Electric Double Layer Simulation on Transient State for Sensitivity Enhancement of Affinity-Based Biosensor

Jun-Myung Woo*, Seok Hyang Kim* and Young June Park*

*School of Electrical Engineering and Computer Science, Seoul National University,
Daehak-dong, Gwnak-gu, Seoul, Korea, woojm99@isis.snu.ac.kr

ABSTRACT

We present a transient simulation of a system consisting of the electrolyte and the metal electrode including the electric double layer(EDL). The motivation of the transient simulation is to enhance the sensitivity of the biosensor based on the electrical signal detection. The Poisson equation and drift-diffusion equation are calculated on steady and transient state. De-ionized water (DIW) and phosphate buffered saline (PBS) buffer are employed as the electrolyte solution, yielding distinct results due to the difference of the ion concentrations. From the simulation results in various conditions, we can find the measurement method that can get the high sensitivity in the sensing of charged molecules.

Keywords: electrical double layer, affinity-based biosensor, sensitivity, step pulse

1 INTRODUCTION

The electronic detection of the biomolecules is emerging as an effective alternative to the optical detection methods. In the affinity-based biosensors based on the label free electronic detection, the semiconductors (or gate oxide) are functionalized by the probe molecules, which are complementary to target molecules[1,2]. Because most biological processes involve electrostatic interactions, the probe-target bound molecules induce the charge variation in the semiconductors so that the conductance of semiconductors is modulated.

However, there exists a space charge layer called the electric double layer (EDL) in the interface between the solution and the electrode, which screens the electrostatic field induced from the charged molecule in over Debye length[3]. General sensing environment involves the buffer solution, where Debye length is ~1 nm in, while the size of biomolecule is several nanometers. In this case, due to the screening effect by the ions, it is difficult to achieve high sensitivity of the BioFETs.

Recent researches[4,5] have focused on the reduction of the screening effect through the forced electro-diffusion flow of the mobile ions and calculated the enhancement of the sensitivity. But the DC electro-diffusion flow is difficult to be applied to the practical measurement scheme since the Faradaic current may change the pH of the solution, etc. Therefore, more feasible sensing method to overcome the screening effect is needed. Here, we propose a new sensing method based on 'the transient state' measurement after step-pulse input bias. Numerical simulations have been developed to investigate the feasibility of the method.

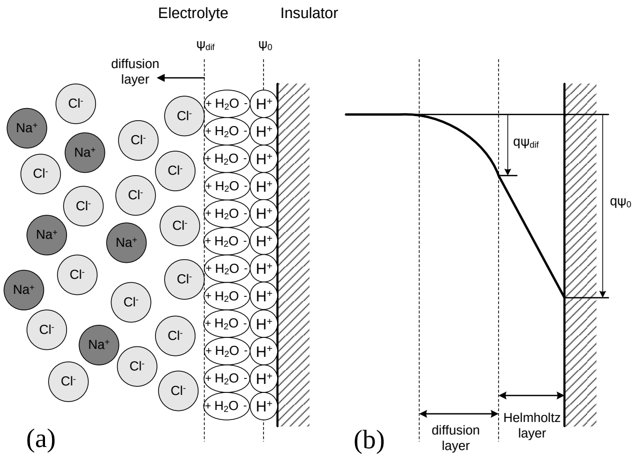


Figure 1. Schematic diagrams of (a) the EDL, and (b) the energy diagram across the EDL for the electrolyte containing Na^+ and Cl^- ions. EDL consists of two layers, the diffuse and Helmholtz lavers.

2 GOVERNING EQUATION

The electrical potential and charged carriers in the electrolyte solution are governed by the Poisson equation,

$$\nabla \cdot \varepsilon(-\nabla \psi) = q([n^+]-[n^-]), \tag{1}$$

where ε is the permittivity of electrolyte solution, ψ is the electrical potential, and $[n^+]$ and $[n^-]$ are the cation and anion in the electrolyte solution, respectively.

In the electrolyte solutions, ion carriers accelrate through the drift and diffusion similar to the transport of the electrons and holes in the semiconductor. Accordingly, the ion flux is represented by

$$F_{[n^\pm]} = \pm \mu_{n^\pm}[n^\pm]\nabla \psi - D_{n^\pm}\nabla [n^\pm] , \tag{2}$$

where $\mu_{n\pm}$ and $D_{n\pm}$ are the mobility and the diffucion

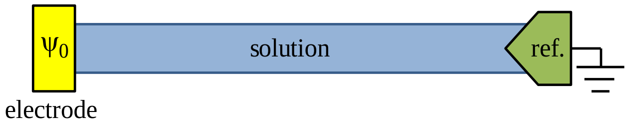


Figure. 2. One-dimensional simulation condition. The electrical voltage bias ψ_0 is applied to the electrode.

coefficient of cation and anion, respectively, in the electrolyte solution.

