# Surface Charge Modulated Ionic Conductance of Closed Solid State Nanopore Biosensors

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**Abstract:** This paper aims to explore the surface charge modulated ionic conductance of closed solid state nanopores for providing a physical explanation to an important observation of significant nonlinear length dependent variation in ionic current in such nanopore biosensors with a view to design improved sensors without increasing the fabrication cost for biomolecule detection. Although extensive work has been done in modelling open pore conductance, closed nanopores have not been considered. For open pore sensors, electrolyte flow rate adjustment is crucial for maximum target molecule binding, limiting the detection limit to 1pg/ml. In closed silicon oxide nanoporous structure on silicon substrate, the depletion layer capacitance at the pore bottom plays a major role in impedance sensing, enabling unique peak frequency based detection selective only to the target antigen. Using COMSOL simulations, we aim to provide a novel framework for modelling the surface charge modulated ionic conductance in closed nanopores.

**Keywords:** solid state nanopore, surface charge modulation, Poisson-Nernst Planck equation, steady state continuum, ionic conductance.

## 1. Introduction

In the past few years there has been a major thrust in the area of solid state nanopore biosensors to detect a wide range of biomolecules like biotin, proteins, toxins, DNA virus and others by surface charge modulated ionic conductance effect [1-21]. Although extensive work has been done in modelling open pore conductance, closed nanopores have not been considered. For open pore sensors, adjustment of the electrolyte flow rate is crucial for maximum target molecule binding, preventing such sensors from achieving a limit of detection below 1pg/ml [1,19]. In closed silicon oxide nanoporous structure on silicon substrate, the depletion layer capacitance at the

pore bottom plays a major role in impedance sensing, enabling unique peak frequency based detection selective only to the target antigen [20]. Figure 1 depicts an open pore and a closed pore nanoporous system. In this paper, we aim to provide a novel framework for modelling the surface charge modulated ionic conductance in closed nanopores using COMSOL, highlighting the significant nonlinear length dependent variation in ionic current.

## 2. Governing Equations

Since in the steady state continuum regime ((i.e. no pore blocking or significant volume exclusion effects and concentration of analyte is large enough so that ensemble average distribution can be considered amongst the pores), nanopore conductance is governed by the
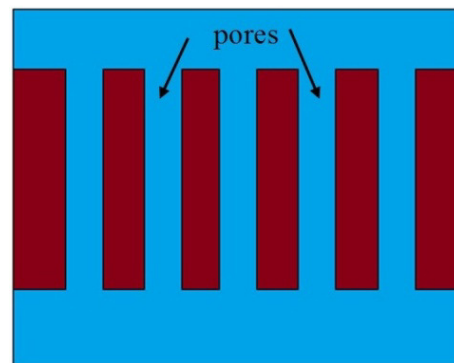


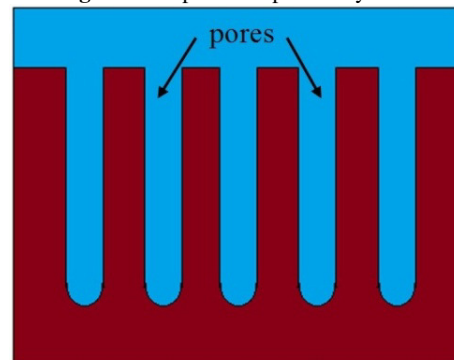**Figure 1a.** Open Nanoporous System



**Figure 1b.** Closed Nanoporous System

Poisson-Nernst Planck (PNP) equations, we have

solved the 2-Dimensional (2D) PNP equations using COMSOL. The Nernst Planck flux equations for each ionic species $i$ is given by

$$J_i = -D_i \nabla c_i - \frac{z_i F}{RT} D_i c_i \nabla \varphi \qquad (1)$$

where $J_i$, $D_i$, $c_i$, and $z_i$ are, respectively, the flux, diffusion constant, concentration, and charge of species $i$. $\varphi$ is the local electric potential and $F$, $R$, and $T$ are the Faraday constant, universal gas constant, and absolute temperature respectively. The relationship between $\varphi$ and $c_i$ is described by the Poisson equation as follows:

