

Development of Electrochemical Analyzer for Polymer-Coated Electrode

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A program, called PLEC-1, has been developed with Visual Basic to simulate and analyze the electrochemical measurement of a polymer-coated electrode with dispersed functional molecules. The program has two independent buffers for oxidant and reductant per one material and can concurrently treat seven materials and three chemical reactions of either first- or second-order. The user can not only experience virtual cyclic voltammetry and potential-step chronoamperometry but also analyze cyclic voltammograms by the Gauss-Newton method using the program. In PLEC-1, simultaneous partial differential equations are solved by the combination of Crank-Nicolson and iteration methods.

Keywords: Electrochemical analyzer, Polymer-coated electrode, Iterative Crank-Nicolson method, Cyclic voltammogram, PLEC-1

1 Introduction

Increasing attention has been paid to polymer metal complexes since these complexes were synthesized in the 1950's [1–3]. Since many studies have been done on electrodes modified with these complexes [4–16], these electrodes have come to be applied in chemical sensors [4], electrocatalysis [5, 6], and fuel cell power systems. These electrodes have a potential to develop new devices because of many combinations of a polymer matrix and a functional complex.

For developing high-performance devices, it is important to understand the processes involved in the system. The processes are described as follows: After the oxidized or reduced species is produced on a base electrode, the concentration distribution of the species changes constantly not only by the diffusion of the redox species but also by the following chemical reactions. Hence, the analysis used in a homogeneous solution cannot be applied to the electrode system except in a few cases. Such a situation can be expressed by partial differential equations, which can be solved not analytically but numerically. However, a computer with a high process capability is required to solve the equations. In 2002, the capa-

bility of a personal computer, e.g., the Pentium III machine, becomes more than six times as high as that of a first commercial supercomputer, CRAY-1 (80MFLOPS), which would be enough to solve the equations.

In the present study, we have developed a program, called PLEC-1, which can simulate electrochemical measurements with a polymer-coated electrode, and analyze cyclic voltammograms by the Gauss-Newton method. PLEC-1 can simultaneously treat seven materials and three reactions in both simulation and analysis.

2 Design of an Electrochemical Analyzer

Figure 1 shows a polymer-coated electrode with up to seven kinds of dispersed or covalently bonded materials soaked in an electrolyte solution. It was assumed that a conventional three-electrode system is employed in the electrochemical measurement. PLEC-1 has two buffers per one material to estimate the concentration distribution of an oxidant and a reductant independently.

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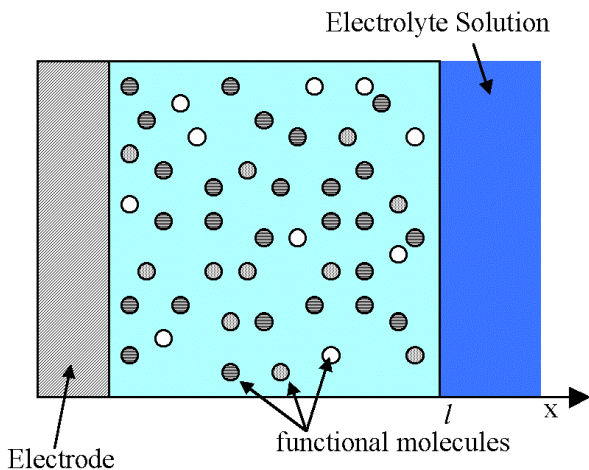


Figure 1. Illustration of a polymer-coated electrode soaked in an electrolyte solution.

The program can treat four kinds of chemical reactions as follows:



where S is a substrate, P a product, E an enzyme, and B a by-product. k_f (s^{-1} or $\text{mol}^{-1}\text{cm}^3\text{s}^{-1}$) and k_b are rate constants of a forward reaction and backward reaction, respectively.

2.1 Diffusion equations in the bulk of the polymer

In a solution, almost all the electrons are transferred by physical diffusion of the redox species. Whereas in a polymer matrix, the electrons are transferred not only by the physical diffusion but also electron hopping because the physical diffusion is suppressed in the polymer matrix. In such a case, when a material exists in a polymer matrix homogeneously, the molar flux of the electrons is proportional to the concentration gradient [13, 14], which is known as Fick's law.

