VOLTAMMETRIC MODELLING BY A SEMIANALYTICAL ROUTE

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In today's electrochemistry, it is no longer considered adequate to base conclusions on such sparse information as that provided by the peak separation in cyclic voltammetry. Trustworthy results can come only by comparing the *entire* experimental results with model predictions. Thus the ability to model elaborate electrochemical systems with precision is vital.

There are three routes for modelling voltammetric experiments. The best is purely mathematical analysis, though unfortunately this approach is tractable only for simple systems. The most popular route is digital simulation, a sophisticated technique in which the governing equations are approximated and solved arithmetically by computer. This approach requires elegant programming and is accessible to most electrochemists only by reliance on "canned" programs. This presentation is about a third route – semianalytic modelling – that has the precision of the mathematical approach, while requiring only modest programming skill.

Semianalytical methods employ a combination of algebraic and numerical analysis. The concept is not new; Nicholson and Shain's seminal work (1) was semianalytical. The version presented here is named "convolutive modelling" (2,3) and is an extension of the semiintegration approach (4). Briefly, the principle is to treat the time-dependence of the voltammetry numerically, but all other aspects – including transport and reactions – analytically.

A voltammetric experiment involves (a minimum of) three distinct processes: (a) The transport of the electroactive substrate S to the electrode surface, possibly involving some homogeneous chemical reaction along the way. (b) The transfer of electrons to or from the substrate, to form the product P, a process than may be reversible, quasireversible or irreversible. (c) The transport of the product back into the solution, possibly accompanied by a chemical transformation. These three processes are "in series" inasmuch as (c) must be preceded by (b), to which in turn (a) is a necessary precursor. Because of the series relationship of the three processes, it follows that, if the factors influencing each of the processes *separately* are known, then the net effect of all three processes *together* is predictable. In fact, the current $I(t)$ is given by the equation

$$\frac{1}{I(t)} = \frac{1}{I_a(t)} + \frac{1}{I_b(t)} + \frac{1}{I_c(t)} \qquad [1]$$

where $I_a(t)$ is the current that *would* flow *if* processes (b) and (c) imposed no kinetic or transport constraint. $I_b(t)$ and $I_c(t)$ have corresponding significances.

Let $k_f(t)$ and $k_b(t)$ be the heterogeneous rate constants of the electrode reaction

$$S - ne^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} P \qquad [2]$$

that converts the substrate into the product. If process (a) imposes no constraint, then the concentration of S at the electrode surface will equal its bulk value c_S^b. Likewise if the product P were initially absent and process (c) imposed no constraint, its concentration at the electrode surface would remain zero and the backward reaction would be unimportant. Therefore, in this hypothetical circumstance,

the current would equal $nFAk_f c_S^b$, and accordingly

$$\frac{I_b(t)}{k_f(t)} = nFA c_S^b \qquad [3]$$

The form adopted by $I_a(t)$, the current that would flow if processes (b) and (c) imposed no constraint, would depend on details of the transport mechanism, the cell geometry, and on the preceding chemical reaction, if any. For linear diffusion in the absence of homogeneous reaction, the following formula (5) would apply

$$I_a(t) * \frac{1}{\sqrt{\pi D_S t}} = nFA c_S^b \qquad [4]$$

where $*$ denotes the operation of convolution, for which simple and efficient algorithms exist (6). In other circumstances different convolutions could apply, all of which may be subsumed in the generic formula

$$I_a(t) * S(t) = nFA c_S^b \qquad [5]$$

where $S(t)$ is a function available from an existing "library" of such functions or, if need be, $S(t)$ can be found by Laplace-transform techniques.

On turning to the $I_c(t)$ term, note that, in the absence of kinetic or transport constraints arising from processes (a) and (b), the concentration of product P at the electrode surface would be given by a nernstian term $c_S^b K(t)$, where $K(t) = k_f(t)/k_b(t)$. Hence, generically

$$\frac{I_c(t)}{K(t)} * P(t) = nFA c_S^b \qquad [6]$$

where $P(t)$ is some function of time, available from the library, dependent on the transport and geometric factors, as well as on any succeeding chemical reactions. For example (2), $P(t) = \exp\{-kt\}/\sqrt{\pi D_P t}$ for linear diffusion with a following reaction of rate constant k.

Putting equations [3], [5] and [6] into [1] leads to the universal "master equation"

$$\left[\frac{1}{k_f(t)} + \left(S(t) + \frac{P(t)}{K(t)} \right) * \right] I(t) = nFA c_S^b \qquad [7]$$

which can be used directly to calculate the voltammetric current for *any* voltage program. Several examples of its application will be presented.

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