



## Effects of the Polarization Resistance on Cyclic Voltammograms for an Electrochemical-Chemical Reaction

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### ABSTRACT

Here I report an electrochemical simulation work that compares voltammetric current and resistance of a complex electrochemical reaction over a potential scan. For this work, the finite element method is employed which are frequently used for voltammetry but rarely for impedance spectroscopy. Specifically, this method is used for simulation of a complex reaction where a heterogeneous faradaic reaction is followed by a homogeneous chemical reaction. By tracing the current and its polarization resistance, I learn that their relationship can be explained in terms of rate constants of charge transfer and chemical change. An unexpected observation is that even though the resistance is increased by the rate of the following chemical reaction, the current can be increased due to the potential shift of the resistance made by the proceeding faradaic reaction. This report envisions a possibility of the FEM-based resistance simulation to be applied to understand a complex electrochemical reaction. Until now, resistance simulations are mostly based on equivalent circuits or complete mathematical equations and have limitations to find proper models. However, this method is based on the first-principles, and is expected to be complementary to the other simulation methods.

**Keywords :** impedance spectroscopy, electrochemistry theory, finite element simulation, electrochemical-chemical reaction.

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### Introduction

Cyclic voltammetry (CV) is the best known electrochemical technique which can show complex electrochemical information such as faradaic and non-faradaic, charge-transfer controlled and mass-transfer controlled processes, reversible and irreversible reactions and so on. Even though CV is the best as a diagnostic tool for electrochemistry, it is strongly recommended to resort to other techniques if precise evaluation of electrochemical parameters is required. [1-2] Various kinds of pulse voltammetry, current-controlled techniques, and hydrodynamic methods

may be used for specific purposes. Among them, electrochemical impedance spectroscopy (EIS) has attracted many attentions in the recent decades [3] because it resolves the electrode/electrolyte interface by frequencies to which individual electrochemical processes differently respond. Nevertheless, EIS is not so frequently used as CV is because it is hard to understand and explain the measured impedance data. [2,4] At that situation, computer-aided simulation can help. [5-6] However, there still remain difficulties such as finding an proper equivalent circuit or mathematical expressions for theoretically modelled electrochemical processes. [7-8] Especially, when the

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electrochemical reaction is complex [9] or the electrode is modified with functional materials [10], it would be harder or could be almost impossible to find a good electrochemical model to carry out the computer-aided simulation.

In this report, I adapt the finite element method (FEM) to conducting the digital simulation, [11-12] where molecular species and their concentrations are digitized as finite elements of time and space at molecular levels and the first-principle calculation based on charge transfer, mass transfer and chemical reaction rate are carried out to find values of each finite element. Using this simulation method, I study an electrochemical reaction coupled with a chemical reaction by finding the relationship between the current of CV and the resistance of EIS.

### Theories and discussion

An electrochemical reaction can be described as  $O + e \rightarrow R$ , and the electrode potential ( $E$ ) and the resulting current ( $i$ ) can be measured by voltammetry. When the potential is scanned along time, it can be expressed as a function of current and concentrations of redox molecules changing with the scanning time. Hence, the time-derivative is described as below.[1]

$$\frac{dE}{dt} = \left(\frac{\partial E}{\partial i}\right)\frac{di}{dt} + \left(\frac{\partial E}{\partial C_O(t)}\right)\frac{dC_O(t)}{dt} + \left(\frac{\partial E}{\partial C_R(t)}\right)\frac{dC_R(t)}{dt} \quad \text{eq (1)}$$

The first term on the right side is known as the polarization resistance,  $R_p$ , which tells the rate of change transfer at the electrified interface as described by eq(2) [13], while the rest part tells the rate of mass transfer through the diffusion layer.

$$-\frac{\partial i}{\partial E} = \frac{1}{R_p} = \frac{n^2 F^2}{RT} [ak_f C_O(t) + (1 - \alpha)ak_r C_R(t)] \quad \text{eq (2)}$$

$k_f$  and  $k_r$  are rate constants for reduction and oxidation reactions,  $\alpha$  transfer coefficient,  $n$  the number of electron transferred,  $F$  faradaic constant,  $R$  gas constant and  $T$  temperature. From the above equation, we can guess that  $1/R_p = 1/R_{p,f} + 1/R_{p,r}$  where each is respectively referred to the following equations.