However, when a material is localized in the polymer matrix because of chemical reactions, the molar flux of

electrons by electron hopping is not always represented by Fick's law. Such a situation causes the reversal of electric potential calculated by Nernstian equation in the direction of electron propagation. Hence, we assumed that the molar flux of electrons by electron hopping, J_{hop} ($\text{mol cm}^2 \text{s}^{-1}$) is expressed by

$$J_{hop,m} = -D_{hop,m} \frac{\partial R_{CT,m}}{\partial x} C_{T,m} \quad (5)$$

where $R_{CT,m}$ is the fraction of charge-transported (or electron-transported) sites, $D_{hop,m}$ ($\text{cm}^2 \text{s}^{-1}$) is an electron hopping diffusion coefficient which is defined by

$$D_{hop,m} = k_{ex,m}' C_{T,m} \quad (6)$$

where $k_{ex,m}'$ ($\text{mol}^{-1} \text{cm}^5 \text{s}^{-1}$) is the rate constant of an electron self-exchange, $C_{T,m}(0, t)$ (mol cm^{-3}) the total concentration of material- m . When the material exists in the matrix homogeneously, eq. 5 is compatible with Fick's law.

Assuming that Material- m ($1 \leq m \leq 7$) consists of an oxidant (abbreviated to ox) and a reductant (abbreviated to rd), the diffusion equations of the oxidant, $C_{ox,m}(x, t)$ (mol cm^{-3}) and reductant, $C_{rd,m}(x, t)$ (mol cm^{-3}) are represented as

$$\begin{aligned} \frac{\partial C_{ox,m}}{\partial t} = & D_{phys,m} \frac{\partial^2 C_{ox,m}}{\partial x^2} \\ & + D_{hop,m} \left(\frac{\partial^2 R_{CT,ox,m}}{\partial x^2} C_{T,m} + \frac{\partial R_{CT,ox,m}}{\partial x} \frac{\partial C_{T,m}}{\partial x} \right) \\ & - R_{ox,m}(0, t) \end{aligned} \quad (7)$$

$$\begin{aligned} \frac{\partial C_{rd,m}}{\partial t} = & D_{phys,m} \frac{\partial^2 C_{rd,m}}{\partial x^2} \\ & + D_{hop,m} \left(\frac{\partial^2 R_{CT,rd,m}}{\partial x^2} C_{T,m} + \frac{\partial R_{CT,rd,m}}{\partial x} \frac{\partial C_{T,m}}{\partial x} \right) \\ & - R_{rd,m}(0, t) \end{aligned} \quad (8)$$

where $D_{phys,m}$ ($\text{cm}^2 \text{s}^{-1}$) is a physical diffusion coefficient of Material- m ($1 \leq m \leq 7$), $R_{ox,m}(0, t)$ ($\text{mol cm}^{-3} \text{s}^{-1}$) and $R_{rd,m}(0, t)$ are the sums of catalytic reaction rates of the oxidant and the reductant, respectively. A boundary condition at the interface between the polymer layer and the electrolyte solution is expressed by

$$\frac{\partial C_m(l, t)}{\partial x} = 0 \quad (\text{B.C})$$

where l (cm) is the thickness of the polymer layer.

2.2 Interface between the electrode and the polymer layer

The electrode reactions are classified into three types by the exchange current density: reversible, irreversible, and inactive. When the exchange current density is large, the redox reaction is reversible [17], whereas when the exchange current density is so small that the ratio of the species does not obey a Nernstian equation, the redox reaction is irreversible [18]. “Inactive” means that the electron exchange between the electrode and a material doesn’t take place in a potential range.

(a) Reversible reaction on a base electrode

Assuming that the concentration ratio on the electrode obeys a Nernstian equation, the concentration of the oxidant on the electrode is represented as

$$C_{ox,m}(0,t) = \frac{C_{T,m}(0,t)}{\left[1 + \exp\left\{-\frac{n_m F}{RT}(E - E_m^\circ)\right\}\right]} \quad (9)$$

where n_m is the number of electrons transferred between the species, F ($C \text{ mol}^{-1}$) the Faraday constant, E_m° (V) the redox potential of the material- m , and E (V) the applied potential on the electrode.

