

Visualization of Electrochemical Measurements under Finite Conditions using JAVA and Its Application for Assisted Learning (2)

Hidehiko SHIROISHI^{a,*}, Toshifumi SHOJI^a, Tomoyo NOMURA^a,
Sumio TOKITA^b and Masao KANEKO^{a, ‡}

^aFaculty of Science, Ibaraki University, Bunkyo 2-1-1, Mito, Ibaraki 310-8512, Japan

^bFaculty of Engineering, Saitama University, Shimo-Ohkubo 255, Saitama, Saitama 338-8570, Japan

**e-mail*: cpx26485@mopera.ne.jp

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A program written in JAVA language was developed for the virtual electrochemical measurement of a modified electrode with a finite diffusion thickness, e.g., an electrode coated with polymer film in which functional molecules were dispersed. This program, called ES-2, can simulate cyclic voltammetry and potential-step chronoamperometry by considering the rate of charge injection from the electrode to the functional molecule and the diffusion of charge. The results are shown by a voltammogram (I-V curve), and concentration distribution in the layer at a series of voltages at cyclic voltammogram mode, I-t curve, and time dependence of concentration distribution in the layer at potential step mode and a text of current values, the fraction of the oxidized molecules (R_{CT}) and parameters used for the simulation in both modes. A dynamic textbook of electrochemistry can be constructed by this program combined with HTML text.

Keywords: Finite differential method, Electrochemical measurements, Cyclic voltammogram, Polymer-coated electrode, JAVA, Education

1 Introduction

The processing capabilities of a personal computer increased by two orders of magnitude in the last decade. Today a personal computer is capable of doing many jobs which could be processed only by a workstation before. Theoretical calculation using a personal computer is widely applied to the analysis of experimental data, e.g., chemical equilibrium, the rate of reaction and molecular orbital calculation.

Functional molecules incorporated into a polymer film coated on an electrode have been investigated during the last twenty years [1–4] for wide applications such as chemical sensors [5], electrocatalyses [6] and energy conversion devices [7]. Studies of charge propagation in a polymer membrane are indispensable for developing high-performance devices.

We have made the program, called ES-1, which can simulate an electrochemical behavior using an electrode with a finite diffusion layer under diffusion rate-limiting

step considering a catalytic reaction [8]. When the interaction between the electrode and the functional molecule is weak, it is possible that a charge injection from the electrode to the molecule is the rate-determining step. ES-1 cannot simulate electrochemical behavior under such a condition. It is also difficult to solve the differential equation analytically because the ratio of the reduced molecule concentration to the oxidized one differs from that calculated from the Nernst equation.

From an educational point of view, a dynamic textbook can be made by using the program written in JAVA language because JAVA has the advantage of the affinity for HTML. Construction of such a textbook on the internet has a great significance for the application of information technologies (IT) to university education and lifelong education.

In the present paper, electrochemical behavior considering a finite diffusion layer and the reaction rate between the electrode and the functional molecule confined in a polymer membrane was simulated using JAVA lan-

‡Correspondence to be addressed

guage. A dynamic textbook of electrochemistry was constructed with ES-2 and HTML text.

2 Method

2.1 Theory of an Electrochemical Simulation

The concept of the simulation is shown in Figure 1. An electrode is coated with a finite polymer layer in which functional molecules are dispersed randomly. The electrode is dipped in an electrolyte solution. Electrochemical measurement is performed by a conventional three-electrode system.

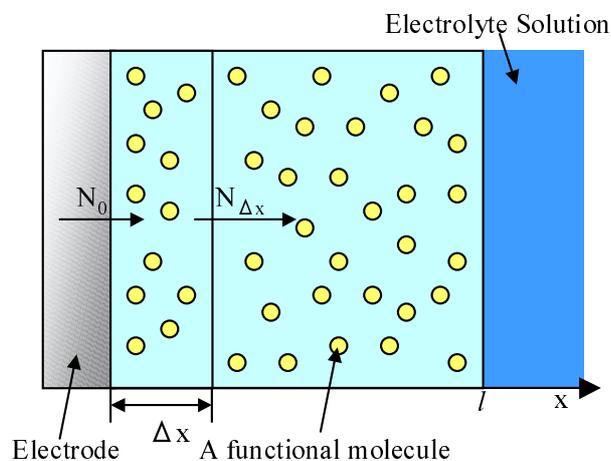


Figure 1. A concept of the electrochemical simulation. The area of the electrode is $S \text{ cm}^2$.

