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Visualization of Electrochemical Behavior under Finite Conditions using JAVA and its Application for Assisted Learning

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Electrochemical measurements in a three electrode system under finite conditions, e.g., at an electrode coated with a polymer film incorporating functional molecules have been simulated using a program written in the JAVA language. The simulation with or without a catalytic reaction by the functional molecules has been performed using the program. The shape of a cyclic voltammogram under finite conditions is different from that under infinite conditions applied to ordinary solution electrochemistry. The fraction of the functional molecules that accepted charges (R_{CT}) has been calculated by integrating a concentration distribution. The current under finite conditions in a potential-step measurement deviated from that under infinite conditions above $R_{CT} \approx 0.5$. The program was introduced to a document on the electrochemistry written in HTML. It can be used by many students in an electrochemistry class without heavy loads on the server computer.

Keywords: Electrochemical measurements, Cyclic voltammogram, Charge propagation, Polymer-coated electrode, Finite condition, JAVA, Education

1 Introduction

Polymer-coated electrodes dispersing functional molecules have been studied during the last two decades [1–4]. These electrodes have wide application such as chemical sensors [5], electrocatalysis [6], and energy conversion devices [7]. It is important to study the charge propagation in polymer membranes for developing high-performance devices.

Needless-to-say a polymer layer coated on an electrode has a finite thickness. This causes a discrepancy in electrochemical results between the finite condition and the infinite condition from which equations in the solution system are derived. Another difference between these two systems

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is that the diffusion of molecules in a polymer layer is much slower than that in a solution. The contribution of the charge hopping mechanism to the whole charge propagation in a polymer-coated electrode would become greater than that in a solution system, so that equations in a solution cannot be applied to the polymer-coated electrode system depending on the situation. Under such finite conditions, it is difficult to solve diffusion equations, when the condition is altered a little. Thus an environment to analyze an electrochemical behavior easily and simply is needed.

In an educational respect, it is a problem to teach electrochemistry attractively because of a lot of abstruse equations. It is instructive to make an environment where every student can perform virtual electrochemical measurements using a network. Such a program has to satisfy the following requirements.

1. Calculations should be performed in each computer to prevent the concentration of calculations on the server.
2. The program should be distributed to each computer easily.
3. The program should be platform-independent for wide use.

JAVA is the best language to meet the above conditions.

In the present paper, we have developed a platform-independent program, called ES-1 (Electrochemical Simulator), written in JAVA language, which can calculate electrochemical behavior under finite conditions. This program is intended for a beginner using a modified electrode.

2 Method

2.1 Theory of the Electrochemical Simulation

Figure 1 shows the scheme of a polymer-coated electrode in which functional molecules were dispersed. In an electrode-coated polymer layer, functional molecules (redox center) are randomly dispersed. The electrode is dipped in an electrolyte solution. Electrochemical measurement is performed by the conventional three electrode system. A conventional diffusion equation including first-order catalytic reaction was used for the simulation:

$$\frac{\partial C(x,t)}{\partial t} + kC(x,t) = D\frac{\partial^2 C(x,t)}{\partial x^2} \tag{1}$$

where $C(x, t)$ (mol cm^{-3}) is the concentration of the oxidized molecule at the time t (s), k (s^{-1}) is the first-order rate constant for the catalysis by the oxidized molecule, D (cm^2 s^{-1}) is the diffusion coefficient of the charge. Assuming that a functional molecule(M) can catalyze a reaction, the first-order catalytic reaction is expressed by

$$\mathrm{M}_{ox} + \mathrm{S} \rightarrow \mathrm{M}_{red} + \mathrm{P} \tag{2}$$

where M_{ox} and M_{red} are the oxidized and reduced forms of the redox center, respectively, S is a substrate, P is a product.