The concentration of the reductant, $C_{rd,m}(0, t)$ (mol cm^{-3}), is expressed as

$$C_{rd,m}(0,t) = C_{T,m}(0,t) - C_{ox,m}(0,t) \quad (10)$$

(b) Irreversible reaction on a base electrode

Total material balance of the species in the immediate neighborhood of the electrode is expressed as

$$SN_{ox,m}(0,t) - \left\{ S\Delta x \frac{\partial C_{ox,m}(0,t)}{\partial t} + S\Delta x R_{ox,m}(0,t) \right\} = SN_{ox,m}(\Delta x, t) \quad (11)$$

$$SN_{rd,m}(0,t) - \left\{ S\Delta x \frac{\partial C_{rd,m}(0,t)}{\partial t} + S\Delta x R_{rd,m}(0,t) \right\} = SN_{rd,m}(\Delta x, t) \quad (12)$$

where S (cm^2) is the area of the electrode, $N_{ox,m}$ (mol cm^{-2}) and $N_{rd,m}$ are the molar fluxes of charges and electrons, respectively. Molar fluxes of the species on the electrode are expressed as

$$N_{ox,m}(0,t) = k_{2,m}C_{rd,m}(0,t) - k_{1,m}C_{ox,m}(0,t) \quad (13)$$

$$N_{rd,m}(0,t) = k_{1,m}C_{ox,m}(0,t) - k_{2,m}C_{rd,m}(0,t) \quad (14)$$

where $k_{1,m}(t)$ (cm s^{-1}) and $k_{2,m}(t)$ are the rate constants for the reduction and the oxidation of the material- m by the electrode, respectively. These constants are defined as functions of electrode potential:

$$k_{1,m} = \frac{i_{0,m}'}{n_m F} \exp\left[-\frac{\alpha_m n_m F (E - E_m^\circ)}{RT}\right] \quad (15)$$

$$k_{2,m} = \frac{i_{0,m}'}{n_m F} \exp\left[\frac{(1 - \alpha_m) n_m F (E - E_m^\circ)}{RT}\right] \quad (16)$$

where $i_{0,m}'$ ($A \text{ mol}^{-1} \text{ cm}$) is the exchange current density at 1 mol cm^{-3} of material- m , and α_m the transfer coefficient.

(c) In case of an inactive material

When the material- m and the electrode do not exchange charges and electrons, boundary conditions are expressed as

$$\frac{\partial C_{ox,m}(0,t)}{\partial x} = 0 \quad (17)$$

$$\frac{\partial C_{rd,m}(0,t)}{\partial x} = 0 \quad (18)$$

2.3 The finite difference method used in PLEC-1

The finite difference method is widely used for approximating solutions to partial difference equation (PDE) problems [19], and classified into three types: explicit, implicit, and iteration. The forward difference method belonging to the explicit types is simple and easy to implement. However, a very small time step is often needed for accuracy.

Implicit types allow using larger values of Δt . The Crank-Nicolson method reduces the error in time by using an average of the terms evaluated at time t and $t + \Delta t$.

When an electron exchange reaction between a base electrode and a material is slow or the chemical reactions are included in the electrode system, the Crank-Nicolson method cannot be applied to solve PDEs. Thus, we adopted an “iterative” Crank-Nicolson method in the program as mentioned below. The following equations do not include the charge hopping mechanism to explain the iterative Crank-Nicolson method concisely.

(a) Irreversible reaction on a base electrode

When the electron exchange reaction is slow, the finite differential equation of the oxidant evaluated as an average at the time $t = j$ and $j - 1$ is expressed by

$$(2 + k_{1,m}(j)r\Delta x)C_{ox,m}(0,j) + D_m r C_{ox,m}(1,j)$$

$$-D_m r C_{ox,m}(2,j)$$

$$= (2 - k_{1,m}(j-1)r\Delta x)C_{ox,m}(0,j-1)$$

$$-D_m r C_{ox,m}(1,j-1) + D_m r C_{ox,m}(2,j-1)$$

$$+ \{k_{2,m}(j)C_{rd,m}(0,j)$$

$$+ k_{2,m}(j-1)C_{rd,m}(0,j-1)\}r\Delta x \quad (19)$$

where D_m ($\text{cm}^2 \text{s}^{-1}$) is an apparent diffusion coefficient of electrons through Material- m ($1 \leq m \leq 7$), r ($\text{cm}^{-2} \text{s}$) is defined by

