Universal Electrochemical/Chemical Simulator Based on an Exponentially Expanding Grid Network Approach

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A universal simulator capable of simulating virtually any user-defined electrochemical/chemical problems in one-dimensional diffusion geometry was developed based on an exponentially expanding grid modification of the existing network approach. Some generalized reaction-diffusion governing equations of an arbitrary electrochemical/chemical process were derived, and program controlled automatic generation of the corresponding PSPICE net-list file was realized. On the basis of the above techniques, a universal simulator package was realized, which is capable of dealing with arbitrarily complex electrochemical/chemical problems with one-dimensional diffusion geometry such as planar diffusion, spherical diffusion, cylindrical diffusion and rotational disk diffusion-convection processes. The building of such a simulator is easy and thus it would be very convenient to have it updated for simulations of newly raised electrochemical problems.

Keywords   electrochemical simulator, electrode process, network approach, exponentially expanding grid

Introduction

Digital simulation is a very powerful tool in both theoretical and experimental aspects of electrochemical researches. Construction of a universal simulator towards simplifying obtaining theoretical electrochemical responses has been the motives of many research groups in recent years. Among these, Digisim[1] series developed by Feldberg in collaboration with Rudolph, and ELSIM series[2-4] by Bieniasz might be the most well known ones. Besides, other simulators such as EASIEST,[5] CVSIM,[6] as well as those distributed by EG&G Princeton Applied Research and CH Instruments[7,8] also appear to be effective for the simulations of a variety of electrochemical problems. However, not all of these simulators are truly universal solvers for electrochemical problems except Digisim and ELSIM. The Digisim employs Rudolph's FIFD (fast implicit finite difference) algorithm, which is an unconditionally stable algorithm especially suitable for solving stiff electrochemical problems with satisfactory accuracy and speed. Digisim can be used for the simulations of electrochemical reactions coupled with any steps of single electron transfer process and homogeneous chemical reactions with reaction orders up to 2. ELSIM is another powerful electrochemical simulator. Different simulation algorithms were integrated into this package, and these algorithms can be selectively used during the simulations in order to achieve the highest simulation efficiency.

Although some of these simulators are available commercially, it is usually difficult or even impossible for users to make modifications to them or build con-nections between them and other laboratory programs. In addition, these packages are usually not portable. All these make the development of an easy-to-build universal simulator become very necessary, especially for those who are not adept at operating sophisticated numerical methods.

We herein report a program interface between electrochemical problems and an electronic simulation package, PSPICE, based on a modified version of a recently developed network approach,[9] exponentially expanding grid network approach (EEGNA).[10] The most attractive feature of this approach is that direct operation of complicated numerical methods is no longer necessary. When the program is connected with PSPICE, a universal electrochemical simulator capable of simulating electrochemical processes with arbitrary heterogeneous or homogeneous complexity in one-dimensional diffusion geometry could be constructed.

Generalized governing difference equations for electrochemical/chemical processes

Owing to the inherent advantages of the network simulation approach, obtaining the corresponding difference equations of an electrochemical problem under consideration is the only necessary procedure for conducting a simulation, because the numerical resolution of these equations could be readily carried out using PSPICE, a commercially available software package originally designed for the simulations of electric circuit problems.

Difference equations for a semi-infinite linear diffusion process

According to Fick's second law, the partial differential equation (PDE) mathematically describing the diffusion of substance *i* can be written as

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} \tag{1}$$

where *c*, *D*, *t*, and *x* represent concentration, diffusion coefficient, time and distance from the electrode surface, respectively. Here we use the maximum initial concentration c_{max}^0, total experimental time τ and the maximum diffusion layer thickness $(D_{max}\tau)^{1/2}$ to normalize Eq. (1) and the resulting dimensionless form is

$$\frac{\partial \theta_i}{\partial H} = \xi_i^2 \frac{\partial^2 \theta_i}{\partial X^2} \tag{2}$$

where θ, *H* and *X* designate dimensionless concentration, time and distance, $\xi_i = (D_i/D_{max})^{1/2}$, *i* corresponds to the *i*th species. Eq. (2) can be approximated into the following Eq. (3) through finite difference discretization of the spatial variable *X*, while keeping the time variable still continuous.

