Simulation of Cyclic Voltammetry Using Finite Difference Methods

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This article discusses the application of finite difference methods to the simulation of cyclic voltammograms with particular reference to the BAS simulation software DigiSim®.

In a previous article (1), we discussed how cyclic voltammetry could be used to achieve a qualitative understanding of electrochemical mechanisms, particularly those that involve chemical reactions coupled to the electron transfer reaction(s). However, since the effects of mass transport, electron transfer kinetics and the kinetics of coupled chemical reactions on a cyclic voltammogram cannot generally be separated, the extraction of quantitative data from a cyclic voltammogram typically requires comparison of the experimental data with simulated data or predictions of a theoretical model. The simulated data are generated by software that requires input of the reaction mechanism, and the appropriate parameters. One approach that often has been used for calculation of theoretical voltammograms is the method of finite differences (2-5), which is the subject of this paper. Particular reference is made to DigiSim, the BAS simulation program for cyclic voltammetry.

Finite difference methods require that the electrochemical experiment be discretized into space and time grids. The space grid is generated by dividing the solution in which concentration changes occur during the experiment into small, discrete volume elements. During the simulation, the concentrations of all the species involved in the electrochemical reaction are calculated for each of the volume elements (***F1***). Since these concentrations change during the experiment, the concentration calculation must be carried out at many time points during the experiments. Therefore, the electrochemical experiment is described by knowing the concentrations in all the volume elements at each of the selected time points.

The accuracy of the simulation depends upon the size of the time and space grids; that is, the number of volume elements and the number of time points. Increasing these numbers increases the accuracy of the simulation, but also increases the time required for the simulation. The selection of these numbers (i.e., how the grids are set up) is discussed in more detail below. The other aspect discussed in this article is the method used for calculation of the concentrations (the explicit and implicit methods), and their advantages and disadvantages.

Optimization of the Space Grid

In a typical cyclic voltammetry experiment, the concentration changes are greatest at the electrode surface, and decrease with increasing distance from the electrode surface. Therefore, a large number of volume elements are required at the electrode surface in order that the changes of concentration with time and distance are described accurately, but fewer are needed at large distances from the surface. The most efficient way to achieve this distribution is to use an exponentially expanding grid (as is shown in ***F1***) (6,7). The thickness of the first element (that adjacent to the electrode surface) is Δx, and the rate of exponential expansion is defined by β.

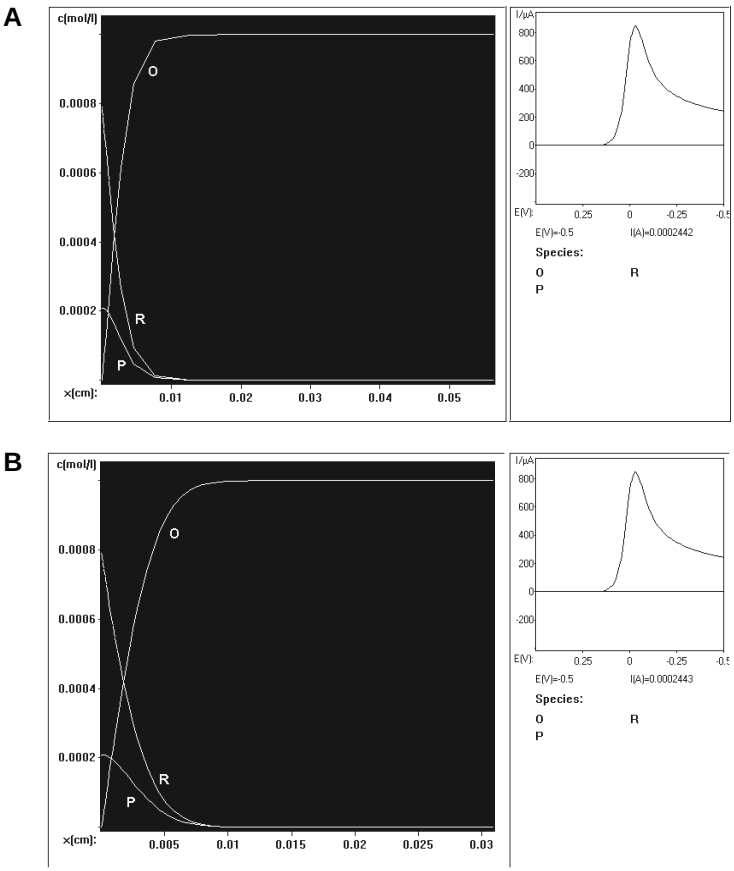
F1

Space grid for finite difference simulation methods.

