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A new approach to electrochemical simulations based on eigenvalue–eigenvector solutions of the diffusion equation

Part II. Cyclic voltammetry and heterogeneous kinetics

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ABSTRACT

We extend our new approach to the digital simulation of electrochemical systems to the analysis of cyclic voltammetry experiments. The linear equation systems are handled by an eigenvalue–eigenvector decomposition of the solution (carried out using the Lanczos algorithm) and the time-dependent boundary conditions are incorporated via a convolution integral formalism. The accuracy of the method is displayed by comparing numerical solutions for several one-dimensional cases with analytical results. As has been shown previously, large gains in efficiency are possible for simulations involving complicated geometries and/or stiff kinetic equations.

(I) INTRODUCTION

In a recent paper [1], we have presented a new approach to electrochemical simulations based on an eigenvector–eigenvalue analysis of the diffusion-kinetic equations. For the simple case of potentiostatic boundary conditions it was shown that that this type of simulation is not only viable for large systems, but considerably superior to conventional calculations in terms of computational cost. In this paper, we extend the technique to include time-dependent boundary conditions at the electrode, including those limited by electron transfer kinetics.

To clarify the formalism of the approach, we first consider the simplest possible cyclic voltammetry experiment with a linearly swept potential: a one-dimensional reversible, or Nernstian, system [2,3]. Initially, we assume the rate of electron transfer is infinitely fast; thus the boundary condition at the electrode is not dependent on kinetic or charge transfer coefficients. We then extend our method to include quasi-reversible systems [2,3], which contain kinetic electron transfer limita-

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tions, where the reverse reaction has to be considered. In addition to a linearly swept potential, the boundary condition at the electrode also includes a dependency on the standard rate constant, and a charge transfer coefficient.

In both cases the matrix equations for the flux are solved using Green's function parameters (eigenvalues and residues). These are calculated using the Lanczos algorithm and the recursive residue generation method (RRGM) [4,5] outlined in Part I. Once evaluated, they can be used to obtain a solution for an arbitrary electrode process. Thus, the Green's function parameters need to be produced only once for a given geometry and set of bulk diffuse parameters. The current can then be calculated for any set of electrode dynamics by, in the simplest situation, evaluating a set of one-dimensional integrals, or, in the most complicated, by solving an integral equation. In that case, however, the resulting integral equation can be reduced to a row by row multiplication of a matrix with a vector, thus expediently solving for the current.

We present below only one-dimensional examples. However, as was demonstrated in Part I, complex two- or three-dimensional systems can be handled in a straight-forward manner.

(II) GENERAL APPROACH

We will study a cyclic voltammetry experiment in which there are two redox species, A and B, initially containing only species A, with the electrode held initially at a potential E_i. In this experiment, the potential is swept linearly, so that at time t the potential is $E(t) = E_i - vt$, where v is the linear potential scan rate. We assume the rate of electron transfer is so rapid at the electrode surface that species A and B adjust immediately to the ratio dictated by the Nernst equation

$$A_0/B_0 = \exp\left[nF/RT(E_i - vt - E^\circ)\right] \tag{1}$$

where F is the Faraday constant, $A_0 = A(0, t)$, and $B_0 = B(0, t)$. Here $A(x, t)$ = the concentration A at position x and time t. Assuming that the total concentration $A + B$ is constant at all x and t, which implies that the diffusion coefficients of A and B are equal to unity, we obtain the boundary condition at the electrode:

$$A_0^*(0, t) = \frac{\exp\left[nF/RT(E(t) - E^\circ)\right]}{1 + \exp\left[nF/RT(E(t) - E^\circ)\right]} \tag{2}$$

where $A_0^*(0, t)$ is the normalized concentration $A_0(0, t)/(A + B)$, the denominator corresponding to the constant value of the total concentration.

We will now solve for current dictated by this boundary condition. Fick's second law governs the bulk diffusion in most electrochemical problems:

$$\partial c_A(x, t)/\partial t = D \nabla^2 c_a(x, t) \tag{3}$$

Here, $c_A(x, t)$ is the concentration of species A at position x and time t, and D is the diffusion coefficient. The system can be written in matrix form [1] as

$$d\boldsymbol{c}_A/dt = \boldsymbol{W}\boldsymbol{c}_A + D'\boldsymbol{s}_0 \tag{4}$$

where

$$\boldsymbol{c}_A = \begin{bmatrix} c_{A1} \\ c_{A2} \\ \vdots \\ c_{An} \end{bmatrix} \tag{5}$$

with $c_{Ai} = c_A(x = i, t)$, and where $\boldsymbol{W}$ is the $N \times N$ matrix whose elements are given by

$$\begin{aligned} [\boldsymbol{W}]_{ij} &= -2D' && \text{if } i = j,\ i \neq N \\ &= -D' && \text{if } i = j,\ i = N \\ &= D' && \text{if } |i - j| = 1 \\ &= 0 && \text{otherwise} \end{aligned}$$

The problem also requires specification of boundary concentrations (c_0 and c_{n+1} for one-dimensional problems) and an initial concentration profile $c(x, t = 0)$. In eqn. (4), D' is a dimensional constant, $D' = D/\Delta x^2$ (here the temporal variable Δt is continuous) with D the diffusion coefficient. The column vector $\boldsymbol{s}_0$ contains the electrode boundary condition in all volumes adjacent to the electrode and is zero elsewhere. The semi-infinite boundary condition $c_{n+1} = 1$ is incorporated in the definition of $\boldsymbol{W}$.