(i) Molar flux in the immediate neighborhood of the electrode

First, charge is injected from the electrode to a reduced molecule in the micro-volume ($S\Delta x$). The injected charge raises the fraction of the oxidized molecules (R_{CT}). The concentration of an oxidized molecule in the micro-volume is reduced by diffusion of the molecules or by a catalytic reaction. Total material balance in the micro-volume ($S\Delta x$) in contact with the electrode is represented as

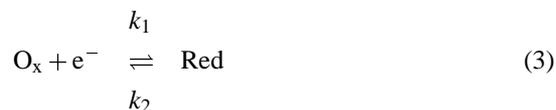
$$SN(0,t) - \left\{ S\Delta x \frac{\partial C_{ox}(0,t)}{\partial t} + S\Delta x R_A(0,t) \right\} = SN(\Delta x,t) \quad (1)$$

where $S \text{ (cm}^2\text{)}$ is the area of the electrode, $N(x,t) \text{ (mol cm}^{-2}\text{s}^{-1}\text{)}$ is the molar flux of charge (or the oxidized molecules), $C_{ox}(x,t) \text{ (mol cm}^{-3}\text{)}$ is the concentration of the oxidized molecule, $R_A(x,t) \text{ (mol cm}^{-3}\text{s}^{-1}\text{)}$ is the rate of the catalytic reaction.

Assuming that convection flux is negligible, $N(\Delta x,t)$ is expressed by Fick's law as

$$N(\Delta x,t) = -D \frac{\partial C_{ox}(\Delta x,t)}{\partial x} \quad (2)$$

A redox reaction between the electrode and the functional molecule is shown by eq. 3



where $k_1 \text{ (cm s}^{-1}\text{)}$ and $k_2 \text{ (cm s}^{-1}\text{)}$ are the rate constants for the reduction and the oxidation of the functional molecules by the electrode, respectively. These constants can be expressed as functions of electrode potential [9]:

$$k_1 = \frac{i_0'}{nF} \exp \left[-\frac{\alpha nF(E - E_{RP})}{RT} \right] \quad (4)$$

$$k_2 = \frac{i_0'}{nF} \exp \left[\frac{(1 - \alpha)nF(E - E_{RP})}{RT} \right] \quad (5)$$

where $i_0' \text{ (Amol}^{-1}\text{cm)}$ is the exchange current density at 1 mol cm^{-3} , n is the charge number of the electrode reaction, α is the transfer coefficient, $E_{RP} \text{ (V)}$ is the redox potential of the molecule, and $E \text{ (V)}$ is the applied potential.

A molar flux from the electrode is represented as

$$N(0,t) = k_2 C_{red}(0,t) - k_1 C_{ox}(0,t) \quad (6)$$

where $C_{red}(0,t) \text{ (mol cm}^{-3}\text{)}$ is the concentration of the reduced molecules. A finite difference equation is derived from eqs. 1, 2 and 6, and used for the simulation [10].

(ii) Diffusion of charge in the bulk of the polymer layer

A diffusion equation in the bulk of the polymer layer is expressed as

$$\frac{\partial C(x,t)}{\partial t} + R_A(0,t) = D \frac{\partial^2 C(x,t)}{\partial x^2} \quad (7)$$

A boundary condition at the interface between the polymer layer and the electrolyte solution is represented as

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

where l is the thickness of the polymer layer.

2.2 Implementation

We used a PC-9821 machine (NEC) with Microsoft Windows 2000. Microsoft Visual J++ version 6(SP3) was installed for developing ES-2. However, Windows Foundation Class library (WFC) was not used to keep a platform-independent feature. ES-2 was tested using PC-9821, IBM/AT compatible, and Macintosh with Internet Explorer and Netscape Navigator.

3 Results and Discussion

3.1 The Feature of ES-2

The combination of ES-2 and electrochemical text written in HTML is shown in Figure 2 [11]. The parameters used for a simulation are shown in Table 1. The feature of ES-2 is similar to that of ES-1. ES-2 has only one button in the control panel for simple operation. A text of electrochemistry written in HTML containing ES-2 can be used for a dynamic textbook. ES-2 shows a voltammogram (I-V curve) and concentration distribution at a series of voltages in the layer in CV mode or a current-time curve and time dependence of concentration distribution in the layer in the potential-step mode (PS mode), and a text of current values, the fraction of the oxidized

molecules and parameters used for the simulation. The results in the text area can be copied by using a shortcut key ([Ctrl]+[C]). Table 2 shows the simulation times in various environments.

