

## PHYSICAL AND MOLECULAR ELECTROCHEMISTRY

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### Summary

We describe first the basic ideas underlying mechanistic investigations in molecular electrochemistry. Propagation of a diffusional flux into the solution is used as an adjustable standard that is compared to the reaction of interest. This principle is applied to resolution of several mechanisms. Then, the advantages of using micrometric or smaller electrodes are considered for accessing smaller timescales or perform very local analysis.

### 1. Introduction

Molecular electrochemistry is a field where the consequences of a current flow through molecules is analyzed. Why is it important to understand the behavior of the molecules for which one electron has been added or removed? Many reasons can be invoked. Often, this event is followed by further chemical reactions in the vicinity of the electrodes because the initially produced species is an unstable intermediate. Analysis of the current recorded then allows us to understand the future of the produced species. In life sciences, many reactions imply electron transfer events in living organisms. This is for example the case in some steps of photosynthesis, or in respiration. In the developing field of molecular electronics, electrochemistry may provide useful information on the way the candidate systems to perform logical functions will be efficient. Molecular electrochemistry is also a tool to understand better what happens when large scale electrolysis are undertaken, such as the Monsanto industrial electrosynthesis of adiponitrile ( $\text{NCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CN}$ ), a key intermediate in the manufacture of nylon 66); what actually occurs is the reductive dimerisation of acrylonitrile ( $\text{CH}_2 = \text{CHCN}$ ). Finally, recording an electrical current is quite an easy operation, so that there is a great interest in producing electrochemical sensors (cf. *Analytical Electrochemistry (Instrumentation and Electroanalytical Methods)* and *Sensors (Bio and Non-bio Sensors)*). Knowing precisely the parameters that influence a mechanism is then important for conceiving efficient devices.

This chapter will consider a progressive complexity of electrochemical mechanisms. Simple electron transfer will be described first, in order to demonstrate that the current recorded at an electrode is related to diffusion in solution. Then, influence of chemical reactions inside the solution will be considered, focusing whenever possible onto examples relevant to biology. In a final part, we describe the various advantages of using electrodes of reduced dimensions. We do not aim at providing an exhaustive account, but rather seek to provide a taste of the wealth and potentialities of physical and molecular electrochemistry.

Since this chapter treats electrochemical kinetics, a pre-requisite for a good comprehension is to dominate the equilibrium aspects of electrochemical systems, particularly Nernst law.

## 2. Principle of Electrochemical Investigations

### 2.1 Electron Transfer at the Interface

The present section is devoted to establishing the general philosophy underlining most of electrochemical investigations[1-2]. This will be first established considering a simple electron transfer where a compound Ox is reduced in Red, without any subsequent chemical reaction:



In homogeneous solutions, kinetic rates refer to volumic quantities. In electrochemistry,

reaction occurs at the electrode surface so that the rate may be expressed relatively to its area  $A$ :

$$v = -\frac{1}{A} \frac{dn_{\text{Ox}}}{dt} = +\frac{1}{A} \frac{dn_{\text{Red}}}{dt} = -\frac{1}{A} \frac{dn_e}{dt} \quad (2)$$

$v$  is thus a flux (in moles.m<sup>-2</sup>s<sup>-1</sup>). In this expression,  $n_{\text{Ox}}$ ,  $n_{\text{Red}}$  and  $n_e$  are the number of moles of Ox, Red, and electrons participating in the electrochemical reaction during time  $dt$ . The flux of electrons from or to the electrode is therefore related directly to the flux of electroactive species inside the solution. The link to the current is straightforward:

$$v = -\frac{1}{AF} \frac{dq}{dt} = -\frac{i}{AF} \quad (3)$$

using IUPAC conventions (oxidation currents are positive).

Since electron transfer steps are elementary reactions,  $v$  can be expressed as:

$$v = k_a[\text{Red}]_{\text{el}} - k_c[\text{Ox}]_{\text{el}} \quad (4)$$

where  $k_a$  and  $k_c$  are the rate constants for anodic (oxidation) and cathodic (reduction) steps respectively.  $[\text{Red}]_{\text{el}}$  and  $[\text{Ox}]_{\text{el}}$  are the concentrations of Ox and Red at the electrode surface. Contribution Electron Transfer and Single Molecular Events by W. Schmickler in this issue defines the parameters that influence the dependence of  $k_a$  and  $k_c$  onto the electrode potential. The most simple (and often sufficient) dependence is to consider an exponential dependence, which leads to the well-known Butler-Volmer formulation:

$$\frac{i}{FA} = k_0 \left\{ [\text{Red}]_{\text{el}} \exp \left[ \frac{(1-\alpha)F(E-E^0)}{RT} \right] - [\text{Ox}]_{\text{el}} \exp \left[ -\frac{\alpha F(E-E^0)}{RT} \right] \right\} \quad (5)$$

$k_0$  is called the electron transfer rate constant and  $\alpha$  the symmetry coefficient. For  $k_0$  very large, electrons can cross the interface very easily, so that thermodynamic equilibrium is reached at the electrode. Mathematically, since  $i/k^0$  then tends to zero:

$$E = E^0 + \frac{RT}{F} \ln \left( \frac{[\text{Ox}]_{\text{el}}}{[\text{Red}]_{\text{el}}} \right) \quad (6)$$

which is the well-known Nernst law. Such redox couples are denoted as fast. Small departure of potential from equilibrium will thus produce an appreciable current since concentrations at the electrode adjust instantaneously. Conversely, when  $k_0$  is very small (slow couples), large overpotentials are needed to get an appreciable rate of oxidation or reduction, i.e.  $k_a$  or  $k_c$  not negligible, so that oxidation and reduction can only occur at very different potentials.

