Cellular Automata for Electrochemistry.
A Practical Approach to the Understanding of Voltammograms
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ABSTRACT
One-dimensional multicomponent cellular automata, with the addition of a reactive boundary, can model electrochemical processes such as cyclic voltammetry. Electron transfer probabilities at the boundary are derived from the Butler-Volmer type kinetic equation. The model is applied successfully to coupled irreversible systems in which an escaping species is involved in addition to oxidized and reduced species.

Keywords : Cellular Automata, Simulation of E-I and I-t Relations, Cyclic Voltammetry, Pedagogical Approach

1. Introduction

Cyclic voltammetry, one of the most popular electrochemical methods, is widely used for the diagnosis of chemical reactions and the analysis of the species participating in the reactions. The interpretation of cyclic voltammograms, however, requires some experience since the peaks result from the interaction of reactions and the analysis of the species participating in the chemical methods, is widely used for the diagnosis of chemical species. The internal state of each cell is represented by the vector $p^i$, which designates the concentration of the two species at time $t = k\Delta t$ and position $x = i \Delta x$ as

$$P^i = \begin{pmatrix} P(Ox) \\ P(Rd) \end{pmatrix}$$

where $P(Ox)$ and $P(Rd)$ are the concentrations of oxidized (Ox) and reduced (Rd) forms, respectively. In the region where the boundary has no effect, the transition is described by the following set of recursion equations,

$$P^{i+1}_j = q_j P^{i-1}_j + (1 - \Gamma) P^i_j + \Gamma P^{i+1}_j \quad (i \geq 2)$$

$$P^{i+1}_i = q_0 P^{i-1}_i + (1 - \Gamma) P^i_i + \Gamma P^{i+1}_{i+1} \quad (i = 1)$$

where $p$ and $q$ are the probabilities for moving to the left and right adjacent cells, respectively. $q_0 = 1 - p_0$ is the probability of moving out of the electrode. $\Gamma$ is a diagonal matrix having the form

$$\Gamma = \begin{pmatrix} \gamma(Ox) & 0 \\ 0 & \gamma(Rd) \end{pmatrix}$$

where $\gamma(Ox)$ and $\gamma(Rd)$ denote the values of $\gamma$ specific to the species; the diffusion coefficient is proportional to $\gamma(0 < \gamma \leq 1)$.

At the boundary ($i=0$), on the other hand, it is necessary to specify how Ox and Rd are produced or converted to each other on the electrode. For this purpose, the following transition rules are introduced.

(i) Ox changes to Rd with a probability of $r_1 p_0$. Ox thus remains unchanged with a probability of $(1 - r_1) p_0$.

(ii) Rd changes to Ox with a probability of $r_2 p_0$. Ox thus remains unchanged with a probability of $(1 - r_2) p_0$.
Here the reaction probabilities \( r_t \) and \( r_b \) are implicit functions of the potential on the electrode, \( E \). \( p_0 \) is the probability of moving toward the boundary and is set to 1/2 in this study.

The rules (i) and (ii) are effected by the first term of the following boundary condition

\[
P_{0}^{t+1} = p_0 A P_0^t + p \Gamma P_1^t
\]

where \( A \) is a 2 × 2 transition matrix defined by

\[
A = \begin{pmatrix}
1 - r_t & r_b \\
r_t & 1 - r_b
\end{pmatrix}
\]

The second term of Eq. (6) comes from the species diffusing from the cell at \( i = 1 \).

The electrical current \( I \) for time \( t = k \Delta t \) may be given by

\[
l = w[r_1 P_0^t(\text{Ox}) - r_b P_0^t(\text{Rd})]
\]

where \( w \) is a constant that may depend on experimental parameters, but hereafter it is set simply to unity.

### 2.2 1D-CA for coupled irreversible systems

Some systems deviate from Scheme (1), as shown in Scheme (9).

\[
\text{Ox} + ne^{-} \xleftrightarrow{k_i} \text{Rd} \xrightarrow{k_b} \text{Ex}
\]

(9)

Here \( \text{Rd} \) may lead to another species \( \text{Ex} \) that escapes from the electrochemical system with the rate constant \( k_b \). This behavior is possible, for example, if \( \text{Ex} \) is a radical.\(^4\) This type of reactions is often called coupled irreversible system.\(^5\)

The variable \( P_1^t \) now contains three components:

\[
P_1^t = \begin{pmatrix}
P(\text{Ox}) \\
P(\text{Rd}) \\
P(\text{Ex})
\end{pmatrix}
\]

(10)

which satisfies the recursion relation (3) and the boundary condition (6). The transition matrix (7) should be modified as follows.

\[
A = \begin{pmatrix}
1 - r_t & r_b & 0 \\
r_t & 1 - r_b & 0 \\
0 & 0 & 0
\end{pmatrix}
\]

(11)

It is possible that \( \text{Ox} \) has an escape channel, and such systems can be modeled by

\[
\text{Ex} \xrightarrow{k_i} \text{Ox} + ne^{-} \xleftrightarrow{k_b} \text{Rd}
\]

(12)

and the transition matrix becomes

\[
A = \begin{pmatrix}
1 - r_t & r_b & 0 \\
r_t & 1 - r_b & 0 \\
r_e & 0 & 0
\end{pmatrix}
\]

(13)

### 2.3 Reaction probabilities at the boundary

In order to determine the values of \( r_t \) and \( r_b \), let us start with the Butler-Volmer type kinetic formula.\(^6\)

\[
\frac{d[Rd]}{dt} = k_b e^{-\alpha n E/V_T} [\text{Ox}] - k_0 e^{\beta n E/V_T} [\text{Rd}]
\]