For the problems under consideration, we monitor only the concentration profile of the species A. Relaxation of the conservation condition $A + B =$ constant would necessitate simulation of both the A and B profiles. This is easily accomplished by increasing the number of variables in eqn. (5) to include both A and B species. The resulting composite vector would be

$$\boldsymbol{c} = \begin{bmatrix} c_{A1} \\ \vdots \\ c_{An} \\ c_{B1} \\ \vdots \\ c_{Bn} \end{bmatrix} \tag{6}$$

We specify $\boldsymbol{c}(0)$ as the vector containing the initial concentration in each volume element, for both the Nernstian and quasi-reversible problems, as well as the Cottrell problem outlined in Part I. The vector $\boldsymbol{c}(0)$ is given by

$$\boldsymbol{c}(0) = \begin{bmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{bmatrix} \tag{7}$$

In the single species case, the effect of the source term $A_0(t)$ is to increase the concentration in the volume one by the increment $D'A_0(t)\,\Delta t$. In our matrix formulation, the diffusion equation is modified to read

$$\mathrm{d}\boldsymbol{c}_\mathrm{A}/\mathrm{d}t = \boldsymbol{W}\boldsymbol{c}_\mathrm{A} + \boldsymbol{f}D'A_0(t) \tag{8}$$

Here $\boldsymbol{f}$ is a vector containing unity in all volumes adjacent to the electrode (in this case, only volume 1), and zero elsewhere:

$$\boldsymbol{f} = \begin{bmatrix} 1 \\ 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix} \tag{9}$$

To solve eqn. (8) we transform to the eigenvector representation

$$\mathrm{d}\,\boldsymbol{y}_\mathrm{A}/\mathrm{d}t = \Lambda\,\boldsymbol{y}_\mathrm{A} + \boldsymbol{M}^{-1}\boldsymbol{f}D'A_0(t) \tag{10}$$

where $\boldsymbol{y}_\mathrm{A} = \boldsymbol{M}^{-1}\boldsymbol{c}_\mathrm{A}$, $\boldsymbol{M}$ is the eigenvector matrix of $\boldsymbol{W}$ and Λ is the diagonal eigenvalue matrix. Equation (10) is now decoupled into one-variable equations of the form

$$\mathrm{d}\,y_j/\mathrm{d}t = \lambda_j y_j + \sigma_j D'A_0(t) \tag{11}$$

where $y_j = [\mathrm{y_A}]_j$, and $\sigma_j = [\boldsymbol{M}^{-1}\boldsymbol{f}]_j = \langle\, y_i \mid \boldsymbol{f}\,\rangle$, which is the dot product, or projection of the eigenvector $\boldsymbol{y}_j$ onto $\boldsymbol{f}$.

Using the convolution theorem, eqn. (11) is solved to yield

$$y_j(t) = \mathrm{e}^{\lambda_j t}y_j(0) + \sigma_j\,\mathrm{e}^{\lambda_j t}D'\int_0^t \mathrm{e}^{-\lambda_j \tau}A_0(\tau)\,\mathrm{d}\tau \tag{12}$$

We now apply the Greens function approach of Part I. The quantity of interest is the concentration in the volume adjacent to the electrode, c_1, which, as we show in Appendix A, can be written as

$$G_{if}(t) = \sum_j R_{if}^{(j)}\,\exp(\lambda_j t) + D'\left\{\sum_j R_{ff}^{(j)}\,\exp(\lambda_j t)\right\}\int_0^t \exp(-\lambda_j \tau)\,A_0(\tau)\,\mathrm{d}\tau = c_1 \tag{13}$$

where $R_{if}^{(k)} = \langle\, \boldsymbol{f} \mid y_k\rangle\langle y_k \mid \boldsymbol{i}\,\rangle$, and $R_{ff}^{(k)} = \langle\, \boldsymbol{f} \mid y_k\rangle\langle y_k \mid \boldsymbol{f}\,\rangle$, $\boldsymbol{i}$ being identical with the initial concentration vector $\boldsymbol{c}(0)$.

As in Part I, the RRGM [4,5] can be used to calculate the eigenvalues λ_j and the residues $R_{if}^{(j)}$ and $R_{ff}^{(j)}$. Once these are known, obtaining $G_{if}(t)$ requires only evaluation of the convolution integrals and summation of terms.

Notice that in eqn. (13) a free diffusion term can be completely separated from the convolution integral, which contains all the useful information of the voltammetry experiment. Only the diffusion modes coupled to the vector $\boldsymbol{f}$ contribute to this term.

We can rewrite $G_{if}(t)$ as

$$G_{if}(t) = G_{if}^{\circ}(t) + D'\int_0^t \left\{\sum_j R_{ff}^{(j)}\,\exp(\lambda_j(t-\tau))\right\}A_0(\tau)\,\mathrm{d}\tau \tag{14}$$

If we substitute the boundary condition A_0 into eqn. (14), we obtain a set of one-dimensional integrals that are easily solved for $G_{if}(t)$, and thus for the concentration of the volume element adjacent to the electrode, c_1.