$$r = \Delta t / \Delta x^2 \quad (20)$$

The diffusion equation of a reductant is represented as

$$(2 + k_{2,m}(j)r\Delta x)C_{rd,m}(0,j) + D_m r C_{rd,m}(1,j)$$

$$-D_m r C_{rd,m}(2,j)$$

$$= (2 - k_{2,m}(j-1)r\Delta x)C_{rd,m}(0,j-1)$$

$$-D_m r C_{rd,m}(1,j-1) + D_m r C_{rd,m}(2,j-1)$$

$$+ \{k_{1,m}(j)C_{ox,m}(0,j)$$

$$+ k_{1,m}(j-1)C_{ox,m}(0,j-1)\}r\Delta x \quad (21)$$

Eqs. 19 and 21 have the other unknown quality; eq. 19 has $C_{rd,m}(0,j)$ and eq. 21 has $C_{ox,m}(0,j)$. Hence, each equation can be solved not independently but simultaneously. Two methods were considered to solve the equations.

One is the method where we must solve the large matrix containing the two species. In this method, it is complicated to accelerate the Gauss method for solving the simultaneous equations, and the second-order chemical reactions cannot be treated by the method.

The other is an "iterative" Crank-Nicolson method. Although the amount of calculation is higher than the above method, it is easy to introduce the calculation of the chemical reactions into the program. However, this method may not have the stability and accuracy of the Crank-Nicolson method.

In the present study, the "iterative" Crank-Nicolson method was adopted for solving PDEs including the second-order chemical reactions.

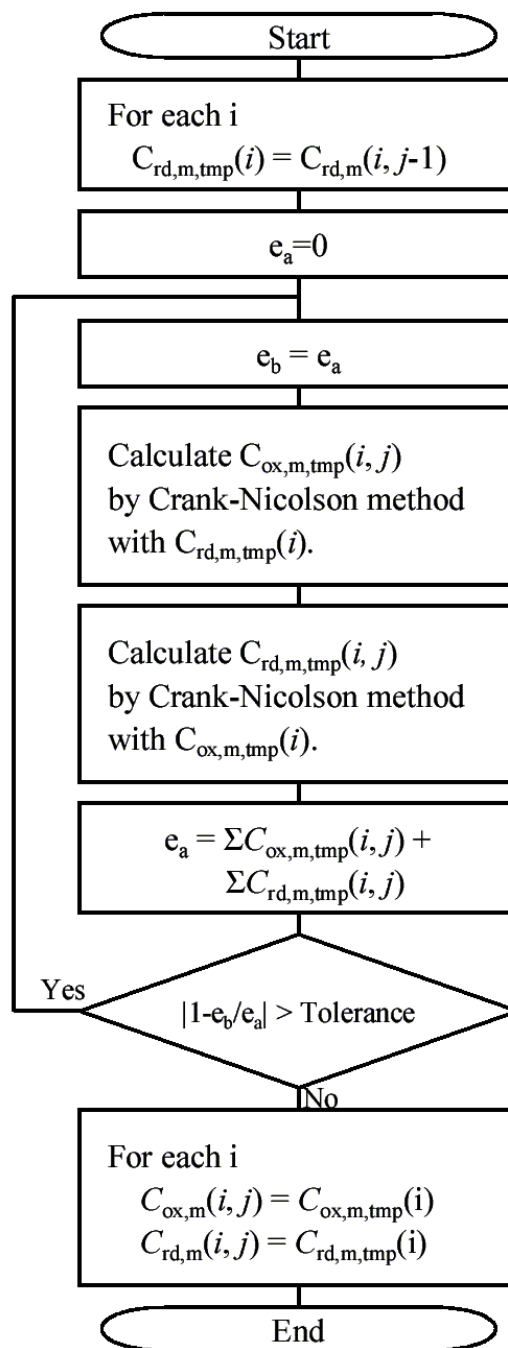


Figure 2. Simplified flow chart of the estimation of the concentration distribution under the condition where the electron exchange reaction is the rate-determining step on the electrode. $C_{ox,m,tmp}(i)$ and $C_{rd,m,tmp}(i)$ are temporary variables, respectively.