Assuming that the concentration of the redox species obeys a Nernstian equation [8], a boundary condition on the electrode (x = 0) is represented as

$$C(0,t) = C_T \Big/ \left[1 + \exp\left\{-\frac{nF}{RT}(E - E^o)\right\}\right] \tag{B.C.1}$$

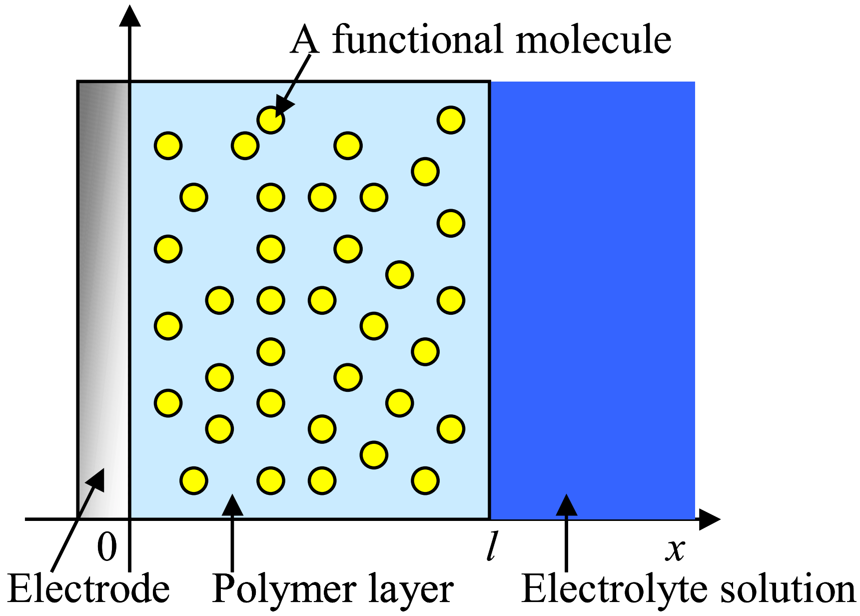


Figure 1. Scheme of a polymer-coated electrode with dispersed functional molecules

where C_T (mol cm^{-3}) is the total concentration of the molecule, E is the applied potential on the electrode, E° is the redox potential of the molecule, n is the number of electrons, F (C mol^{-1}) is the Faraday constant. Another boundary condition under finite conditions is represented as

$$\frac{\partial C(l,t)}{\partial x} = 0 \tag{B.C.2}$$

where l is the thickness of the polymer layer. A finite differential method (FDM) was used for the simulation.