To facilitate evaluation of the integral, the simple variable substitution $u = t - \tau$ is made, and eqn. (14) becomes

$$G_{if}(t) = G_{if}^{\circ}(t) + D' \int_0^t \left\{ \sum_j R_{ff}^{(j)} \exp(\lambda_j \tau) \right\} A_0(t-\tau)\, d\tau \tag{15}$$

We can simplify the notation further by writing

$$G_{if}(t) = G_{if}^{\circ}(t) + D' \int_0^t G_{ff}(\tau) A_0(t-\tau)\, d\tau \tag{16}$$

where $G_{ff}(\tau)$ is

$$G_{ff}(\tau) = \left\{ \sum_j R_{ff}^{(j)} \exp(\lambda_j \tau) \right\}$$

The flux (and thus the current) is dependent on c_1 and c_0, the electrode boundary condition, which for this case is A_0. The current density, $i/(\text{area})$, is related to the flux of species A at the electrode surface ($x = 0$) by the equation

$$\frac{i}{K} = D\left[\frac{\partial c}{\partial x}\right]_{x=0} \tag{17}$$

where $K = (nF(\text{area}))$. For the problems considered here, the discrete representation of the flux is

$$\frac{i}{K} = \left(\frac{D}{\Delta x}\right)[c_1 - c_0] \tag{18}$$

Since c_1 is obtained through G_{if}, and the boundary condition c_0 is defined here as $A_0(t)$, a simple subtraction yields the current.

(III) QUASI-REVERSIBLE SYSTEMS: ELECTRODE KINETICS

Having developed a general algorithm for obtaining the current with a time-dependent boundary condition, we now treat the conventional cases of electrode kinetic systems, or quasi-reversible systems [2,3].

For a quasi-reversible system, the net current, or flux, involves appreciable activated components from both forward and reverse charge transfers. The boundary condition for these cases is

$$D\left(\frac{\partial A_0}{\partial x}\right)_{x=0} = k^{\circ} \exp(-\alpha nf[E(t) - E^{\circ}])\{A_0 - B_0 \exp(nf[E(t) - E^{\circ}]\} \tag{19}$$

where $f = F/RT$, α is the charge transfer coefficient, and k° is the standard rate constant. The left hand side of this equation is the flux, which is equal to the current i divided by a constant (eqn. 16). The right hand side can also be expressed in terms of i and known functions of t. To accomplish this, we make the substitution

$$A_0 = (i + k_b)/(k_f + k_b) \tag{20}$$

where $k_f = k^{\circ} \exp(-\alpha nf[E(t) - E^{\circ}])$ and $k_b = k^{\circ} \exp((1-\alpha)nf[E(t) - E^{\circ}])$.

As in the reversible problem, c_1 is obtained through G_{if}. Inserting the boundary condition into eqn. (15), the result is:

$$G_{if}(t) = G_{if}^{\circ}(t) + D' \int_0^t G_{ff}(\tau) \frac{i(t-\tau) + k_b(t-\tau)}{k_f(t-\tau) + k_b(t-\tau)} d\tau = c_1(t) \tag{21}$$

The boundary condition $A_0(t)$ implies that $c_0(t) = A_0(t)$, and with $c_1(t)$ given by eqn. (21), the equation for flux (eqn. 18) becomes

$$\left[G_{if}^{\circ}(t) + D' \int_0^t G_{ff}(\tau) \frac{i(t-\tau) + k_b(t-\tau)}{k_f(t-\tau) + k_b(t-\tau)} d\tau \right] - \left[\frac{i(t) + k_b(t)}{k_f(t) + k_b(t)} \right] = \frac{i(t)}{KD'} \tag{22}$$

Equation (22) is an integral equation for the unknown quantity $i(t)$ in terms of the known functions k_b, k_f, G_{if}°, and G_{ff}. Various numerical approaches to the solution of this equation are possible. Below, we exploit the fact that i, k_b, and k_f are slowly varying functions of time as compared to G_{ff}. This allows a coarse graining of the operator G_{ff} which permits the integral equation to be solved on a relatively sparse mesh, thus reducing the computation time considerably.

We consider integration over $G_{ff}(\tau)$ to be a matrix operator which maps the function $A_0(t-\tau)$ defined on a coarse time grid onto another function, also defined on a coarse grid. That is

$$\left\{ \int_0^t G_{ff}(\tau) \, d\tau \right\} A_0(t-\tau) = j(t) \tag{23}$$

We now seek an $N_c \times N_f$ matrix representation of this integral operator, where N_c and N_f are the number of coarse and fine mesh points, respectively. The most conceptually straightforward approach to this is to interpolate $A_0(t-\tau)$ onto a fine mesh, carry out the integration over t, and return to the coarse mesh. In matrix form, this procedure can be represented as $\boldsymbol{j} = \boldsymbol{GZA}_0$, where $\boldsymbol{G}$ is the $N_c \times N_f$ matrix

$$\begin{bmatrix} G_{ff}(\tau=0) & G_{ff}(\tau_1) & . & G_{ff}(\tau=1) & 0 & . & . \\ G_{ff}(\tau=0) & . & . & . & G_{ff}(\tau=2) & 0 & . \\ . & . & . & . & . & . & . \\ G_{ff}(\tau=0) & . & . & . & . & . & G_{ff}(\tau=1) \end{bmatrix}$$