As mentioned above, eq. 19 which is the finite difference equation of the oxidant contains the unknown reductant concentration, $C_{rd,m}(i, j)$, and eq. 21 for the $C_{rd,m}(i, j)$ also contains the unknown oxidant concentration, $C_{ox,m}(i, j)$. The following procedures were adopted for solving problems: First, $C_{rd,m}(i, j-1)$ was substituted for an initial value of $C_{rd,m}(i, j)$. Eq. 19 and eq. 21 were solved alternately until tolerance was satisfied. The simplified flow chart is shown in Figure 2.

(b) Following chemical reaction with reversible reaction on base electrode

We obtained a finite differential equation of a substrate in a bulk polymer by evaluating an average at the time $t = j$ and $j - 1$ as

$$\begin{aligned} & -D_s r C_s(i-1, j) + (2 + 2D_s r + Q_f(i, j)\Delta t) C_s(i, j) \\ & -D_s r C_s(i+1, j) = D_s r C_s(i-1, j-1) \\ & + (2 - 2D_s r - Q_f(i, j-1)\Delta t) C_s(i, j-1) \\ & + D_s r C_s(i+1, j-1) \\ & + \frac{1}{2} \{R_b(i, j) + R_b(i, j-1)\} \Delta t \end{aligned} \quad (22)$$

where D_s ($\text{cm}^2 \text{s}^{-1}$) is the diffusion coefficient of the substrate, C_s (mol cm^{-3}) is the concentration of the substrate, R_b ($\text{mol cm}^{-3} \text{s}^{-1}$) is the increasing concentration caused by the reverse reaction, and the relation between Q_f (s^{-1}) and R_f ($\text{mol cm}^{-3} \text{s}^{-1}$) is expressed by

$$Q_f(i, j) = R_f(i, j) / C_s(i, j) \quad (23)$$

In the same manner as above, the finite difference equation of a product in the bulk polymer is represented as

$$\begin{aligned} & -D_p r C_p(i-1, j) + (2 + 2D_p r + Q_b(i, j)\Delta t) C_p(i, j) \\ & -D_p r C_p(i+1, j) = D_p r C_p(i-1, j-1) \\ & + (2 - 2D_p r - Q_b(i, j-1)\Delta t) C_p(i, j-1) \\ & + D_p r C_p(i+1, j-1) \\ & + \frac{1}{2} \{R_f(i, j) + R_f(i, j-1)\} \Delta t \end{aligned} \quad (24)$$

where D_p ($\text{cm}^2 \text{s}^{-1}$) is the diffusion coefficient of the product and C_p (mol cm^{-3}) is the concentration of the

product. The relation between Q_b (s^{-1}) and R_b ($\text{mol cm}^{-3} \text{s}^{-1}$) is given by

$$Q_b(i, j) = R_b(i, j) / C_p(i, j) \quad (25)$$

For example, when the chemical reaction expressed by eq. 1 takes place in the polymer layer of the electrode, eq. 22 contains an unknown quantity, $C_p(i, j)$, because R_b is defined by eq. 25. Eq. 22 cannot be solved independently, so the following procedures were adopted for solving equations: $C_p(i, j-1)$ is substituted for an initial value of $C_p(i, j)$. Until tolerance was satisfied, eq. 22 and eq. 24 were solved alternately as the electrode reaction was irreversible.

In short, the concentrations that should be simultaneously estimated are processed in a loop, and the loop is repeated until tolerance is satisfied, which is the algorithm adopted in PLEC-1.

3 Implementation

We used an IBM/AT compatible in which Microsoft Visual Basic 6(SP5) was installed for developing PLEC-1. The program was tested with Windows 98, Me, and XP installed in IBM/AT compatibles.

4 Feature of PLEC-1

Figure 3 shows the screen shot of PLEC-1 that can simulate the cyclic voltammogram of a polymer coated electrode with up to seven materials and three chemical reactions and is equipped with the analysis of electrochemical properties, concentrations, and reaction rates by the Gauss-Newton method. Table 1 shows the commands of PLEC-1. The details of the usage were described in a help file.

5 Results and Discussion

Stability of iterative Crank-Nicolson method

On the basis of the algorithm, it is anticipated that the stability of the iterative Crank-Nicolson method is between the forward difference and Crank-Nicolson methods. Figure 4 shows cyclic voltammograms simulated with three methods. The cyclic voltammogram calculated by the forward difference diverged at 1.46V, while those by Crank-Nicolson and iterative Crank-Nicolson methods could be simulated without divergence. It is suggested that the iterative Crank-Nicolson method is more stable than the forward difference one.

