

Surface Charge Modulated Ionic Conductance of Closed Solid State Nanopore Biosensors

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Abstract

There has been a major thrust in solid state nanopore biosensors to detect biomolecules by surface charge modulated ionic conductance effect[1-8]. For open pore sensors, adjustment of electrolyte flow rate is crucial for maximum target molecule binding, preventing such sensors from achieving LOD below 1pg/ml[1,9]. In closed silicon oxide nanoporous structure on silicon substrate, depletion layer capacitance at pore bottom plays a major role in impedance sensing, enabling unique peak frequency based detection selective only to target antigen[10]. We aim to provide a framework for modeling the surface charge modulated ionic conductance in closed nanopores.

Since in steady-state, nanopore conductance is governed by Poisson-Nernst Planck(PNP)equation, we have solved 2D PNP equation using COMSOL Multiphysics software. The 2D structure simulated is shown in Figure 1. The electrolyte used is KCl.

Nernst Planck flux equations:-

$$J_i = -D_i \nabla c_i - z_i F / (R * T) * D_i * c_i * \nabla \varphi \quad (1)$$

where J_i , D_i , c_i , and z_i are, respectively, the flux, diffusion constant, concentration, and charge of species i . φ is the local electric potential and F , R , and T are the Faraday constant, universal gas constant, and absolute temperature respectively.

The relationship between φ and c_i is described by the Poisson equation as follows:

$$\nabla^2 \varphi = -F / (\epsilon * \epsilon_0) * \sum (z_i * c_i) \quad (2a)$$

where ϵ_0 is the dielectric constant of free space, ϵ 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 φ :-

$$c_i = c(i,0) * \exp(-z_i * F * \varphi / (R * T)) \quad (2b)$$

where $c(i,0)$ is the bulk concentration of species i .

In order to solve the PNP equation, we have coupled 'Electrostatics'(Poisson equation) and 'Transport of Diluted Species'(Nernst Planck equation) physics.

'Electrostatics' boundary conditions:-

Constant potential difference is applied between AB and GFE.

For proper appreciation of the effect of surface charge, four conditions are considered. Surface charge is applied (1) on the walls (HG,DE) and bottom (GFE), (2) only on the pore walls (HG,DE) (3) only on the pore bottom(GFE). (4) Surface charge is not applied.

'Transport of Diluted Species' boundary conditions:-

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

Figure 2 shows effect of surface charge modulation. In order to compare the numerical results with a theoretical model, the potential profile 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 3. Figure 4 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. Finite-element simulations demonstrate role of surface charge in ion transport. The results can be validated and compared by developing an analytical model. The two combined can provide a thorough explanation of the unexplored surface charge modulated ionic conductance in closed nanopores.

Reference

- 1) R. Wei et. al., 'Stochastic sensing of proteins with receptor-modified solid-state nanopores', *Nature Nanotechnology* 7, 257-263 (2012).
- 2) C. Lee et. al., 'Large Apparent Electric Size of Solid-State Nanopores Due to Spatially Extended Surface Conduction', *NanoLetters* 12, 4037-4044 (2012).
- 3) F. Baldessari, 'Electrokinetics in nanochannels Part I. Electric double layer overlap and channel-to-well equilibrium', *Journal of Colloid and Interface Science* 325, 526-538 (2008).
- 4) G. Jagerszki et. al., 'Hybridization-Modulated Ion Fluxes through Peptide-Nucleic-Acid-Functionalized Gold Nanotubes. A New Approach to Quantitative Label-Free DNA Analysis', *NanoLetters* 7, 1609-1612 (2007).
- 5) Y. Yan et. al., 'Ion current rectification inversion in conic nanopores: Nonequilibrium ion transport biased by ion selectivity and spatial asymmetry', *Journal of Chemical Physics* 138, 044706(1-6) (2013).
- 6) A. Yochelis, 'Spatial Structure of Electrical Diffuse Layers in Highly Concentrated Electrolytes: A Modified Poisson–Nernst Planck Approach', *Journal of Physical Chemistry C* 118, 5716-5724 (2014).
- 7) K. Zhou et. al., 'Transport and Sensing in Nanofluidic Devices', *Annual Review of Analytical Chemistry* 4, 321-341 (2011).
- 8) H.S. White, A. Bund, 'Ion Current Rectification at Nanopores in Glass Membranes', *Langmuir*, 24, 2212-2218 (2008).
- 9) X. Wang, S. Smirnov, 'Label-Free DNA Sensor Based on Surface Charge Modulated Ionic Conductance', *ACS Nano* 3, 4, 1004-1010 (2009).
- 10) H. Ghosh, C. RoyChaudhuri, 'Ultrasensitive food toxin biosensor using frequency based signals of silicon oxide nanoporous structure', *Applied Physics Letters* 102, 243701(1-4) (2013).