$$\frac{d\theta_{i,j}}{dH} \Delta Y_{i,j} = \frac{\theta_{i,j+1} - \theta_{i,j}}{Y_{i,j+1} - Y_{i,j}} - \frac{\theta_{i,j} - \theta_{i,j-1}}{Y_{i,j} - Y_{i,j-1}} \tag{3}$$

where $Y_{i,j} = X_j/\xi_i$, *j* represents the *j*th spatially discretized volume unit, $\Delta Y_{i,j}$ is the thickness of the *j*th volume unit, $Y_{i,j}$ corresponds to the position of the concentration center in the *j*th volume unit. Using EEGNA[10] can cause dramatic enhancement in simulation speed and accuracy, and make it more suitable for constructing a universal simulator. In EEGNA, the spatial variable *Y* is divided into exponentially increasing small simulation units according to the following equations.[11]

$$\Delta Y_{i,j} = \Delta Y_i e^{\beta(j-1)} \tag{4}$$

$$Y_{i,j} = \Delta Y_i \frac{e^{\beta(j-0.5)} - 1}{e^\beta - 1} \tag{5}$$

$$\Delta Y_i \xi_i = \frac{L_{max}(e^\beta - 1)}{e^{N\beta} - 1} \tag{6}$$

where β is an exponentially expanding factor, ΔY_i the thickness of the first volume unit right adjacent to the electrode surface, L_{max} the dimensionless thickness of the simulation layer and *N* the number of the volume units comprised in the whole simulation space.

Spherical or cylindrical diffusion item

If a spherical or cylindrical diffusion exists, the corresponding terms corresponding to spherical or cylindrical diffusion should be included in Eq. (1), resulting in Eq. (7).

$$\frac{\partial c_i}{\partial t} = D_i \left(\frac{\partial^2 c_i}{\partial x^2} + \frac{\Omega}{x} \frac{\partial c_i}{\partial x} \right) \tag{7}$$

where *x* represents the radial coordinate in a spherical or cylindrical coordinates system, Ω is a constant decided by the geometry of the working electrode: $\Omega = 2$ or 1 corresponds to the spherical or cylindrical case, and the second item in the right hand side of Eq. (7) is the so called spherical or cylindrical diffusion term. Similarly, the spherical/cylindrical diffusion term in Eq. (7) can be normalized as

$$\frac{\Omega}{Y_{i,0} + Y_{i,j}} [(\theta_{i,j+1} - \theta_{i,j})R_r + (\theta_{i,j} - \theta_{i,j-1})R_l] \tag{8}$$

where $Y_{i,0}$ is the dimensionless electrode radius, R_r and R_l have the following forms

$$R_r = \frac{1 - e^{-0.5\beta}}{e^{0.5\beta} - e^{-0.5\beta}}; \quad R_l = \frac{e^{0.5\beta} - 1}{e^{0.5\beta} - e^{-0.5\beta}} \tag{9}$$

Convectional item for the diffusion equation of the rotational disk electrode (RDE) system

Under appropriate conditions,[12] the diffusion towards a rotational disk electrode could be described by the following equation

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} + B'x^2 \frac{\partial c_i}{\partial x} \tag{10}$$

where $B' = 0.5102326\omega^{3/2}\nu^{-1/2}$, ω is the angular velocity of the rotational disk electrode and ν the kinematic viscosity of the electrolyte solution. Therefore contribution from convection effect could be expressed by

$$B_i' Y_{i,j}^2 [(\theta_{i,j+1} - \theta_{i,j})R_r + (\theta_{i,j} - \theta_{i,j-1})R_l] \tag{11}$$

where, $B_i' = B'\xi_i\tau(D_{max}\tau)^{1/2}$.

Based on the above discussions, the differential equations describing the evolution of concentrations could be expressed in a more generalized form

$$\frac{d\theta_{i,j}}{dH} \Delta Y_{i,j} = \Theta_L(i,j) + S_{SC}\Theta_{SC}(i,j) + S_{RDE}\Theta_{RDE}(i,j) \tag{12}$$

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where $\Theta_L(i,j)$, $\Theta_{SC}(i,j)$ and $\Theta_{RDE}(i,j)$ correspond to linear, spherical-cylindrical and rotational convection (for a RDE system) items, which are depicted by Eqs. (3), (8) and (11), respectively. The subscripts "SC" and "RDE" correspond to the spherical-cylindrical and rotational disk electrode, respectively. S_P is a 0/1 function with a value switched between "1" and "0" corresponding to systems with or without the "P (P=SC or RDE)" effect.