A measure of the current consequently represents a relative easy access to the kinetics of a system, the potential scale being the reference to the thermodynamic driving force.

## 2.2. Propagation into the Solution

Electron transfer induces a modification of surface concentrations for Ox and Red. In a first stage, we consider a macroscopic electrode where a single space coordinate  $x$  can be considered ( $x=0$  is the location on the electrode). As soon as concentration gradients appear diffusion then tends to compensate them. This is translated physically by Fick's first law:

$$J_i = -D_i \frac{\partial [i]}{\partial x} \quad (7)$$

where  $J_i$  is the flux of  $i$  and  $D_i$  the diffusion coefficient ( $i$  – Ox or Red).

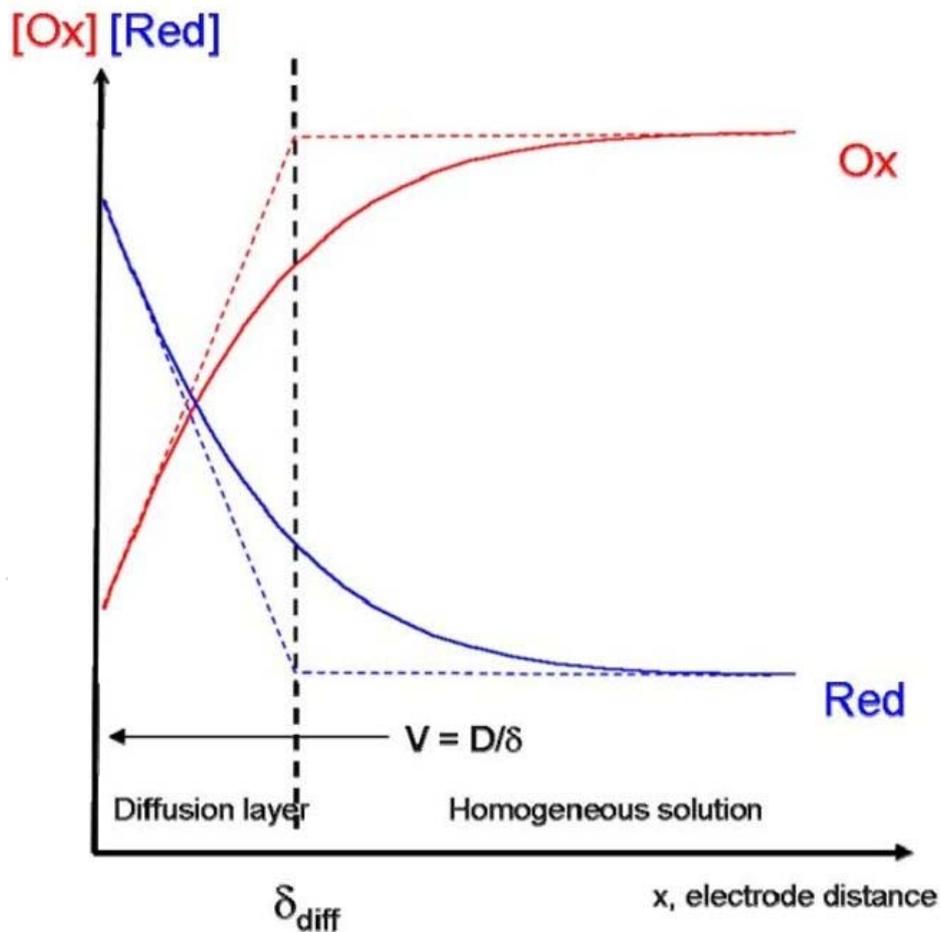


Figure 1. Evolution of concentration profiles with electrode distance

The characteristic distance over which the solution composition is quantitatively modified, and thus where significant diffusion fluxes are involved is defined as the

diffusion layer length  $\delta_{\text{diff}}$ , which may be more accurately defined as:

$$\delta_{\text{diff}} = -D_i \frac{\Delta[i]}{J_i|_{x=0}} \quad (8)$$

$\Delta[i]$  is the concentration difference between the electrode and bulk solution. An initial perturbation thus propagates from the electrode to the solution. In addition to diffusion, intervention of other transport phenomena should also be considered. Ox or Red (or both) is (are) charged, so that electrical migration effects may be important. Usually, an inert supporting electrolyte is added to the solution in large quantities to transport the current so that migration of the solute of interest can be neglected in standard conditions. Secondly, convection gradients are always present, and sometimes purposely generated. Convection is a semi-macroscopic movement of the liquid that then also tends to restore homogeneity. However, conversely to diffusion, convection increases when going far from the electrode. Since diffusion operates by a random walk process, the diffusion layer length grows proportionally with  $t^{1/2}$  ( $\delta_{\text{diff}} \approx \sqrt{D_i t}$ ) until convection restores homogeneity of the solution. Consequently, there is a critical distance, namely the convection layer  $\delta_{\text{conv}}$  from which convection plays a major role. The situation is thus as follows. For small time, i.e.  $t \ll \delta_{\text{conv}}^2 / D_i$  convection effects can be neglected and the diffusion layer length is solely controlled by the perturbation duration:  $\delta_{\text{diff}} \approx \sqrt{D_i t}$ . This is the domain of transient electrochemistry. Conversely, when  $t \gg \delta_{\text{conv}}^2 / D_i$  the diffusion layer cannot grow anymore and  $\delta_{\text{diff}} \approx \delta_{\text{conv}}$ . A steady state behavior is observed in this regime. In steady state methods, the diffusion layer is varied by adapting the flow of solution, high flows corresponding to small  $\delta_{\text{conv}}$ . The global situation may then appear quite complicated, but different techniques indeed operate in one or the other limiting situation which simplifies the problem.

The Nernst model is very simple but nevertheless integrates in a simple way all the physical parameters present in each specific method. This model considers linear diffusion profiles inside the diffusion layer, so that the current may be expressed as:

$$i = \frac{nFAD_i[i]}{\delta_{\text{diff}}} \quad (9)$$

where  $n$  is the number of electrons transferred per redox molecule. This model applies in transient or steady state conditions. It amounts to assuming that convection does not interfere for  $x < \delta_{\text{conv}}$ , and that the solution is homogeneous for  $x > \delta_{\text{conv}}$ . There is then a formal equivalence between both approaches. Advantage of steady states methods is that interferences of double layer charging (cf. *The Electrochemical Double Layer at the Metal/Electrolyte Junction and the Interfaces*) are negligible. Advantages of transient methods is that they allow a simpler visualization of intermediates produced when complicated mechanisms are involved.

For small electrodes, edge effects may become predominant so that radial diffusion may occur. At long timescales, steady state can be achieved without interference of convection, whereas at short timescales transient behavior will be observed. This will be detailed in section 4.

The electrochemical strategy consists in comparing the time  $\tau_i = \delta_{diff}^2 / (\pi D_i)$  or the velocity  $\pi D_i / \delta_{diff}$  needed to cross the diffusion layer to the characteristic one of the reaction of interest. Table 1 gives different electrochemical techniques and their corresponding pertinent parameters, as well as their influence onto the diffusion layer sizes.

Technique	Characteristic parameter	Diffusion layer length $\delta_{diff}$	Characteristic time $\tau_i$
Rotating disk electrode	rotation velocity $\omega$ (in $\text{rad.s}^{-1}$ ).	$1.61 \omega^{-1/2} D^{1/3} \nu^{-1/6}$	$0.83 \times (\omega D^{1/3} \nu^{1/3})^{-1}$
Chronoamperometry	Step duration $\tau$	$\sqrt{\pi D \tau}$	$\tau$
Cyclic voltammetry	Scan rate $\nu$ (in $\text{V.s}^{-1}$ )	$\sqrt{\frac{\pi D R T}{F \nu}}$	$\frac{R T}{F \nu}$
Impedancemetry	Frequency $f$	$\sqrt{\frac{\pi D}{f}}$	$\frac{1}{f}$
Ultramicroelectrode	electrode radius $r_0$	$\frac{\pi r_0}{4}$ (in steady state)	$\frac{\pi r_0^2}{16 D}$
Scanning Electrochemical Microscopy	$d/r_0$ with: d: distance between the electrode and the surface $r_0$ : electrode radius	d	$\frac{d^2}{\pi D}$

Table 1. Electrochemical method, main characteristic parameter, diffusion layer length and characteristic time.

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### Biographical Sketches

**Emmanuel Maisonhaute** is professor at Université Pierre et Marie Curie (Paris 6). He did his Ph D at Ecole Normale Supérieure under the supervision of Pr. Christian Amatore and a post-doctoral stay in the Compton group in Oxford. He is interested in pushing transient electrochemistry to the very short (nanoseconds) timescales, adsorbed electroactive systems related to molecular electronics and coupling electrochemistry with other physicochemical methods such as scanning probe microscopies or radiolysis.

**Jay Wadhawan** is a lecturer at Hull University, UK. He studied at Oxford University with Professor Richard Compton and Dr Frank Marken, and undertook research training with Professor Emmanuel Maisonhaute and Professor Christian Amatore at Ecole Normale Supérieure, Paris. Current research focus is on (1) molecular (photo) electrochemistry and its applications in energy conversion, (2) in the use of electrochemistry to unravel biophysical phenomena, and (3) in the development of electrochemical sensor technologies, and associated mathematical modeling.