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## MODELING OF ION DIFFUSION INDUCED CURRENT THROUGH A NANOCHANNEL

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### ABSTRACT

In this article, a theoretical model that takes into consideration both the diffusion and electric osmosis fluxes to estimate the diffusion current through a nanochannel is proposed. Equivalent impedance of a nanochannel is modeled as a series connection of finite RC circuits. The impedances of the electrical double layer and buffer solution in each infinitesimal RC circuit are represented by a capacitor and a resistor, respectively. Due to the electrical double layer effect, the diffusion induced current in the proposed model is position dependent. Computer simulations and experiments using a nanoporous anodic aluminum oxide (AAO) thin film as the filter to separate electrolysis with ion concentration gradient are conducted. A high degree coincidence between the theoretical and experimental data is observed.

### 1. INTRODUCTION

Diffusion process due to concentration gradient allows particles to travel from higher concentration area to lower concentration area. It is a phenomenon that is frequently presented in our day-to-day life. Many useful applications such as diffuser, mixer, reactor, doping in solid state using diffusion process have been implemented [1-4]. Fick's law and its derivatives [5-7] are used as the basis for mathematical modeling of diffusion processes.

When a thin film with porous nanochannels is implemented to separate solutions with ion concentration gradient, diffusion induced current can be detected. For ions with relatively low diffusivity, the constant gradient approximation (CGA) approach [8] can be implemented to model the linear decreasing concentration profile. Based on the CGA model, the ion diffusion electrical

potential across a membrane can be estimated. When a membrane with through nanochannels is utilized as the separating filter to produce concentration gradient, the simple CGA model is not adequate to well describe the ion diffusion properties. The main reason is that both the concentration gradient and osmosis effect affect the ions' behaviors inside a nanochannel [9-11]. In nano domain, it seems interesting to have deeper examinations on the ions movement inside the nanochannels. Furthermore, the diffusion induced current is more attractive when the diffusion mechanism is implemented to the development of a photovoltaic system such as the dye-sensitivity solar cell [12-14].

In this research, a mathematical model that considers both the diffusion and electric osmosis effects to describe the property of the diffusion current through a nanochannel is investigated. Equivalent impedance of a nanochannel is modeled as a series connection of finite RC circuits. The impedance of the electrical double layer that causes the electric osmosis flux is characterized by a capacitor and the buffer solution is modeled by a resistor. Computer simulations and experiments using a nanoporous anodic aluminum oxide (AAO) [15, 16] thin film as the filter to separate electrolysis with ion concentration gradient are conducted to verify the proposed model.

### 2. DIFFUSION GRADIENT THROUGH A NANO POROUS MEMBRANE

#### 2.1 Diffusion flux of a membrane

Diffusion of ions across a membrane can be described by the Fick's law as,

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$$\psi = -D \frac{\partial c}{\partial x} \quad (1)$$

$\psi$  denotes the flux of ions due to diffusion,  $c$  is the ion concentration,  $x$  is the thickness of the membrane,  $D$  is the diffusion coefficient ( $m^2/s$ ).

For ions with sufficiently low diffusivity, the concentration profile across the membrane can be modeled by the constant gradient approximation (CGA) [8] as schematically illustrated in Figure 1. Assume the area of the membrane is  $A$ , the volume of each vessel is  $v_1$  and  $v_2$ , and the ion concentration in each vessel is  $c_1$  and  $c_2$ , respectively.

Under the CGA, the diffusion coefficient of the membrane is constant. The rate of change of the flux can be described by,

$$\frac{\Delta\psi}{\Delta t} = -\frac{DA}{l} \left( \frac{1}{v_1} + \frac{1}{v_2} \right) \psi \quad (2)$$

Combining Equation (1) and (2), the ion concentration difference between vessel 1 and 2 can be calculated as,

$$\Delta c(t) = \Delta c(0) \exp\left(-\frac{DA}{l} \left( \frac{1}{v_1} + \frac{1}{v_2} \right) t\right) = \Delta c(0) \exp(-t/\tau) \quad (3)$$

Where  $\Delta c(t) = c_1(t) - c_2(t)$  and

$$\tau = l \left[ DA \left( \frac{1}{v_1} + \frac{1}{v_2} \right) \right]^{-1}$$

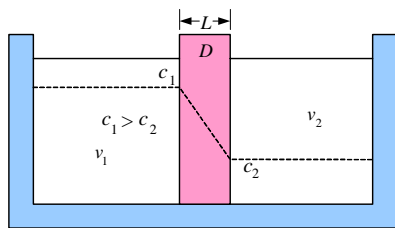


Figure 1. Schematic illustration of the constant gradient approximation (CGA)

## 2.2 Ion diffusion induced electrical potential

Based on the CGA model, the ion diffusion induced electrical potential across a membrane with through nanochannels can be calculated as,

$$V = V_1 - V_2 = \frac{\kappa T}{q} \ln\left(\frac{c_2}{c_1}\right) \quad (4)$$

Similar to Equation (3), the above expression can only describe the ion diffusion induced electrical potential across a membrane.