Homogeneous chemical reactions

When homogeneous chemical reactions must be considered and each of these reactions can be viewed as two single-direction reactions,[13-15] the equation for reaction (r) will have the following form

$$\sum_{s=1}^{S} \mu_{s,r}^{f} A_s \leftrightarrow \sum_{s=1}^{S} \mu_{s,r}^{b} A_s \qquad (13)$$

where $\mu_{s,r}^{f}$, $\mu_{s,r}^{b}$ are stoichiometric coefficients of species A_s in reaction (r). S is the total number of species involved in the chemical reactions. Consequently, the right-hand side of Eq. (12) will involve a homogeneous reaction item, $S_{HOM}\Theta_{HOM}(i,j)$ (S_{HOM} is a 0/1 function with a value equal to 1 when there is at least one homogeneous reaction), with the following expression for $\Theta_{HOM}(i,j)$

$$\Theta_{HOM}(i,j) = \sum_{r=1}^{R} f_r(i,j) \qquad (14)$$

where R is the total number of homogeneous chemical reactions. The right-hand side of Eq. (14) is a sum corresponding to all the reactions (r) that produce or consume substance A_i (referred to as substance i, briefly). The expression of $f_r(i,j)$ is

$$f_r(i,j) = \Delta Y_{i,j}(\mu_{i,r}^{b} - \mu_{i,r}^{f}) \times$$
$$\left[k_{r,f}' \prod_{s=1}^{S} \theta_{s,j}^{\lambda_{sr}^{f}} - k_{r,b}' \prod_{s=1}^{S} \theta_{s,j}^{\lambda_{sr}^{b}} \right] \qquad (15)$$

$$k_{r,f}' = \tau k_r^{f}(\theta_{max}^{0})^{\sum_{s=1}^{S}\lambda_{sr}^{f}-1}$$
$$k_{r,b}' = \tau k_r^{b}(\theta_{max}^{0})^{\sum_{s=1}^{S}\lambda_{sr}^{b}-1} \qquad (16)$$

where, λ_{sr}^{f} and λ_{sr}^{b} are the forward and backward reaction orders of substance A_s in reaction (r).

Considering the homogeneous chemical reactions, Eq. (12) becomes

$$\frac{d\theta_{i,j}}{dH} \Delta Y_{i,j} = \Theta_L(i,j) + S_{SC}\Theta_{SC}(i,j) +$$
$$S_{RDE}\Theta_{RDE}(i,j) + S_{HOM}\Theta_{HOM}(i,j) \qquad (17)$$

Boundary conditions

In electrochemical simulations, diffusion is typically limited to happen within a finite thickness of a solution layer, which is usually called a simulation layer. The thickness of this layer was defined to be $L_{max}(D_{max}\tau)^{1/2}$ with a dimensionless form of L_{max}. Concentrations of all the species beyond the outer boundary of the simulation layer are thought to be constant with values always determined by initial system parameters:

$$\theta_{i,N+1} \equiv \theta_i^0 \qquad (18)$$

where N is the total number of the simulation boxes (volume units) within the simulation layer, and $N+1$ corresponds to the $(N+1)$th simulation box, which lies outside of the simulation layer and is the neighbor of the Nth box. For a finite diffusion process with a blocked boundary condition such as that in a thin layer electrochemical cell, the corresponding boundary conditions will be

$$\theta_{i,N+1} \equiv \theta_{i,N} \qquad (19)$$

The boundary conditions at the surface of the electrode are determined by the electron transfer kinetics and the flux balances. Assuming that all the electrode reactions are first order elementary reactions adhering to the Butler-Volmer kinetics, the electrode reactions could then be expressed in a form similar to Eq. (13)

$$\sum_{se=1}^{Se} \mu_{se,re}^{f} A_{se} \leftrightarrow \sum_{se=1}^{Se} \mu_{se,re}^{b} A_{se} \qquad (20)$$
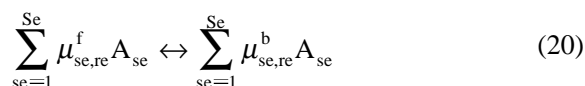
where $\mu_{se,re}^{f}$ and $\mu_{se,re}^{b}$ are the forward and backward stoichiometric coefficients[13-15] of an electrode reaction with a value of 0 or 1 under our assumptions. Se is the total number of species involved in electron transfer processes and Re is the total number of the electron transfer reactions. Therefore, the boundary conditions at the electrode surface can be expressed in a form of Eq. (21).