The continuity equation for ion carriers can be written as

$$\frac{\partial [n^{\pm}]}{\partial t} = -\nabla \cdot F_{[n^{\pm}]} \quad . \tag{3}$$

In the steady state, the left term of Eq. (3) becomes zero, yielding the Boltzmann distribution for ions,

$$[n^{\pm}] = n_0 \exp(\mp \psi / V_t) \quad , \tag{4}$$

where n_0 is bulk ion concentration of the electrolyte solution. The diffuse layer derives from this distribution, suggested by Gouy and Chapman[6,7].

After Stern's modification[8] that considers the Helmholtz layer due to the minimum distance between the ions and the electrode surface, the EDL has been regarded as a series capacitance made up of the Helmholtz layer and diffuse layer, as shown in Figure 1.

3 SIMULATION RESULTS AND DISCUSSION

Parameter	Value	Note
ε	78 * ε_0	aqueous solution in room temperature
μ_{H+}	33.3 * 10^{-4} cm^2/V-s	
μ_{OH-}	18.8 * 10^{-4} cm^2/V-s	
μ_{Na+}	5.9 * 10^{-4} cm^2/V-s	
μ_{Cl-}	7.0 * 10^{-4} cm^2/V-s	
$D_{n\pm}$	$\mu kT/q$	Einstein relation
n_0	10-7 M 0.1 M	in DIW in PBS buffer
d_H	5 Å	thickness of Helmholtz layer

Table 1: Values Used for Variables and Constants Used to Calculate the Theoretical Value

The parameters and simulation conditions used in this work are summarized in Table 1 and Figure 2. In Figure 2, the electrical potential ψ_0 is applied to the electrode with respect to bulk solution, which is grounded by the reference electrode. Generally, the semiconductors are employed as the electrode in the affinity-based biosensors to detect the charge induced by charged molecules.

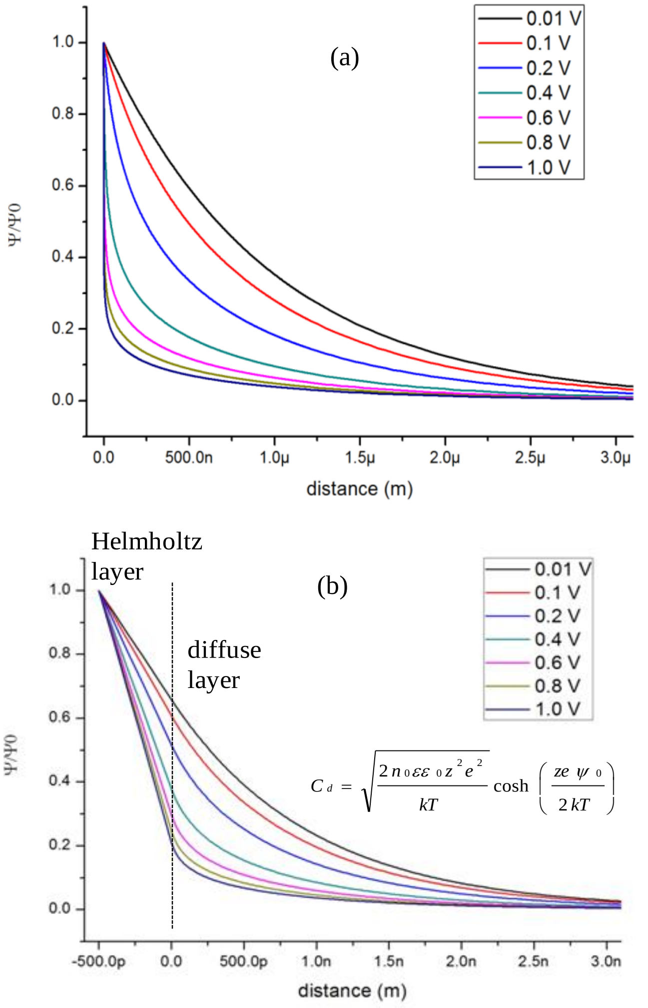
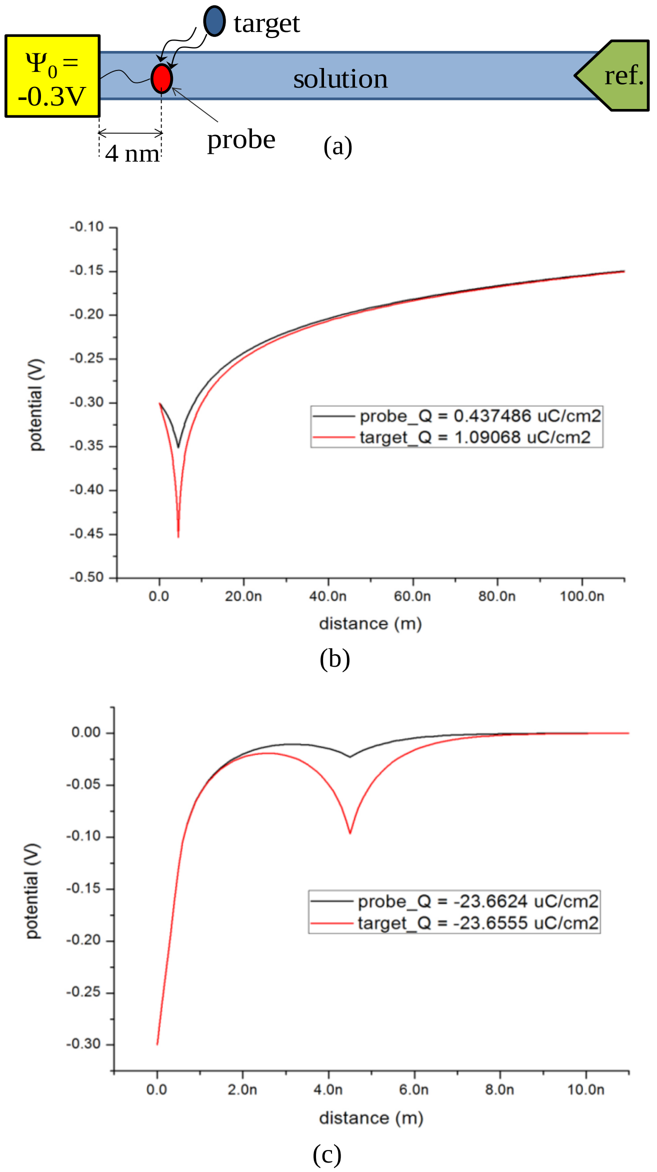