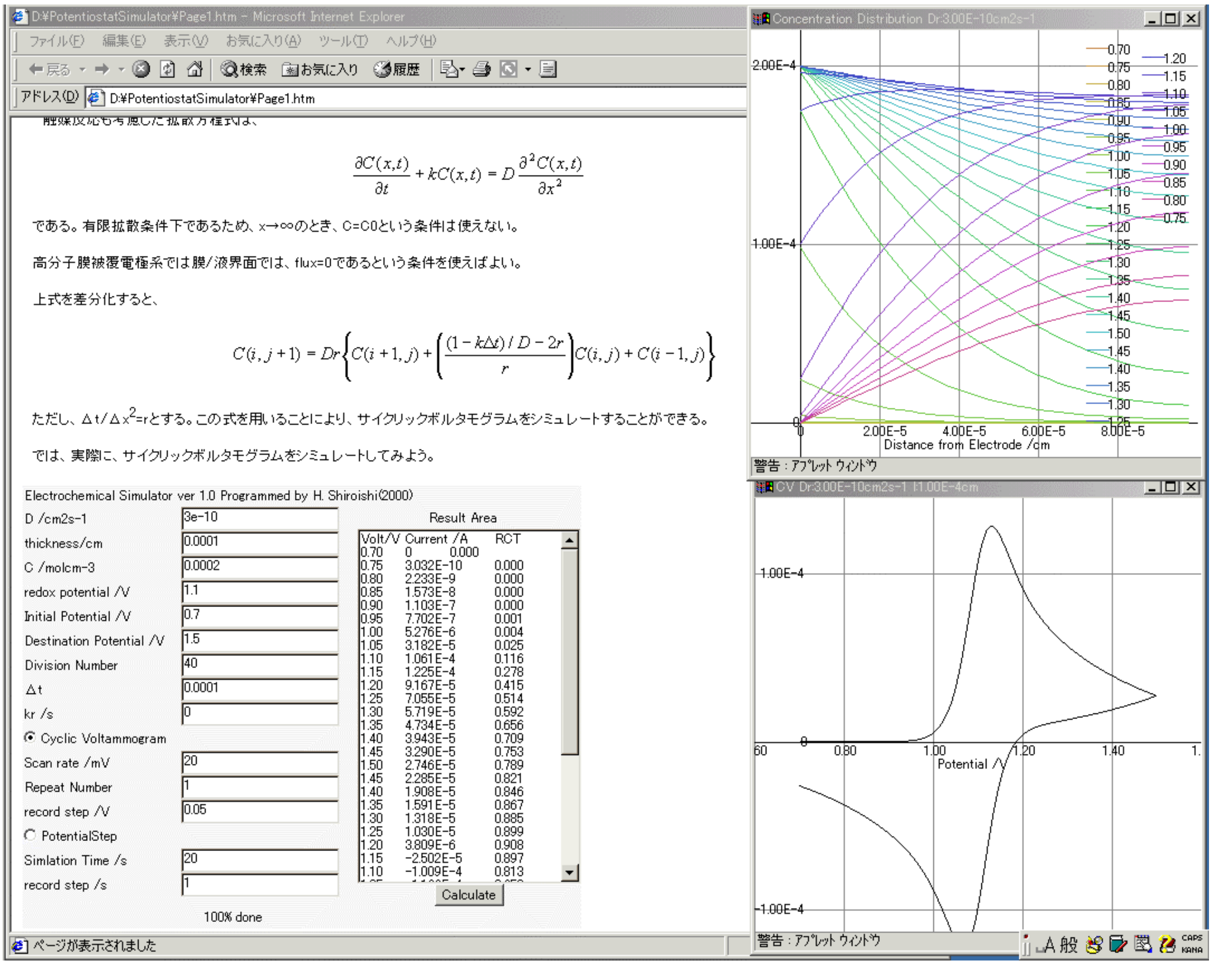
2.2 Implementation

We used a PC-9821 machine (NEC) in which Microsoft Windows 2000 was installed for developing ES-1 with the Microsoft Visual J++ version 6(SP3). However, we didn't use a Windows Foundation Class library (WFC) to keep a platform-independent feature. ES-1 was tested using IBM/AT compatible with Internet Explorer version 5.5.

3 Results and Discussion

3.1 The Feature of ES-1

Figure 2 shows the combination of the ES-1 and electrochemical texts written in HTML. Students can learn electrochemistry by electrochemical text blended with the simulation program smoothly[9]. ES-1 has only one button in the control panel. Simple operation is very important for use in an electrochemistry class because most of the time in class should be spent for teaching electrochemistry itself, and not for teaching the usage of the program. The numerical results are put into a text area since JAVA applets are prohibited from accessing any local disks. The results in the text area can be copied by using a shortcut key ([Ctrl]+[C]).



触媒反応も考慮した拡散方程式は、

$$\frac{\partial C(x,t)}{\partial t} + kC(x,t) = D\frac{\partial^2 C(x,t)}{\partial x^2}$$

である。有限拡散条件下であるため、x→∞のとき、C=C0という条件は使えない。

高分子膜被覆電極系では膜/液界面では、flux=0であるという条件を使えばよい。

上式を差分化すると、

$$C(i,j+1) = Dr\left\{C(i+1,j) + \left(\frac{(1-k\Delta t)/D-2r}{r}\right)C(i,j) + C(i-1,j)\right\}$$

ただし、$\Delta t/\Delta x^2$=rとする。この式を用いることにより、サイクリックボルタモグラムをシミュレートすることができる。

では、実際に、サイクリックボルタモグラムをシミュレートしてみよう。

Electrochemical Simulator ver 1.0 Programmed by H. Shiroishi(2000)

D /cm2s-1	3e-10
thickness/cm	0.0001
C /molcm-3	0.0002
redox potential /V	1.1
Initial Potential /V	0.7
Destination Potential /V	1.5
Division Number	40
Δt	0.0001
kr /s	0
● Cyclic Voltammogram	
Scan rate /mV	20
Repeat Number	1
record step /V	0.05
○ PotentialStep	
Simlation Time /s	20
record step /s	1