Inside a nanochannel, both the concentration gradient and osmosis effect affect the ions' behaviors. The flux of ions that counts both the concentration gradient and osmosis effect [9-11] can be described by,

$$\psi = -cz\mu \frac{\partial V_x}{\partial x} - \frac{\mu\kappa T}{q} \frac{\partial c}{\partial x} \quad (5)$$

The first item is the electric osmosis flux and second item denotes the ion diffusion flux. Where  $c$  is the ion concentration,  $z$  is the valence of ions,  $\mu$  denotes the mobility of ions,  $V_x$  is the electrical potential at a distance  $x$  from the entrance of a nanochannel,  $q$  is the charge on each ion,  $T$  is absolute temperature,  $\kappa$  is the Boltzman constant.

## 3. DIFFUSION INDUCED CURRENT INSIDE A NANOCHANNEL

### 3.1 Impedance of a Nanochannel

The ion diffusion induced electrical potential across a membrane with through nanochannels can be described by Equation (4). To further identify the ion diffusion induced current through the nanoporous membrane, the impedance of the membrane has to be modeled.

As aforementioned, diffusion ions traveling along a nanochannel are influenced by both the diffusion flux and the electric osmosis flux that results from the electrical double layer as schematically depicted in Figure 3. The electrical double layer consisting of the fixed stern layer and the diffuse Gouy-Chapman layer [17], gives to an electrical potential (zeta potential) between the wall of the nanochannel and bulk of the buffer solution that carries the ions [18]. Equivalent impedances of a nanochannel can be modeled as a series connection of finite RC circuits as shown in Figure 4. The capacitor  $C_d$  and resister  $r$  in each infinitesimal RC circuit denote the impedance of the electrical double layer and the buffer solution, respectively.

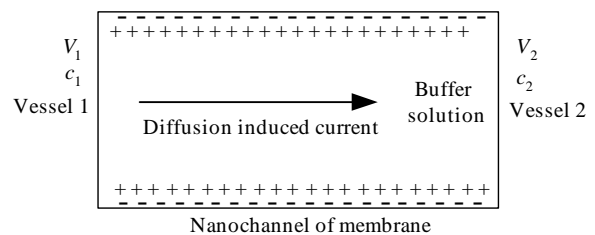


Figure 3. Nanochannel double layer

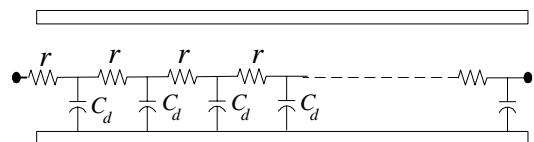


Figure 4. Nanochannel impedance model

### 3.2 Ion diffusion induced current

As depicted in Figure 3, the electric double layer induced potential at the wall of a nanochannel will trap cations that travel along the axial direction, resulting in reducing of the ion diffusion current stage by stage. The

equivalent circuit of an infinitesimal unit with a distance  $x$  from the inlet of this nanochannel is schematically illustrated in Figure 5.

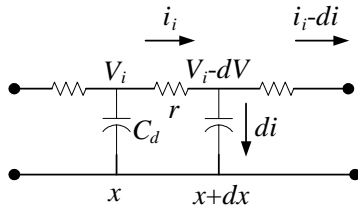


Figure 5. The equivalent circuit of an infinitesimal unit. The time dependent potential gradient and diffusion current gradient along the axial direction at position  $x$  can be described as,

$$\frac{\partial V_i(t)}{\partial x} = -ri_i(t) \quad (6)$$

$$\frac{\partial i_i(t)}{\partial x} = -C_d \frac{\partial V_i(t)}{\partial t} \quad (7)$$

Equations (6) and (7) can be rearranged as,

$$\frac{\partial^2 V_i(t)}{\partial x^2} = -rC_d \frac{\partial V_i(t)}{\partial t} \quad (8)$$

$$\frac{\partial^2 i_i(t)}{\partial x^2} = -rC_d \frac{\partial i_i(t)}{\partial t} \quad (9)$$