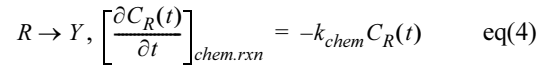
$$\frac{1}{R_{p,f}} = \frac{n^2 F^2}{RT} \alpha C_O(t) k^0 \exp\left[\frac{\alpha F}{RT}(E - E^0)\right] \quad \text{eq (3-1)}$$

$$\frac{1}{R_{p,r}} = \frac{n^2 F^2}{RT} (1 - \alpha) C_R(t) k^0 \exp\left[\frac{n(1 - \alpha)F}{RT}(E - E^0)\right] \quad \text{eq(3-2)}$$

Here, we can learn that  $\ln R_{p,f}$  and  $\ln R_{p,r}$  are linear

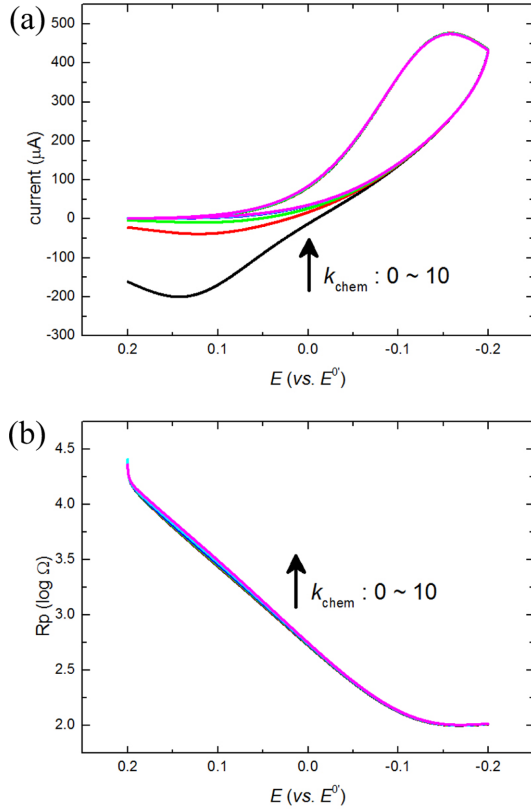
with the electrode potential and the slopes are the same as those of the Tafel plots [1] and the total resistance,  $R_p$ , is sum of them. By the way, the intercepts are different due to the concentrations of O and R at the electrified interface.

When an electrochemical reaction becomes complex by the proceeding or following chemical reactions,  $R_p$  should be changed because  $R_{p,f}$  and  $R_{p,r}$  are dependent on concentrations of O and R species. When a 1-order homogeneous reaction follows the heterogeneous faradaic reaction,[14]



the changing concentrations are taken into account at eq(3). Simulations with changing  $k^0$  and  $k_{chem}$  leads us to a short conclusion that  $R_{p,f}$  and  $R_{p,r}$  can be almost separately modulated to manipulate  $R_p$ . Decrease of  $k^0$  increases the intercept of  $R_{p,f}$  while increase of  $k_{chem}$  increases that of  $R_{p,r}$ . In other words, the decreased  $k^0$  slows down the electron transfer rate of the forward reaction of which the resistance is increased, and the increased  $k_{chem}$  decreases  $C_R(t)$  so that the resistance of eq (3-2) is increased. As results of properly controlling  $R_{p,f}$  and  $R_{p,r}$ , we observe different behavior of  $R_p$ . First, even when  $R_{p,f}$  increases by decreased  $k^0$ ,  $R_{p,r}$  can be almost unchanged due to the facile consumption of the R species by the following chemical reaction ( $R \rightarrow Y$ ). Consequently, the unbalanced change of  $R_{p,f}$  and  $R_{p,r}$  will make a shift of the lowest  $R_p$  to the positive potential direction. Eventually at a very small  $k^0$ , huge value of  $R_{p,f}$  overwhelms  $R_{p,r}$  such that the electrochemical reaction is totally controlled by the slow forward reaction. This situation is described as an irreversible faradaic reaction because only the forward reaction is dominantly observable and confirmed by simulation of cyclic voltammetry as shown in Fig. 1(a). Also, the total  $R_p$  is seen to be mostly determined by the overwhelming  $R_{p,f}$  no matter  $R_{p,r}$  is controlled by  $k_{chem}$  as shown in Fig. 1(b).

