252

Single Alternating Group Explicit (SAGE) Method for Electrochemical Finite Difference Digital Simulation

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The four different schemes of Group Explicit Method (GEM): GER, GEL, SAGE and DAGE have been claimed to be unstable when employed for electrochemical digital simulations with large model diffusion coefficient D_M. However, in this investigation, in spite of the conditional stability of GER and GEL, the SAGE scheme, which is a combination of GEL and GER, was found to be unconditionally stable when used for simulations of electrochemical reaction-diffusions and had a performance comparable with or even better than the Fast Quasi Explicit Finite Difference Method (FQEFD) in some aspects. Corresponding differential equations of SAGE scheme for digital simulations of various electrochemical mechanisms with both uniform and exponentially expanded space units were established. The effectiveness of the SAGE method was further demonstrated by the simulations of an EC and a catalytic mechanism with very large homogeneous rate constants.

Keywords   digital simulation, single alternating group explicit method, Cottrell process, cyclic voltammetry

Introduction

Electrochemical simulation has proved to be very useful for both theoretical and experimental investigations of complicated electrochemical process.[1-7] Among the existing methods, finite difference technique is most frequently used, and has experienced successful developments during the past decades. For the simulation of electrochemical problems, classical explicit finite difference (EFD),[8] fast quasi explicit finite difference (FQEFD),[9] hopscotch,[10] Saul'yev,[11] Crank-Nicolson (CN),[12] and fast implicit finite difference (FIFD),[13] methods have been developed. Incorporating an expanded grid technique,[14] these methods can deal with most of electrochemical problems with different performances.

Although implicit methods have showed better stabilities than the explicit ones, efforts in search of explicit simulation algorithms with satisfactory stability and accuracy have never been ceased due to their attractive simplicity[15-19] in programming. In addition, parallelization of the explicit simulation is usually much easier than the implicit ones, which makes the explicit methods very promising in simulations of very complicated mechanisms. Nevertheless, the most serious problem for the explicit methods exists in its conditional stability. This makes the use of a model diffusion coefficient (D_M) with a value larger than 0.5 impossible, and leads to a difficulty in simulating an electrochemical process coupled with fast homogenous reactions. In addition, as pointed out by Feldberg, such a difficulty also exists in the simulation of a system involving species with extremely different diffusion coefficients. In order to overcome these difficulties, FQEFD and Hopscotch methods were developed.

Another member among the explicit methods, the single alternating group explicit (SAGE) method,[20] also has attractive D_M stability, as well as the mathematical simplicity in solving numerically parabolic partial differential equations (PDEs). Like other explicit methods, it is easy for SAGE to realize parallel programming. Besides, SAGE is also suitable for the numerical resolution

of two-dimensional problems as is the truth mathematically. Unfortunately, this method was claimed to be unstable for the simulation of a Cottrell process when $D_M > 5.0$.[21]

In the present work, difference equations with both uniform and expanding space units were established for the SAGE scheme when applied to the simulations of various electrochemical problems. The stability and accuracy of the SAGE difference scheme were demonstrated by applying it to the simulations of some typical electrochemical mechanisms (some of them are usually thought to be challenging for an explicit method).

Theory

Saul'yev difference algorithm

A pair of finite difference equations which are explicit and unconditionally stable were developed by Saul'yev in 1964.[22] One of them is called the Saul'yev -RL equation and can be written as

$$C_i' - C_i = D_M(C_{i-1} - C_i - C_i' + C_{i+1}') \quad (1)$$

It can be rearranged into

$$(1 + D_M)C_i' - D_M C_{i+1}' = D_M C_{i-1} + (1 - D_M)C_i \quad (2)$$

while the other is known as the Saul'yev-LR equation and can be written in the following form:

$$\begin{aligned} &- D_M C_i' + (1 + D_M) C_{i+1}' \\ &= (1 - D_M) C_{i+1} + D_M C_{i+2} \end{aligned} \quad (3)$$

Using Eqs. (2), (3) to solve parabolic partial differential equations was first suggested by Larkin[23] and then was applied in electrochemical digital simulation. Among these applications, the Saul'yev-RL method showed better efficiency and higher precision than the Hopscotch method,[21] and the < LR, RL > Saul'yev algorithm[11] has also been found to have a simulation efficiency similar to the Crank-Nicolson method. In addition, both of the above two methods need much lower programming effort.

