Monte Carlo Simulation of Electrochemical Detection of Redox Molecules with Nanoscale Redoxcycling

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ABSTRACT

Nanoscale redoxcycling is widely used in electrochemical detection of low analyte concentration because of its high sensitivity, rapid response and the ability to conduct microscale sample measurement. Diffusion equation is usually used for this analyte sensing, but in this paper, Monte Carlo simulation with nanoscale redoxcycling is performed to test the effectiveness of this equation for low analyte concentration sensing. In this simulation, each analyte molecule is expressed by a particle. The results show that even in extremely low analyte concentration, the steady-state current is equal to that obtained using diffusion equation. This suggests that the diffusion equation is applicable even for exthemely low concentration analyte sensing.

Keywords: Nanoscale redoxcycling, Monte Carlo

INTRODUCTION

Biosensors that can detect minute quantities of important biomolecules in the human body are increasingly gaining attention nowadays[1,2,3,4]. Currently, electrophoresis, fluorescence and amperometric detection methods are the common techniques used for such purpose. The electrophoresis method requires large equipment[5], and fluorescence method requires long detection time[6]. On the other hand, amperometric detection by nanoscale redoxcycling method shown in Fig. 1 can be more reliable due to its high sensitivity, rapid response and the ability to conduct microscale sample measurement. Therefore, many works on this method are published[7, 8], and most of them include simulation to optimize the design and to predict the performance of the sensors. In the previous studies, mass transport of analyte molecules is expressed by the diffusion equation as follows:[9,10]

$$\frac{\partial c(x,t)}{t} = D \frac{\partial^2 c(x,t)}{x^2},$$ (1)

where, c is bulk concentration of analyte, D is diffusion coefficient, x is distance from electrode, and t is the time. In the case of nanoscale redoxcycling, the diffusion layer is essentially one dimensional, and the steady-state current is given by

$$I = \frac{nFDAc}{d},$$ (2)

where, n is number of electron transfer per oxidation-reduction reaction, F is Faraday constant, D is diffussion coefficient, A is electrode area, c is bulk concentration of analyte, and d is distance between cathode and anode. However, in low concentration analtye molecule, the effectiveness of Eqs. (1) and (2) has not been proved.
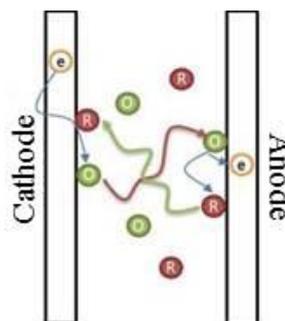

Fig. 1 Illustration of redox cycling. The reducing species are oxidized at the cathode, and after diffusing to the anode, they are reduced to original state when diffusing to the anode.

In this paper, Monte Carlo (MC) simulation of nanoscale redoxcycling is performed, where analyte molecules are expressed by particles. The simulation results show that even in extremely low analyte concentration, the steady-state current is in accord with the result obtained using Eqs. (1)-(2). This indicates that the diffusion equation is applicable to extremely low analyte concentration cases.

Method

We assumed that the analtye molecules are potassium ferricyanide $K_3[Fe(CN)_6]$ (Ferri), potassium ferrocyanide $K_4[Fe(CN)_6]$ (Ferro) in the simulation. The basic equations are based on those used in a previous report.[11] The particle momentum comes from Newton's second law, and assuming that the gravity force and fluid-

particle interaction can be ignored, the motion of particles in aqueous solution can be expressed by

$$m\frac{d\boldsymbol{v}}{dt} = -\beta\boldsymbol{v} + \boldsymbol{\eta}(t) \ , \tag{3}$$

$$-\beta\boldsymbol{v} = F_D = \frac{18\mu m_p\,(\boldsymbol{u}-\boldsymbol{v})}{d_p^{\;2}\rho_p} \ , \tag{4}$$

$$\boldsymbol{\eta}(t) = F_B = \zeta\sqrt{\frac{12\pi r_p k_B T}{\Delta t}} \ , \tag{5}$$

where F_D expresses drag force, F_B expresses brownian force, μ is fluid viscosity, m_p is particle mass, $\boldsymbol{u}$ is fluid velocity $\boldsymbol{v}$ is particle velocity, d_p is particle diameter, ρ_p is particle density, ζ is zero mean three-dimension ramdom numbe, r_p is particle radius, k_B is Boltzman's constant, T is temperature, and Δt is time step used in the simulation . We obtained the value of diffusion coefficient D from experimental data and determined the value of r_p by