When the following parameter substitution is applied, the above Equations become the ordinary differential equations as Equations (11) and (12).

$$y^2 = \frac{c_d r x^2}{4t} \quad (10)$$

$$\frac{\partial V_i(t)}{\partial t} = -\frac{\partial V_i(t)}{\partial y} \sqrt{\frac{c_d r}{4}} x t^{-3/2} \quad (11)$$

$$\frac{\partial V_i(t)}{\partial x} = \frac{\partial V_i(t)}{\partial y} \sqrt{\frac{c_d r}{2\sqrt{t}}} \quad (12)$$

Equations (11) and (12) can be integrated to obtain a 2<sup>nd</sup> order differential equation as,

$$\frac{d^2 V_i(t)}{dy^2} + 2y \frac{dV_i(t)}{dy} = 0 \quad (13)$$

Hence,

$$\frac{dV_i(t)}{dy} = A_1 \exp(-y^2) \quad (14)$$

and

$$V_i(t) = A_1 \int_0^y e^{-y^2} dy + B = A_1 \text{erf}(y) + B \quad (15)$$

$$\text{erf}(y) = \frac{2}{\sqrt{\pi}} \int_0^y e^{-y^2} dy$$

where  $\text{erf}(y)$  denotes the error function.

Equation (15) indicates that  $V_i(t)$  only depends on  $y$ .

When  $t=0$  and  $x=0$ ,  $V_i(0) = V_1(0)$  is the initial voltage in vessel 1. The constants  $A_1$  and  $B$  in Equation (15) are,

$$A_1 = -B = -V_1(0) \quad (16)$$

The ion diffusion induced potential and current inside a nanochannel can be solved from Equation (15) respectively as,

$$V_i(t) = V_1(0) \left[ 1 - \text{erf}\left(\frac{1}{\sqrt{\tau}}\right) \right] \quad (17)$$

and

$$i_i(t) = \frac{V_1(0)}{rx} \frac{2}{\pi\tau} \exp\left(-\frac{x}{\tau}\right) \quad (18)$$

where  $\tau = \frac{4t}{c_d r x^2}$  is the time constant.

### 3.3 Impedence of Nanochannel

To fully utilize Equation 18 to estimate the diffusion current through a nanochannel, the unit resistance  $r$  and capacitance  $C_d$  defined in Figure 5 have to be determined in advanced. In general, it is difficult to experimentally measure them.

For a nanochannel as shown in Figure 3 with thickness  $l$ , the overall diffusion impedance across it can be modeled by [19],

$$Z(s) = R_w \frac{D \Delta c(s)}{l \psi(s)} \quad (19)$$

where  $R_w$  denotes the resistance across the channel.  $R_w$  can be furthered calculated according to,

$$R_w = \frac{l}{qAD} \left( \frac{V}{\Delta c} \right) \quad (20)$$

The overall capacitance across the nanochannel can also be estimated in terms of  $R_w$  as,

$$C_w = \frac{l^2}{R_w D} \quad (21)$$

The unit resistance  $r$  and capacitance  $C_d$  defined in Figure 5 are then approximated by Equation 22 and 23, respectively.

$$r = \frac{R_w}{l} \quad (22)$$

$$C_d = \frac{C_w}{l}$$

## 4. COMPUTER SIMULATIONS

Computer simulations of the diffusion current through an anodic aluminum oxide (AAO) thin film with nanochannels by using Equation 18 are conducted. The overall resistance  $R_w$  and capacitance  $C_w$  of an AAO thin film are  $8.9 \Omega$  and  $0.108 \mu\text{F}$ , respectively [20]. Accordingly, the unit resistance  $r$  and capacitance  $C_d$  can be calculated.

Figure 6 illustrates the profiles of the position dependent diffusion current through an AAO thin film for an electrochemistry cell as shown in Figure 1 with initial ion concentration ratio  $c_1(0)/c_2(0)=6$ .

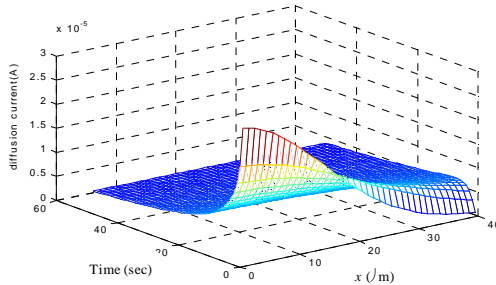


Figure 6. Profiles of the position dependent diffusion current through an AAO thin film

Figure 7 depicts the trajectories of the diffusion currents at  $x=l$  for ion concentration ratios 6 and 3, respectively.