Group explicit method

Another practical ways of using the Saul'yev equations in a combined manner were developed by Evans and Abdullah.[20] The heart of this method is to apply the Saul'yev-RL and Saul'yev-LR equations to successive pairs of two points along every line of the space-time grid. Thus the concentration pairs can be easily solved by combining Eqs. (2), (3). The resulted equations are totally explicit which can be written as follows:

$$C_i' = \Delta_i/\Delta \quad (4)$$

$$C_{i+1}' = \Delta_{i+1}/\Delta \quad (5)$$

where $\Delta = r_{11} r_{22} - r_{12} r_{21}$, $\Delta_i = r_{22} a - r_{12} b$, $\Delta_{i+1} = r_{11} b - r_{21} a$, with $r_{11} = r_{22} = 1 + D_M$, $r_{12} = r_{21} = - D_M$, $a = D_M C_{i-1} + (1 - D_M) C_i$ and $b = (1 - D_M) \cdot C_{i+1} + D_M C_{i+2}$. Eqs. (4), (5) can be used following four different schemes: GER, GEL, SAGE and DAGE. For the GER scheme, the Saul'yev-RL equation is used for the last point and Eqs. (4), (5) are then used for all the remained points. Similarly, the Eqs. (4), (5) are used for every space point in the GEL scheme except for the first point for which the Saul'yev-LR equation should be used. As for the SAGE, the single alternating group explicit method, the GER and GEL schemes are used alternatively on successive time levels of the grid. The DAGE is a double alternating group explicit method, which means the GER scheme is used for the first time level, and the GEL for the next two levels, and again the GER for the next two time levels, and so on. The first two are unstable for $D_M > 1$. However, the last two algorithms are unconditionally stable for all positive values of D_M, as claimed by Evans and Abdullah.[20] In spite of the attractive possibilities outlined by the authors, the results[21] show that the simulated results by these schemes also suffered strong instabilities when large D_M was employed. Obviously, this unexpected instability is worthy of being investigated again in more detail to explore the real reason that leads to such numerical oscillations. The simplest and very effective method to evaluate the stability of a finite difference algorithm is the simulation of a Cottrell experiment because the abrupt change of the surface concentration,[24] which initiates the diffusion, is usually a factor causing the numerical instability.

Simulation of the Cottrell experiment by SAGE method

The following discussion is on the basis of the following electrode reaction:

$$Ox + e^- \leftrightarrow Red \quad (E^0, \ \alpha, \ k^0) \quad (6)$$
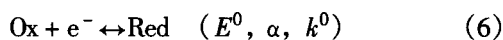
where E^0 is the formal electrode potential, α is the transfer coefficient and k^0 is the standard heterogeneous rate constant. They are the operational parameters in Butler-Volmer rate expressions for the interfacial process.

1. Uniform grid equations

For the uniform grid difference SAGE method, calculations of the concentrations in the GER step are based on Eqs. (4), (5), except for the first two space grids where two different equations must be used:

$$C_1' = \Delta_1/\Delta \quad (7)$$

$$C_2' = \Delta_2/\Delta \quad (8)$$

where $\Delta = r_{11}^0 r_{22}^0 - r_{12}^0 r_{21}^0$, $\Delta_1 = r_{22}^0 a^0 - r_{12}^0 b^0$, $\Delta_2 = r_{11}^0 \cdot b^0 - r_{21}^0 a^0$, with $r_{11}^0 = 1 + D_M$, $r_{22}^0 = 1 + 2D_M$, $r_{12}^0 = -D_M$, $r_{21}^0 = -2D_M$, $a^0 = 2D_M C_0 + (1 - 2D_M) C_1$ and $b^0 = (1 - D_M) C_2 + D_M C_3$. Calculation of the first point in the GEL step follows the Saul'yev-LR equation, which can be rewritten as follows:

$$C_1' = [C_1 + D_M(C_2 - C_1) + 2D_M C_0']/(1 + 2D_M) \quad (9)$$

As for the last point in the GER step, we put it in pair with an extra point with the bulk concentration. This simplifies the programming a little and does not influence the simulation accuracy because the added point is far beyond the "diffusion layer". In all the simulations, the currents were calculated and stored for analysis at the end of every GEL step. Possible cancellations of the

truncation errors after a cycle of GER and GEL steps should improve the simulation accuracy further.[21]

2. Exponentially expanded grid equations

If the exponentially expanded space grid is employed for the simulation, Eqs. (4), (5) are still used in the same form but with different parameters: $r_{11} = 1 + D_i'$, $r_{22} = 1 + D_{i+1}'$, $r_{12} = -D_i''$, $r_{21} = -D_{i+1}'$, $a = D_i' C_{i-1} + (1 - D_i') C_i$ and $b = (1 - D_{i+1}') C_{i+1} + D_{i+1}'' C_{i+2}$. Thus Eqs. (4), (5) can be used for the calculations of all space points in the GER step following the definitions of D_i' and D_i'' by Feldberg.[14]

In the GEL step of the SAGE scheme, the equation used to calculate the concentration of the first point becomes

$$C_1' = [C_1 + D_1''(C_2 - C_1) + D_1' C_0']/(1 + D_1') \quad (10)$$

Development of SAGE scheme for the simulation of the cyclic voltammetric experiment