and $\boldsymbol{A}_0$ is a vector. Here $(\tau = 0, \tau_1, \tau_2, \tau_3 \ldots \tau = t)$ corresponds to the integration steps over τ. The simplest interpolation scheme approximates A_0 on the fine grid by its closest value on the coarse grid. The $N_f \times N_c$ matrix $\boldsymbol{Z}$ reproduces a Simpsons's rule integration on the coarse grid. Equation (22) can now be written as

$$\boldsymbol{G}_{if}^{\circ}(t) + D'\tilde{\boldsymbol{G}}\boldsymbol{A}_0 - \boldsymbol{A}_0 = \boldsymbol{i}(t)/KD' \tag{24}$$

where $\tilde{\boldsymbol{G}} = \boldsymbol{GZ}$. A typical matrix element of $\tilde{\boldsymbol{G}}$ is

$$\begin{aligned} (\tilde{G})_{11} = \frac{h}{3} \big[& G_{ff}(0) + 4\big[G_{ff}(\tau_1) + G_{ff}(\tau_3) + \ldots G_{ff}(\tau_{t-1})\big] \\ & + 2\big[G_{ff}(\tau_2) + G_{ff}(\tau_4) + \ldots + G_{ff}(\tau_{t-2})\big] + G_{ff}(1)\big] \end{aligned} \tag{25}$$

where h represents the step difference of the sum: $\tau_{i+1} - \tau_i = h$. Using eqn. (20), we can write eqn. (24) as

$$\boldsymbol{G}^\circ + D'\tilde{\boldsymbol{G}}\left\{\frac{\boldsymbol{i}}{k_b + k_f} + \frac{k_b}{k_b + k_f}\right\} - \left\{\frac{\boldsymbol{i}}{k_b + k_f} + \frac{k_b}{k_b + k_f}\right\} = \boldsymbol{i}\frac{1}{nFAD'} \tag{26}$$

In matrix form, eqn. (26) becomes

$$\boldsymbol{G}^\circ + D'\tilde{\boldsymbol{G}}\boldsymbol{S}\boldsymbol{i} + D'\tilde{\boldsymbol{G}}\boldsymbol{H} - [\boldsymbol{S}\boldsymbol{i} + \boldsymbol{H}] = \boldsymbol{I}\boldsymbol{i}(1/nFAD') \tag{27}$$

where $\boldsymbol{I}$ is the identity matrix and $\boldsymbol{S}$ is a diagonal matrix defined by

$$[\boldsymbol{S}]_{mm} = \left[\frac{1}{k_b(t_m) + k_f(t_m)}\right]$$

and $\boldsymbol{G}^\circ$ and $\boldsymbol{H}$ are vectors of length N_c with

$$\boldsymbol{H}_m = \frac{k_b(t_m)}{k_b(t_m) + k_f(t_m)}$$

Rearranging, eqn. (27) becomes

$$\boldsymbol{G}^\circ + D'\tilde{\boldsymbol{G}}\boldsymbol{H} - \boldsymbol{H} = \left[\boldsymbol{I}\frac{1}{nFAD'} + \boldsymbol{S} - D'\tilde{\boldsymbol{G}}\boldsymbol{S}\right]\boldsymbol{i} \tag{28}$$

Equation (28) is an extremely important result. As was noted in Section (I), the boundary condition A_0 is completely separated from the convolution term, G_{ff}, and thus from the matrix $\tilde{\boldsymbol{G}}$. Since A_0 contains all the useful information of the voltammetry experiment, we only need construct the matrix $\tilde{\boldsymbol{G}}$ once. These calculations represent the bulk of computation time, and once solved for a given geometry, we can then apply any boundary condition at the electrode, or a set of boundary conditions, to obtain currents (fluxes) dependent on a variety of k°'s and α's in minimum computation time.

To obtain more accurate results, we use Lagrange interpolation [6] on the elements of the matrix $\boldsymbol{GZ}$. In this case, the $\boldsymbol{Z}$ matrix is somewhat more complicated (see Appendix B), and leads to a final $\tilde{\boldsymbol{G}}$ matrix with typical elements

$$(\tilde{\boldsymbol{G}})_{11} = h/3\left[\tau_1 \times 4G_{ff}(\tau_1) + \tau_2 \times 2G_{ff}(\tau_2) + \ldots + 1.0 \times G_{ff}(1.0)\right.$$

$$(\tilde{\boldsymbol{G}})_{12} = h/3\left[1.0 \times G_{ff}(1.0) + (1 - \tau_1) \times 4G_{ff}(\tau_1) + \ldots + 0.0 \times G_{ff}(0.0)\right]$$

where for this example, we use an step difference of h for the integration.