$$\int_i = \frac{(\theta_{i,1} - \theta_{i,0})}{\Delta Y_i} = \sum_{re=1}^{Re}(\mu_{i,re}^{f} - \mu_{i,re}^{b})\xi_i^{-1} \times$$
$$\left[\Psi_{re}^{f}\prod_{se=1}^{Se}\theta_{se,0}^{\lambda_{se,re}^{f}} - \Psi_{re}^{b}\prod_{se=1}^{Se}\theta_{se,0}^{\lambda_{se,re}^{b}} \right] \qquad (21)$$

where $\int_i$ is a dimensionless simulation flux, $\lambda_{se,re}^{f}$ and $\lambda_{se,re}^{b}$ represent the orders of the forward and backward electrode reactions[15] with value of 0 or 1 under our assumptions, Ψ_{re}^{f} and Ψ_{re}^{b} are dimensionless rate constants corresponding to the forward and backward electron transfer reactions defined by the following expressions

$$\Psi_{\text{re}}^{\text{f}} = k_{\text{re}}^{\text{f}} (\tau / D_{\text{max}})^{1/2}$$

$$\Psi_{\text{re}}^{\text{b}} = k_{\text{re}}^{\text{b}} (\tau / D_{\text{max}})^{1/2} \tag{22}$$

where k_{re}^{f} and k_{re}^{b} are conditional (apparent) rate constants of the forward and backward electrode reactions defined by the Butler-Volmer equations

$$k_{\text{re}}^{\text{f}} = k_{\text{re}}^{0} \exp\left[\frac{-\alpha_{\text{re}} n_{\text{a,re}} F(E - E^0)}{RT}\right]$$

$$k_{\text{re}}^{\text{b}} = k_{\text{re}}^{0} \exp\left[\frac{(1 - \alpha_{\text{re}}) n_{\text{a,re}} F(E - E^0)}{RT}\right] \tag{23}$$

where k_{re}^{0}, α_{re} and $n_{\text{a,re}}$ are standard heterogeneous rate constant, electron transfer coefficient and the number of transferred electrons in an activation step. E, E^0, F, R and T are polarizing electrode potential, conditional electrode potential, Faraday constant, gas constant and thermodynamic temperature, respectively.

Conversion of an electrochemical problem into a PSPICE netlist file

A sub-network designating the semi-infinite diffusion process

A network model designating a purely linear diffusion process is termed a diffusion sub-network hereafter. The diffusion sub-network can be viewed as a trapezoidal combination of a series of capacitors and resistors. The first step to construct such a network is to label all the network nodes (corresponding to the simulation boxes) involved. For convenience, we define the node label to be in the form of "$S_i Z_j$", with "S_i" corresponding to the ith species and "Z_j" corresponding to the jth simulation box. The voltage on node $S_i Z_j$ represents the concentration of the ith species at the jth simulation box, *i.e.* $V(S_i Z_j) = \theta_{i,j}$. The distribution of all the nodes in a diffusion sub-network is shown in Figure 1.

S_1Z_0	S_1Z_1	S_1Z_2	$\cdots$	S_1Z_{j-1}	S_1Z_i	S_1Z_{j+1}	$\cdots$	S_1Z_N	S_1Z_{N+1}
$\vdots$	$\vdots$	$\vdots$		$\vdots$	$\vdots$	$\vdots$		$\vdots$	$\vdots$
S_iZ_0	S_iZ_1	S_iZ_2	$\cdots$	S_iZ_{j-1}	S_iZ_i	S_iZ_{j+1}	$\cdots$	S_iZ_N	S_iZ_{N+1}
$\vdots$	$\vdots$	$\vdots$		$\vdots$	$\vdots$	$\vdots$		$\vdots$	$\vdots$
S_MZ_0	S_MZ_1	S_MZ_2	$\cdots$	S_MZ_{j-1}	S_MZ_i	S_MZ_{j+1}	$\cdots$	S_MZ_N	S_MZ_{N+1}

Figure 1   Generalized node labels in the electric network for an electrochemical diffusion process. M is the total number of the interested species and N the total number of the discretized simulation boxes. S_iZ_0 represents the nodes at the left boundary, *i.e.* the electrode surface, while S_iZ_{N+1} designates the first nodes outside the "simulation layer" whose concentrations will never be influenced by diffusion and can always be assumed to be constant during the whole simulation process.