3.2 The Result of the Simulation

The time dependence of the concentration distribution at a potential-step measurement is shown in Figure 3. The concentration of the oxidized molecule near the electrode increased gradually at $i_0' = 1.0 \times 10^{-3} \text{ Amol}^{-1}\text{cm}$ (Figure 3(a)) after the potential at which a reduced molecule is oxidized completely under the Nernstian condition was applied, while the curve of the oxidized molecule rose immediately at $1 \text{ Amol}^{-1}\text{cm}$ (Figure 3(b)).

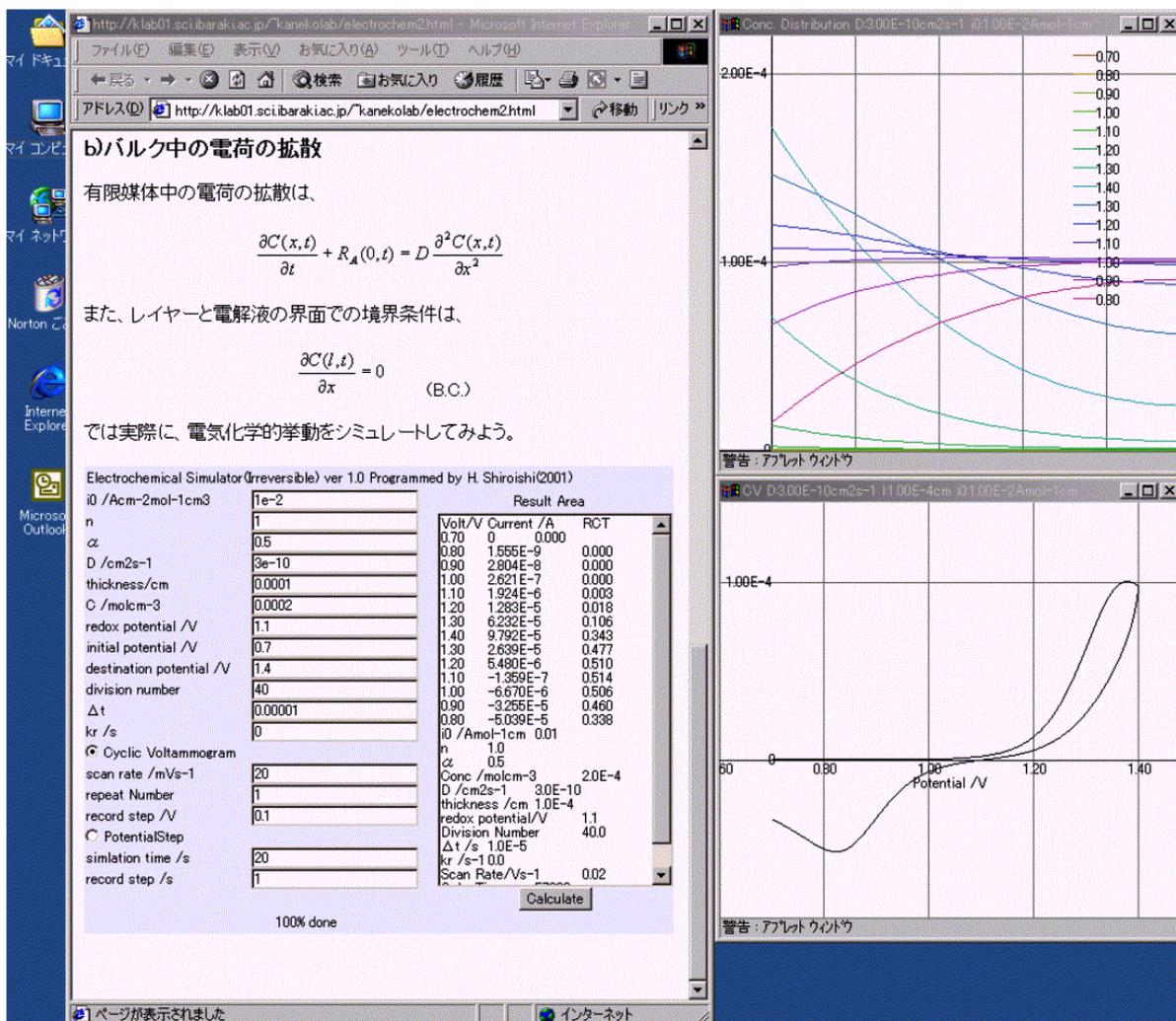


Figure 2. Combination of the ES-2 and electrochemical texts written in HTML.