(IV) RESULTS

For the Nernstian (reversible) case, results were compared to a numerical solution by Nicholson and Shain [2,3] (see Table 1). The results shown in Fig. 1 were obtained with $v = 1.0$ V/s, $RT/nF = (28.5/1.109)/n$ mV at 25 °C, $D' = 8.0$, and the integration was carried out with 100 steps per unit time. The diffusion coefficient D' must be very large to obtain eigenvalues associated with short times;

TABLE 1

Current functions $i/[D'(nF/RT)]^{1/2}$ for reversible charge transfer

$(E-E_{1/2})n$ /mV	N and S [a]	RRGM [b]	$(E-E_{1/2})n$ /mV	N and S [a]	RRGM [b]
80	0.042	0.041	−10	0.418	0.410
60	0.084	0.083	−20	0.441	0.433
50	0.117	0.115	−28.5	0.4463	0.439
40	0.160	0.157	−40	0.438	0.431
30	0.211	0.206	−50	0.421	0.415
20	0.269	0.263	−60	0.399	0.393
10	0.328	0.321	−80	0.353	0.346
0	0.380	0.371	−100	0.312	0.302

[a] Nicholson and Shain [3].
[b] Recursive residue generation method.

these eigenvalues are large in absolute value. When t is close to τ, the modes of high frequency (large algebraic eigenvalues) make a substantial contribution to the $\exp(\lambda(t-\tau))$ terms. At times far from τ, eigenvalues large in absolute value also make a contribution to this term. This was not true in the cases outlined in Part I. There, the eigenvalues occurred only in a term $\exp(\lambda t)$, and eigenvalues associated with short times were quickly damped.

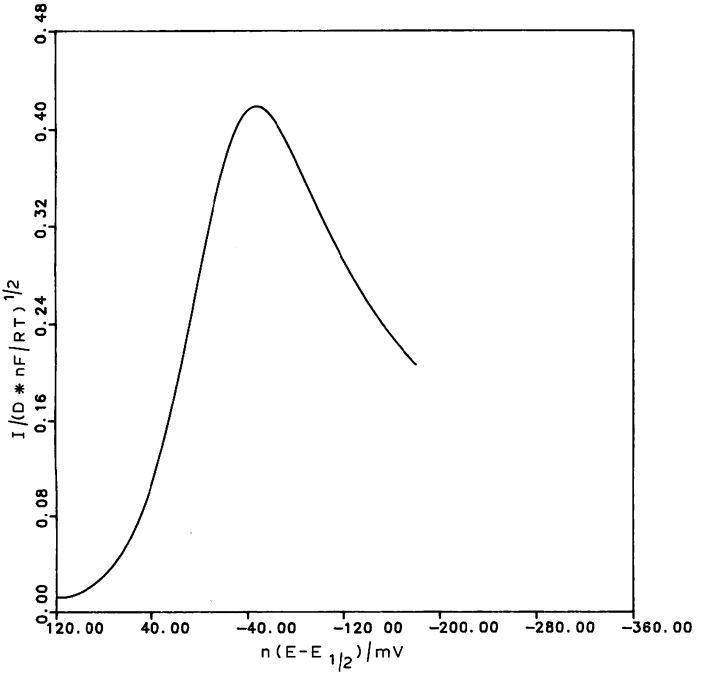

Fig. 1. Current with Nernstian boundary condition.

TABLE 2

Current functions $i/[D'(nF/RT)]^{1/2}$ for irreversible charge transfer

$(E - E_{1/2})n$ /mV	N and S [a]	RRGM [b]	$(E - E_{1/2})n$ /mV	N and S [a]	RRGM [b]
110	0.016	0.021	10	0.462	0.462
100	0.035	0.034	0	0.492	0.490
80	0.073	0.072	−5	0.496	0.495
60	0.145	0.145	−10	0.492	0.491
40	0.264	0.266	−20	0.472	0.470
30	0.337	0.338	−30	0.441	0.439
20	0.406	0.408	−40	0.406	0.399
15	0.437	0.438	−50	0.374	0.365

[a] Nicholson and Shain [3].
[b] Recursive residue generation method.

By increasing the diffusion coefficient D' and the system size (and the number of integration steps), the values obtained by the RRGM can be made to converge exactly with the values obtained by Nicholson and Shain, with some sacrifice in CPU time. With the RRGM these parameters are easily adjusted, and the program can be run with varying degrees of accuracy, according to need and available CPU time. For the calculations reported here, we used a uniform spatial grid with 700 discrete volumes, enough to ensure adequate representation of the diffusion profile.

Results for the irreversible system $O + n\ e^- \rightarrow R$ are given in Table 2. The boundary condition is $i(t)/nFA = k_f C_0(0, t)$, where k_f is given in eqn. (20). Here we use $\alpha = 1.0$ and $v = 1$ V/s. Again, these parameters are easily adjusted to suit users' needs.

For the quasi-reversible systems, results were again compared to previous numerical results (see Figs. 2–4). The results shown are with $v = 1$ V/s, $D' = 8.0$, and $\alpha = 0.7$, 0.5 and 0.3. The rate constants were defined with the parameter $\Lambda = k^\circ/[D'(nF/RT)]^{1/2}$. Λ values in these figures are 1.0, 0.1 and 0.01. The calculation was performed on a CRAY X-MP; the simulation required 1.18 s for 1 set of kinetic and charge transfer coefficients; and for 9 sets of parameters at once (Figs. 2–4), the simulation required 1.43 s. Thus for a given geometry, the bulk of the computation time is done only once, and many sets of parameters can be used without sacrifice in time.