i=1	i=2	i=3	i=4	
c_1^m	c_2^m	c_3^m	c_4^m	• • • • •
Δx	$e^{\beta}\Delta x$	$e^{2\beta}\Delta x$	$e^{3\beta}\Delta x$	

F2

DigiSim concentration profiles for an EC mechanism (O + e = R, R = P) for β = 0.5 (a) and 0.2 (b).



The effect of β is illustrated in ***F2***, which compares concentration profiles generated by the BAS simulation software DigiSim for β = 0.5 (a) and 0.2 (b); the finer grid (β = 0.2) leads to a smoother profile.

The other parameters that determine the number of volume elements are X_{max}, which is the total distance described by the simulation, and Δx. X_{max} is given by the formula:

$$X_{max} = 6(Dt)^{1/2}$$

where D is the largest diffusion coefficient specified for the simulation, and t is the time required for the experiment (2). The optimum value for Δx is also dependent upon the diffusion coefficient, as well as Δt (the interval between sampling times). D, Δx, and Δt are related by the following equation:

$$D_m = D\,\frac{\Delta t}{\Delta x^2}$$

where D_m is referred to as the model diffusion coefficient. The default value for D_m in DigiSim is 10. Δt is calculated from the user-specified value of the scan rate, and the size of the potential step. For example, let us consider a simulation with a scan rate of 1 V s^{-1}, a potential range between -0.3 V to + 0.3 V, a potential step of 0.005, with all species having a diffusion coefficient of 1 x 10^{-5} cm^2 s^{-1}. Therefore, Δt = 0.005 s, and Δx = 7.07 x 10^{-5} cm for D_m = 10.

The magnitude of Δx requires special consideration if the simulated mechanism involves a chemical reaction. A typical concentration profile for an EC mechanism (i.e., the electron transfer reaction O + e = R is followed by a chemical reaction R = P) is shown in ***F2***. In addition to changes in concentration due to diffusion, there are also changes in concentration due to the chemical reaction. The layer in which the concentrations are perturbed by the chemical reaction is referred to as the reaction layer, and it is important that this layer contain enough volume elements to describe accurately the changes in the concentrations due to the chemical reaction. The thickness of this layer (μ) is typically expressed in terms of Δx, and the default setting in DigiSim is that $\mu^2 = 50(\Delta x)^2$; that is, the reaction layer contains about 7 volume elements.

μ is defined by the equation

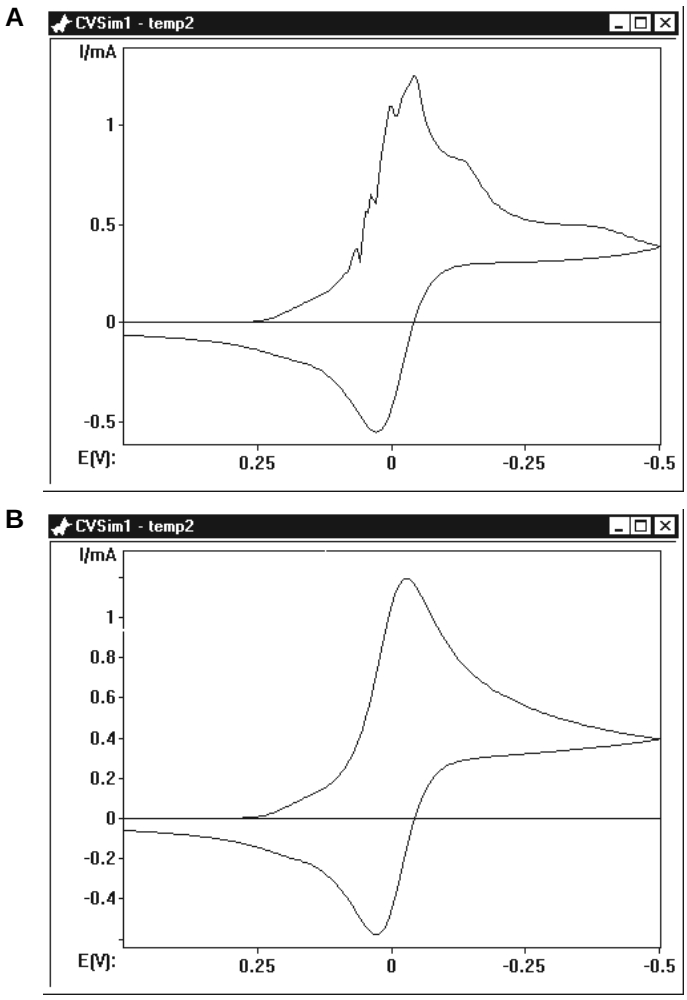
$$\mu = \sqrt{\frac{D_R}{k_2 + k_{-2}}}$$