100% done

Result Area

```
Volt/V Current /A   RCT
0.70   0         0.000
0.75   3.032E-10    0.000
0.80   2.233E-9     0.000
0.85   1.573E-8     0.000
0.90   1.103E-7     0.000
0.95   7.702E-7     0.001
1.00   5.276E-6     0.004
1.05   3.182E-5     0.025
1.10   1.061E-4     0.116
1.15   1.225E-4     0.278
1.20   9.167E-5     0.415
1.25   7.055E-5     0.514
1.30   5.719E-5     0.592
1.35   4.734E-5     0.656
1.40   3.943E-5     0.709
1.45   3.290E-5     0.753
1.50   2.746E-5     0.789
1.45   2.285E-5     0.821
1.40   1.908E-5     0.846
1.35   1.591E-5     0.867
1.30   1.318E-5     0.885
1.25   1.030E-5     0.899
1.20   3.809E-6     0.908
1.15   -2.502E-5    0.897
1.10   -1.009E-4    0.813
```

Calculate

Figure 2. Combination of the ES-1 and electrochemical texts written in HTML. Upper window illustrates the concentration distribution of the oxidized molecule. Lower window shows the cyclic voltammogram of the molecule.

3.2 Results of the Simulation

Figure 3 shows the time dependence of R_{CT} estimated by absorption spectral change at potential step measurement using ITO/Nafion[Ru(bpy)$_3$$^{2+}$] electrode. A curve calculated with ES-1, shown in Figure 3, coincides with the actual measurement suggesting that the simulation is reasonable. The diffusion coefficient used in the simulation was estimated by conventional equation in the solution system in the initial time region.

Students can see the electrochemical behavior shown below using ES-1. Figure 4(a) shows a series of cyclic voltammograms at various thicknesses of a finite layer. The increase of the layer thickness raised the anodic current beyond the potential at the peak current, where the anodic current is derived from the diffusion of charges, but reduces the cathodic current on the reverse scan. This is because a thinner layer makes a steeper concentration gradient of the redox molecules.

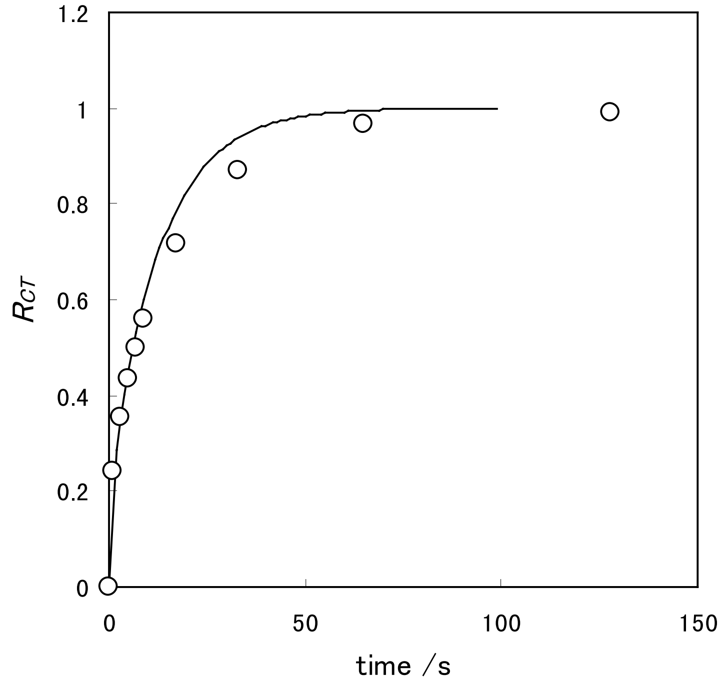


Figure 3. Time dependence of R_{CT} estimated by absorption spectral change at potential step measurement from 0.6V (versus Ag|AgCl) to 1.4V using ITO/Nafion[Ru(bpy)$_3^{2+}$] electrode in 0.1mol dm^{-3} KNO$_3$ (pH 1). The solid line was calculated with ES-1. ($D = 3.2 \times 10^{-10}$ cm^{2}s^{-1}, $l = 1 \times 10^{-4}$ cm, $C_T = 4.2 \times 10^{-4}$ mol cm^{-3})