1. Quasi reversible reaction

The only difference in the simulation of this system from the Cottrell simulation exists in the calculations for the boundary points, C_0 and C_1, for both the reactant and the product. These unique calculations are only necessary in the GEL step of the SAGE simulation. For the GER step, all the calculations are the same as described above, bearing in mind that the surface concentration, C_0, is now not a constant any more (equal to zero for the Cottrell process), but varies with time or potential levels. To calculate the boundary concentrations in the GEL step, the following four-variable linear algebra equations which are the discrete forms of the flux balance condition: the Butler-Volmer kinetic equation and the Saul'yev LR equations for the concentrations of the first points of both the reactant and the product. These equations can be written into a matrices expression:

$$\begin{bmatrix} -D_{ox,1}' & 1 + D_{ox,1}' & 0 & 0 \\ 1 + k_f \Delta t/D_{ox,1}'\Delta x & -1 & k_b \Delta t/D_{ox,1}'\Delta x & 0 \\ 0 & 0 & -D_{red,1}' & 1 + D_{red,1}' \\ -D_{ox,1}' & D_{ox,1}' & -D_{red,1}' & D_{red,1}' \end{bmatrix} \begin{bmatrix} C_{ox,0}' \\ C_{ox,1}' \\ C_{red,0}' \\ C_{red,1}' \end{bmatrix} = \begin{bmatrix} C_{ox,1} + D_{ox,1}''(-C_{ox,1} + C_{ox,2}) \\ 0 \\ C_{red,1} + D_{red,1}''(-C_{red,1} + C_{red,2}) \\ 0 \end{bmatrix} \quad (11)$$

where $D'_{p,1}$ and $D''_{p,1}$ (the subscript "p" represents "ox" or "red", corresponding to the reactant and product of the electrode reaction) are the left and right dimensionless diffusion coefficients, which were defined by Feldberg,[14] of the species in the first space grid for an exponentially expanded space grid model, k_f and k_b are the forward and backward heterogeneous rate constants defined in the Butler-Volmer expression, Δt is the time increment in the simulation and Δx is the thickness of the first space element, the concentration variables marked with the superscript "$'$" designate the concentrations at the current time level of the simulation and concentration variables without superscript "$'$" represent the previous time level. Defining parameters: $m_{11} = -D'_{ox,1}$, $m_{12} = 1 + D'_{ox,1}$, $m_{21} = 1 + k_f\Delta t/(D'_{ox,1}\Delta x)$, $m_{23} = -k_b\Delta t/(D'_{ox,1}\Delta x)$, $m_{33} = -D'_{red,1}$, $m_{34} = 1 + D'_{red,1}$, $m_{41} = -\zeta$, $m_{42} = \zeta$, $a^0 = C_{ox,1} + D''_{ox,1}(-C_{ox,1} + C_{ox,2})$, $b^0 = C_{red,1} + D''_{red,1}(-C_{red,1} + C_{red,2})$, Eq. (11) can be written into En. (12) by appropriate matrices transformations.

$$\begin{bmatrix} C'_{ox,0} \\ C'_{ox,1} \\ C'_{red,0} \\ C'_{red,1} \end{bmatrix} = \begin{bmatrix} a^{0'}/m'_{11} \\ [c^0 - m'_{21}C'_{ox,0}]/m'_{22} \\ [b^0 - m'_{31}C'_{ox,0} - m'_{32}C'_{ox,1}]/m'_{33} \\ -m_{41}C'_{ox,0} - m_{42}C'_{ox,1} + C'_{red,0} \end{bmatrix} \tag{12}$$

where $a^{0'} = a^0 + m_{12}c^0/[1 - m_{34}m_{42}m_{23}/(m_{33} + m_{34})]$, $m'_{11} = m_{11} + [m_{21} + m_{34}m_{41}m_{23}/(m_{33} + m_{34})]m_{12}/[1 - m_{34}m_{42}m_{23}/(m_{33} + m_{34})]$, $c^0 = -m_{23}b^0/(m_{33} + m_{34})$, $m'_{21} = m_{21} + m_{34}m_{41}m_{23}/(m_{33} + m_{34})$, $m'_{22} = -1 + m_{34}m_{42}m_{23}/(m_{33} + m_{34})$, $m'_{31} = -m_{34}m_{41}$, $m'_{32} = -m_{34}m_{42}$, and $m'_{33} = m_{33} + m_{34}$.

Eq. (12) is a four-variable linear algebra equations group and can be solved directly without much difficulty, resulting in the explicit expressions for all the four concentration variables at the boundary points.

2. First order irreversible EC mechanism

The first order irreversible EC mechanism couples an electron transfer (Eq. 6) with an irreversible homogeneous first-order chemical reaction

$$\text{Red} \xrightarrow{k_1} \text{Prd} \tag{13}$$

The EFD algorithm is not satisfactory in simulating such a process when the homogeneous rate constant k_1 is very large, because the extremely thin reaction layer needs space units with very small thickness to describe it accurately. This means the simulation will take very long CPU time. The D_M stability of the SAGE method should be advantageous in dealing with this problem. For the programming, the equations used for this mechanism are mostly the same as those for the quasi-reversible scheme, only the definitions of r_{11} and r_{22} in the corresponding Eqs. (4), (5) for the calculations of product concentrations and m_{34} in Eq. (12) for the calculations of the boundary concentrations of both the reactant and the product in the GEL step are different. The above differences in calculating r_{11}, r_{22} and m_{24} are due to the fact that not only the diffusion but also the coupled chemical reaction (Eq. 13) alters the concentration of "Red". The influence of the coupled chemical reaction on the change of the product concentration is reflected by a term $k_t C_i \Delta t$ in the following equation (corresponding to Eq. 2).