Figure 3. Normalized potential profile in (a) DIW condition and (b) buffer condition. The screening length in buffer solution is very shorter than that in DIW, because of the difference of ion concentration. The bias dependence of the screening length corresponds to diffusion capacitance.

Figure 3 shows the normalized potential profiles in the DIW and PBS buffer condition. Theoretical values for the Debye length in DIW and PBS buffer are about 1 μm and 1 nm, respectively. In the PBS buffer, the Helmholtz layer which has 5 Å-thickness can be observed. As the bias voltage increases, the screening length becomes shorter because the counter ions accumulate on the electrode surface exponentially to the electrode potential.

3.1 The steady state condition



(a)

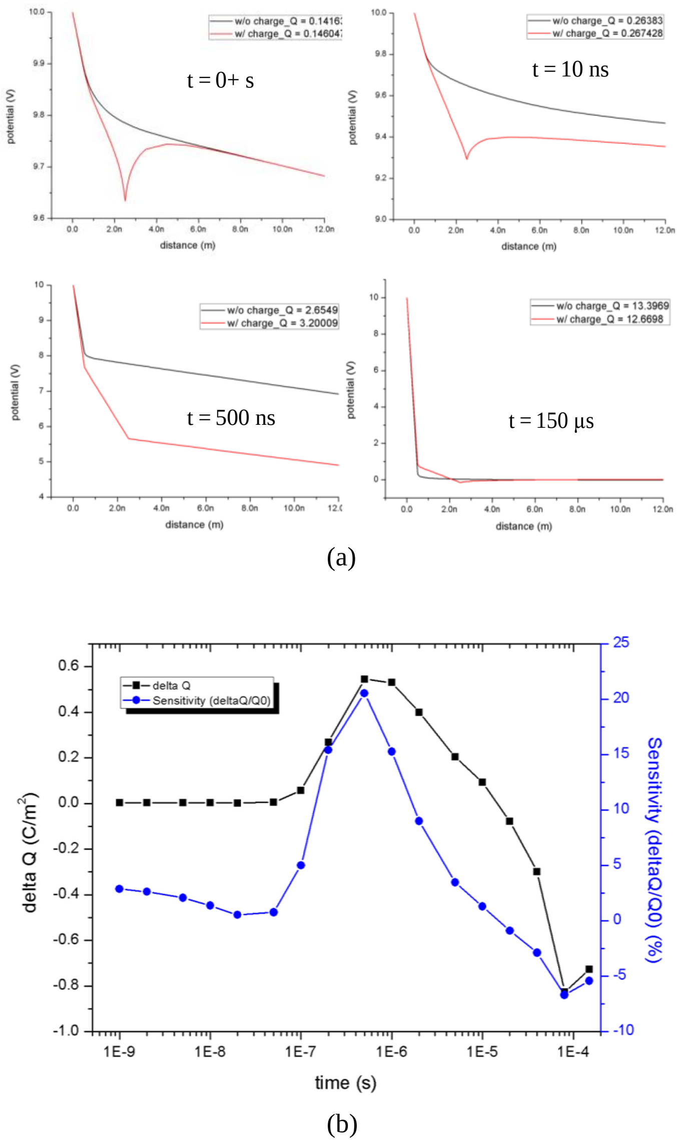
(b)