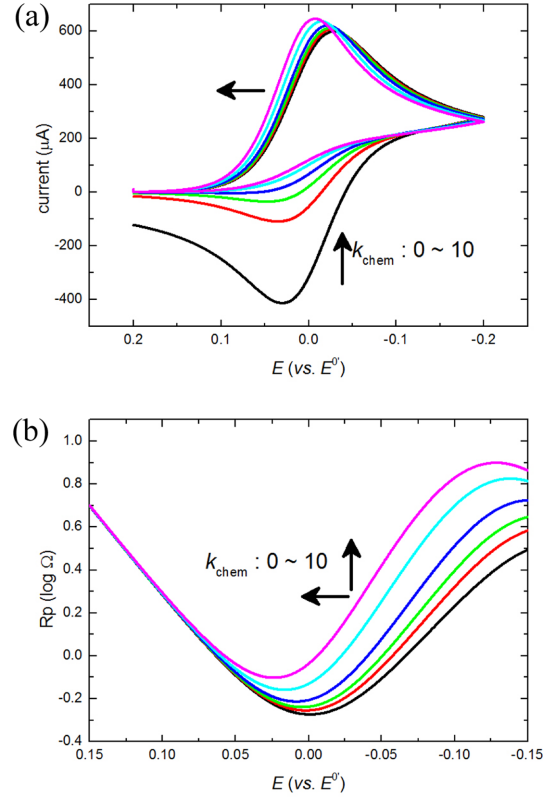
On the other hand, when  $k_{chem}$  is gradually increased with high  $k^0$ , the concentration of R,  $C_R(t)$ , is decreased by eq(4) and  $R_{p,r}$  is increased by eq(3) subsequently while little change of  $R_{p,f}$  is expected from the change of  $k_{chem}$ . Fig. 2(b) shows how the total  $R_p$  changes according to the change of  $k_{chem}$ . The value of the lowest  $R_p$  increases and its position shifts to the positive direction as  $k_{chem}$  increases. These



**Fig. 1.** The cyclic voltammogram (a) and the polarization resistance (b) are obtained by the FEM-based simulation. Simulation parameters are following: the scan rate = 100 mV/s,  $k^0 = 0.001$  cm/s,  $\alpha = 0.5$  and varying  $k_{chem} = 0, 0.5, 1, 2, 5$  and  $10$  mM/s. The arrow shows the increasing direction of  $k_{chem}$ .

results can be clearly shown by simulations of cyclic voltammograms in Fig. 2(a). It is not surprising that the position shifts are in accordance with the shifts of the current curves because the lowest  $R_p$  goes with the current peaks. However, it is surprising to observe that the current peaks increase with increase of  $R_p$  values.

This ironic observation is explained from the aspect of overpotential. When the  $R_p$  curves or the current curves of a reduction reaction shift to the positive direction of potential, less overpotentials are required to activate such faradaic reactions. The reduced overpotential generates extra potential at a certain electrode potential. Such superfluous potential can facilitate the charge transfer process, and when the facilitation effect is large enough, it can beat the resistance of charge transfer,  $R_p$ . The reduced



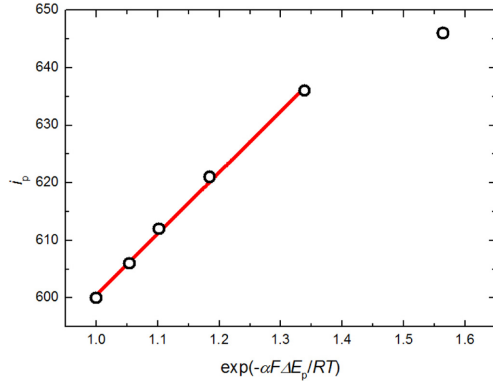
**Fig. 2.** The cyclic voltammogram (a) and the polarization resistance (b) are obtained by the FEM-based simulation. Simulation parameters are following: the scan rate = 100 mV/s,  $k^0 = 1$  cm/s,  $\alpha = 0.5$  and varying  $k_{chem} = 0, 0.5, 1, 2, 5$  and  $10$  mM/s. The arrow shows the increasing direction of  $k_{chem}$ .