(14)

\[
e = E - E_{eq}
\]

where \([\text{Rd}]\) and \([\text{Ox}]\) are concentrations of \( \text{Rd} \) and \( \text{Ox} \), respectively, and \( E_{eq} \) is the equilibrium potential at which no current flows. The prefactors \( k_b \) and \( k_0 \) implicitly depend on the electrode potential \( E \). The positive parameters \( \alpha \) and \( \beta \) satisfy the relation \( \alpha + \beta = 1 \). The voltage parameter \( V_T = k_b T/e \) approximately equals 25 mV, where \( k_b \) is the Boltzmann constant, \( e \) the elementary charge, and \( T \) the absolute temperature.

For an infinitesimal change \( t \to t + \Delta t \), Eq. (14) leads to

\[
X(t + \Delta t) = \begin{pmatrix}
1 - \Delta t k_0 e^{(-\alpha n E/V_T)} & \Delta t k_0 e^{(\beta n E/V_T)} \\
\Delta t k_0 e^{(-\alpha n E/V_T)} & 1 - \Delta t k_0 e^{(\beta n E/V_T)}
\end{pmatrix} X(t)
\]

(15)

where

\[
X(t) = \begin{pmatrix}
[\text{Ox}] \\
[\text{Rd}]
\end{pmatrix}
\]

(16)

The transition probabilities for such short time steps can be written as

\[
r_t = \Delta t [k_b e^{(-\alpha n E/V_T)} + O(\Delta t)]
\]

(17)

\[
r_b = \Delta t [k_0 e^{(\beta n E/V_T)} + O(\Delta t)]
\]

(18)

where higher-order terms in \( \Delta t \) have been taken into consideration. The transition probabilities \( r_t \) and \( r_b \) are not necessarily what we seek for, however, since the time resolution in the observation is many orders of magnitude larger than that for molecular dynamics.

Here let us assume that the relative transition probabilities change only a little as the value of \( \Delta t \) is increased. Equations (17) and (18) thus lead to a relation applicable to 1D-CA,

\[
\frac{r_t}{r_b} = K_{RO} e^{(-\alpha n E/V_T)} + O(\Delta t)
\]

(19)

where \( K_{RO} \) is defined by

\[
K_{RO} = \frac{k_b}{k_0}.
\]

(20)

Let us further assume that the correction term of \( \Delta t \) is of little importance. Since the probabilities should obey the restriction \( r_t, r_b \leq 1 \), a reasonable choice of the transition probabilities may be the following set of equations,

\[
r_t = \frac{K_{RO}}{1 + K_{RO} e^{(-\alpha n E/V_T)} + \exp[\beta n E/V_T]} e^{(-\alpha n E/V_T)}
\]

(21)

\[
r_b = \frac{1}{1 + K_{RO} e^{(-\alpha n E/V_T)} + \exp[\beta n E/V_T]}
\]

(22)

but these relations can readily be arranged to the following forms,

\[
r_t = \frac{1}{1 + K_{RO} e^{-n(E - E_{eq})/V_T}}
\]

(21)

\[
r_b = \frac{1}{1 + K_{RO} e^{-n(E - E_{eq})/V_T}}
\]

(22)

Note that Eqs. (21) and (22) are allowed to be multiplied by the same factor.

### 3. Results and Discussion

The preceding algorithm has been implemented on the personal computer, and already been applied to the step response and cyclic voltammograms for simplest systems.\(^7\)

The algorithm is now applied to the coupled irreversible system (9). The electrode potential is changed in such a way that \( E = E_i \to E_b \to E_j \to E_b \to \cdots \). The potential is changed gradually with a step size \( \Delta E \), and at each value of \( E \) the calculation is iterated \( N_{step} \) times. Therefore the sweep rate \( v \) is proportional to \( 1/N_{step} \).

The following parameters have been chosen: \( E_i = 0 \, mV \), \( E_b = -1000 \, mV \), \( E_j = -500 \, mV \), \( |\Delta E| = 10 \, mV \), \( \gamma = 1 \), and \( K_{RO} = 1 \). The spatial range was \( i = 0, 1, 2, \ldots, N_i - 1 \) with \( N_i = 256 \). For the escape channel we have chosen \( r_e = k_0 T/e \) with \( k = 0.2 \).
The results are shown for $N_{\text{step}} = 8$ and $N_x = 256$ in Fig. 2(a) and for $N_{\text{step}} = 64$ and $N_x = 512$ in Fig. 2(b). Note that the intensity decreases gradually because of the escape channel.

These figures, with the calculations for more values of $N_{\text{step}}$, suggest that the peak position shifts systematically as $v$ is increased and that the peak intensity increases essentially in proportion to $\sqrt{v}$. The calculations for Scheme (12) yield similar increases in the peak intensity but opposite shifts in the peak position.

4. Conclusion

The transition probabilities Eqs. (21) and (22) have been derived from the basic kinetic equation. The features of the coupled irreversible systems (9) and (12) have been accounted for, and the extension to more complex systems is within the scope of the present 1D-CA.

References


Figure 2. (Color online) Cyclic voltammograms for the coupled irreversible system (9). $r_e = 0.2 r_i$. The ordinate is in arbitrary units.
(a) $N_{\text{step}} = 8$ and $N_x = 256$. (b) $N_{\text{step}} = 64$ and $N_x = 512$. 

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