$$r_P = \frac{k_B T}{6\pi\mu D} \ . \tag{6}$$

As m_p is determined from Ferri molar mass (329.24g/mol), ρ_p is expressed by

$$\rho_p = \frac{3m_p}{4\pi r_p^{\;3}} \ . \tag{7}$$

We adjusted Δt to ensure that simulation can be properly executed, And it is approximately equal to particle momentum relaxation time[12] which is defined as

$$\Delta t \cong \frac{\rho_P d_p^{\;2}}{18\mu} \ . \tag{8}$$

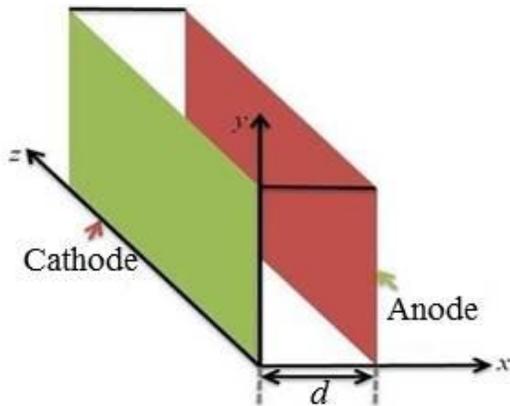The variables and constants are summarized in Table I. Fig. 2 illustrates the model structure.

Fig. 2 Model of electrodes. x axis demonstrate the electrode distance. y, z axis demonstrate the electrode length and width.

In the MC simulation, Ferri is randomly introduced between the electrodes with zero velocity and an initial charge of $-3e$. Then we simulated the particle motion based on Eqs. (3)-(5) by Comsol Multiphysics 4.3b. All of the boundaries is set to 'bounce' (incident angle and reflection angle are same, and the value of velocity will not change) to retain the particle energy. The left boundary in Fig. 2 is assumed to be cathode and the right one is anode. Ferri ($-3e$) will become Ferro ($-4e$) when it collides onto the cathode, and Ferro ($-4e$) will become Ferri ($-3e$) when it collides onto the anode. The interactions between particles are neglected. Simulation time is set for 0~1.0 μs, and the number of events of particle charge interchange is recorded. The data is then analyzed by using Matlab R2013a to calculate electric current given as the time differential to the number of charge interchange events. Ferri loses an electron by the cathode and be oxidized become Ferro, where electric current is called oxidation current. On the other hand, when Ferro diffusing to the anode, it supplies an electron to the anode and be reduced to Ferri. The produced electric current is called reduction current.

Table I Parameters of simulation

Parameter	Value(Ferri,Ferro)	Description
m_p	5×10^{-24}kg	Particle mass
D	$5\times10^{-10}\,\mathrm{m^2/s}$	Diffusion coefficient
$\boldsymbol{u}$	0	Fluid velocity
μ	$8.9\times10^{-4}\,\mathrm{pa\cdot s}$	Fluid viscosity
T	298.15K	temperature
k_B	$1.3806488\times10^{-23}\,\mathrm{m^2kg\;s^{-2}K^{-1}}$	Boltzmann's constant
Δt	$1\times10^{-13}\,\mathrm{s}$	Time step
r_p	$4.9\times10^{-10}\,\mathrm{m}$	Particle radius
ρ_p	$10100\mathrm{kg/m^3}$	Particle density
d_p	$9.8\times10^{-10}\,\mathrm{m}$	Particle diameter
$\boldsymbol{v}$	variable	Particle velocity
ζ	variable	Random number
c	variable	concentration
x	variable	Distance from electrode
t	variable	Time