where D_R is the diffusion coefficient of R, and k_2 and k_{-2} are the rates of the forward and reverse chemical reactions. A consequence of these relationships is that the magnitude of Δx must decrease with increasing k in order to maintain the accuracy of the simulation. If Δt is not varied, the magnitude of D_m must also increase. In DigiSim, the minimum value of D_m is 10, unless the value of k requires a larger value. To illustrate the relationships, let us extend the calculations given above to include a chemical reaction with an equilibrium constant of 1000 for various values of the forward rate constant k_2 of the B = C forward reaction (note that k_{-2} is negligible in comparison with k_2, and hence is not included in the calculation of μ). For D_m = 10, Δx = 7.07 x 10^{-5} cm; therefore, this value for D_m is adequate if μ needs to be 5 x 10^{-4} cm or larger. This value of μ corresponds to a k_2 value of 40 s^{-1}. For larger values of k_2, Δx must be smaller than 5 x 10^{-4} cm, and hence a larger value is required for D_m (if Δt is to remain constant). For example, if k_2 = 100 s^{-1}, Δx = 4.5 x 10^{-5}cm, and D_m = 25.

The default space grid parameters values set by DigiSim should be optimal for a planar electrode geometry for most mechanisms. Although decreasing β from its default value of 0.5 improves the smoothness of the concentration profiles, there is typically little improvement in the accuracy of the simulation for values of β less than 0.5. However, there are exceptions. The simulated cyclic voltammogram for a catalytic mechanism (O + e = R, R + S = O + T, with the diffusion coefficients of S and T being an order of magnitude

F3

DigiSim simulations for a catalytic mechanism (O + e = R, R + S = O + T) for β = 0.5 (a) and 0.05 (b).



smaller that those of O and R) is shown in ***F3*** for β = 0.5 (a) and β = 0.1 (b). The uneven appearance of the voltammograms in ***F3a*** suggests that it may not be accurate, and this is confirmed by the improvement achieved by decreasing the value of β.

Calculation of Concentrations

There have been two general approaches used for finite difference simulations — the explicit finite difference (EFD) method, and the implicit finite difference (IFD) method. (DigiSim is based on an IFD method.) These will be discussed in turn.

