

NETWORK SIMULATION OF A REVERSIBLE ELECTRON TRANSFER UNDER CYCLIC VOLTAMMETRIC CONDITIONS

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Reversible electron transfer reaction of a freely diffusing species has been studied using the network approach. A network model for this process under cyclic voltammetric conditions has been proposed, and a numerical simulation has been made with the help of the electrical circuit simulation routine PSPICE. A great accuracy in simulated voltammograms has been reached with a personal computer at a moderate cost in computer time.

Cyclic voltammetry is a convenient technique for extracting thermodynamic and kinetic information from electrochemical experiments.

The interpretation of cyclic voltammetric results is greatly facilitated by the comparing experimental and theoretical curves, the latter being obtained from a mathematical model of the electrochemical system. Since an analytical solution of the differential equations of the model is nearly impossible in a great number of interesting situations, several authors have tackled this problem with analog methods of simulation^{1,2} and numerically³. Digital simulation has contributed to the development of electrochemical methodology when more efficient methods have been applied, such as orthogonal collocation⁴, expanding space and time grids⁵, spline collocation⁶ or eigenvector-eigenvalue analysis⁷. All these methods reduce the CPU time at the expense of increasing the mathematical and programming complexity and decreasing the accessibility of the methodology to the electrochemical community.

We present in this paper a network method, which can be used with advantage for the simulation of a cyclic voltammetric experiment. The technique is derived from the theories of Peusner⁸ and Oster et al.⁹, which permit coupled flows and driving forces to be analyzed in terms of graphs. Highly developed methods of circuit analysis may then be employed to obtain the dynamic behaviour of the system directly from the graph, without having the deal with the differential equations explicitly, thus providing a very powerful tool and a rigorous basis for understanding the behaviour of the whole system.

Network approach principles have been introduced elsewhere⁸⁻¹¹ and need not be elaborated here.

We begin by proposing a network model which is an appropriate discrete approximation to the mathematical equations of the cyclic voltammetric behaviour of freely diffusing reversible redox species (E mechanism). Secondly, the numerical simulation of the resulting network model is realized by using the electric simulation routine PSPICE (ref.¹²), which is very easy to use even with personal computers. It yields voltammetric current-potential solutions in a general working curve format.

RESULTS AND DISCUSSION

Mathematical Model

Let us consider a reversible electron transfer reaction



where n is the number of electrons transferred and E^0 is the formal electrode potential.

By assuming the semi-infinite linear diffusion to the electrode, the reaction (1) can be described by Fick's first law of diffusion

$$J_i = -D_i (\partial c_i / \partial x), \quad (2)$$

where J_i is the flux of a chemical species i , c_i is the concentration of i and D_i is the diffusion coefficient. So, the mathematical description of the mass balances in the diffusion process near the electrode can be written as

$$\partial c_O / \partial t = D_O \partial^2 c_O / \partial x^2, \quad (3)$$

$$\partial c_R / \partial t = D_R \partial^2 c_R / \partial x^2. \quad (4)$$

These equations are subject to the initial and boundary conditions,

$t = 0, x \geq 0$ and $t > 0, x \rightarrow \infty$:

$$c_O = c_O^* \quad (5)$$

$$c_R = c_R^* = 0 \quad (6)$$

$t > 0, x = 0$:

$$D_O (\partial c_O / \partial x)_{x=0} = -D_R (\partial c_R / \partial x)_{x=0} \quad (7)$$

$$c_0(0, t) / c_R(0, t) = \Theta S_\lambda(t), \quad (8)$$

where a Nernstian charge transfer is assumed in Eqs (7) and (8) and Θ and $S_\lambda(t)$ take (for cyclic voltammetric conditions) the forms

$$\Theta = \exp \{ (nF / RT) (E_{\text{start}} - E^0) \} \quad (9)$$

and

$$S_\lambda(t) = \begin{cases} \exp(-at) & \text{for } t \leq t_\lambda \\ \exp(at - 2at_\lambda) & \text{for } t_\lambda \leq t \leq 2t_\lambda \end{cases} \quad (10)$$

as defined by Nicholson and Shain³, where t_λ is the potential switching time and a is a constant

$$a = (nF / RT) v, \quad (11)$$

where R , T , F have their usual significance and v is the potential scan rate.

Network Model

The general procedure for obtaining the network model representative of a transport process consist in dividing the physical region of interest into volume elements or compartments sufficiently small, so that spatial variations within each subregion can be ignored. Logically, the precision of quantitative modelling is greatly improved as the degree of subdivision increases because the longer the number of compartments, the closer we come to continuum behaviour. In this way, the diffusive flux of a chemical species i to the electrode (Eq. (2)) can be replaced by that corresponding to the discrete case,

$$J_i = -D_i (\Delta c_i / \Delta x) = D_i \{ c_i(x) - c_i(x + \delta) \} / \delta, \quad (12)$$

where δ is the compartment thickness.