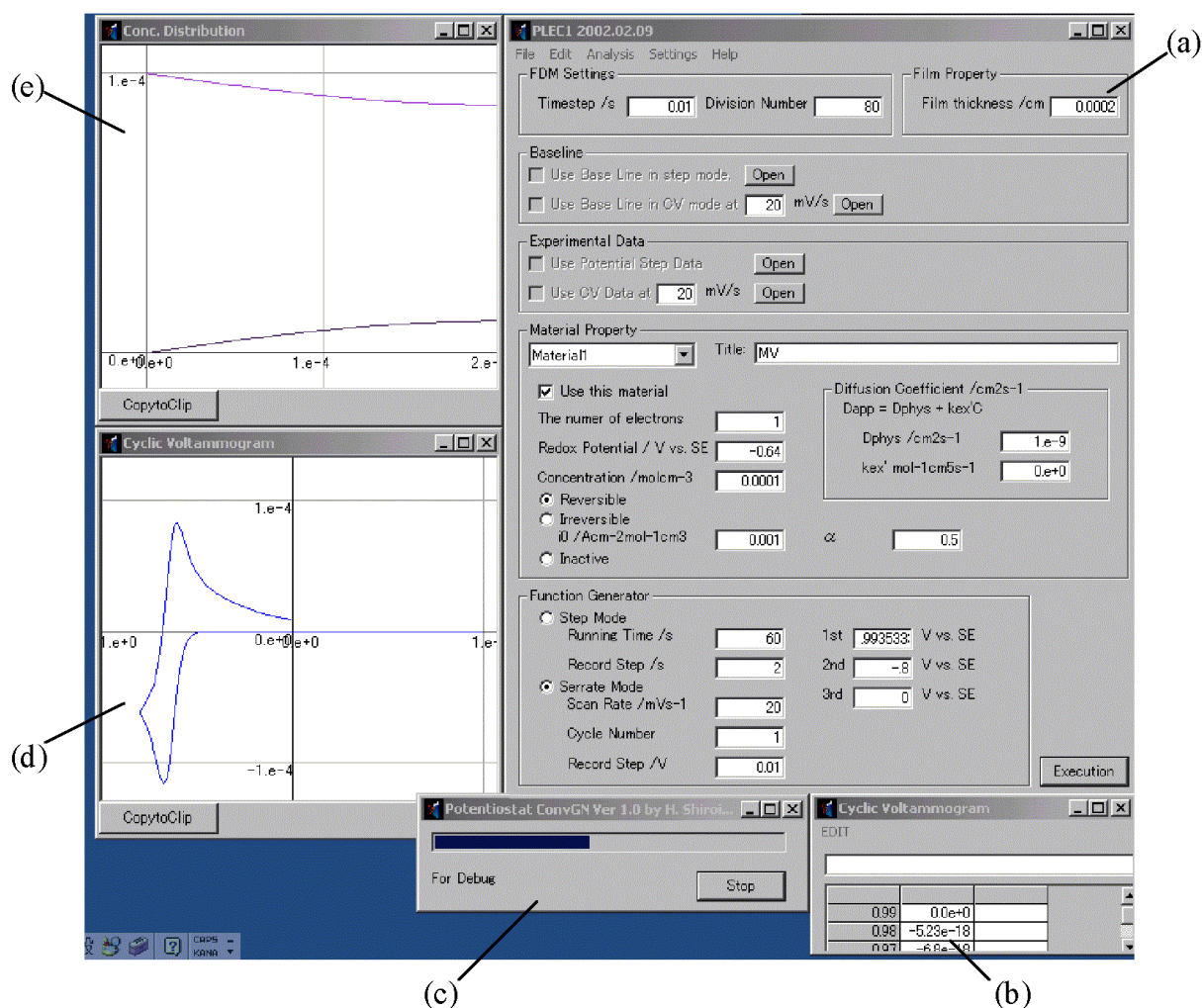


Figure 3. Screen shot of PLEC-1. (a) Control panel. (b) Numerical values of a simulated cyclic voltammogram. (c) Potentiostat PLEC-1. (d) Graph window of cyclic voltammogram. (e) Concentration distribution of material species.

Table 1. Commands in PLEC-1.