(V) CONCLUSION

In this paper we have established the validity of the Lanczos algorithm and RRGM procedures for time-dependent potential electrochemical simulations of arbitrary geometry. Our approach should increase the utility of digital simulations, since it yields a greater time improvement than other sophisticated numerical methods, without introducing constraints on the boundary conditions.

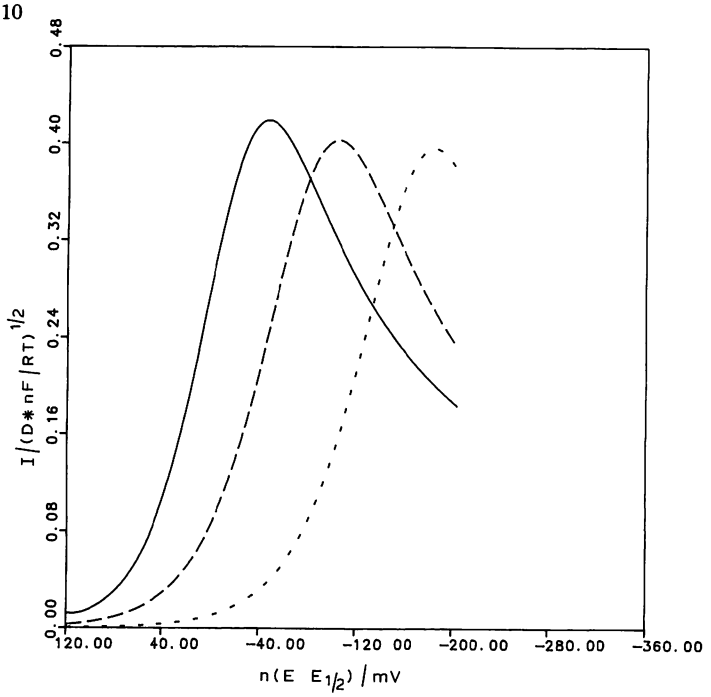

Fig. 2. Variations of quasi-reversible current function for $\alpha = 0.7$, and the following values of Λ: $\Lambda = 1$ (———), $\Lambda = 0.1$ (— — —), $\Lambda = 0.01$ (- - - - - -). $\Lambda = k°/(D'nF/RT)^{1/2}$.

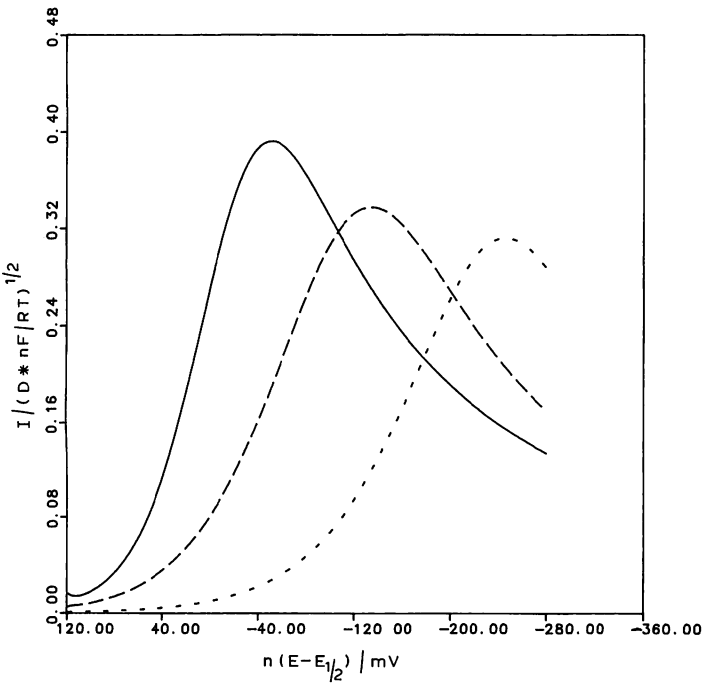

Fig. 3. Variations of quasi-reversible current function for $\alpha = 0.5$, and the following values of Λ: $\Lambda = 1$ (———), $\Lambda = 0.1$ (— — —), $\Lambda = 0.01$ (- - - - - -). $\Lambda = k°/(D'nF/RT)^{1/2}$.

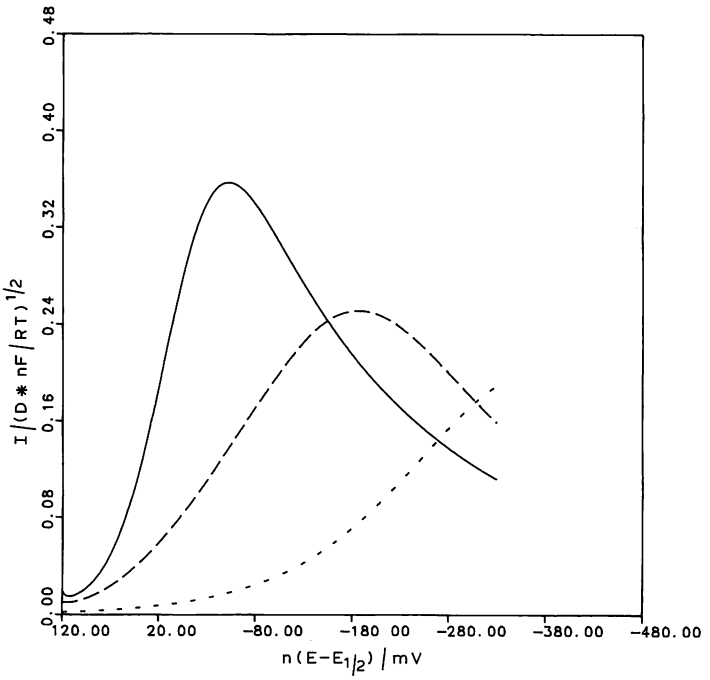

Fig. 4. Variations of quasi-reversible current function for $\alpha = 0.3$, and the following values of Λ: $\Lambda = 1$ (———), $\Lambda = 0.1$ (— — —), $\Lambda = 0.01$ (- - - - -). $\Lambda = k°/(D'nF/RT)^{1/2}$.