Using this numbering fashion can easily avoid repetitive node names, and it is also very easy to position a simulation box corresponding to any substance in the whole network. In addition, it is also necessary to name all the resistors, capacitors and sources, and place them into corresponding locations in the network. A capacitor with a name of C_CS$_i$Z$_j$ is located between an electric node S$_i$Z$_j$ ($j \neq 0$, $j \neq N+1$) (corresponding to the position with the average concentration of a species in one simulation box) and the analog ground (with a node label of 0). A resistor with a name of R_RS$_i$Z$_j$ is placed between two neighboring nodes, S$_i$Z$_j$ and S$_i$Z$_{j+1}$. Thus a network model for the ith species has a structure as depicted in Figure 2.
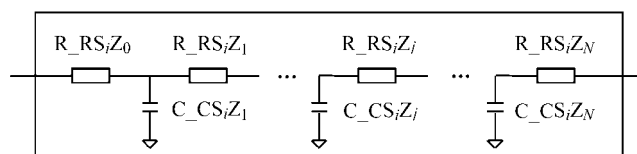

Figure 2   Schematic diagram of a ladder-like network model standing for the linear diffusion process for species i (boundary conditions are not shown).

Typical program codes for generating the network model shown in Figure 2 are as follows

DO

    WRITE TO FILE: "R_RS$_i$Z$_j$ S$_i$Z$_j$ S$_i$Z$_{j+1}$ R(i,j)"

    WRITE TO FILE: "C_CS$_i$Z$_j$ S$_i$Z$_j$ 0   C(i,j)   IC(i,j)"

LOOP

    WRITE TO FILE: "R_RS$_i$Z$_0$ S$_i$Z$_0$ S$_i$Z$_1$ Y$_{i,1}$"

where, R(i,j) is the resistance of R_RS$_i$Z$_j$, C(i,j) is the capacitance of C_CS$_i$Z$_j$ and IC(i,j) is the initial voltage (initial condition) on the capacitor C_CS$_i$Z$_j$. Based on Eqs. (5) and (6), the expressions of R(i,j), C(i,j) and IC(i,j) are defined by Eqs. (24)—(26), respectively.

$$R(i,j) = Y_{i,j+1} - Y_{i,j} \tag{24}$$

$$C(i,j) = \Delta Y_{i,j} \tag{25}$$

$$IC(i,j) = \theta_i^0 \tag{26}$$

Add spherical/cylindrical diffusion, rotational convection and homogeneous reaction terms to the linear diffusion network model

The method we used to introduce spherical/cylindrical diffusion, rotation disk diffusion-convection or homogeneous reaction terms is to add dependent power sources such as a multi-variable voltage dependent current source decided by Eqs. (8), (11) and (14) to appropriate network nodes. The form of this source is expressed by:

$$G(i, j) = S_{\text{SC}} \Theta_{\text{SC}}(i, j) +$$

$$S_{\text{RDE}} \Theta_{\text{RDE}}(i, j) + S_{\text{HOM}} \Theta_{\text{HOM}}(i, j) \tag{27}$$

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According to the input language for PSPICE, addition of a spherical/cylindrical diffusion term can be realized by the following program lines:

IF (S_{SC}＝1 or S_{RDE}＝1 or S_{HOM}＝1)

  DO

    WRITE TO FILE: "G_GS$_i$Z$_j$ S$_i$Z$_j$ 0   VALUE＝{−G(i,j)}"

  LOOP

ENDIF

Boundary conditions

The boundary conditions in an electrochemical system involve the right (corresponding to the semi-infinite position) and left (at the surface of an electrode) ones. The right boundary conditions [Eqs. (18), (19)] can be realized by adding constant-voltage (semi-infinite diffusion) or constant-current (blocked finite diffusion) sources to the nodes labeled as S$_i$Z$_{N+1}$. And this corresponds to the following program lines.