The equation of the time dependent R_{CT} value under infinite conditions is represented by eq. 3 [10, 11], where R_{CT} is the fraction of the redox molecule that accepted a charge.

$$R_{CT} = \frac{2D^{1/2}\, t^{1/2}}{\pi^{1/2}\, l} \tag{3}$$

Figure 4(b) shows the plots of R_{CT} vs. $t^{1/2}l^{-1}$ simulated by ES-1. The simulated curve under the finite conditions deviated from the curve calculated by eq. 3 above $R_{CT} \approx 0.5$.

Figure 5(a) shows a series of cyclic voltammograms at various k values. The anodic current beyond the redox potential increased with the k value. Time dependence of R_{CT} under finite conditions at various k values in potential step measurement is shown in Figure 5(b). The increase of k value reduced the time to reach the plateau, and also lowered the plateau value.

4 Conclusion

An electrochemical simulator (ES-1) under finite conditions for redox centers confined in an electrode coated polymer layer was developed for an electrochemistry class. ES-1 was written in JAVA language which has characteristics of platform-independence, an easy cooperation with HTML and small load on a server computer. The R_{CT} value under finite conditions deviated from that under infinite conditions above $R_{CT} \approx 0.5$.

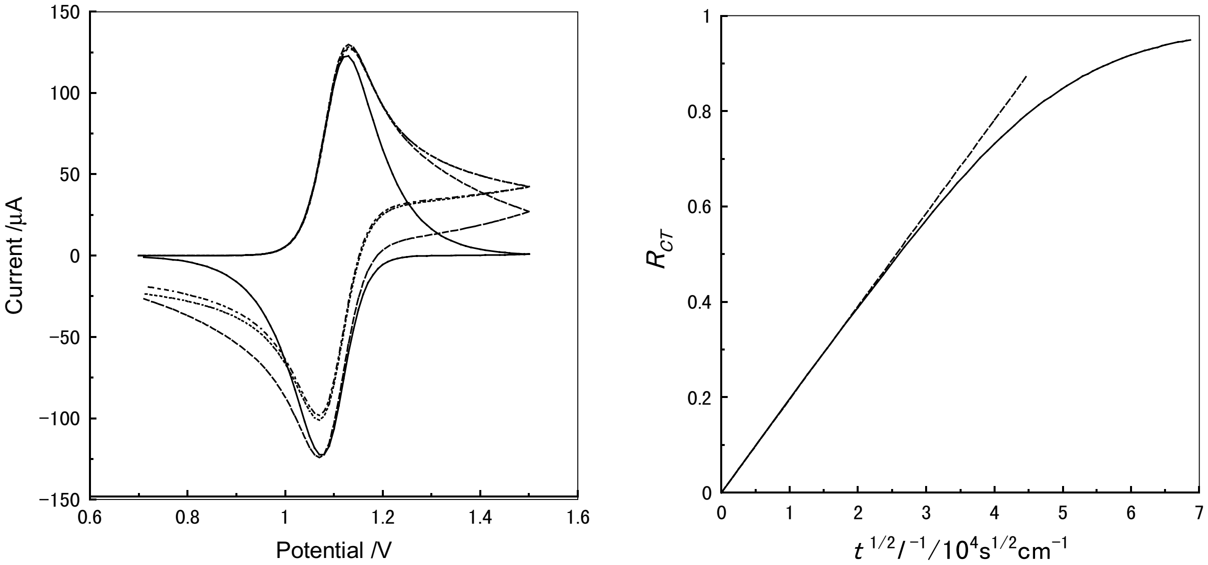


Figure 4. Virtual electrochemical measurements of a material ($D = 3\times10^{-10}$cm^{2}s^{-1}, $k = 0$ s^{-1}, $E^\circ = 1.1$ V vs. a standard electrode) at various thicknesses using ES-1. (a) Cyclic voltammogram from 0.7 V to 1.5 V at 20mV/s. —, $l = 0.5\times10^{-4}$ cm; - - -, 1.0×10^{-4} cm ; ···, 2.0×10^{-4} cm ; - · - 3.0×10^{-4} cm. (b) The plots of R_{CT} vs. $t^{1/2}l^{-1}$ at applied potential from 0.7V to 1.5V. —, A simulated curve under finite condition; - - -, calculated by eq.3 (under infinite condition).