(c)

Figure 4. (a) Schematic diagram of the probe-target binding event in the affinity-based biosensor. Potential profiles in (b) DIW and (c) PBS buffer condition on steady state. The electrode bias voltage is set to -0.3 V and charged molecules are on the 4 nm from the interface. *Q* represents the induced charge on the electrode surface.

The electrode surface charge induced by charged molecules is calculated from $Q = -\int D \cdot ds$. The size of molecules is set to be 4 nm, and their charge density is considered as the sheet charge density. The sensor system detects the probe-target binding event by the difference of induced surface charge between before and after the event.

As shown in Figure 4(b), in the DIW condition, there is considerable variance of induced charge by the target binding because the screening length is quite longer than the size of the molecule. On the other hand, in PBS buffer condition as shown in Figure 4(c), the sensor cannot detect the target molecules due to relatively shorter screening length.



(a)

(b)

Figure 5. (a) Potential profiles at 0+ s, 10 ns, 500 ns and 150 μs. (b) Variance of induced surface charge and corresponding sensing ability with respect to time after step-pulse biasing in the buffer solution.

Accordingly, in view of high sensitivity, the ionic solution with low ionic concentration is better environment to detect the charged molecules.

3.2 The transient state condition

In DC forced electro-diffusion flow, the driving force behind the reduction of screening effect is the external high electric field. We can observe similar effect on the transient response after the high bias step input pulse.

Figure 5(a) demonstrates the potential profiles according to the time flow. At t = 0 sec, high bias voltage, 10 V, is applied to the electrode (distance = 0) in the PBS buffer condition. As discussed before, the high sensitivity cannot be achieved because of the short screening length in the PBS buffer. However, high step pulse bias induces the electro-diffusion flow of mobile ions on transient state, so that the screening length is extended instantaneously. We need to notice that after 500 ns from pulse biasing, extended screening length makes the difference in the induced surface charge as shown in Figure 5(a).

Figure 5(b) shows change of the induced charge variation and the sensitivity with the time. As the screening length is extended, the sensitivity becomes the maximum, and decreases again as the system settles down at the steady state.

4 CONCLUSION

We have presented a numerical simulation for the affinity-based electrical biosensor system on the steady and transient state. Considering the screening length in the solutions, the solution with low ion concentration can be better measurement condition to get the high sensitivity. The transient electro-diffusion ionic flow caused by step-pulse input bias leads to the enhancement of the sensitivity. From these results, we can find a new sensing measurement scheme to achieve high sensitivity in the biosensor applications.

ACKNOWLEDGMENT

This work was supported by the BK21Program, the Nano System Institute National Core Research Center (NSI-NCRC) program of KOSEF, and the Industrial Source Technology Development program (10033590) of the Ministry of Knowledge Economy (MKE), Korea.

REFERENCES

[1] J. Wang, “Carbon-nanotube based electrochemical biosensors: A review,” *Electroanalysis*, Vol. 17, pp. 7-14, 2005.
[2] D. Landheer, G. Aers, W. R. McKinnon, M. J. Deen, and J. C. Ranuarez, “Model for the field effect from layers of biological macromolecules on the gates of metal-oxide-semiconductor transistors,” *Journal of Appl. Phys.*, Vol. 98, 044701, 2005.
[3] P. Bergveld, “Thirty years of ISFETOLOGY: What happened in the past 30 years and what may happen in the next 30 years,” *Sensors and Actuators B*, Vol. 88, pp. 1-20, 2003.
[4] Y. Liu, J. Sauer, R. W. Dutton, “Effect of electrodiffusion current flow on electrostatic screening in aqueous pores,” *Journal of Appl. Phys.*, Vol. 103, 084701, 2008.
[5] Y. Liu, K. Lilja, C. Heitzinger, and R. W. Dutton, “Overcoming the screening-induced perfomance limits of nanowire biosensors: a simulation study on the effect of electro-diffusion flow,” *IEEE IEDM*, pp. 491-494, 2008.
[6] G. Gouy, *J. Phys. Radium*, Vol. 9, p. 457, 1910.
[7] D. L. Chapman, *Phil. Mag.*, Vol. 25, p. 475, 1913.
[8] O. Stern, *Z. Elektrochem*., Vol. 30, p. 508, 1924