$$C'_i - C_i = D_M(C_{i-1} - C_i - C'_i + C'_{i+1}) - k_t C_i \Delta t \tag{14}$$

Therefore, the Saul'yev-RL and -LR equations for the calculation of the concentration of the electrode reaction product (Red) using an exponentially expanding grid algorithm should be written as:

$$(1 + D''_{red,i} + k_1\Delta t)C'_{red,i} - D''_{red,i}C'_{red,i+1} = D'_{red,i}C_{red,i-1} + (1 - D''_{red,i})C_{red,i} \tag{15}$$

$$-D''_{red,i+1}C'_{red,i} + (1 + D'_{red,i+1} + k_1\Delta t)C'_{red,i+1} = (1 - D''_{red,i+1})C_{red,i+1} + D''_{red,i+1}C_{red,i+2} \tag{16}$$

These above two equations show that the expressions of r_{11} and r_{22} now used for the calculations of the product

concentrations of the non-boundary points are: $r_{11} = 1 + D''_{red,i} + k_1\Delta t$, $r_{22} = 1 + D'_{red,i+1} + k_1\Delta t$. The calculation of the boundary concentrations in the GEL step is based on three relationships: the flux balance equation, the Butler-Volmer equation, and the Saul'yev LR equations for the first grid point. Among these, only the one corresponding to the concentration of Red is different from the quasi-reversible case, and this equation has the following form:

$$- D''_{red,1} C'_{red,0} + (1 + D'_{red,1} + k_1\Delta t) C'_{red,1}$$
$$= (1 - D'_{red,1}) C_{red,1} + D''_{red,1} C_{red,2} \qquad (17)$$

It means that $m_{34} = 1 + D'_{red,1} + k_1\Delta t$ should be used instead of $m_{34} = 1 + D'_{red,1}$ for the boundary concentration calculations.

After the replacements of r_{11}, r_{22} and m_{34}, calculation of the concentrations at the boundary points in the GEL step and the product concentration in both the GEL and the GER step could be conducted in a similar way to that for the quasi-reversible scheme. In addition, the calculations for the concentrations of the reactant at non-boundary points do not need to be changed and are the same as those in the quasi-reversible scheme.

3. Irreversible first order catalysis mechanism

For the above EC mechanism, only those parameters corresponding to the product of the electrode reaction need to be modified. However, in the case of the simulation of the irreversible catalysis reaction,

$$\text{Red} \xrightarrow{k_c} \text{Ox} \qquad (18)$$

parameters corresponding to calculations of the concentrations for both the reactant and the product of the electrode reaction must be modified. For the product, the definitions of r_{11} and r_{22} are modified in the same way as for the EC mechanism with the homogeneous kinetics constant k_1 replaced by k_c. However, for the reactant, the corresponding r_{11} and r_{22} are kept unchanged with the expressions of parameters a^0 and b^0 changed into: $a^0 = D'_{ox,i}C_{ox,i-1} + (1 - D'_{ox,i}) C_{ox,i} + k_c C'_{red,i}\Delta t$ and $b^0 = (1 - D''_{ox,i+1}) C_{ox,i+1} + D''_{ox,i+1} C_{ox,i+2} + k_c C'_{red,i+1}\Delta t$. The values of $C'_{red,i}$ and $C'_{red,i+1}$ are known because the concentrations of the product of the

heterogeneous reaction at every point are calculated firstly. Other differences exist in the parameters of Eq. (12), which is used to calculate the concentrations of the reactant and the product at the boundary points. For the catalysis system, the following modifications are necessary on the basis of simple mathematical deductions. First the expression of m_{34} becomes: $m_{34} = 1 + D'_{red,1} + k_c\Delta t$, then m_{11}, m_{12} and a^0 are changed into: $m_{11} = -D'_{ox,1} + k_c\Delta tm_{33}m_{41}/(m_{33} + m_{34})$, $m_{12} = 1 + D'_{ox,1} + k_c\Delta tm_{33}m_{42}/(m_{33} + m_{34})$ and $a^0 = C_{ox,1} + D'_{ox,1}(-C_{ox,1} + C_{ox,2}) + k_c\Delta tb^0/(m_{33} + m_{34})$, thus the equations for the boundary concentrations of the catalytic mechanism also have the form of Eq. (11) and can be solved analogously resulting in a solution with the form described by Eq. (12).

Simulation results and discussion

All the programs were written in Turbo C 2.0 and executed in double precision on an IBM-PC compatible microcomputer with a Pentium 120 MHz processor. The programs are available from the authors upon request.