DO

  IF (Diffusion Type=Semi Infinite)   THEN

    WRITE TO FILE: "V_VS$_i$Z$_{N+1}$ S$_i$Z$_{N+1}$ 0 DC VDC(i)"

  ENDIF

  IF (Diffusion Type=Finite)   THEN

    WRITE TO FILE: "I_IS$_i$Z$_{N+1}$ S$_i$Z$_{N+1}$ 0 DC 0"

  ENDIF

LOOP

where $\mathrm{VDC}(i)=\theta_i^0$.

And the left boundary conditions [Eq. (21)] were introduced by

DO

  IF (The ith Species is Electroactive)   THEN

    WRITE TO FILE: "G_GS$_i$Z$_0$ S$_i$Z$_0$ 0   VALUE＝{G(i)}"

  ELSE

    WRITE TO FILE: "I_IS$_i$Z$_0$ S$_i$Z$_0$ 0 DC 0"

  ENDIF

LOOP

where $\mathrm{G}(i)=\displaystyle\int_i$.

Dimensionless simulation current

Based on Eq. (20) the dimensionless simulation current could be calculated by

$$I=\sum_{re=1}^{Re}\left(n_{re}\left[\Psi_{re}^{f}\prod_{se=1}^{Se}\theta_{se,0}^{\lambda_{se,re}^{f}}-\Psi_{re}^{b}\prod_{se=1}^{Se}\theta_{se,0}^{\lambda_{se,re}^{b}}\right]\right)\qquad(28)$$

where, n_{re} is the number of electrons involved in an electron transfer reaction. According to the normalization procedure we are using, the relationship between the dimensionless current, I, and the real electric current, i, is

$$I=\frac{i\sqrt{\tau}}{FA\theta_{max}\sqrt{D_{max}}}\qquad(29)$$

Based on the above discussions, a computer program in Qbasic 4.5 could be written for the automatic generation of the netlist file, and is referred to as a reaction complier in the following text.

Input file of the reaction complier

An input file[16] is necessary in building a universal simulator, which should contain all necessary experimental and simulation parameters of the system to be simulated in order to enable communications between the user and the simulator. Here we define an ASCII file with a name of "INPUT.ATN" to server this purpose. The reaction complier can exactly scan every line of this file and convert it into the corresponding netlist file, which is an approximation of the simulated electrochemical problem based on the above introduced exponentially expanding grid network modeling approach. The input file we have designed is self-explanatory and has a concise and easy-to-understand grammar with a typical format as in Figure 3. In this file, all the contents in the square brackets act as prompts for the contents of the following lines and any modification or removal of these contents is prohibited.

A program module for error check of the input file was also employed to minimize possible failures or mistakes of the simulations caused by wrong input data, and thus could facilitate finding invalid parameters entered by the user. Two kinds of techniques were designed for the error check, one is called run time error check (RTEC), and the other is a postfactum error check (PFEC). RTEC will find and report any invalid input data and logic errors in the input file, and then terminate the reaction compilation. The PFEC will store the compiled results back into an ASCII file with a name of "INPUT.CHK", possible input errors can be found by looking at this file.

Thermodynamic self-consistency (TSC)[15,17] of an electrochemical/chemical system is important and must be considered during assigning the thermodynamic and kinetic parameters to the reaction system. Methods for checking the thermodynamic consistency in an electrochemical/chemical reaction system have been discussed in detail by Luo[17] and Bieniasz.[15] In our simulator, both a Gauss-Jordan elimination algorithm[15] and a rank algorithm[18] are employed for TSC check.

Construction of the universal electrochemical/chemical simulator

On the basis of the above developed reaction complier, as well as the program modules for the check of

[Method(CV/CA: cyclic voltammetry/chronoamperometry) (no period)]

CV

[Number of reaction-diffusion species (no period)]

4

[Electron transfer reactions |E_0 (V)|arfa|na|k_0 (cm/s or s^{-1} for SF) (with period)]

1+e→2|0.0|0.5|1|1e-1;

3+e→4|0.5|0.5|1|1e-5.

