

VIRTUAL CYCLIC VOLTAMMETRY

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Abstract

In this paper we discuss the advantages of using interactive simulation programmes for electrochemical dynamical experiments to help both researchers and students in understanding the phenomena underlying these experiments, as well as in obtaining meaningful chemical and electrochemical parameters associated with the redox transformation mechanisms. A PC computer programme developed for this purpose, and which is available to anyone interested, is also presented and applied to the demonstration of virtual cyclic voltammetry.

Key words – Virtual electrochemistry, interactive simulation, cyclic voltammetry

Introduction

Digital simulation is a very powerful technique that can be used with enormous advantages by electrochemists in many fields of research and teaching.

Computational Models as a Tool for Electrochemists

Digital simulation can be very helpful to the experimental electrochemist [1] and is gaining in popularity, with a gradual increase in the number of users, because it has proved to be a very powerful technique to interpret experimental data, either by assisting the researchers in proposing mechanisms for the electrochemical transformations or by allowing them to estimate chemical and electrochemical parameters.

The fitting of simulations to experimental data, to help in the establishment of the mechanisms of electrochemical processes and in the estimate of the kinetic parameters is compatible with off-line simulation and is usually performed in this way. After the collection of the experimental data, simulations can be carried out at leisure. This type of simulation has also some uses in the teaching area, as it can be applied to show the students how a certain type of system is expected to behave, by performing the relevant simulations and compiling the results.

Moreover, the power of computer systems has increased enormously in the last few years. Computers are getting smaller and faster and fast computing is now accessible to everybody. This can be exploited by using simulation techniques interactively, allowing the users, namely the students, to interact with the experiment, as they would with a real equipment. This allows the extension of the use of simulation techniques to teaching, training specialised personnel and, even

experiment planning. For instances, if we suspect how a certain compound, sometimes a difficult one to synthesise, is expected to behave, we can test our proposal by simulating, in a virtual system, the experiments to be performed, before venturing into the real system. This will allow us to anticipate the results of the experiment and, if right, perform the best set of experiments to obtain the desired data.

Advantages of Interactive Simulation

The use of a virtual electrochemical experiment set (and this is true for many other virtual instruments) can have two main advantages for didactical purposes.

The first one is the fact that we can perform experiments without the need for the real equipment. Computers are getting cheaper all the time. This is partially true for electronic equipment also, but a full set of electrochemical equipment is still much more expensive than a computer. Using virtual equipment, it is possible to show the student a much larger number of situations than would be practicable using only real equipment. It would even allow the remote use of these "electrochemical apparatus", namely at home.

But there is also another very important pedagogical advantage. Sometimes the best systems to show a certain aspect of the study of electrochemical behaviour are not easy to obtain. It may involve delicate synthetical procedures or the use of sensitive compounds. In a virtual experiment, the choice of the system is our own. We can have any particular ECE system we choose, and it is easy to illustrate the way the system reacts to the change, for instance, of the relative values of the formal potentials of the different redox pairs.

Problem Description

In order to simulate a physical process, we must first describe it mathematically and understand the way it behaves in a real experiment. A brief explanation of the general problem follows.

Mathematical Description

The problem is described for cyclic voltammetry experiments, although the application to other dynamic techniques is quite straightforward.

In figure 1 we can see how the concentration profiles, of the two species involved in a reversible electrochemical redox process, evolve with the scanning of the potential, for the cathodic (fig. 1-a) and anodic (fig. 1-b) portions of the voltamogram. The current, induced by the corresponding changes in the concentration profiles, is also depicted as a function of the applied potential.

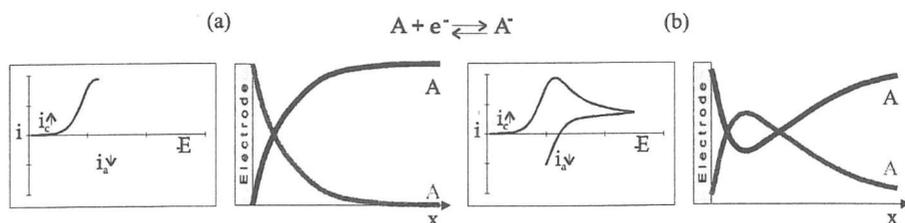


Figure 1 – Voltammograms for a reversible redox process and the corresponding concentration profiles for the cathodic (a) and anodic (b) portions of the curves. (x = distance to the electrode surface).