Simulation of the Cottrell problem

The accuracy of simulated current can be estimated from the ratio $R(j)$ between the simulated current and the analytical value as a function of the iteration number.[9]

$$R(j) = f_s[\pi(j + \tau)/D_M]^{1/2}\Delta t/\Delta x \qquad (19)$$

where j is the iteration number, f_s is the simulated flux and τ is an arbitrary parameter with a value chosen to give best fitting with the analytical results. As shown in Table 1, the simulation was stable even with very large D_M, this confirms the unconditional stability of the SAGE method. Bearing in mind that the real iteration number is $2j$ for two steps (GER and then GEL) are involved in "one iteration". The SAGE simulation was accurate enough with $D_M < 1.0$. Slower convergence appeared for $D_M > 10$. This could be attributed to the so-called propagational inadequacy[24] due to the lower propagation speed of computation relative to diffusion for a uniform grid algorithm. The convergence can be accelerated by using an exponentially expanded space grid tech-

nique.[24] In order to prove this prediction, an exponentially expanded space grid was also used for the simulation of a Cottrell process and the results are tabulated in Table 2. As shown in Table 2, the accuracy was not improved but slightly decreased when the expanded grid was employed. In addition, the stability became worse for the expanded grid SAGE method. Strong computation oscillations appeared with $D_M > 100$. As the fully implicit calculation can always enhance the stability of an algorithm, the implicit calculation of the boundary concentration (C_1'), which was calculated following the Saul'yev-RL scheme for the uniform grid simulation in the GER step, was tried and found to be able to damp the oscillations and thus improve the accuracy efficiently (shown in Table 3). By comparison with the simulated results of the uniform grid simulation employing the same implicit calculation of C_1' (shown in Table 4), a faster convergence was observed for the expanded grid technique. Thus we conclude that the instability in the expanded grid SAGE simulation was caused by the abrupt change of the interfacial concentration, which led to a negative value of the calculated boundary concentration at the first iteration and thus made the calculation unstable.

Table 1 $R(j)$ values for a simulation of the Cottrell experiment obtained with the uniform grid SAGE method[a]

j	D_M					
	0.4	1	5	10	100	4000
10	1.001431	0.979650	0.890498	0.757906	0.091502	0.000437
20	1.000370	0.989787	0.947917	0.892926	0.215954	0.001236
30	1.000179	0.993183	0.965725	0.931334	0.333397	0.002262
40	1.000112	0.994884	0.974449	0.949313	0.435205	0.003468
50	1.000080	0.995906	0.979631	0.959802	0.520332	0.004824
60	1.000062	0.996588	0.983065	0.966687	0.590292	0.006312
70	1.000051	0.997075	0.985507	0.971556	0.647339	0.007916
80	1.000044	0.997441	0.987334	0.975182	0.693753	0.009626
90	1.000039	0.997726	0.988752	0.977987	0.731571	0.011430
100	1.000036	0.997953	0.989884	0.980223	0.762508	0.013323

[a] Optimal value of τ is -0.16 for this case.

Table 2 $R(j)$ values for a simulation of the Cottrell experiment obtained with the expanded grid SAGE method

j	D_M					
	0.4	1	5	10	100	300
10	1.000507	0.979723	0.860240	0.739608	− 11.527455	− 19.429897
20	1.000092	0.988589	0.931161	0.859551	0.989325	− 15.444766
30	1.000147	0.992855	0.953610	0.905968	− 0.068550	2.164761
40	0.999343	0.994276	0.965414	0.929255	0.285547	− 0.351084
50	0.999433	0.995076	0.972390	0.943588	0.432571	− 1.231617
60	0.999871	0.995914	0.976825	0.953144	0.522214	− 0.424053
70	1.000167	0.996692	0.979936	0.959836	0.590858	− 0.179712
80	1.000210	0.997275	0.982333	0.964747	0.642287	− 0.079577
90	1.000082	0.997638	0.984292	0.968528	0.682643	0.046496
100	0.999896	0.997832	0.985930	0.971569	0.714851	0.146598

[a] Optimal value of τ is 0.0 for this case.

Table 3 $R(j)$ values for a simulation of the Cottrell experiment obtained with the expanded grid SAGE method with the implicitly calculated boundary concentration C_j at the GER step at every time level[a]

j	D_M						
	0.4	1	5	10	100	1000	100000
10	1.000900	0.996755	0.997612	1.000879	0.989522	1.904237	0.404522
20	1.000314	0.997450	0.998075	0.998388	1.003620	1.136939	1.014347
30	1.000508	0.998850	0.997967	0.998608	0.998983	0.814406	1.560731
40	0.999639	0.998863	0.998502	0.998447	0.999061	0.991041	1.918514
50	0.999639	0.998736	0.998922	0.998671	0.999333	1.020820	2.064326
60	1.000037	0.998943	0.998993	0.999013	0.999358	0.997406	2.020298
70	1.000321	0.999284	0.998936	0.999215	0.999239	0.996143	1.840130
80	1.000360	0.999552	0.998926	0.999257	0.999148	0.999203	1.585531
90	1.000227	0.999676	0.999009	0.999215	0.999152	0.999466	1.313810
100	1.000030	0.999676	0.999155	0.999168	0.999235	0.999396	1.069084

[a] Optimal value of τ is -0.7 for this case.