The diffusive flux and the concentration play the same role, respectively, as the current and voltage in an electrical circuit. Thus, a comparison of Eq. (12) and Ohm's law allows us to represent the dissipative effect of the diffusion in the compartment by means of a linear resistor of a value

$$R_i = \delta / D_i. \quad (13)$$

Moreover, as

$$J_i = \partial n_i / \partial t = \gamma (\partial c_i / \partial t), \quad (14)$$

where n_i is the number of moles of a species i , is a relationship characterizing a monoport capacitor, the value of the capacitance, γ , must be equal to the thickness of each compartment, i.e., $\gamma = \delta$.

The elementary network model for a nonstationary diffusion process of species O and R in a volume element is the well-known model of Fig. 1 obtained by connecting the two monoports, resistive and capacitive, in such a way that Kirchhoff's current law is fulfilled.

The next step is to include initial and boundary conditions in the network model.

Equations (5) and (6) for $t = 0$ and $x \geq 0$ point out the uniformity of the initial concentrations of O and R throughout the system, i.e., a unique value of the "voltages" c_0^* and c_R^* , respectively, in each node of the network. These conditions have been incorporated by means of the initial potential of the capacitors in Fig. 1, which is the resulting model for nonstationary diffusion in a single compartment. Any number of them can be connected in series to form a network model for the entire physical region.

On the other hand, Eqs (5) and (6) for $t > 0$, $x \rightarrow \infty$ and imply that the concentrations of the substances O and R in points far from the electrode maintain their initial values. Thus, for $x \geq L$, where L is a "real" distance from the electrode, where no concentration changes occur during the process. For the network modelling purpose, these conditions can be represented by two suitable constant voltage sources of outputs c_0^* and c_R^* at $x = L$. As c_R^* is equal to zero, this voltage source is replaced by an ideal conductor connected to ground in Fig. 2.

According to the Fick's first law (Eq. (2)), the boundary conditions Eqs (7) and (8) can be rewritten as

$$J_0(0, t) = -J_R(0, t) \quad (15)$$

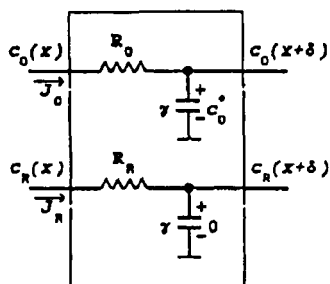


FIG. 1
Network model for a non-stationary diffusion process of species O and R in a volume element

and

$$c_0(0, t) = \Theta S_\lambda(t) c_R(0, t). \quad (16)$$

Equations (15) and (16) in which the "current" J_R is a linear function of the "current" J_0 and the "voltage" c_0 is a function of two "voltages" ΘS_λ and c_R , can be modelled, respectively, by a linear current-dependent current source and a non-linear voltage dependent voltage source, as it is shown in Fig. 2, case of $x = 0$. Here, the function ΘS_λ has been considered as a voltage-type variable, which is modelled by a time-exponential source of output $\Theta S_\lambda(t)$, cf. Eq. (10). Figure 2 shows the global E-network model, with boundary and initial conditions.

As the network model and mathematical equations are the same, the simulation of the network model can provide the temporal evolution of the fluxes and concentrations in each volume element, and, more importantly, the theoretical voltammograms for different sets of values of the characteristic system parameters.

Network Simulation

By means of the network model of Fig. 2, with the appropriate numerical values for the system parameters, the theoretical cyclic voltammograms expected for a system following the E-mechanism can be easily obtained using the electric network simulation program PSPICE (ref.¹²). To this effect, a fifty-compartment reticulation model for the diffusion layer ($N = 50$) has been used. This choice gives a reasonable numerical accuracy at a low cost in computer time. Network simulations were performed for selected parameter values, for which the results can be compared with those obtained by Nicholson and Shain³. The parameter values used^{3, 13} are given in Table I, where the thickness of the diffusion layer under the non-stationary conditions¹³ $L = (\pi D t)^{1/2}$ is estimated for $t = 3$ s.

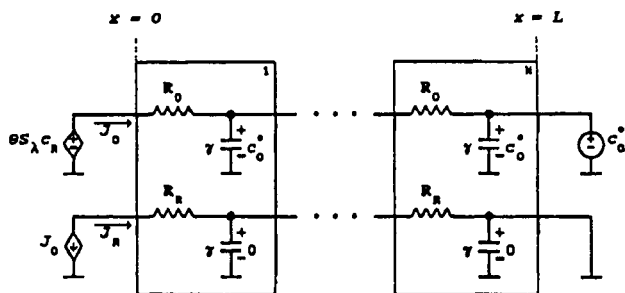


FIG. 2
Network model for a reversible electron transfer under cyclic voltammetric conditions

Results are shown in Fig. 3 and Table I. In Fig. 3 the cyclic voltammograms for the different switching potentials $E_{1/2} - E_{\lambda} = 75, 100, 150, 200, 300$ mV are displayed, which were obtained from the simulation of the E-network model (Fig. 2). As the current I is proportional to the flux at the electrode surface,

$$I / nFA = D_0 (\partial c_0 / \partial x)_{x=0} = -J_0(0, t), \quad (17)$$

it is evaluated through the determination of the flux at $x = 0$ in the branch of the network corresponding to the specie O.