$$\nabla^2 \varphi = -\frac{F}{\epsilon \epsilon_0} \sum_i z_i c_i \qquad (2a)$$

where $\epsilon_0$ is the dielectric constant of free space, $\epsilon$ is the relative dielectric constant of the medium. The equilibrium distribution of $c_i$ follows a Boltzmann distribution given in equation 2b which can be obtained by setting $J_i = 0$ in equation 1 followed by spatial integration of $c_i$ and $\varphi$:

$$c_i = c_{i,0} \exp\left(-\frac{z_i F \varphi}{RT}\right) \qquad (2b)$$

where $c_{i,0}$ is the bulk concentration of species $i$.

## 3. Use of COMSOL Multiphysics

In order to model the surface charge modulated ionic conductance in closed solid state nanopores, we have considered a single
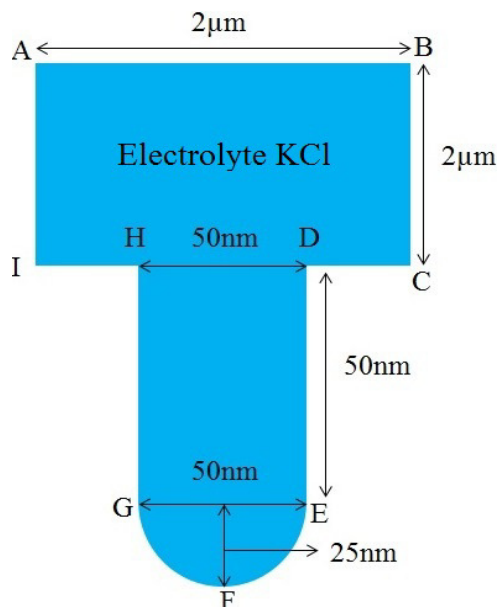


**Figure 2.** Geometry of the 2D computational domain (structure not to scale). ABCI represents the bulk electrolyte well and DEFGH represents the pore.

closed pore with a bulk solution layer at the mouth of the pore as shown in figure 2. The 2D structure is simulated using COMSOL. The computational domain assumed a room temperature aqueous KCl solution for which the following parameters were used:-

- $T = 298$ K
- $D_K = 1.957 \times 10^{-9}$ m$^2$/s
- $D_{Cl} = 2.032 \times 10^{-9}$ m$^2$/s
- $\epsilon = 80$
- $c_{K,0} = c_{Cl,0} = 1$ mole/m$^3$

In order to solve the PNP equations, we have coupled 'Electrostatics' (Poisson equation) and 'Transport of Diluted Species' (Nernst Planck equation) physics. The boundary conditions for 'Transport of Diluted Species' physics are as follows:-

- Concentration of electrolyte at AB, GEF is held constant at the bulk value.

The boundary conditions for 'Electrostatics' physics are as follows:-

- Constant potential difference is applied between AB and GFE.
- Using surface charge on the pore walls and bottom as the adjustable parameter here, simulations were carried out for four different conditions:-
1) Surface charge is applied on both the walls (HG, DE) and pore bottom (GFE).
2) Surface charge is applied only on the pore walls (HG, DE).
3) Surface charge is applied only on the pore bottom (GFE).
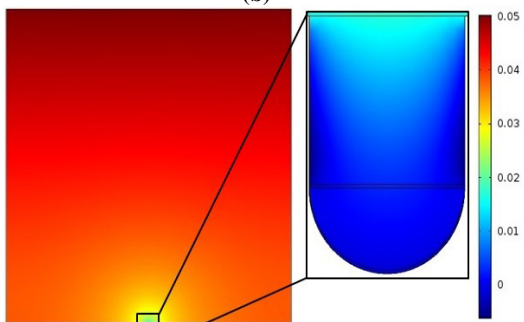4) No surface charge is applied.