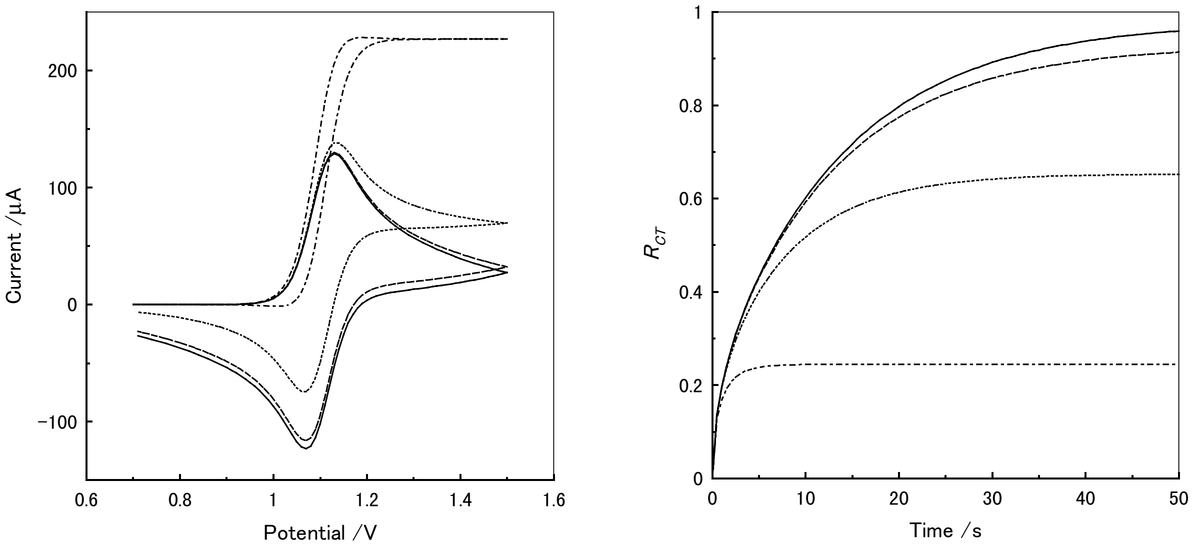


Figure 5. Virtual electrochemical measurements of a material ($D = 3\times10^{-10}$cm^{2}s^{-1}, $E^\circ = 1.1$ V vs. a standard electrode) at various k values using ES-1. —, $k = 0$ s^{-1}; - - -, 5×10^{-3} s^{-1} ; ···, 5×10^{-2} s^{-1} ; - · - 5×10^{-1} s^{-1}. (a) Cyclic voltammogram from 0.7 V to 1.5 V at 20mV/s. (b) Time dependence of R_{CT} at an applied potential from 0.7V to 1.5V.

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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

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機能分子分散高分子被覆電極などの有限境界条件を有する電極を用いた電気化学測定において、電極からの電荷伝播を、差分法を用いて可視化した。電気化学測定法として最も広く用いられるサイクリックボルタモグラムとポテンシャルステップ法に対応させて、電極からの伝播の様子をグラフ化した (Figure 2)。また、それらを用いた、化学センサー、電気触媒系の反応解析にむけ、運搬の途中で電荷が消費される場合についても可視化できるようにした (Figure 5)。また、開発言語は授業での活用に向け、サーバーへの負担が少なく、HTML 中に導入することにより、プログラムの配布が容易であり、機種依存性がないといった点から、JAVA を用いた。

キーワード : Electrochemical measurements, Cyclic voltammogram, Charge propagation, Polymer-coated electrode, Finite condition, JAVA, Education