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ABSTRACT

The method of orthogonal collocation is used to discretize the differential equations describing quasi-reversible electrode processes under conditions of potential scanning. The resulting set of ordinary differential equations is solved to give numerical simulations. The numerical values are compared to literature data. A method for optimization of the dimensionless parameter is given.
INTRODUCTION

The mathematical description of electrochemical processes at stationary electrodes yields partial differential equations of the type

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - f(c)$$  \hspace{1cm} (1)

for each species, where $f(c)$ is determined by the homogeneous kinetics of the electrochemically produced intermediates and the substrate and $x$ is a distance coordinate. The initial condition normally is that the substrate is the only species present in solution and is homogeneously distributed in the $x$ direction.

The boundary conditions are dictated by the experiment performed and by the kind of electron transfer, i.e. reversible or irreversible. It has been shown for a variety of boundary conditions [1-4] that orthogonal collocation [5,6] provides a powerful, fast, and easily applied method to simulate kinetic diffusion problems of this kind. Up to now, however, only boundary conditions related to reversible electron transfer reactions have been used.

We now report the theory for application of this mathematical method to quasi-reversible electrode mechanisms:

$$A \xrightleftharpoons{\Delta E} B$$  \hspace{1cm} (2)

$$B \rightarrow C$$  \hspace{1cm} (3)

where the electrode reaction of $A$ to $B$ is described by a standard potential $E^*$, a standard rate constant for electron transfer $k_0$, the transfer coefficient $n$ and the number $n$ of transferred electrons. Product $B$ may react in a chemical reaction (3) with a homogeneous rate constant $k$.

INITIAL AND BOUNDARY CONDITIONS

To simulate a reaction scheme (2)-(3) we have to solve equations of the type (1) for three species $A$, $B$ and $C$ (assuming equal diffusion coefficients for each species):

$$\frac{\partial c_A}{\partial t} = D \frac{\partial^2 c_A}{\partial x^2} - k c_B$$  \hspace{1cm} (4)

$$\frac{\partial c_B}{\partial t} = D \frac{\partial^2 c_B}{\partial x^2} + k c_B$$  \hspace{1cm} (5)

and

$$\frac{\partial c_C}{\partial t} = D \frac{\partial^2 c_C}{\partial x^2} + k c_B$$  \hspace{1cm} (6)

The calculation of $c_C$ is not essential to simulate purely electrochemical responses for this reaction scheme. However, if one wishes to do so, this calculation may be included without any problem.

The initial conditions are:

$$t=0, c_A, c_B, c_C$$  \hspace{1cm} (7)
The boundary conditions at an infinite distance from the electrode are given by:

\[ t > 0, \ y \to \infty : \quad c_A = c_A^0, \ c_B = c_B^0 = 0 \]  

(9)  

whereas at the electrode

\[ t > 0, \ x = 0 : \quad \frac{\partial c_A}{\partial x} \big|_{x=0} = -\left( \frac{\partial c_B}{\partial x} \big|_{x=0} \right) \]  

(11)  

holds. Here \( A_1 = \frac{\alpha_1}{\alpha_1 + \alpha_2} \) \( \exp \left[ (\alpha_1 - \alpha_2) \frac{RT}{RT} (E - E^0) \right] \)  

(13)  

and

\[ A_2 = \frac{\alpha_2}{\alpha_1 + \alpha_2} \exp \left[ -\frac{\alpha_1}{\alpha_1 + \alpha_2} \frac{RT}{RT} (E - E^0) \right] \]  

(14)

Introducing Nicholson's definitions \( \theta \) for potential scan conditions (cyclic voltammetry)

\[ \Theta = \exp \left[ \frac{RT}{RT} (E^* - E^*) \right] \]  

(15)

The system of partial differential equations (6)-(10) has to be solved under the initial conditions (7) and (8) and the boundary conditions (10)-(11), (13) and (14).

**Transformation into a Dimensionless System of Equations**

We have to transform this system of partial differential equations and the conditions under which it is to solve into a
dimensionless form. We use the following transformation equations:

\[ T' = \alpha t \]
\[ X = x/L \]
\[ C_x^* = c_x/c_0^* \]
\[ C_y^* = c_y/c_0^* \]
\[ C_z^* = c_z/c_0^* \]
\[ X = A_0 \theta \]
\[ \theta = \Lambda_0 \theta \]

with

\[ L = D/L \]

where \( L \) is a distance from the electrode where no diffusion occurs during the simulation. Thus, the dimensionless system is

\[ \frac{\partial c_x^*}{\partial T'} = \beta \frac{\partial^2 c_x^*}{\partial X^2} \]
\[ \frac{\partial c_y^*}{\partial T'} = \beta \frac{\partial^2 c_y^*}{\partial X^2} - \lambda c_y^* \]
\[ \frac{\partial c_z^*}{\partial T'} = \beta \frac{\partial^2 c_z^*}{\partial X^2} + \lambda c_z^* \]

under the conditions

\[ T'=0,0 \leq X \leq 1: \]
\[ c_x^* = 1 \]
\[ c_y^* = c_z^* = 0 \]