Figure 4(a) shows a series of cyclic voltammograms at various i_0' values. The decrease of the i_0' value increased the potential difference between the anodic and cathodic peaks, and at the same time their peak current decreased.

Cottrell plots at various i_0' values are shown in Figure 4(b). The current at the initial time reduced with decreasing i_0' value. Further decrease of the i_0' value causes a constant current value in the initial time region.

4 Conclusion

A virtual electrochemical simulator, called ES-2, written in JAVA language, was developed. ES-2 can simulate potential-step measurement and cyclic voltammetry under finite conditions by considering the rate of charge injection from the electrode to the functional molecule and the diffusion of charges. The current value at the initial time reduced with decreasing i_0' value.

Table 1. Parameters used for the simulation.

Caption in ES-2		restriction
$i_0' / \text{Acm}^{-2}\text{mol}^{-1}\text{cm}^3$	exchange current density	$i_0' > 0$
n	the number of electrons	$n > 0$
α	transfer coefficient	$0 < \alpha < 1$
$D / \text{cm}^2\text{s}^{-1}$	diffusion coefficient	$D > 0$
thickness / cm	layer thickness	thickness > 0
$C / \text{mol cm}^{-3}$	concentration of a material	$C > 0$
redox potential / V	redox potential of a material	
initial potential / V	potential induced at initial time	
destination potential / V	maximum potential	
division number	the division number used in the finite difference method	$0 < \text{Div. Num.} < 200$, integer
Δt	time step used in the finite difference method	$\Delta t > 0$
kr / s	first-order rate constant of catalysis	$kr \geq 0$
CV mode		
scan rate / mV s^{-1}	scan rate per second	scan rate > 0
repeat number	cycle number	repeat number > 0 , integer
record step / V	the voltage by which the results are recorded as text and concentration distribution	record step > 0
Potential Step mode		
simulation time / s		simulation time > 0
record step / s	the time by which the results are recorded as text and concentration distribution	record step > 0

Table 2. Simulation times in various environments using default parameters^a

	CPU	machine	OS	browser	Time / s
CV mode ^b	Pentium 90MHz	PC9821Xa	Windows 95	Internet Explorer 4.0	106
	Pentium III 600MHz	IBM PC/AT Compatible	Windows 2000	Netscape Navigator 4.7	14
	Athlon 800 MHz	IBM PC/AT Compatible	Windows 2000	Internet Explorer 5.5	9
	Power PC G4 400MHz	Macintosh	Mac OS 8.6	Internet Explorer 4.5	17
PS mode ^c	Pentium 90 MHz	PC9821Xa	Windows 95	Internet Explorer	359
	Pentium III 600 MHz	IBM PC/AT Compatible	Windows 2000	Netscape Navigator 4.7	48
	Athlon 800 MHz	IBM PC/AT Compatible	Windows 2000	Internet Explorer 5.5	32
	Power PC G4 400MHz	Macintosh	Mac OS 8.6	Internet Explorer 4.5	60

^a $i_0'=0.01\text{A mol}^{-1}\text{cm}^{-3}$, $n=1$, $C=2 \times 10^{-4}\text{mol cm}^{-3}$, $D=3 \times 10^{-10}\text{cm}^2\text{s}^{-1}$, thickness= $1 \times 10^{-4}\text{cm}$, division number=40, $\Delta t=1 \times 10^{-5}\text{s}$, $kr=0\text{ s}^{-1}$