The timing results reported above could be improved significantly by various optimizations procedures, including improved interpolation procedures and numerical grids for solving eqn. (11). The development of general purpose, numerically efficient routines will be a subject of future communications.

Looking to the future, we comment briefly here on the limitations of our present procedures and how these might be overcome. First, there is an obvious restriction to first order systems. We are currently developing a modified version of the Lanczos time propagation scheme which takes moderate sized (as opposed to global) timesteps; the convolution integral is used to correct for nonlinear as well as external time-dependent terms over this restricted time interval. Preliminary results indicate that order of magnitude improvements over explicit schemes, as well as implicit approaches like the Gear package, are routinely realized, as in the present case. This approach will be applicable to any type of electrochemical simulation.

Secondly, there is the question of accessibility of the methodology to the electrochemical community. As stated in Part I, given a modular version of our code, for first order problems one has only to write a subroutine specifying the action of the diffusion operator on concentration vector to carry out the Lanczos part of the calculations. As this procedure is identical to the usual computation required in an explicit scheme to advance the concentration to the next timestep,

there should be no problem in accomplishing this once the matrix/vector notation is understood.

Such a procedure does, of course, require a user-friendly version of the Lanczos driver program and associated subroutines. We intend to explore the modified algorithm described above which is applicable to non-linear problems before pursuing the development of such a program in detail. In principle, however, there is no difficulty in carrying out this task.

There is clearly a large set of problems in electrochemistry for which simpler existing methods are quite adequate; in this case, there is no particular reason to switch to the method proposed in this paper. However, for stiff systems in complex geometries, the order of magnitude improvements attainable may make the effort involved worthwhile. Our next objective is to attack an important electrochemical problem for which such computational demands are a significant barrier to solution, and to demonstrate that methods of the type described here can overcome the barriers. Only in this fashion can the practical advantages of the method (whatever they turn out to be) be determined definitively.

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(VI) APPENDIX A

In the following, we apply Green's function formalism to eqn. (12), and show how we arrive at eqn. (13). Equation (12) reads

$$y_j(t) = e^{\lambda_j t} y_j(0) + \sigma_j \, e^{\lambda_j t} D' \int_0^t e^{-\lambda_j \tau} A_0(\tau) \, d\tau \tag{29}$$

Remember $\sigma_j = [\boldsymbol{M}^{-1}\boldsymbol{f}]_j$, $y_j = y_{A\,j}$, and $\boldsymbol{y}(t) = \boldsymbol{M}^{-1}\boldsymbol{c}_A$. We can write eqn. (29) as

$$\boldsymbol{y}(t) = \exp(\Lambda t)\,\boldsymbol{y}(0) + \exp(\Lambda t)\boldsymbol{M}^{-1}\boldsymbol{f}\int_0^t \exp(\Lambda\tau)\,A_0(\tau)\,d\tau \tag{30}$$

Equation (30) is now multiplied by $\boldsymbol{M}$ to transform $\boldsymbol{y}(t)$ into $\boldsymbol{c}(t)$, which is the desired result. The result is

$$\begin{aligned}\boldsymbol{c}(t) &= \boldsymbol{M}\exp(\Lambda t)\boldsymbol{M}^{-1}\boldsymbol{c}(0) + \boldsymbol{M}\exp(\Lambda t)\boldsymbol{M}^{-1}\boldsymbol{f}\int_0^t \exp(-\Lambda\tau)\,A_0(\tau)\,d\tau \\ &= \exp[\boldsymbol{W}t]\,\boldsymbol{c}(0) + \exp[\boldsymbol{W}t]\,\boldsymbol{f}\int_0^t \exp(-\Lambda\tau)\,A_0(\tau)\,d\tau \\ &= \boldsymbol{G}(t)\,\boldsymbol{c}(0) + \boldsymbol{G}(t)\,\boldsymbol{f}\int_0^t \exp(-\Lambda\tau)\,A_0(\tau)\,d\tau \end{aligned} \tag{31}$$