Now we use orthogonal collocation to derive a system of simultaneous ordinary differential equations from each of the three partial differential equations (28)–(30). We fit the coefficients of a polynomial in \( c^*(x,t) \) such that the differential equations are fulfilled exactly at certain points. It has been shown that a very efficient collocation method can be constructed if we use orthogonal polynomials and if those points are the zeroes of the polynomial \( \phi \). Furthermore, in this case, the distance derivatives of the concentration at those "collocation points" are given by [1,5,6]

\[ \frac{d^2 c^*}{dx^2} \mid _{x_i} = \sum_{i=1}^{N_k} A_i c^*(x_i,y) \]
where the $A_{i,j}$ and $B_{i,j}$ are matrix elements only dependent on the kind and degree of the polynomial chosen. A polynomial of degree $n$ has $n$ roots in the open interval between zero and one and we have to include the boundary points at $x = 0$ and $x = 1$. Thus, the dummy variable $j$ varies from 1 to $M_2$.

Substituting the second derivatives with respect to $x$ in equation (29) we get

$$
\frac{d^2 c^A}{dx^2}_{[i,j]} = \sum_{j=1}^{M_2} \hat{B}_{i,j} \frac{d}{dx} c^A(x_{i,j})
$$

(39)

where the sum can be expanded and the boundary conditions (33) be introduced:

$$
\frac{d c^A}{dx}_{[i,j]} = \beta \sum_{j=1}^{M_2} \hat{B}_{i,j} \frac{d}{dx} c^A(x_{i,j})
$$

(40)

The concentration of species $A$ at the electrode surface is not known explicitly but may be derived from the boundary conditions (35) and (36). Using (38), equation (35) yields:

$$
\sum_{j=1}^{M_2} A_{i,j} a^A(x_{i,j}) e^{-\gamma_{i,j}} = -\sum_{j=1}^{M_2} A_{i,j} c^A(x_{i,j})
$$

(41)

or

$$
\frac{d c^A}{dx}_{[i,j]} = \frac{1}{A_{[i,j]}} \left[ A_{[i,j]} = \sum_{j=1}^{M_2} A_{i,j} c^A(x_{i,j}) \right]
$$

(42)

Equation (36) gives (again using (38))

$$
\sum_{j=1}^{M_2} A_{i,j} c^A(x_{i,j}) e^{-\gamma_{i,j}} \frac{d}{dx} c^A(x_{i,j}) = \frac{\gamma_{i,j}}{\gamma_{i,j}} c^A(x_{i,j}) \frac{d}{dx} c^A(x_{i,j})
$$

(43)

or after expansion of the sum, collection of the terms containing $c^A(x_{i,j})$ and solution for $c^A(x_{i,j})$:

$$
\frac{\gamma_{i,j}}{\gamma_{i,j}} c^A(x_{i,j}) \frac{d}{dx} c^A(x_{i,j}) = \frac{\gamma_{i,j}}{\gamma_{i,j}} c^A(x_{i,j}) \frac{d}{dx} c^A(x_{i,j})
$$

(44)

Equations (43) and (45) can be solved for $c^A(x_{i,j})$:

$$
\frac{\gamma_{i,j}}{\gamma_{i,j}} c^A(x_{i,j}) \frac{d}{dx} c^A(x_{i,j}) = \frac{\gamma_{i,j}}{\gamma_{i,j}} c^A(x_{i,j}) \frac{d}{dx} c^A(x_{i,j})
$$

(46)

Now it is possible to substitute for $c^A(x_{i,j})$ in equation (46) and we finally get

$$
\frac{d c^A}{dx}_{[i,j]} = \frac{1}{A_{[i,j]}} \left[ A_{[i,j]} = \sum_{j=1}^{M_2} A_{i,j} c^A(x_{i,j}) \right]
$$

(47)

It follows from equation (29) after insertion of (39), expansion of the sum and introduction of the boundary condition (44):
Again, \( c_1(0, T^*) \) may be calculated. If we insert (43) into (45), we arrive at

\[
\frac{dc_1}{dT} = \beta \left[ \sum_{j=2}^{m_1} \frac{A_{j1} c_j(x_j, T^*)}{A_{1j}} \right] - \frac{1}{T^*} \frac{dc_1}{dT} \]  

(48)