Table 4 $R(j)$ values for a simulation of the Cottrell experiment obtained with the uniform grid SAGE method with the implicitly calculated boundary concentrations of C_1 at the GER step at every time level[a]

j	D_M					
	0.4	1	5	10	100	1000
10	1.008411	1.001367	1.026174	1.071629	0.887692	0.334799
20	1.004152	1.001011	1.012194	1.032600	1.080953	0.472909
30	1.002753	1.000733	1.007910	1.020117	1.146717	0.571448
40	1.002060	1.000570	1.005853	1.014559	1.163185	0.649187
50	1.001646	1.000466	1.004645	1.011416	1.158957	0.713368
60	1.001372	1.000393	1.003850	1.009393	1.146529	0.767751
70	1.001176	1.000341	1.003287	1.007980	1.131656	0.814609
80	1.001030	1.000300	1.002868	1.006936	1.116959	0.855450
90	1.000917	1.000269	1.002544	1.006135	1.103541	0.891343
100	1.000826	1.000243	1.002286	1.005499	1.091765	0.923083

[a] Optimal value of τ is -0.7 for this case.

Simulation of the cyclic voltammetric experiment

1. *Reversible electron transfer reaction (Nernst process)*

Reversible reaction can be considered as a limiting case of the quasi reversible process when $k^0/(DFv/RT)^{1/2} \to \infty$. This case was chosen to demonstrate the stability and accuracy of the SAGE method. The simulated results are given in Table 5. Similar to the FQEFD method, the SAGE method was stable even for very large D_M. For the results in Table 5, the following condition,[9] the same as that proposed empirically by Feldberg for his FQEFD method, must be met in order to get accurate simulation results:

$$D_{max,M} \leq 2 \times 10^{-9}/ \mid v\Delta t \mid^3 \qquad (20)$$

where $v\Delta t$ is the potential increment in each iteration, and $D_{max,M}$ is the larger between $D_{ox,M}$ and $D_{red,M}$. Equilibrium initial concentrations were not used and no obvious oscillations were observed in our simulations with an initial potential set to be $(E_0 + 0.2$ V$)$. As seen from Table 5, the results for the simulations with $\beta = 0.5$ agree well with those computed by Nicholson and Shain.[25] In addition, simulations using $\beta = 1$ also produced good results with only slight deviations from those obtained with $\beta = 0.5$. This means $\beta = 1$ can be used for the SAGE simulation and thus shortens the computation time considerably. Since the fully implicit calculations for the boundary concentrations, as done for the Cottrell simulation, were not used for all the simulations here and no obvious oscillations were observed even for very

large D_M, we conclude again that the instability for the expanded grid simulation of the Cottrell process is caused by the strong discontinuity of boundary concentrations and this discontinuity is minimized for voltammetric simulations.

2. Irreversible electron transfer reaction

Simulated results for an irreversible process were also obtained by the SAGE method by assuming the di-

mensionless heterogeneous rate constant $\Lambda = 10^{-4}$ ($\Lambda = k^0/(DFv/RT)^{1/2}$) and the electron transfer coefficient $\alpha = 0.5$. The results are shown in Table 6 and agree well with the values of Nicholson and Shain.[25] Following the constraint of Eq. (20), the D_M as large as 10^{12} could be used and presented excellent results. Similarly, accurate results were also gained even with a larger value of $\beta = 1$. This saved the computation time significantly.

Table 5 Simulated curre functions for a reversible cyclic voltammogram[a]

$(E - E_0)$/V	NS	$\|v\Delta t\|$ (V) D_M β	10^{-3} 1		10^{-4} 10^3		10^{-5} 10^6		10^{-6} 10^9		10^{-7} 10^{12}	
			0.5	1	0.5	1	0.5	1	0.5	1	0.5	1
0.120	0.009		0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009
0.100	0.020		0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020
0.080	0.042		0.041	0.041	0.041	0.041	0.041	0.041	0.041	0.041	0.041	0.041
0.060	0.084		0.084	0.084	0.084	0.084	0.084	0.084	0.084	0.084	0.084	0.084
0.040	0.160		0.160	0.160	0.160	0.160	0.160	0.160	0.160	0.160	0.160	0.160
0.020	0.269		0.269	0.269	0.269	0.269	0.269	0.269	0.269	0.269	0.269	0.269
0	0.380		0.379	0.379	0.380	0.380	0.380	0.380	0.380	0.380	0.380	0.380
-0.0285	0.4463		0.4467	0.4469	0.4476	0.4466	0.4476	0.4478	0.4476	0.4465	0.4476	0.4473
-0.020	0.441		0.441	0.441	0.442	0.441	0.442	0.442	0.442	0.441	0.442	0.442
-0.040	0.438		0.439	0.439	0.439	0.438	0.439	0.440	0.439	0.438	0.439	0.439
-0.060	0.399		0.400	0.402	0.400	0.398	0.400	0.401	0.400	0.400	0.400	0.399
-0.080	0.353		0.354	0.356	0.353	0.352	0.353	0.353	0.353	0.354	0.353	0.351
-0.100	0.312		0.313	0.314	0.313	0.312	0.313	0.311	0.313	0.315	0.313	0.310
-0.120	0.280		0.281	0.281	0.280	0.281	0.280	0.278	0.280	0.283	0.280	0.278
-0.150	0.245		0.245	0.243	0.245	0.248	0.245	0.242	0.245	0.247	0.245	0.245

[a] Simulation parameters: $D_M = D_{ox,M} = D_{red,M} = 2 \times 10^{-9}/|v\Delta t|^3$, $E_{start} = E^0 + 0.200$ V.