[Homogeneous chemical reactions|k_{fc}|k_{bc} (with period)]

1↔3|13.622e7|3.892e12;

2↔4|3.892e12|3.892e8;

1+4↔2+3|1.38e-4|3.892e4.

[Diffusion type(L/S/C/RDE/FD/SF: linear/spherical/cylindrical/rotational disk/finite diffusion/surface) (no period)]

L

[Area (cm^2)/radius (μm)/radius, length (cm)/angular velocity (rad/s),kinematic viscosity (cm^2/s),area/area,thickness (cm)/area (no period)]

1E-6

[Experimental: cycles, E_i (V), E_s (V), E_t (V), v (V/s) or time (s) for CA, temper (C.D.) (no period)]

1, 0.7, −0.3, 0.6, 0.1, 25.0

[Simulation: boxnum,beta,dE (mV) or dt (s) for CA (no period)]

20, 1, 1

[IR drop: Ru(ohm),Cdl(F) (no period)]

0, 0

[Initial concentrations (mmol•L^{-1} or mol•cm^{-2} for SF) (with period)]

1|1000;

2-4|0.

[Diffusion coefficients (cm^2/s) (with period)]

1-4|1e-5.

[Current output (CF/DF:current function/default) (no period)]

DF

[Dimensionless simulation layer: Lmax (no period)]

6

[END]

Figure 3　An example of the input file "INPUT.ATN" to the reaction complier.

the input errors and the thermodynamic self-consistency, a general-purpose electrochemical/chemical simulator could be easily realized. The schematic structure of such a simulator is shown in Figure 4. The electrochemical/chemical reactions system and the experimental and simulation parameters are specified in the input file. The RTEC and PFEC modules will check all possible errors happening in the input file. The thermodynamic self-consistency will be analyzed by another program module, and the user will be notified if any thermodynamic or kinetic parameter of the reaction system is out of self-consistency. If all these checks pass successfully, the reaction complier will scan every line of the input file and automatically transform the problem under simulation into a PSPICE netlist file. Thus the electrochemical responses of the reaction system can be readily obtained by calling the simulation program, PSPICE.

Application to the simulation of an electrochemical square-scheme problem

As an example, we choose a square scheme to demonstrate the efficiency of this simulator. Square scheme is a usually encountered reaction mechanism in electrochemical researches.[19] This scheme is ideal for testing the efficiency of an electrochemical simulation algorithm.[20,21] We now employ it to give initial test of the EEGNA method, more detailed investigation was reported elsewhere.[22] Using our simulator, the simulation process of this complicated system becomes quite simple. A typical input file for this scheme has the form as in Figure 3. The square scheme could be illustrated as follows [Eq. (30)].
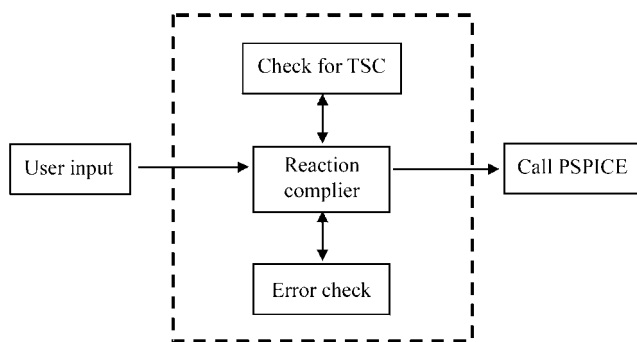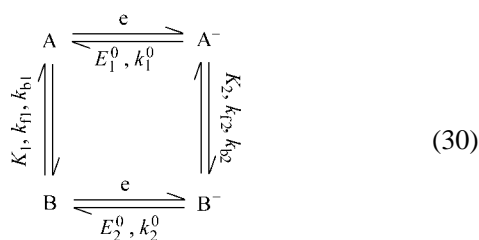

Figure 4　Block structure of the as-designed electrochemical/chemical simulator.

$$
\begin{array}{c}
\text{A} \xrightleftharpoons[E_1^0,\,k_1^0]{e} \text{A}^- \\[4pt]
K_1,k_{f1},k_{b1} \quad\quad\quad K_2,k_{f2},k_{b2} \\[4pt]
\text{B} \xrightleftharpoons[E_2^0,\,k_2^0]{e} \text{B}^-
\end{array}
\qquad\qquad (30)
$$

where K is chemical equilibrium constant and k is forward (f) or backward (b) kinetic rate constant.