The problem at hand is essentially a diffusion-reaction problem. There is one or more species that are involved in an electrochemical reaction, taking place at the surface of an electrode. As a rule,

these species also exist in solution and when they are consumed or produced at the electrode's surface, they must be transported to or from the electrode.

The way this mass transfer process occurs (and if we assume that a sufficient concentration of supporting electrolyte exists so that we can neglect migration effects) can be described by Fick's Laws, as shown in figure 2

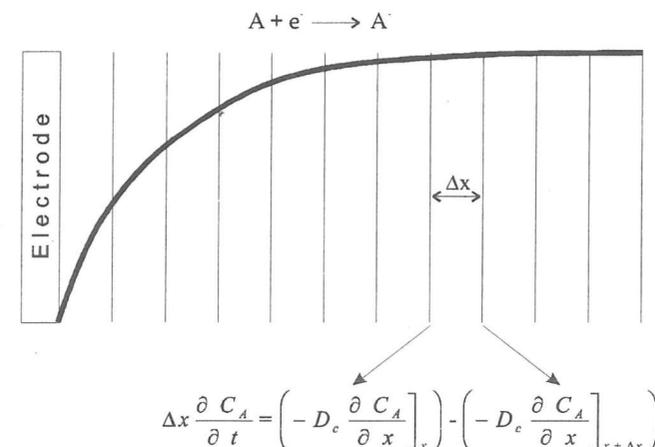


Figure 2 – Mass balance for species A, with an effective diffusion coefficient D_e , inside a slice of solution of thickness Δx , in an equally spaced divided solution – deduction of the Fick's second law.

The final set of equations that is used to describe the reaction-diffusion problem is, thus, constituted by a partial differential equation for each species; each equation describes the way one of the species involved diffuses throughout the solution, and which corresponds, in the simplest case, to Fick's second law (some modifications are needed if we encounter homogeneous chemical reactions) [2].

$$\frac{\partial C_A}{\partial t} = D_e \frac{\partial^2 C_A}{\partial x^2}$$

In this equation D_e represents the effective diffusion coefficient for the species and C_A its concentration.

These partial differential equations are completed by the following set of boundary conditions, which includes the condition correspondent to the actual electrochemical reaction term,

$$\begin{aligned} t &= 0 \\ C_A(x) &= C_A^b \\ t &> 0 \\ -D_e \left. \frac{\partial C_A}{\partial x} \right|_{x=0} &= r_{\text{heterogeneous}} \\ \lim_{x \rightarrow \infty} C_A &= C_A^b \end{aligned}$$

where C_A^b is the bulk concentration of species A and $r_{heterogeneous}$ is the rate of transformation of species A at the electrode.

Programme Development - Tools and Methodologies

Main Features

The computer programme was developed for Windows 95, using Visual Basic version 4, from Microsoft, thus taking advantage of modern graphical interfaces. The choice of the programming environment was made taking into account the ease of programming and development of the interface with the user.

The programme was developed as several separate modules, which interact through a series of global data variables. The modularity assures a good amount of flexibility, so that one can easily change the programme to add new features.

The main problem, as seen previously, is solving the set of differential equations that describe these phenomena. According to our previous experience and work, the method of lines [3, 4] was selected to perform the time-course integration of the relevant equations.

Structure of the Programme

The core of the whole programme is the integration module, represented in the scheme depicted in figure 3. This is a separate module, which contains the description of all the systems that can be dealt with by the programme, and the routines that are required to compute the concentrations as a function of the time and space coordinates, for each mechanism.