Again, \( c_1(0, T^*) \) may be calculated. If we insert (43) into (45), we arrive at

\[
\frac{dc_1}{dT} = \beta \left[ \sum_{j=2}^{m_1} \frac{A_{j1} c_j(x_j, T^*)}{A_{1j}} \right] - \frac{1}{T^*} \frac{dc_1}{dT} \]  

(49)

\[
\left[ A_{11} - \frac{1}{T^*} \beta \left( \sum_{j=2}^{m_1} \frac{A_{j1} c_j(x_j, T^*)}{A_{1j}} \right) \right] \frac{dc_1}{dT} \]  

The current through the working electrode is given by

\[
I = \alpha F A D \left( \frac{2c_1}{T^*} \right) \]  

(54)

We have shown [2], that Nicholson and Shains current function [44](51) can be related to the dimensionless quantities used in
the transformation equations (20)-(24) by
\[ \frac{\tilde{X}(\tilde{t})}{X(\tilde{t})} = \sqrt{\frac{\alpha}{\pi}} \left( \frac{\partial^2}{\partial x^2} \right) X(0) \] (55)

Thus, calculation of \( x \) or \( y(\tilde{t}) \) requires the calculation of the first derivative of \( \tilde{c}_A \) with respect to \( x \) at the electrode surface. This may be done from equation (36) using equations (66) and (69). It follows

\[ \frac{\tilde{X}(\tilde{t})}{X(\tilde{t})} = \left[ \frac{\partial^2}{\partial x^2} \left( \tilde{c}_A \right) \right] = \left[ \frac{\partial^2}{\partial x^2} \left( \tilde{c}_A \right) \right] \] (56)

**Optimization of the Dimensionless Parameter \( \beta \)**

In the case of a reversible electrode reaction it has been shown that the value of the dimensionless parameter \( \beta \) has a significant influence on the accuracy of the simulation [2]. Also, a method to optimize this value in terms of stability of the solution of the differential equation system has been given [10].


\[ \lambda < \frac{0.45}{|f_0|} \] (57)

which relates the maximum stepwidth of the integration \( h \) to the absolute value of the time derivative of \( x \) at the electrode surface.

For solutions of type (26-30), it is possible to calculate a maximum value of \( \beta \) without causing instability of the solution. For \( \beta = \frac{\partial^2}{\partial x^2} \) requires the calculation of the maximum value of

\[ \tilde{X}(\tilde{t}) \] (58)

from equations (26-28), it is possible to calculate the maximum value of \( \beta \) without causing instability of the solution. For (157) may be fulfilled for all species and collocation points. From equation (47) follows

\[ \lambda = \left( \frac{\partial^2}{\partial x^2} \right) X(0) \] (59)

In analogy equation (50) yields

\[ \lambda = \left( \frac{\partial^2}{\partial x^2} \right) X(0) \] (60)

while equation (55) gives

\[ \lambda = \left( \frac{\partial^2}{\partial x^2} \right) X(0) \] (61)

As in the case of a reversible electron transfer, we have to make sure that (57) is fulfilled at the extreme points of a possible scan, i.e. \( S_i(T) = 0 \) (\( T^* \)) and \( S_i(T) = 1 \) (\( T^* \)).

Inserting the corresponding expressions for \( f_0 \) into inequality (57) would yield inequalities which are difficult to solve for \( \beta \). If we assume, however, that the scan starts at a potential well before the standard potential (which is the general experimental procedure) we can set
Thus, for $a > 0$

$$\theta \gg 1 \quad \text{(62)}$$

and

$$\theta < 1 \quad \text{(63a)}$$

Equations (59) and (60) reduce for $S_i(T') = 0$ to

$$f_y = \alpha \left[ - \frac{B_{ii}}{A_{ii}} A_{ii} + B_{ii} \right] \quad i = 2, \ldots, N+4 \quad \text{(64)}$$

and

$$f_y = \beta \left[ - \frac{B_{ii}}{A_{ii}} A_{ii} + B_{ii} \right] - \mathcal{R} \quad i = 2, \ldots, N+4 \quad \text{(65)}$$

while for $S_i(T') = 1$

$$f_y = \alpha \left[ - \frac{B_{ii}}{A_{ii}} A_{ii} + B_{ii} \right] \quad i = 2, \ldots, N+4 \quad \text{(66)}$$

and

$$f_y = \beta \left[ - \frac{B_{ii}}{A_{ii}} A_{ii} + B_{ii} \right] - \mathcal{R} \quad i = 2, \ldots, N+4 \quad \text{(67)}$$

Finally, stability is maintained if inequalities (68)-(70) are fulfilled.

\[
\begin{align*}
\frac{0.65}{|\beta_i A_i |} & \quad i = 2, \ldots, N+4 \\
\frac{0.65}{|\beta_i A_i |} & \quad i = 2, \ldots, N+4 \\
\frac{0.65}{|\beta_i A_i |} & \quad i = 2, \ldots, N+4 \\
\\end{align*}
\]

As pointed out for the reversible case [10], $\theta$ must be chosen as large as possible to give reliable results.