The EFD method is simpler, both conceptually and mathematically. It is based on the calculation of concentrations at time **t** + Δ**t** from concentrations at time **t**. Since the starting concentrations are known for all the volume elements, the concentrations at other time points can be calculated. However, this simplicity is accompanied by considerable limitations. The most fundamental limitation is that, during one time period Δt (or iteration), any change in concentration can only propagate to the next volume element (this is referred to as "propagational inadequacy" (8)). For example, if there are any changes in concentrations at the electrode surface during the first iteration (e.g., due to charge transfer), the EFD method will only calculate changes in concentration in the first volume element. Since perturbations due to diffusion occur over a distance $x = 6(D\Delta t)^{1/2}$, the EFD method can only be accurate if $x \approx \Delta x$ for the first iteration (first time element). Further restrictions are placed on the EFD method by the requirement that D_m must be less than 0.5 (for numerical stability of the calculation). The effect of these limitations can be illustrated using the simulation example discussed above; if $k_2 = 100$, $\Delta x = 4.5 \times 10^{-5}$ cm, $\Delta t = 1 \times 10^{-4}$ s, and the number of time points = 12,000. Hence, even for this relatively low value of k_2, a large number of time points is required, and such a simulation would require about 80s on a 486 DX 33 MHz. Furthermore, for each order of magnitude increase in k_2, the number of time points required for the EFD method, and the time required for the simulation, also increase by an order of magnitude. Therefore, the EFD method is not practical for simulation of mechanisms with even moderately fast chemical reaction kinetics. (It has been suggested that a smaller value should be used for μ (9). Although this will decrease the time required for the simulation, it will also decrease the accuracy.)

Variations of the EFD method have been developed, based on the Hopscotch (10) and the DuFort-Frankel (11) algorithms. The increased stability of these methods has permitted the use of larger values of D_m, with a corresponding decrease in the computational time required, but very small values of Δt are still required for systems with large kinetic parameter values.

The IFD method calculates concentrations at time **t** + Δ**t** using the concentrations at **t** + Δ**t** and **t**. It is less intuitive, and more computationally complex, but it is more stable, and more accurate than the EFD method. However, early studies based on the two common IFD algorithms (Lassonen (12) and Crank-Nicolson(13)) concluded that, despite their advantages, IFD methods were too inefficient to be suitable for mechanisms involving chemical reactions coupled to electron transfer reactions. However, more recently, Rudolph developed an IFD method (referred to as the fast implicit finite difference or FIFD method) that was considerably more efficient than previous attempts (4,14,15). In addition to the stability and accuracy of IFD methods, the FIFD method is not

restricted to small values of Δt, and this leads to a dramatic improvement in efficiency relative to the EFD methods, particularly for systems with large kinetic rate constants.

The FIFD method has been applied to both the Lassonen and Crank-Nicolson algorithms. The Crank-Nicholson algorithm had better accuracy, but it was more complicated to program than the Lassonen algorithm, and, more importantly, it was less stable, particularly for second order equations. In addition, the accuracy of the Lassonen algorithm was improved significantly by using the Richtmeyer modification (4,16). Therefore, the modified Lassonen algorithm is the algorithm of choice for the FIFD method.

The stability and efficiency of the FIFD method makes it suitable as the basis for a general simulator; that is, a simulator that can be used for virtually any mechanism, and that can run efficiently for a wide range of kinetic parameter values. A study that compared various finite difference simulation programs showed that, for a given square scheme mechanism, a basic EFD program (developed by Gosser (9)) required 24 hours on a mainframe computer; a modified EFD method (the fast quasi-explicit method by Feldberg (17)) required six minutes on the mainframe computer, 30 seconds on a supercomputer, and 45 minutes on a 386 SX PC; whereas the FIFD required 30 seconds on the PC (18). A latter study on the same mechanism using DigiSim (which is based on a later version of the FIFD method) showed that only 8 seconds were required using a 486DX 33 MHz PC (19). A more recent comparison of DigiSim with simulation programs based on methods other than the finite difference method showed that DigiSim was significantly faster than these other methods (5).

This article has provided a brief description of the parameters that need to be considered when setting up a simulation. Although the constraints of these parameters can be severe for some mechanisms, these can be readily accommodated by the FIFD method upon which DigiSim is based. DigiSim can therefore be considered to be a general simulator, as it can be used for any redox mechanism (20) that can be described in terms of single or multiple electron transfer reactions and first- or second-order chemical reactions. In addition, a wide range of kinetic parameter values can be handled efficiently. The combination of DigiSim with the computing capabilities of modern day PCs means that only a few seconds are now required for simulations that, even ten years ago, required hours of computing time.

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20. DigiSim can be used for redox mechanisms that entail semi-infinite diffusion (e.g., solution conditions) or finite diffusion (e.g., redox polymer films on an electrode surface).

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