^b repeat number=1, scan rate=20mV/s

^c simulation time=20s

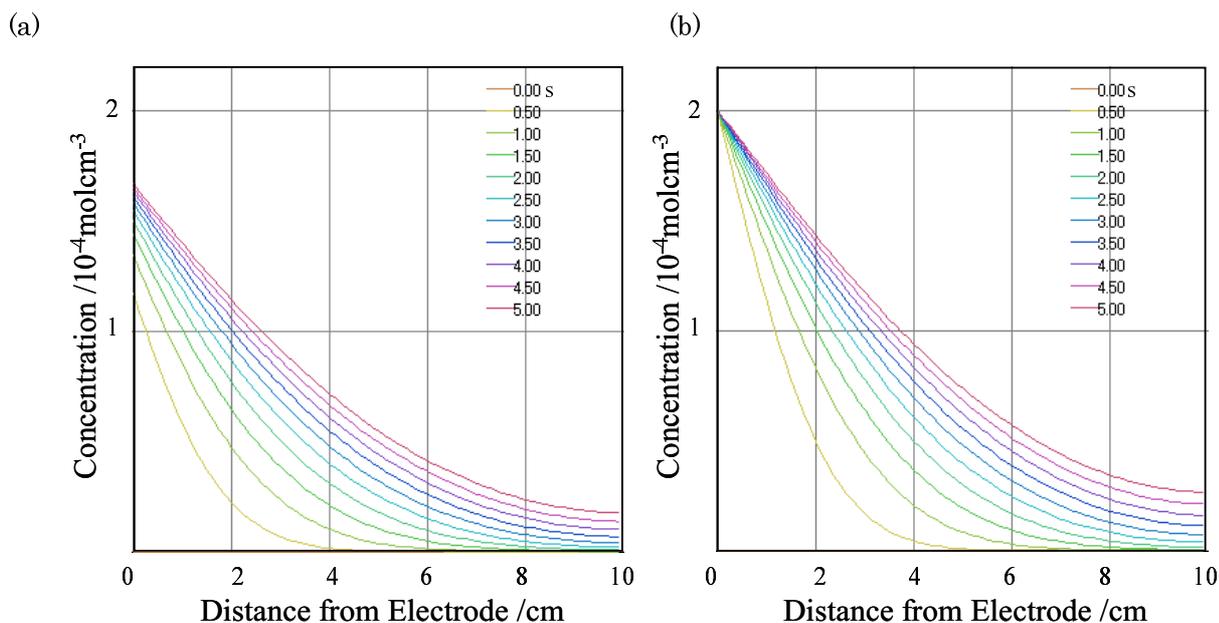


Figure 3. Time dependence of the concentration distribution of a molecule ($\alpha=0.5$, $D=3.0 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$, $l=1.0 \times 10^{-4} \text{ cm}$, $k=0 \text{ s}^{-1}$, $E_{RP}=1.1 \text{ V}$ vs. standard electrode) at a potential-step measurement from 0.7V to 1.5V. (a) $i_0' = 1.0 \times 10^{-3} \text{ Amol}^{-1} \text{ cm}$ (b) $i_0' = 1 \text{ Amol}^{-1} \text{ cm}$.