	Menu/Submenu	Description
File	Open parameters	Load the parameters from the PLEC-1 format file
	Save parameters	Save the parameters as PLEC-1 format
	Quit	Quit PLEC-1
Edit	Paste parameters	Paste parameters from Microsoft Excel
Analysis	CV analysis (one material)	Analysis of the cyclic voltammogram with Gauss-Newton method
	Concentration Analysis	Concentration analysis using a cyclic voltammogram with Gauss-Newton method
	Reaction Analysis	Reaction analysis using a cyclic voltammogram with Gauss-Newton method
Settings	AVI Setting	Settings for the animation of the concentration distribution graph
	Reaction Setting	Settings for the reactions among materials
	Gauss-Newton Setting	Settings for the Gauss-Newton method
Help	Help	Show help file. (English and Japanese)
	About	Show information about PLEC-1

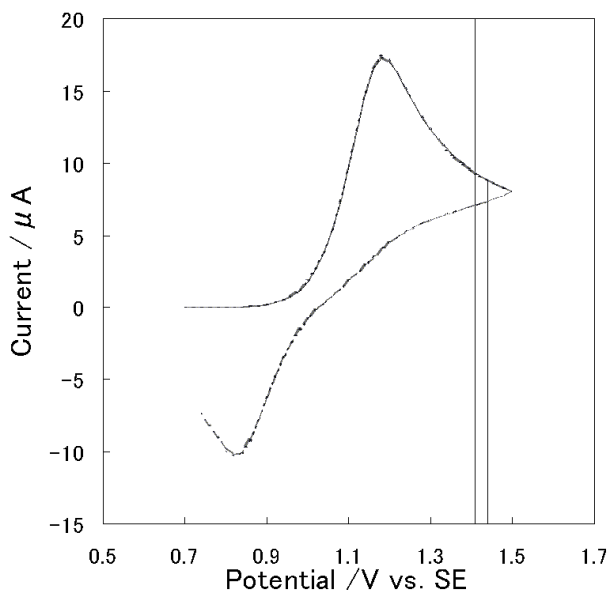


Figure 4. Cyclic voltammogram of a virtual material with three methods. Scan rate is 20mVs^{-1} . —, the forward difference method; ---, Crank-Nicolson method; ···, Iterative Crank-Nicolson method. ($\Delta t = 0.01\text{ s}$, Div. Num. = 40, $l = 1 \times 10^{-4}\text{ cm}$) The properties of the material are as follows: $n = 1$, $E^\circ = 1\text{ V vs. SE}$, $D_{\text{phys}} = 1 \times 10^{-11}\text{ cm}^2\text{ s}^{-1}$, $k_{\text{ex}} = 0\text{ mol}^{-1}\text{cm}^5\text{s}^{-1}$, $C_T = 2 \times 10^{-4}\text{ mol cm}^{-3}$, $i_0 = 1 \times 10^{-2}\text{ Acm}^{-2}\text{mol}^{-1}\text{cm}^3$, $\alpha = 0.5$.

6 Conclusion

We have developed an electrochemical analyzer called PLEC-1 which can simulate the electrochemical behavior of a polymer-coated electrode and estimate the electrochemical properties, concentrations, and reaction rates by the Gauss-Newton method.

7 Agreements for using the program

The “PLEC-1” is freeware. We cannot be responsible for damages that you might receive when using this program. Please feel free to contact us, when you find bugs. We would welcome suggestions for the improvement of the program. The program can be downloaded at the CSJ ftp server.

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高分子修飾電極のための電気化学測定解析 ソフトウェアの開発

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機能性物質分散高分子膜修飾電極の電気化学測定結果を解析するソフトウェア PLEC-1 を作成した。このプログラムはサイクリックボルタモグラム測定およびポテンシャルステップ測定のシミュレーションおよび Gauss-Newton 法による実験データの解析ができる。また、7 種類までの物質と物質間の 1 次と 2 次の化学反応を同時に 3 つまで取り扱うことができる。そのため、1 つの物質に対して酸化体と還元体のための 2 つのバッファを持つ。数値計算は、Crank-Nicolson 法と反復法を組み合わせることによって行われた。

キーワード：電気化学アナライザ, 高分子膜被覆電極, 反復 Crank-Nicolson 法, サイクリックボルタモグラム, PLEC-1