Next, after meshing the structure, steady state stationary simulations have been performed.

## 4. Results and Discussions

In order to model the ionic conductance, the simulated potential distribution and the concentration profile has been studied. The effect of surface charge modulation can be observed by comparing the potential profiles in figure 3a and 3b. In order to compare the numerical results with a theoretical model, the potential distribution in the pore has to be solved analytically. For that, we need to apply superposition theorem and sum up the two potential profiles shown in figure 4. Here the distribution in only one half of the pore is
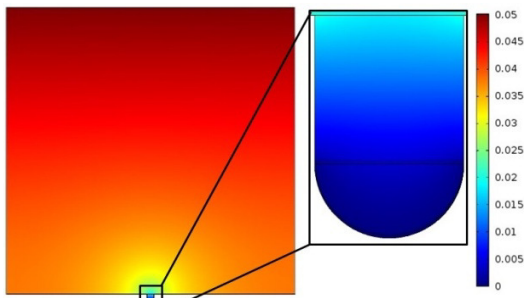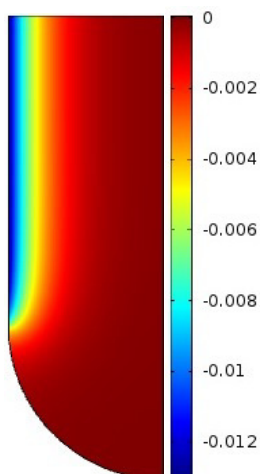
**Figure 3a.** Potential profile (V) when no surface charge is applied

**(b)**



**Figure 3b.** Potential profile (V) when surface charge is applied on both walls and bottom of the pore

considered using axial symmetry. Figure 5 depicts that even ignoring the edge effect [2] at the pore entrance, i.e., the well-pore junction, there is a significant nonlinear dependence of current on pore length. This can be exploited for the optimization of pore geometry, leading to performance enhancement.



**Figure 4a.** Potential profile when surface charge is applied only on the pore walls
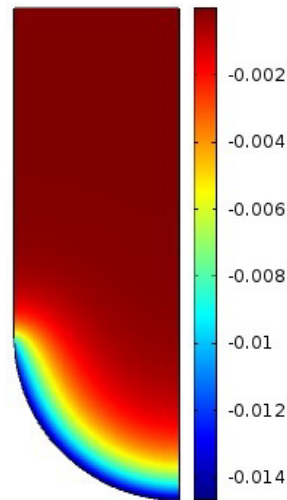


**Figure 4b.** Potential profile when surface charge is applied only on the pore bottom
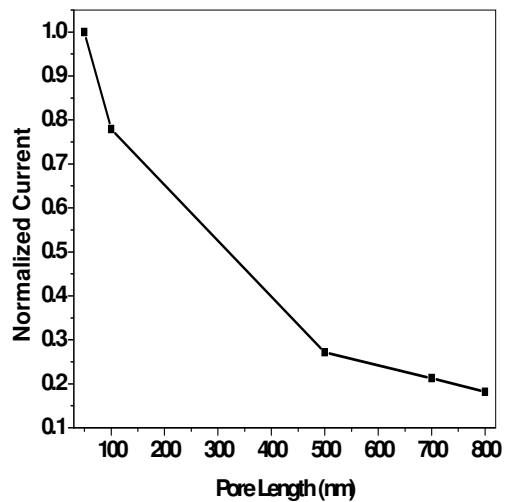


**Figure 5.** Normalized ionic current versus pore length for pore diameter = 50 nm

## 5. Conclusions

Finite-element simulations demonstrate the role of surface charge in ion transport in closed nanopores. The results can be validated and compared by developing a proper analytical model. The two combined can provide a thorough understanding and analysis of the unexplored surface charge modulated ionic conductance in closed nanopores.

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