overpotentials ( $\Delta E_p$ ) are estimated from the potentials of the lowest  $R_p$ , and plotted with the increased peak currents ( $\Delta i_p$ ) in Fig. 3. The linear relationships is explained by the Butler-Volmer equation below,

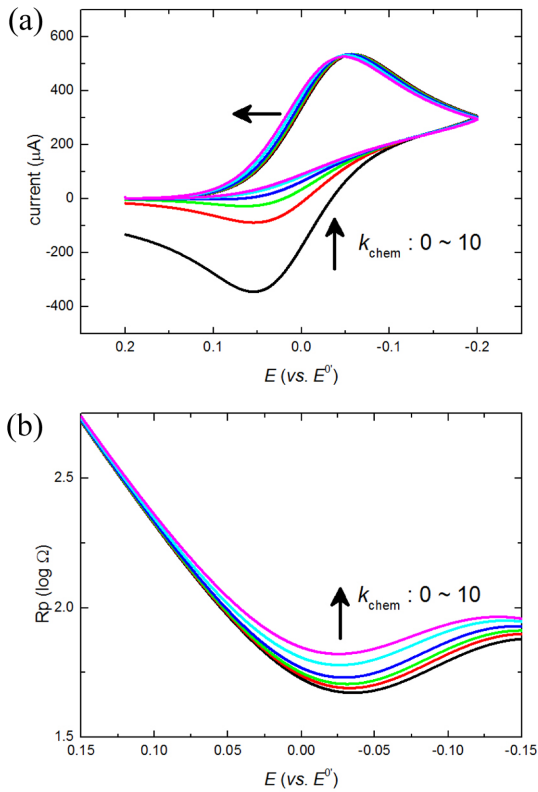
$$\Delta i_p = \exp\left(-\frac{\alpha F}{RT} \Delta E_p\right) \quad \text{eq (5)}$$

This is very similar to the Frumkin effect but works oppositely; the Frumkin effect corrects the current with decreased overpotential, [15-16] however this effect does with increased over potential.

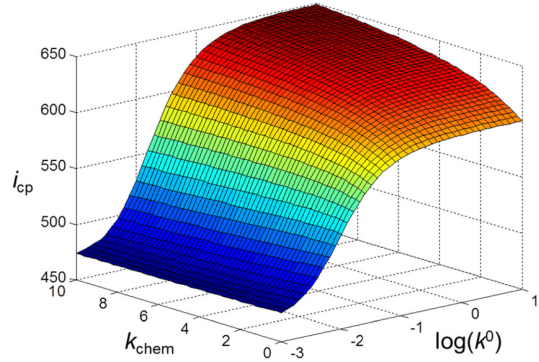
Nevertheless, the accelerated charge transfer by the redundant potential is not always observable. When the extra-potential is not enough to overcome the resistance of transferring charges at the electrified interface, we can only observe potential shift without current increase. Such conditions can be made with



**Fig. 3.** The potential shifts and peak currents obtained by varying values of  $k_{chem}$  are plotted. The plots are fitted to the Butler-Volmer equation as down the red line. Deviation is shown when the chemical reaction rate is too high because it severely decrease  $C_R(t)$  in eq(3-2). As a result of that,  $R_{p,r}$  is increased more than  $\exp[-\alpha F \Delta E / RT]$  so that the current becomes less than the expected value.



**Fig. 4.** The cyclic voltammogram (a) and the polarization resistance (b) are obtained by the FEM-based simulation. Simulation parameters are following: the scan rate = 100 mV/s,  $k^0 = 0.1$  cm/s,  $\alpha = 0.5$  and varying  $k_{chem} = 0, 0.5, 1, 2, 5$  and 10 mM/s.