Here, $\boldsymbol{G}(t) = \exp[\boldsymbol{W}t]$ is the Green's function operator; its matrix elements $G_{mn}(t)$ give the probability of an ion initially in volume element n diffusing into cell m at time t. The matrix $\boldsymbol{G}(t)$ acting on the initial concentration vector gives the probability profile of a ion initially at $\boldsymbol{c}(0)$, and $\boldsymbol{G}(t)$ acting on $\boldsymbol{f}$ gives the probability profile of an ion initially at the electrode, and after time t, still at the electrode. $\boldsymbol{G}(t)$ may be evaluated in terms of the eigenvalues and eigenvectors of $\boldsymbol{W}$. From eqn. (31),

$$G_{fi}(t) = \mathrm{e}^T\boldsymbol{G}(t)\boldsymbol{c}(0) + \mathrm{e}^T\boldsymbol{G}(t)\,\boldsymbol{f}\int_0^t \exp(-\Lambda\tau)A_0(\tau)\,\mathrm{d}\tau$$

$$= \mathrm{e}^T\{\boldsymbol{M}\exp[\Lambda t]\boldsymbol{M}^{-1}\}\boldsymbol{c}(0) + \mathrm{e}^T\{\boldsymbol{M}\exp[\Lambda t]\boldsymbol{M}^{-1}\}\boldsymbol{f}$$

$$\times\int_0^t \exp(-\Lambda\tau)A_0(\tau)\,\mathrm{d}\tau \tag{32}$$

Equation (32) becomes

$$\sum_{k=1}^{N} \mathrm{e}^T\boldsymbol{y}_k \exp(\lambda_k t)\,\boldsymbol{y}_k^T\boldsymbol{c}(0) + \sum_{k=1}^{N} \mathrm{e}^T\boldsymbol{y}_k \exp(\lambda_k t)\,\boldsymbol{y}_k^T\boldsymbol{f}\int_0^t \exp(-\lambda_k\tau)A_0(\tau)\,\mathrm{d}\tau$$

$$= \sum_{k=1}^{N} R_{if}^{(k)} \exp\lambda_k t + \sum_{k=1}^{N} R_{ff}^{(k)} \exp\lambda_k t\int_0^t \exp(-\lambda_k\tau)A_0(\tau)\,\mathrm{d}\tau \tag{33}$$

The products $R_{if}^{(k)}$ and $R_{ff}^{(k)}$ are the residues [4,5] of the system. They are a direct measure of the coupling to both the initial concentration distribution and the concentrations at the electrodes. Note that the residues associated with eigenvalues small in absolute value determine long-time behavior (when t is much greater than τ), while all residues, including those associated with large absolute eigenvalues contribute to short time response (when t is close to τ).

(VII) APPENDIX B

In this appendix we will use Lagrange two point, or linear, interpolation on the elements of the matrix $\boldsymbol{GZ} = \bar{\boldsymbol{G}}$. Lagrange interpolation evaluates the function $f_p = f(x_0 + ph)$ as

$$f(x_0 + ph) = (1-p)f_0 + pf_1 \tag{34}$$

where $x_{i+1} - x_i = h$. For example, the first element of $\boldsymbol{G}$, which corresponds to the integral (before interpolation) from 0 to 1 over τ, can be written

$$(\tilde{G})_{11} = \int_0^t G_{ff}(\tau)\,\mathrm{d}\tau = \frac{h}{3}\left[G_{ff}(0.0) + 4.0G_{ff}(\tau_1) + 2.0G_{ff}(\tau_2) + \ldots + G_{ff}(1.0)\right] \tag{35}$$

With interpolation, this splits into two matrix elements

$$(\tilde{G})_{11} = \frac{h}{3}\left[0.0G_{ff}(0.0) + \tau_1 4G_{ff}(\tau_1) + \tau_2 2G_{ff}(\tau_2) + \ldots + 1.0G_{ff}(1.0)\right]$$

$$(\tilde{G})_{12} = \frac{h}{3}\left[1.0G_{ff}(0.0) + (1-\tau_1)4G_{ff}(\tau_1) + (1-\tau_2)2G_{ff}(\tau_2) + \ldots + 0.0G_{ff}(1.0)\right] \tag{36}$$

The matrix element $(\tilde{G})_{32}$ becomes

$$(\tilde{G})_{32} = \frac{h}{3}\left[1.0G_{ff}(2.0) + (1-\tau_1)4G_{ff}(\tau_1) + (1-\tau_2)2G_{ff}(\tau_2) + \ldots + 0.0G_{ff}(3.0)\right]$$
$$+ \frac{h}{3}\left[0.0G_{ff}(1.0) + \tau_1' 4G_{ff}(\tau_1') + \tau_2' 2G_{ff}(\tau_2') + \ldots 1.0G_{ff}(2.0)\right] \tag{37}$$

In general,

$$\begin{aligned}(\tilde{G})_{xy} &= \int_{x-y}^{x-y+1} G_{ff}(\tau)\,\mathrm{d}\tau \\ &= \frac{h}{3}\left[1.0G_{ff}(x-y+1) - (1-\tau_1)4G_{ff}(1-\tau_1) + \ldots\right. \\ &\quad \left. + 0.0G_{ff}(x-y+2)\right] \\ &\quad + \frac{h}{3}\left[0.0G_{ff}(x-y) + \tau_1' 4G_{ff}(\tau_1') + \ldots + 1.0G_{ff}(x-y+1)\right] \\ &\quad x \geqslant y\end{aligned} \tag{38}$$

$$(\tilde{G})_{xy} = (\tilde{G})_{12} \quad x = y-1$$

$$(\tilde{G})_{xy} = 0.0 \quad x < y-1$$

With interpolation, the accuracy is improved without much sacrifice in CPU time.

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