Results and discussion

In order to confirm the validity of using diffusion equation for low analtye concentration sensing, we compared the simulation and theoretical steady-state current with various electrode areas, Ferri concentration and the distance between cathode and anode. Fig. 3(a) shows the current with electrode areas ranging from 0.01μm to 0.32μm for Ferri concentration 0.83mM (M = mol/L) and electrode distance 20nm. It shows that the current increases with the electrode area. Fig. 3(b) shows the relationship between steady-state current and electrode areas. The figure shows that simulation result
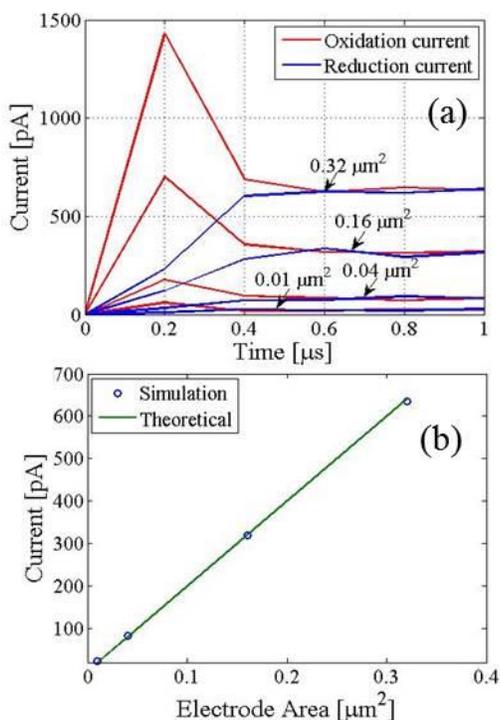
Fig. 3(a) Current for 0.83mM Ferri and various electrode area of 0.01, 0.04, 0.16 and $0.32\mu m^2$. (b) Comparison between simulation and theoretical of steady-state current .
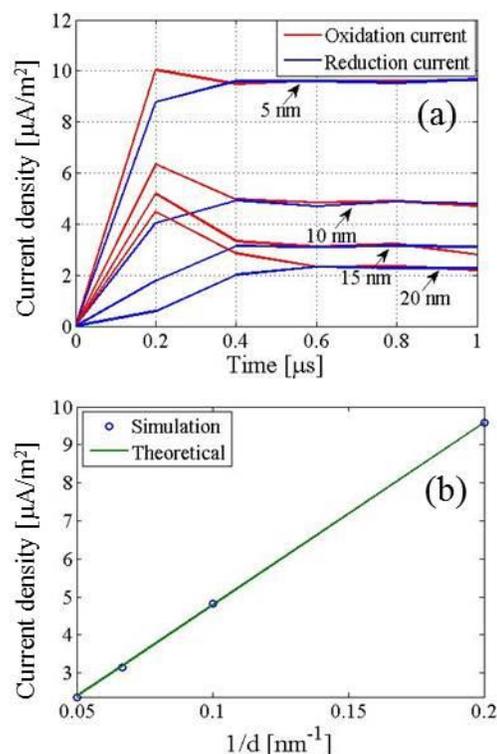

Fig. 4(a) Current density with various Ferri concentration of 1 μM, 1 nM, 1 pM and 1 fM. (b) Comparison between simulation and theoretical of steady-state current density.

Fig. 5(a) Current density for 1 pM Ferri and various electrode distance of 20 nm, 15 nm, 10 nm and 5 nm. (b) Comparison between simulation and theoretical of steady-state current density.
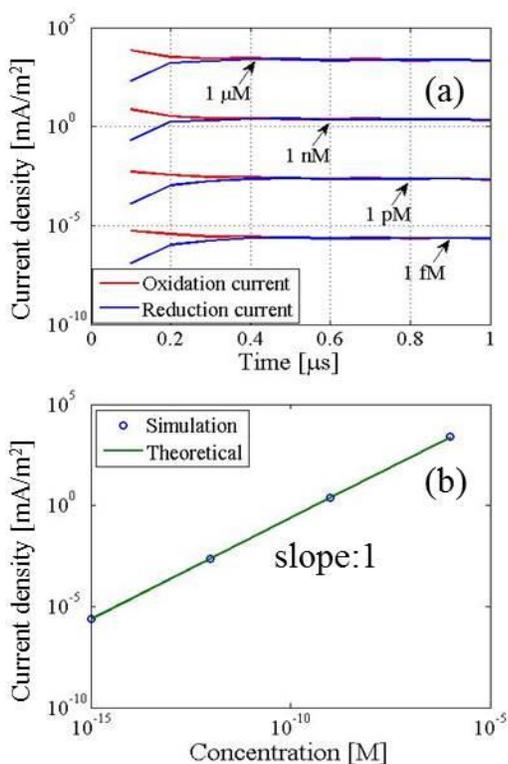
is consistent with the theoretical value from Eq. (2). Fig. 4(a) shows the logarithmic value of current density with Ferri concentrations ranging from 1fM to 1μM for the electrode distance 20nm and the same particles count, while Fig. 4(b) shows that the steady-state current is proportional to the Ferri concentration, and it also concurred with the theoretical value. This indicates that Eqs. (1)-(2) are valid even in low analtye concentration.

Fig. 5(a) shows the current density with electrode distances ranging from 5nm to 20nm for Ferri concentration 1pM and the same particles count, and Fig. 5(b) shows that the steady-state current is inverselyproportional to electrode distance. This result also agreed with the theoretical value.

Conclusion

Monte Carlo simulation of nanoscale redox cycling is performed. The diffusion equation has been proved to be valid even for low analtye concentration. Our next step is to perform the simulation with a lesser particles count.

Acknowlegement

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