The following cross-reaction, a solution electron transfer (SET) reaction, might possibly exist in the above system.

$$
\text{A} + \text{B}^- \leftrightarrow \text{A}^- + \text{B}\ (K_3, k_{f3}, k_{b3}) \qquad (31)
$$
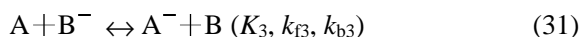
In order to fulfill the requirement of thermodynamic self-consistency, the following equation must hold

$$
K_3 = K_1/K_2 = \exp[(F/RT)(E_1^0 - E_2^0)] \qquad (32)
$$

The simulation parameters were chosen to be: $c_A{}^* = 1$ mmol/L, $E_1^0 = 0.0$ V, $E_2^0 = 0.5$ V, $K_2 = 10^4$, $K_1 = 3.5 \times 10^{-5}$, $k_{b1} = 3.892 \times 10^2$ s^{-1}, $k_{f2} = 3.892 \times 10^{-4}$ s^{-1}, 3.892×10^4 s^{-1}, 3.892×10^{12} s^{-1}, $v = 0.1$ V•s^{-1}, assuming the diffusion coefficients of all the interested substances to be the same: $D = 10^{-5}$ cm^2•s^{-1}. The simulation process is very convenient even for such a complicated mechanism, and the user only needs to enter all the parameters into the input file to start the simulation. The simulation results are listed in Table 1. All the results are in well agreement with those reported elsewhere.[21,23]

Considering the SET reaction with $k_{f3} = 1.38 \times 10^{-2}$, $k_{b3} = 3.892 \times 10^6$, $k_{b1} = k_{f2} = 3.892$ s^{-1}, then the simulated voltammetric response of this process seemed not to be influenced by the SET process for Nernstian electrode process. On the other hand, if the electrode process is not Nernstian ($k_1^0 = 10^{-1}$ cm•s^{-1}, $k_2^0 = 10^{-5}$ cm•s^{-1}, $\alpha = 0.5$) at the potential scan rate considered, the simulated voltammetric response is also blind to the existence of the SET process if reactions A↔B and A$^-$↔B$^-$ are extremely fast, which make the Nernstian equilibrium still hold due to the requirement of thermodynamic self-consistency as shown in Eq. (32). All these results are consistent with the report.[21,23]

Conclusions

We have developed a universal electrochemical simulator capable of simulating virtually any user-defined mechanisms. The simulator we developed can cope with both voltammetric and chronoamperometric problems in planar, spherical, cylindrical and rotational disk electrode systems for semi-infinite, thin layer finite diffusion as well as the electrochemistry of species exclusively adsorbed at electrode surface. Due to the simplicity for the construction of such a simulator, incorporation of some other functions in this simulator should be feasible and easy to realize. The accuracy and speed of the simulator are satisfactory as demonstrated by the simulation of a square scheme electrochemical process.

Finally, it is noteworthy that the simulations of 2-dimensional (2D) diffusions are currently hindered by the slow computation speed of the electronic package for these 2D problems, and there is still a problem in theory to make electric circuitry equivalences for the simulations of chronopotentiometric problems. These difficulties are waiting to be solved in the future.

Table 1 Simulated peak potentials E_{pc} and peak current functions Ψ_{pc} for a square scheme with different $k_{f1}{}^a$

k_{f1}/s^{-1}	EFD[b]		EFDHE[c]		FQEFD[d]		EEGNA	
	E_{pc}	Ψ_{pc}	E_{pc}	Ψ_{pc}	E_{pc}	Ψ_{pc}	E_{pc}	Ψ_{pc}
3.892×10^{-4}	-28.8	0.446			-28.3	0.445	-28.4	0.4455
3.892×10^4			99.6	0.495	98.2	0.494	98.4	0.4947
3.892×10^{12}			208.0	0.447	208.1	0.445	208.1	0.4462

^{a} Simulation parameters: $E_{start} = -0.7$ V, $N = 20$, $\beta = 1$, ptential step, 1 mV; ^{b} explicit finite difference method; ^{c} heterogeneous equivalent method operating in conjunction with EFD; ^{d} fast quasi-explicit finite difference method.

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