[b] Ψ_r is the current function for a reversible process defined by Nicholson and Shain.[25]

Table 6 Simulated current functions for an irreversible cyclic voltammogram[a]

E_{ir} (V)[b]	NS	$\|v\Delta t\|$/V D_M β	10^{-3} 1		10^{-7} 10^{12}	
			0.5	1	0.5	1
0.140	0.008		0.008	0.008	0.008	0.008
0.100	0.035		0.035	0.035	0.035	0.035
0.080	0.073		0.073	0.073	0.073	0.073
0.060	0.145		0.145	0.145	0.145	0.145
0.040	0.264		0.264	0.264	0.264	0.264
0.020	0.406		0.406	0.406	0.406	0.406
-0.0053	0.4958		0.4955	0.4962	0.4961	0.4955
-0.020	0.472		0.472	0.473	0.473	0.472

[a] Simulation parameters: $D_M = D_{ox,M} = D_{red,M} = 2 \times 10^{-9}/|v\Delta t|^3$, $E_{start} = E^0 + 0.200$ V, $\alpha = 0.5$, $\Lambda = 10^{-4}$.

[b] $E_{ir} = \alpha(E - E^0) + (RT/2F)\ln(\pi\alpha/(\Lambda^2))$ (see Ref. [25]).

[c] $\Psi_{ir} = \Psi_r/\alpha^{1/2}$ (see Ref. [25]).

3. Reversible electrode process with an irreversible first-order following up chemical reaction

In simulations of electrochemical systems coupled with homogeneous reactions, it is important to consider the possibility that a reaction layer, whose dimensions will be considerably smaller than the diffusion layer may be produced. This is indeed the case with an EC mechanism. The thickness of the reaction layer, μ, as promised by Feldberg,[9] will be

$$\mu = (D_{ox,M}/k_s)^{1/2} \qquad (21)$$

where $k_s = k_1 + k_{-1}$, and k_{-1} is equal to zero for an irreversible chemical reaction.

For accurate computation a conservative constraint requires that

$$\mu/\Delta x \geq 5 \qquad (22)$$

With the empirically deduced relationship of Eq. (20) one obtains:

$$| v\Delta t | \leq [10^{-9}/(25k_1\Delta t)]^{1/3} \qquad (23)$$

First-order rate constant for cyclic voltammetry is commonly normalized as:

$$k_1^{\neq} = RTk_1/(F | v |) \qquad (24)$$

Combining Eq. (23) and Eq. (24) gives:

$$| v\Delta t | \leq \{10^{-9}/[25(F/RT)k_1^{\neq}]\}^{1/4} \qquad (25)$$

This weak dependence of $|v\Delta t|$ on $k_1^{\neq}$ shows the similarity of effectiveness of the SAGE method to the FQEFD algorithm. If an EFD algorithm were used, $|v\Delta t|$ would be strongly dependent upon the value of $k_1^{\neq}$ (to the -1 power). Table 7 presents the simulated cyclic voltammetric current functions for a reversible electron transfer followed by an irreversible first-order chemical reaction. By appropriate transformation of the potential, it is then valid to compare the simulated data ($k_1^{\neq} \gg 1$) with the computations of Nicholson and Shain for an irreversible electron transfer with $\alpha = 1$.[25] The agreement is excellent. In addition, the computational instabilities didn't

arise in the simulation process although the simulation commenced from non-equilibrium initial concentrations. In another word, there might be some initial instabilities, but too small to be observed.

Table 7 Simulated cyclic voltammetric current functions for a reversible electron transfer followed by an irreversible first-order chemical reaction[a]

E_{ec} (V)[b]	Ψ_{ir}[c]	Ψ_{ec} β	
		0.5	1.0
0.140	0.008	0.008	0.008
0.100	0.035	0.035	0.035
0.080	0.073	0.072	0.073
0.060	0.145	0.145	0.145
0.040	0.264	0.263	0.264
0.020	0.406	0.405	0.405
− 0.0053	0.4958	0.4966	0.4958
− 0.020	0.472	0.474	0.472
− 0.040	0.406	0.407	0.406
− 0.070	0.323	0.323	0.325

[a] Simulation parameters: $\Lambda = \infty$; $k_1^{\neq} = 10^{12}$; $|v\Delta t| = 1.007 \times 10^{-6}$ V; $D_M = D_{ox,M} = D_{red,M} = 9.8 \times 10^8$; $E_{start} = E^0 + 0.7$ V.