Figures used in the abstract

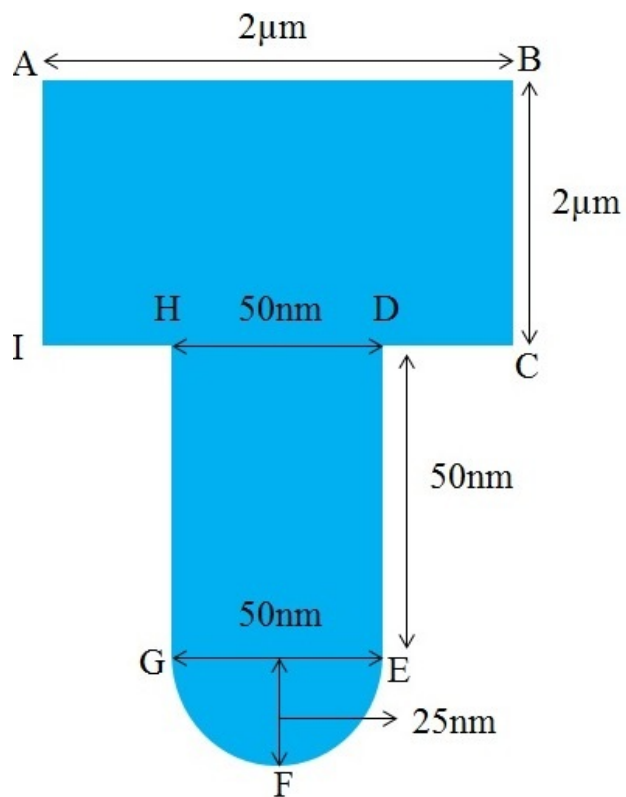


Figure 1: Geometry of Simulated Structure(not to scale). ABCI represents the bulk electrolyte well and DEFGH represents the pore.

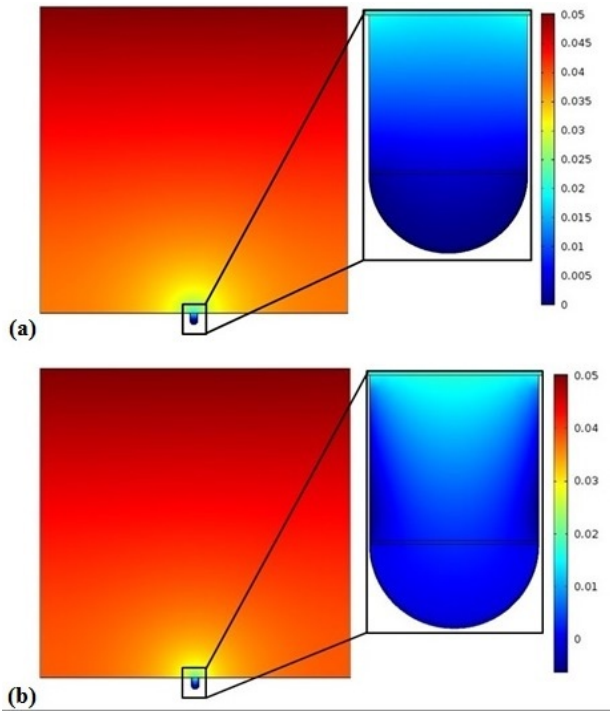


Figure 2: (a) Potential profile (V) when no surface charge is applied. (b) Potential profile (V) when surface charge is applied on both walls and bottom of the pore.

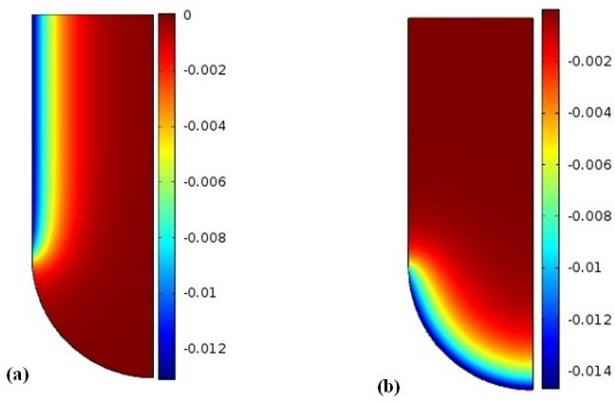


Figure 3: (a) Potential profile when surface charge is applied only on pore walls. (b) Potential profile when surface charge is applied only on pore bottom. (Only one half of pore is simulated considering axial symmetry.)

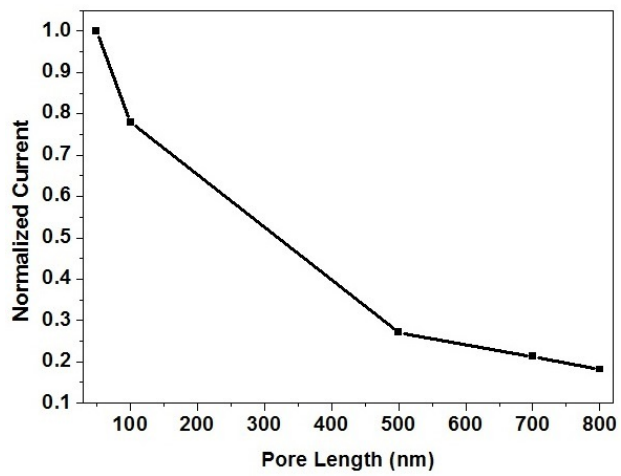


Figure 4: Normalized ionic current versus pore length for pore diameter = 50nm