (I.13) and (I.14), the current is given by

$$I = nF\mathrm{A}kC^{\mathrm{S}} \tag{I.15}$$

Thus one may write that the partial currents for the forward and reverse reactions as:

$$I_{\mathrm{f}} = nF\mathrm{A}k_{\mathrm{f}}C_{\mathrm{o}}^{\mathrm{S}} \tag{I.16}$$

and,

$$I_{\mathrm{r}} = nF\mathrm{A}k_{\mathrm{r}}C_{\mathrm{R}}^{\mathrm{S}} \tag{I.17}$$

where n is the number of electrons transferred, A is the electrode surface area (cm^2), C^{S} is the surface concentration (mol cm^{-3}) and k_{f} and k_{r} are the rate constants (cm s^{-1}) for the forward and reverse heterogeneous reaction.

Unlike conventional reaction rate constants, which vary only with temperature, these rate constants are dependent both on temperature and the applied potential, E_{app}. It is found experimentally that the forward and reverse rate constants vary exponentially as given below [3]

$$k_{\mathrm{f}} = k_{\mathrm{o}} \exp[(-\alpha nF/RT)(E_{\mathrm{app}} - E^{\mathrm{o}})] \tag{I.18}$$

and

$$k_{\mathrm{r}} = k_{\mathrm{o}} \exp[((1-\alpha)nF/RT)(E_{\mathrm{app}} - E^{\mathrm{o}})] \tag{I.19}$$

where k_{o} is the *formal* or the apparent heterogeneous rate constant and α is known as the electron-transfer coefficient.

Thus, the measured current, I_{net}, becomes

$$I_{\mathrm{net}} = I_{\mathrm{r}} - I_{\mathrm{f}} = nF\mathrm{A}\left(k_{\mathrm{r}}C_{\mathrm{R}}^{\mathrm{S}} - k_{\mathrm{f}}C_{\mathrm{o}}^{\mathrm{S}}\right) \tag{I.20}$$

or substituting k_{f} and k_{r} from Equations (I.18) and (I.19)

$$I_{\mathrm{net}} = nF\mathrm{A}k_{\mathrm{o}}\left\{C_{\mathrm{R}}^{\mathrm{S}} \exp[(1-\alpha)(nF/RT)(E_{\mathrm{app}} - E^{\mathrm{o}})] - C_{\mathrm{o}}^{\mathrm{S}} \exp[(-\alpha nF/RT)(E_{\mathrm{app}} - E^{\mathrm{o}})]\right\} \tag{I.21}$$

Equation (I.21) is known as the Eyring equation and relates the surface concentrations to the net current flow, I_{net}. The equation is ideal and cannot be tested experimentally. However, one such equation which can be tested is the Butler-Volmer equation, which relates the bulk concentrations (measurable) with the net current. Discussion below will show how the Eyring equation can be transformed to the Butler-Volmer equation provided that the Nernst equation is considered.

If it is assumed that the surface concentrations and the bulk concentrations of O and R are only equal when the electrode is at equilibrium, that is, $C_{\mathrm{o}}^{\mathrm{S}} = C_{\mathrm{o}}^{*}$ and $C_{\mathrm{R}}^{\mathrm{S}} = C_{\mathrm{R}}^{*}$ when $E_{\mathrm{cell}} = E_{\mathrm{rev}}$, then rearranging the *Nernst* equation [Equation (I.6)] gives

$$\left(C_{\mathrm{R}}^{*}/C_{\mathrm{o}}^{*}\right) \exp[(nF/RT)(E_{\mathrm{rev}} - E^{\mathrm{o}})] = 1 \tag{I.22}$$

If both sides of Equation (I.22) are raised to the power α, one obtains

$$\left(C_{\mathrm{R}}^{*}/C_{\mathrm{o}}^{*}\right)^{\alpha} \exp[(\alpha nF/RT)\,(E_{\mathrm{rev}} - E^{\mathrm{o}})] = 1 \tag{I.23}$$