**RESULTS OF THE CALCULATIONS**

Calculations using the theory derived above have been performed on an AMDahl 470/V4 computer using a dialog program for data input\(^a\). Trial functions have been Legendre polynomials with different degree $N$. Table 1 shows the variation of peak potential separation with $N$ compared to the 'reference' value given by Nicholson [8]. The integration step width was 0.5 (sV), i.e. the simulated cyclic voltammogram between 0.8 and 0.2 (V) was constructed from 1200 data points. The cpu-time needed for different $N$ is also given in Table 1.

For $N = 5$ the peak potential separation is essentially the same as given by Nicholson, the difference being 0.5 (sV), i.e. the same value as the integration step width. For smaller $N$ differ.

\(^a\) Copies of the program which also contains other electrochemical reaction models are available on request.
deviates considerably. The cpu-time, however, decreases. According to this result, all further simulations have been performed with $N = 9$. Table 2 shows variation of $\Delta E_p$ with the kinetic parameter $\Psi$ which is connected to Nicholson's parameter $\Psi$ [8] by

$$\Psi' = \Psi \sqrt{\pi}$$

The maximum deviation from Nicholson's data is 1.5 (mV), a very low value considering that $\Delta E_p$, the integration step width, is 0.5 (mV). It should be noted here that Nicholson's values are simulated as well. With approximately 2.5 cpu-seconds needed for 1200 data points, the program works fast and efficient.

**CONCLUSION**

The technique of orthogonal collocation can be applied to simulate quasireversible electrode processes under potential sweep conditions. The equations describing the time dependence of the concentration of all species are formally very similar to those derived for reversible electron transfers. The dimensionless parameter $\Psi$ can be optimised in terms of stability of the solution of the differential equation system. The numerical results calculated for the "pure" quasireversible electron transfer (i.e., without homogeneous kinetic complications) are very close to the reference values given by Nicholson [8] and computed by a totally different method.

The application of this work is obviously the interpretation of more complicated electrode reaction mechanisms where homogeneous chemical reactions are coupled to the quasireversible electron transfer. The expansion of the theory given here to those cases is, as usual in orthogonal collocation calculations, easily done. Simulation and comparison to experiments with real substrates undergoing complicated reaction sequences will be shown in a further paper.
ACKNOWLEDGMENTS

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REFERENCES

Table 1. Simulations of a quasireversible electrode process with polynomials of different degree N.

<table>
<thead>
<tr>
<th>N</th>
<th>( \Delta E_p ) (mV)</th>
<th>( \Delta E_p^{o3} )</th>
<th>( \Delta E_p^{red} )</th>
<th>cpu-time (s)</th>
<th>( \Delta E_p ) (mV)</th>
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<td>6</td>
<td>110.5</td>
<td>-0.4040</td>
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<td>7</td>
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<td>0.2370</td>
<td>2.536</td>
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a) This work, \( \Delta E = 0.5 \) (mV), \( \gamma = 0.88623 \).
b) Nicholson, ref. [8], \( \gamma = 0.5 \) (\( \gamma = 0.88623 \)).

Table 2. Simulations of a quasireversible electrode processes by orthogonal collocation, variation of \( \gamma' \).

<table>
<thead>
<tr>
<th>( \gamma' )</th>
<th>( \gamma^{1} )</th>
<th>( \Delta E_p^{3} ) (mV)</th>
<th>( \Delta E_p^{3} ) (mV)</th>
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<tr>
<td>0.17725</td>
<td>0.1</td>
<td>210.5</td>
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<tr>
<td>0.44111</td>
<td>0.35</td>
<td>104.0</td>
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<td>0.62036</td>
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<td>120.5</td>
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<td>0.84623</td>
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<td>1.3291</td>
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<td>5.1174</td>
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<td>7.0998</td>
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<td>8.8623</td>
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<td>10.6347</td>
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<td>63</td>
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<tr>
<td>35.4491</td>
<td>20</td>
<td>60.0</td>
<td>61</td>
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a) This work, \( \Delta E = 0.5 \) (mV), \( \gamma = 9 \), \( |\Delta E_p^{3} - \gamma' \Delta E_p^\gamma| < 0.14 \) (mV).
b) Nicholson, ref. [8], \( |\Delta E_p^{3} - \gamma' \Delta E_p^\gamma| < 0.14 \) (mV).
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