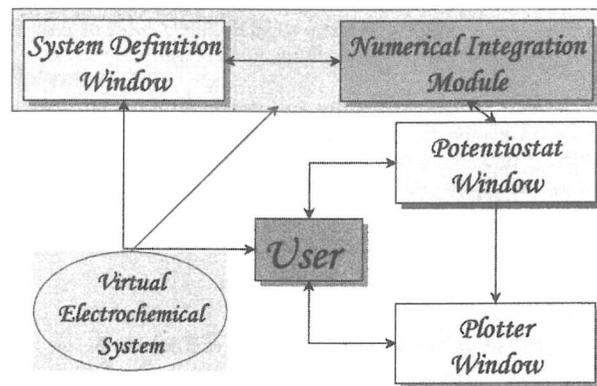


Figure 3 – Block representation of the structure of the programme. The “Numerical Integration Module” is the core engine of the programme while the user’s interface is actually composed by the “System Definition Window”, “Potentiostat Window” and “Plotter Window”. The “System Definition Window” and the “Numerical Integration Module” correspond to the virtual electrochemical system

The interface with the user is mainly composed of three separate windows, one corresponding to the system, “System Definition Window”, and allowing the user to choose the system and change the relevant parameters. The other one is the “Potentiostat/(Programmer) Window”, which enables the user to control the way the potentials are applied to the cell, as well as turning the cell on and off and measuring the current and potential. The third window is the “Plotter Window”, which allows the user to visualise the data from the experiment.

The interaction of all these modules constitutes the whole application itself and allows the interactive simulation of the electrochemical process.

Unified Interface

However, this programme can go beyond the simple virtual experiments. In fact, it is possible to replace the virtual electrochemical system by a real one. To achieve this goal, it is only necessary to substitute the integration module and the system window by an electrochemical cell containing a real system, add an interface to connect the computer to the potentiostat, build a module to control this interface, and we will be able to use the same user interface to operate both real and simulated experiments. This can be easily visualised by comparing figure 3, representing the virtual electrochemical system, with figure 4 that describes the real one.

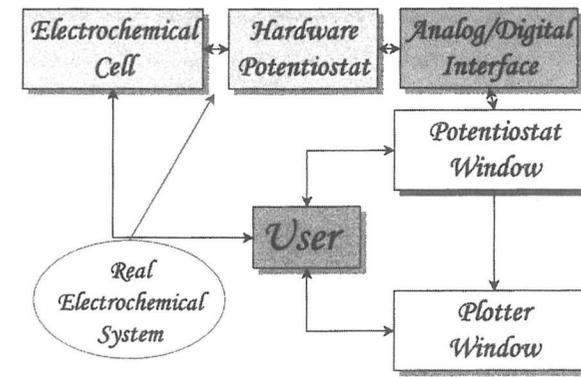


Figure 4 – Unified Interface – The user can use the same interface to operate both the real and the virtual experiments.

This can be used, for instance, to program laboratory work, namely with the involvement of students.

A student can, thus, get trained in this technique and prepare a whole set of experiments using computer simulations, and then carry out a limited number of real experiments, using the same interface he used for the virtual ones.

A Virtual Study of an ECE System

As an example of a virtual experiment we can choose, at the “System Window”, an anodic process following an ECE mechanism, with an irreversible chemical reaction between the two reversible electrochemical steps, the second one having the highest formal potential.

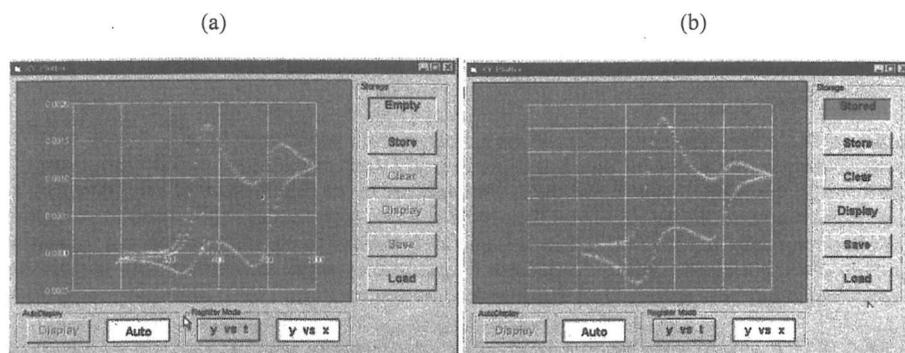


Figure 5 – “Plotter Window” showing a cyclic voltammogram for an ECE anodic process recorded at (a) 200 mV/s and (b) 500 mV/s.