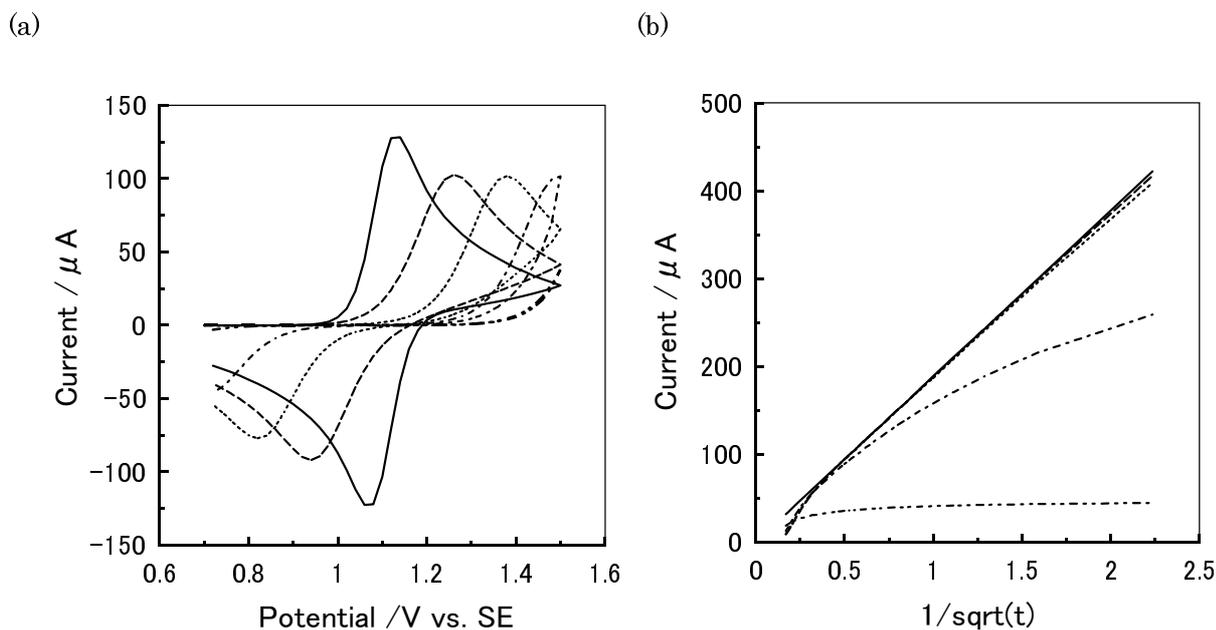


Figure 4. Virtual electrochemical measurements of a molecule ($\alpha=0.5$, $D=3.0 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$, $k=0 \text{ s}^{-1}$, $E_{RP}=1.1 \text{ V}$ vs. standard electrode) at various i_0' values using ES-2. —, Nernstian Condition; ---, $i_0' = 1.0 \times 10^{-1} \text{ Amol}^{-1} \text{ cm}$; ···, $i_0' = 1.0 \times 10^{-2} \text{ Amol}^{-1} \text{ cm}$; -·-·, $i_0' = 1.0 \times 10^{-3} \text{ Amol}^{-1} \text{ cm}$; ·-·-·, $i_0' = 1.0 \times 10^{-4} \text{ Amol}^{-1} \text{ cm}$. (a) Cyclic voltammogram between 0.7V to 1.5V at 20 mV s^{-1} . (b) Cottrell plots at the potential-step from 0.7V to 1.5V.

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H. Shiroishi, T. Nomura, K. Ishikawa, S. Tokita and M. Kaneko, *J. Chem. Software*, **7**, 145 (2001).
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- [10] ES-2 simulates the electrochemical measurement by the forward difference method. In large concentration gradient near the electrode, a larger division number is desirable for an accurate simulation. For large diffusion coefficient or large k value, it is preferable that a small Δt be used for a correct simulation. ES-2 and ES-1 with Crank-Nicolson method are also available at the same addresses.
- [11] This program incorporated into an electrochemical text written in HTML can be seen at <http://klab01.sci.ibaraki.ac.jp/~kanekolab/electrochem2.html>

JAVA 言語を用いた有限境界条件下での電気化学測定の可視化と電気化学教育への応用 (2)

城石 英伸^{a*}, 庄司 俊史^a, 野村 知生^a, 時田 澄男^b, 金子 正夫^a

^a 茨城大学理学部自然機能化学科, 〒 310-8512 茨城県水戸市文京 2-1-1

^b 埼玉大学工学部応用化学科, 〒 338-8570 埼玉県さいたま市下大久保 255

*e-mail: cpx26485@mopera.ne.jp

機能性分子分散高分子膜被覆電極 (Figure 1) などの有限境界条件下において、電極と機能性分子の反応速度を考慮しながら電気化学測定をシミュレートするプログラムを JAVA 言語を用いて作成した。このプログラムでは、サイクリックボルタモグラムおよび、ポテンシャルステップ時における時間電流曲線 (および電荷伝播率)、電極近傍の濃度分布の時間変化をシミュレートすることができる。また、シミュレート結果はテキストボックス内に数値と表示され、クリップボードを介して他のソフトに転送することが可能である。CV において交換電流密度が減少すると、アノードピークとカソードピークのポテンシャル差は増大し、ピーク電流値は減少した (Figure 4(a))。また、コットレルプロットにおいて、交換電流密度が減少すると初期の電流値が減少した (Figure 4(b))。このプログラムは HTML 文書中に組み込むことにより電気化学の動的なテキストとして活用できる (Figure 2)。

キーワード: Finite differential method, Electrochemical measurements, Cyclic voltammogram, Polymer-coated electrode, JAVA, Education