[b] $E_{ec} = E - E^0 - (RT/2F)[-1.56 + \ln(k_1^{\neq})] - 0.0053$ V; With the appropriate transformation of the potential, the current function for an irreversible electron transfer.

[c] Ψ_{ir}, is theoretically identical to, Ψ_{ec}, the current function for a reversible electron transfer followed by an irreversible first-order chemical reaction with $k_1^{\neq} \gg 1$.

4. Reversible electrode process with an irreversible first-order following up catalytic reaction

Using large D_M also becomes critical when the catalytic mechanism in Table 8 is considered. Obviously, the model diffusion coefficient D_M must be chosen carefully to achieve sufficient simulation accuracy. Here, Eq. (25) can also be used with $k_1^{\neq}$ replaced by $k_c^{\neq}$. The simulated results for different $\mu/\Delta x$ are presented in Table 8. It can be seen that the simulations gave accurate results when $\mu/\Delta x \geq 5$, which means that accurate simulation of a first-order catalytic scheme also needs at least five concentration points lying within the "reaction layer".[9]

5. Other aspects concerning the SAGE simulation method

The computation speed of the SAGE simulation is

Table 8 Simulated voltammetric peak current functions (Ψ_p) for a reversible electron transfer followed by an irreversible first-order catalytic chemical reaction[a]

$k_c^{\neq} = k_c/(vF/RT)$	Ψ_p					
	FIFD	$\mu/\Delta x$	$\lvert v\Delta t\rvert /V$	D_M	β 0.5	1.0
10^2	(10.000)					
	8.427	0.5	1.007×10^3	0.98	6.400	7.156
	9.986	5	3.184×10^{-4}	31	9.941	9.965
	10.001	50	1.007×10^{-4}	980	9.999	10.000
10^8	(10000)					
	8427	0.5	3.184×10^{-5}	3.1×10^4	6403	7159
	9986	5	1.007×10^{-5}	9.8×10^5	9941	9965
	10001	50	3.184×10^{-6}	3.1×10^7	9999	10000

[a] Comparisons between the FIFD method and the SAGE method show the effectiveness of the SAGE method for simulation of such system with very large homogeneous rate constant. Simulation parameters: $E_{start} = E_0 + 0.200$ V; $E_{start} - E_{switch} = 0.500$ V (peak currents in parenthesis obtained by numerical integration as reported in Ref.[26])

comparable to the FQEFD method. However, its stability and accuracy are better than that FQEFD method. As known from Tables 2, 3, calculating the boundary concentrations C_0 and C_1 by the fully implicit equations will result in a faster convergence and a better simulation stability. We also extended this idea to the Nernstian system, and found that the allowed potential increment was almost twice that described by Eq. (20), which enhances the computation speed further at the price of solving more complicated six-variable algebra equations for non-Nernstian systems. Therefore, this idea was not explored in any further detail. Another method of using the GER and GEL equations simultaneously in an averaged manner, just like that of the Larkin-4 procedure,[23] was also tried for a voltammetric simulation of a Nernstian system with an expanded grid, and the results showed strong oscillations when $D_M > 2$.

Typical CPU time for the SAGE simulation of a complete (forward and backward scans) cyclic voltammetric curve of an EC system on a 586 PC with a Pentium 120-MHz processor is about 2.5 min with $D_M = 10^9$, β = 1 and the potential range of 500 mV. This time decreases quickly with the decrease of D_M and becomes less than 12 s when $D_M = 10^6$. Since a PC with a CPU clock frequency > 1 GHz is the current state of the art, thus the simulation could still be substantially accelerated if a faster CPU was employed. For explicit methods, enhancing the computation speed can be realized via parallel programming based on parallel processors. Since the digital simulation is facing the problem of considerably long computation time and large memory usage in simulations of rather complicated mechanisms, especially in 2-D or 3-D space, the explicit methods may be superior to implicit ones in processing such cases due to high parallelism of them. Following this idea, dividing simulation space into small finite domains and employing some stable and accurate equations on these separate domains (analogous to SAGE method) may be promising in dealing with these complex systems and is in need of being explored.

Conclusions

The SAGE method shows excellent stability and accuracy for the simulations of electrochemical problems, comparable with or even better than the FQEFD methods in some aspects. On a PC-level computer, the computation does not need too long CPU time if the model diffusion coefficient is not greater than 10^9, which corresponds to a dimensionless first-order homogeneous rate constant of 10^{12} which is enough for most of the electrochemical problems. Using faster or parallel CPU processors could be effective in improving the computation speed further. Application of SAGE to 2-D or 3-D problems is also worthy of being tried, because it is also an unconditionally stable algorithm. Like the FQEFD method, SAGE has great advantages on the EFD method. In addition, this method also shows a similarity

to the FIFD method[13] in the feasibility of using larger value of the exponentially expanding factor (the maximum value of $\beta = 1$ can be used). Although the FIFD algorithm performs well without the restriction of the potential increment, its programming is certainly more complicated.

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