At the “Potentiostat Window” we can choose the adequate potential range and the scan rate (200 mV/s), turn the cell on and start the cycle. In the “Plotter Window” we can see the voltammogram appearing and notice that the cathodic counterpart for the first wave is smaller than the anodic peak, due to the chemical reaction (see figure 5a).

A second oxidation wave is observed, corresponding to the oxidation of the product of the chemical reaction. Unlike the first wave this peak is mainly reversible. Looking at the same system at a higher scan rate, as shown in picture 5b, we can see that the height of the first wave increases, due to the increase in scan rate. At the same time the intensity of the second wave decreases, since the time interval for the chemical reaction to proceed has decreased.

Stored voltammograms can also be saved to disk for future reference and to import to other applications, such as spreadsheets.

This programme is available, upon request, to anyone interested in using it.

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ELECTRO-OXIDATION OF METHANOL ON POROUS UNSUPPORTED Pt-Ru ALLOY ELECTRODES IN STRONG ALKALI AND STRONG ACID

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Abstract

Porous unsupported Pt-Ru single phase alloy electrodes with different compositions viz., 9:1, 7:3 and 5:5 are prepared by NaBH₄ reduction method at room temperature. The reactivity of these alloy electrodes towards the methanol oxidation reaction (MOR) is systematically investigated in different electrolytes of high and low pH with various quantities of methanol at room temperature by using cyclic voltammetric (CV) and steady-state galvanostatic polarisation techniques. Various electrochemical processes occurring in different potential regions are discussed. The highest activity of the MOR is obtained for a 7:3 electrode in 2.5 M H₂SO₄ / 2.5 M CH₃OH and in 6 M KOH / 6 M CH₃OH mixtures, respectively. It is concluded that by choosing the proper ratio of OH⁻ ions and CH₃OH in solution, it is possible to remove completely the intermediate organic species and/or poisonous species that retard the MOR.

Key words: unsupported Pt-Ru electrode, strong alkali, strong acid, MOR activity, intermediate organic poisonous species.

Introduction

While Pt-Ru binary alloy electrodes have been extensively studied for methanol oxidation reaction (MOR) in acid solutions [1-9], very little work has been done in alkaline solutions [10,11]. And that too, these prior studies have focussed mainly on high surface area carbon supported Pt-Ru alloys [10,11] and unsupported arc melted smooth Pt-Ru alloys [6]. The MOR on porous unsupported Pt-Ru alloy in alkaline as well as in acid solutions have not yet been investigated systematically, despite the fact that these alloy electrodes might provide the best activity for the MOR [2,7]. Very recently, Chu and Gilman [7], have prepared unsupported Pt-Ru alloy electrodes and investigated the MOR over a range of temperatures (between 25 and 60°C) by using only 0.5 M H₂SO₄ with 1 M CH₃OH; they have concluded that the Pt-Ru (5:5) provides the highest activity for the MOR.

In this paper, the activity of porous unsupported Pt-Ru single phase alloys with different compositions viz., 9:1, 7:3 and 5:5 is reported. The reactivity of these alloy electrodes towards the MOR was evaluated in different electrolytes of high and low pH that contain various quantities of methanol at room temperature (~25°C) by using the cyclic voltammetric (CV) and steady-state polarisation techniques. It is inferred that the highest activity for the MOR is obtained for the 7:3 alloy electrode in 2.5 M H₂SO₄ / 2.5 M CH₃OH mixture and in 6 M KOH / 6 M CH₃OH mixture at lower overpotentials. The CVs recorded for all the electrodes, exhibit anodic featureless curves for almost all equimolar electrolyte / CH₃OH mixtures and this could be due to complete oxidative removal of poisonous organic species chemisorbed on Pt sites.

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