(where $1^{\alpha} = 1$) and if both sides of Equation (I.22) are raised to the power $(\alpha - 1)$, one also obtains

$$\left(C_{\mathrm{R}}^{*}/C_{\mathrm{o}}^{*}\right)^{(\alpha-1)} \exp[(\alpha - 1)\,(nF/RT)(E_{\mathrm{rev}} - E^{\mathrm{o}})] = 1 \tag{I.24}$$

If both sides of Equation (I.23) are multiplied by $C_{\mathrm{o}}^{\mathrm{S}}$, one may write

$$C_{\mathrm{o}}^{\mathrm{S}}\left(C_{\mathrm{R}}^{*}/C_{\mathrm{o}}^{*}\right)^{\alpha} \exp[(\alpha nF/RT)\,(E_{\mathrm{rev}} - E^{\mathrm{o}})] = C_{\mathrm{o}}^{\mathrm{S}} \tag{I.25}$$

similarly if both sides of Equation (I.24) are multiplied by $C_{\mathrm{R}}^{\mathrm{S}}$, one may write

$$C_{\mathrm{R}}^{\mathrm{S}}\left(C_{\mathrm{R}}^{*}/C_{\mathrm{o}}^{*}\right)^{(\alpha-1)} \exp[(\alpha - 1)\,(n/RT)(E_{\mathrm{rev}} - E^{\mathrm{o}})] = C_{\mathrm{R}}^{\mathrm{S}} \tag{I.26}$$

Inserting Equations (I.25) and (I.26) into Equation (I.21) leads to Equation (I.27)

$$\begin{aligned} I_{\mathrm{net}} = nF\mathrm{A}k_{\mathrm{o}}\left(C_{\mathrm{R}}^{*}\right)^{\alpha}\left(C_{\mathrm{o}}^{*}\right)^{(1-a)} &\left\{\left(C_{\mathrm{R}}^{\mathrm{S}}/C_{\mathrm{R}}^{*}\right)\exp[(1-\alpha)(nF/RT)(E_{\mathrm{app}} - E_{\mathrm{rev}})]\right.\\ &\left.\times\left(C_{\mathrm{o}}^{\mathrm{S}}/C_{\mathrm{o}}^{*}\right)\exp[(-\alpha nF/RT)(E_{\mathrm{app}} - E_{\mathrm{rev}})]\right\} \end{aligned} \tag{I.27}$$

It is also found experimentally that there is a deviation of the applied potential, E_{app}, from the reversible potential, E_{rev}. This 'perturbation' is termed overpotential, η (see later in this section) and is given by:

$$\eta = E_{\mathrm{app}} - E_{\mathrm{rev}} \tag{I.28}$$

Inserting Equation (I.28) into Equation (I.27) leads to Equation (I.29)

$$\begin{aligned} I_{\mathrm{net}} = nF\mathrm{A}k_{\mathrm{o}}\left(C_{\mathrm{R}}^{*}\right)^{\alpha}\left(C_{\mathrm{o}}^{*}\right)^{(1-\alpha)} &\left\{\left(C_{\mathrm{R}}^{\mathrm{S}}/C_{\mathrm{R}}^{*}\right)\exp[(1-\alpha)(nF/RT)\eta]\right.\\ &\left.\times\left(C_{\mathrm{o}}^{\mathrm{S}}/C_{\mathrm{o}}^{*}\right)\exp[(-\alpha nF/RT)\eta]\right\} \end{aligned} \tag{I.29}$$

or

$$I_{\mathrm{net}} = I_{\mathrm{o}}\left\{\left(C_{\mathrm{R}}^{\mathrm{S}}/C_{\mathrm{R}}^{*}\right)\exp[(1-\alpha)(nF/RT)\eta] - \left(C_{\mathrm{o}}^{\mathrm{S}}/C_{\mathrm{o}}^{*}\right)\exp[(-\alpha nF/RT)\eta]\right\} \tag{I.30}$$

with $I_{\mathrm{o}} = nF\mathrm{A}k_{\mathrm{o}}\,(C_{\mathrm{R}}^{*})^{\alpha}\,(C_{\mathrm{o}}^{*})^{(1-\alpha)}$ being the exchange current. Often the exchange current is normalised to unit area to provide the exchange current density, $i_{\mathrm{o}} = I_{\mathrm{o}}/A$.