**Fig. 5.** The effects of the co-play between  $k_{chem}$  and  $k_0$  on change of the cathodic current peak ( $i_{cp}$ ). The simulation conditions are the same in Fig. 1, 2 and 4.

moderate values of  $k^0$  and  $k_{chem}$ . In Fig. 4, we can see that increases of  $k_0$  and  $k_{chem}$  increase both  $R_{p,f}$  and  $R_{p,r}$ , which lead to increase of total  $R_p$  with small potential shifts. At this situation, decrease of overpotential is canceled out by increase of  $R_p$ , so that effective acceleration of charge transfer is hampered by the stronger resistance. Eventually, no current increase is observed even with potential is shifted. Fig. 5 shows the overall effects of the combination of  $k^0$  and  $k_{chem}$  on the peak current. When  $k^0$  is low,  $k_{chem}$  has little effect on the electrochemistry. However, when  $k^0$  is high enough,  $k_{chem}$  makes significant effects onto the electrochemical reaction.

#### Experimental of the FEM-based simulation

All the simulations are done using Matlab. The concentrations of O and R species in the linear transfer space and time are defined by  $C_O(x,t)$  and  $C_R(x,t)$ , and re-defined by  $C_O(n,m)$  and  $C_R(n,m)$  as finite elements and framed in a 2D-matrix. Here,  $n$  and  $m$  are dimensionless parameters determined by  $n = x/\Delta x$ , and  $m = t/\Delta t$ , respectively, as used in electrochemistry simulations. [11,17-18]

For calculation for the diffusion of  $j$  species, the Fick's first and second laws are modified and combined to express a dimensionless concentration,  $C_j(n,m)$ , by the dimensionless parameters as shown below,

$$C_j(n,m+1) = C_j(n,m) + D_M [C_j(n+1,m) - 2C_j(n,m) + C_j(n-1,m)] \quad \text{eq (6)}$$

Here,  $D_M$  is a dimensionless diffusion coefficient

obtained from  $D\Delta t/\Delta x^2$  and called the model diffusion coefficient.[17] For calculation for the flux at the electrified interface, the charge transfer rate and the diffusion rate are balanced to yield the following equation,

$$-J_O(m) = [k_f C_O(1,m) - k_r C_R(1,m)] / (1 + k_f/2D_M + k_r/2D_M). \quad \text{eq(7)}$$

For calculation for the change by the homogeneous chemical reaction, the concentrations are obtained by the following equation,

$$C_j(n,m+1) = C_j(n,m) - k_M C_j(n,m), \quad \text{eq(8)}$$

The constant  $k_M = k_{chem}\Delta t$  is a dimensionless parameter for the chemical reaction rate. To satisfy the conditions of the semi-infinite diffusion and the explicit finite elements,  $D_M < 0.5$  and the maximum  $n > 6(D_M m)^{1/2}/\Delta x$  are set.

## Conclusion

So far, I have discussed on a complex electrochemical reaction, where a heterogeneous faradaic reaction is accompanied by a homogeneous chemical reaction from viewpoints of voltammetric current and resistance using the digital simulation. The digital simulation is conducted in the finite element method discretizing the dimension, time and concentrations of chemicals. The concentrations are used to theoretically calculate polarization resistances and their flux to obtain voltammograms which can be measured by experiments. By changing the rates of heterogeneous and homogeneous reactions respectively, it is learned how the resistance is reflected on the measurable voltammogram. With decreasing  $k^0$ , the resistance increases to lead an irreversible faradaic reaction regardless of the chemical reaction. On the other hand, with increasing  $k_{chem}$ , the resistance increases with lowering overpotential. From this sense, a paradox that current is increased with increased resistance is explained. Also, the co-play of  $k^0$  and  $k_{chem}$  studied to predict how the voltammogram appears.

From this report, I present a vision of FEM-based digital simulation study on impedance, more specifically *resistance*. Even though there are many electrochemical measurement techniques such as voltammetry and electrochemical impedance spec-

troscopy, we still have limitations in understanding the observations especially when the reactions are very complex. As shown in this report, such understandings can be facilitated by computer simulations. [19] While theoretical resistance data are mostly simulated based on the equivalent circuit models, ours are done using the finite elements at the molecular levels. Consequently, it is not necessary to find an appropriate equivalent circuit or mathematical equations of potential and current. For the time being, it is only shown that resistance simulation is possible at the molecular level. In the forth-coming reports, it will be reported how an equivalent circuit is modelled from our FEM-based resistance simulation results.

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