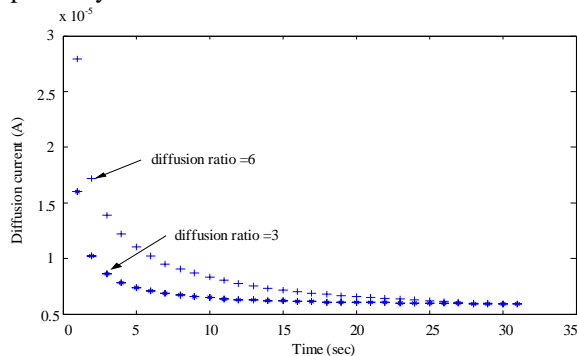


Figure 7. Trajectories of the diffusion currents at  $x=l$

### 5. EXPERIMENTAL VERIFICATION

To further verify the validity of Equation 18, an electrochemistry bath that contains two vessels separated by an AAO thin film with pore diameter around 50 nm as shown in Figure 8 is built. The CH1627A electrochemistry analyzer by CH Instruments is used to measure the ion currents. The electrolysis used is potassium chloride (KCl). In general, pores with diameter of 50 nm should allow both the cation ( $K^+$ , 0.137nm) and anion ( $Cl^-$ , 0.181 nm) to penetrate simultaneously. Therefore, the KCl electrolysis is not suitable to verify Equation 18 that is valid for diffusion current induced by ions with same polarities. However, there are 4.3  $K^+$  ions and 1/15  $Cl^-$  ion on average flowing in the channel due to the electric osmosis inside a nanochannel [21]. It is reasonable to assume that the cations contribute most of the diffusion current.

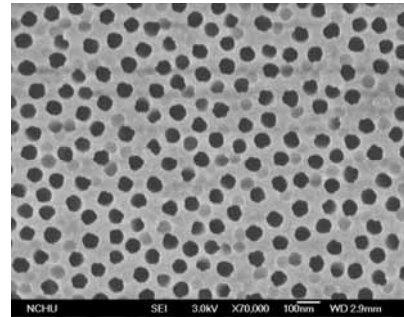


Figure 8. AAO thin film to separate vessels with different ion concentrations

Figure 9 compares the experimental and simulation diffusion currents for the condition of  $c_1(0)/c_2(0)=6$ . There is only a small deviation between the theoretical and experiment data. The validity of the proposed model of diffusion current through nanochannels can be verified.

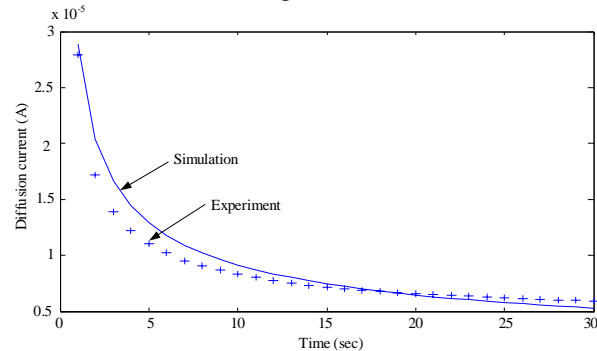


Figure 9. Comparison of the theoretical and experimental diffusion current

### 6. CONCLUSIONS

Diffusion property allows ions to travel from higher concentration area to lower concentration area. When a thin film with porous nanochannels is implemented to separate solutions with ion concentration gradient, diffusion induced current can be detected.

Diffusion ions traveling along a nanochannel are influenced by both the diffusion flux and the electric osmosis flux that results from the electrical double layer. In this article, a novel model that considers both the diffusion and electric osmosis effects to describe the property of the diffusion current through a nanochannel is proposed. Equivalent impedance of a nanochannel is modeled as a series connection of finite RC circuits. The impedance of the electrical double layer that causes the electric osmosis flux is represented by a capacitor and the buffer solution is modeled by a resistor.

Computer simulations using a nanoporous anodic aluminum oxide (AAO) thin film to separate solutions with ion concentration gradient are conducted. An electrochemistry bath that contains two vessels separated

by an AAO thin film is built to carry out the experiments. A high degree coincidence between the theoretical and experimental data is observed.

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