After obtaining $J_0(x=0)$ from the network simulation, the current function $\pi^{1/2}\chi(at)$ is evaluated by the relationship³

$$\pi^{1/2}\chi(at) = [J_0(x=0)] / [c_0^*(D_0a)^{1/2}]. \quad (18)$$

Resulting values of the current function for the cathodic portion of the voltammogram are compared with those given the numerical integration³ and the orthogonal collocation¹³ methods. As it can be seen from Table I, our results are in a very good agreement with the former data, and differ only slightly from the later data.

The values simulated by means of the orthogonal collocation method listed in Table I were obtained¹³ using a dimensionless parameter $\beta = 10^{-3}$ (β being equal to D/aL^2). When β was chosen too high (10^{-2}), the simulation values started to oscillate and no smooth curve were obtained¹³. Nevertheless, in our case $L = 10^{-4}$ m which corresponds to $\beta = 10^{-2}$. In spite of this, the network approach works very well and provides non-oscillating simulation values, which are the same as those predicted by the numerical integration simulation³.

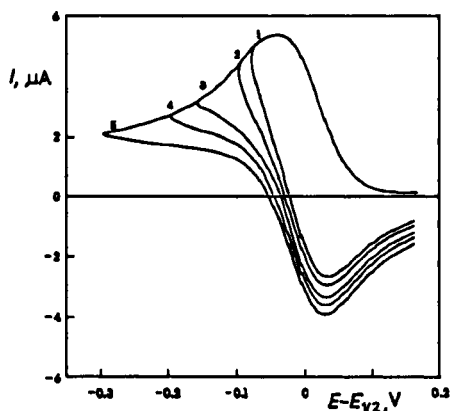


FIG. 3
Cyclic voltammograms of a reversible redox couple simulated by network approach for the different values of $E_{1/2} - E_{\lambda}$: 1 75 mV, 2 150 mV, 3 150 mV, 4 200 mV, 5 300 mV

In summary, the proposed network model together with an electric circuit simulation program such as PSPICE, allows us to easily simulate cyclic voltammetric E model. The main advantage of this method is that it is not limited by the complexity of the processes occurring in the system. Thus, for example, the network method allow to deal

TABLE I

Comparison of simulation data for a reversible charge transfer and the values of the parameters^{3,13}: $D_i = 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $\ln \theta = 6.5$, $T = 298.16 \text{ K}$, $c_0^* = 1 \text{ mol l}^{-1}$, $a = 3.892 \text{ s}^{-1}$ and $L = 10^{-4} \text{ m}$

$E - E_{1/2}$ mV	$\pi^{1/2} \chi$		
	ref. ³	ref. ¹³	this work
120	0.009	0.0092	0.0093
100	0.020	0.0197	0.0198
80	0.042	0.0416	0.0417
60	0.084	0.0846	0.0846
50	0.117	0.1180	0.1179
45	0.138	—	0.1380
40	0.160	0.1608	0.1604
35	0.185	—	0.1851
30	0.211	0.2127	0.2118
25	0.240	—	0.2401
20	0.269	0.2709	0.2693
15	0.298	—	0.2988
10	0.328	0.3299	0.3276
5	0.355	—	0.3548
0	0.380	0.3824	0.3795
-5	0.400	—	0.4009
-10	0.418	0.4213	0.4184
-15	0.432	—	0.4317
-20	0.441	0.4427	0.4406
-25	0.445	0.4468	0.4457
-28	—	—	0.4463
-28.5	0.4463	—	0.44632
-29	—	—	0.4463
-30	0.446	0.4469	0.4461
-35	0.443	—	0.4436
-40	0.438	0.4374	0.4382
-50	0.421	—	0.4212
-60	0.399	0.3967	0.3995
-80	0.353	0.3506	0.3533
-100	0.312	0.3113	0.3127
-120	0.280	—	0.2804
-150	0.245	—	0.2450

also with chemical reactions in a straightforward way, because PSPICE can deal with multidimensional dependent sources specified by nonlinear polynomial functions. Moreover, network approach allows to solve problems of a great mathematical complexity by using microcomputers at a moderate cost in computer time.

On the other hand, one particular advantage of the method used here is that the investigator need not be familiar with computer programming, and rather needs only to learn a few rules for providing information to PSPICE, which uses a simple and concise language for representing circuit diagrams. This is generally not the case when classical numerical methods are to be used.

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