If the solution is well stirred or currents are kept so low that the surface concentrations do not differ appreciably from the bulk values, that is, $C_{\mathrm{o}}^{\mathrm{S}} = C_{\mathrm{o}}^{*}$ and $C_{\mathrm{R}}^{\mathrm{S}} = C_{\mathrm{R}}^{*}$, then Equation (I.30) becomes

$$i_{\mathrm{net}} = i_{\mathrm{o}}\{\exp[((1-\alpha)nF/RT)\eta] - \exp[(-\alpha nF/RT)\eta]\} \tag{I.31}$$

which is known as the Butler-Volmer equation.

Equation (I.31) must be regarded as the fundamental equation of electrode kinetics and it shows how the net current varies with the exchange current density, the overpotential and the electron-transfer coefficient. For practical purposes, it is convenient to consider the limiting behaviour of Equation (I.31) for small and large values of the arguments of the exponential terms. Experimentally, two limiting forms of Equation (I.31) are used:

(a) At small overpotentials.

For small values of overpotential, that is, when $\eta \rightarrow 0$, the exponential terms can be written as Taylor expansions, that is, $\exp(x) \approx (1 + x)$. Thus, Equation (I.31) becomes

$$i_{\text{net}} = \frac{i_{\text{o}} nF}{RT} \eta \tag{I.32}$$

that is, the current density is directly proportional to the overpotential. Thus a plot of i_{net} versus η is linear. By analogy with Ohm's law ($V = Ir$), here (RT/nFi_{o}) can be regarded as an impedance and is often referred to as a Faradaic (or charge transfer or ohmic) resistance. This is particularly important in AC impedance measurements. In practice, the linear approximation can be used for $|\eta| > 10/n$ mV.

(b) At large overpotentials.

At large positive overpotentials, that is, when $\eta \rightarrow +\infty$ that is, $\exp[(-\alpha nF/RT)\eta] \rightarrow 0$, then Equation (I.31) can be approximated to

$$i_{\text{net}} \approx i_{\text{o}} \exp[(1-\alpha)(nF/RT)\eta] \tag{I.33}$$

or

$$\log i_{\text{net}} \approx \log i_{\text{o}} + (1-\alpha)(nF/(2.3RT))\eta \tag{I.34}$$

[where $\ln(x) = 2.3 \log(x)$] or

$$\eta \approx -2.3RT \log i_{\text{o}}/((1-\alpha)nF) + 2.3RT \log i_{\text{net}}/((1-\alpha)nF) \tag{I.35}$$

At large negative overpotentials, that is, when $\eta \rightarrow -\infty$, Equation (I.31) can be approximated to

$$i_{\text{net}} \approx -i_{\text{o}} \exp[(-\alpha nF/RT)\eta] \tag{I.36}$$

or

$$\log |i_{\text{net}}| \approx \log i_{\text{o}} - \alpha nF/(2.3RT)\eta \tag{I.37}$$

or

$$\eta \approx 2.3RT \log i_{\text{o}}/(\alpha nF) - 2.3RT \log |i_{\text{net}}|/(\alpha nF) \tag{I.38}$$

The logarithmic relationships in Equations (I.35) and (I.38) are known as the Tafel equations in the form of $\eta = \text{a} + \text{b} \log i_{\text{net}}$. In practice, the Tafel approximation is generally used for $|\eta| < 120/n$ mV.

A plot of versus η *vs.* $\log i_{\text{net}}$ will be linear in this high overpotential region, and $\log i_{\text{o}}$ and α can be found from the intercept (a) and slope (b) respectively, as shown in Figure I.3.

Having discussed the important parameters in electrode kinetics, the next section considers the effect of overpotential on the electrode potential measurements.

All galvanic cells are said to operate reversibly when they draw zero current, that is, operate at the reversible potential, E_{rev}. However, if the electrode potential is deliberately altered to a value more anodic or cathodic to its equilibrium value, then current will immediately flow in such a direction so as restore the equilibrium, that is, normal battery