ELECTROSTATIC GATING OF ION AND MOLECULE TRANSPORT THROUGH A NANOCHANNEL-ARRAY MEMBRANE

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ABSTRACT

This work presents a predictive and today's most complete model for electrostatic gating of nanofluidic channels. The model is based on the classical mean field equations and accounts for the surface reactivity. The model is successfully verified against previously published experimental data [1]. The fabrication concept of a novel device is introduced and its predicted performances are discussed with the help of the presented model. A $\sim 40\times$ performance improvement, in terms of tunability of the ionic conductivity in the nanochannel, in comparison to the result presented in [1], is expected.

KEYWORDS

Nanofluidics, nanochannels, electrostatic gating, surface charge, model.

INTRODUCTION

Ionic and molecular transport behavior in nanochannels is dominated by the surface charges and/or the surface potential. Indeed, a so-called electrical double layer (EDL) forms in the first tens of nanometers from the solid surface to screen off the surface charges by attracting oppositely charged ions. When the EDL thickness becomes comparable to the characteristic

dimension of the nanochannel, an overlap of the EDL, induced by the two opposite walls of the channel, occurs. This overlap results in an enrichment of the channel with counter-ions (of opposite charge to that of the surface) and a depletion from co-ions, thus generating a quasi-unipolar solution inside the nanochannel.

Controlling the ionic permselectivity of nanochannels by tuning their surface charge promises fundamentally novel tools for biochemical or energy applications [3], and has recently become an area of great interest. Previous research studied the use of the pH, ionic strength or surface material properties [4] as ways to modulate the nanofluidic properties. However, the former two methods are limiting in that they require very controlled and specific liquid properties, and the latter method is static, i.e. cannot be varied once the device has been manufactured.

Electrostatically gated nano/microchannel devices, e.g. "nanofluidic transistors" [1] or "FlowFETs" [2], vary the electrostatic potential of a gate electrode behind the channel walls to tune the ion permselectivity and/or electroosmotic flow (EOF). However, these structures are limited in terms of flow or current because of their planar geometry. Martin *et al.* [16] presented a first attempt of ion transport control through a gold nanotubule membrane, but their approach is limited in terms of gate potential range since the gold is not electrically isolated from the electrolyte, offering a conductive pathway and requiring chemical surface treatment against specific ion absorption. Moreover, the behavior of gated nanochannels is not yet fully understood. Models of *non-gated* nanochannels, e.g. [4-6], use the Poisson-Boltzmann equation and assume a (known) surface charge density, σ_s , or zeta-potential, ζ , to predict the electrokinetic behavior. However, the presence of a gate electrode, with potential V_{Gate} with respect to the bulk solution, modulates σ_s and ζ . Jiang *et al.* [7] provided the first *predictive* 1D model for a metal-oxide-electrolyte (MOE) interface by taking into account the electrostatically modulated surface (de)protonation at the solid-liquid interface. However, their approach cannot address the (2D or 3D) influence of the electrostatic effects along the nanochannel. Other models [1, 6, 8-10] are incomplete because they ignore the gate modulated surface (de)protonation and/or surface charges, and/or require *a posteriori* data fitting to system characteristics.

Novel approach

This work presents the first *predictive* and *most complete* model so far for an electrically gated nanochannel. We also introduce the concept of a novel

Schematics of a gated nanochannel

Figure 1 3D Schematic of a typical nanofluidic transistor structure (top), Out-of-scale 2D schematic of [1] device as implemented in the FE model for validation.

device that promises a ~ 40 times performance improvement in terms of tunability compared to previous work.

Our innovative model circumvents the above-described limitations of previous models by associating the classical electrokinetic equations (the Poisson equation for the electrical potential; the Nernst-Planck equation for the individual ion flux; and the Navier-Stokes equation for the aqueous medium flow) with the site-binding model of an oxide-electrolyte interface, as proposed by Yates *et al.* [11] (Figure 2). This association of equations makes our model exceed previous work in that: i) it is predictive, i.e. requiring only geometrical data and the dissociation constants of the surface material, but not the a-priori knowledge of ζ nor σ_s as boundary conditions; ii) it accounts for the presence of a complex electrolyte or analyte, i.e. non-binary electrolyte, mixed electrolytes or supporting electrolyte and specific analyte; and iii) it is complete, i.e. allowing to predict the entire 2D or 3D source-drain-gate configuration as well as all important system parameters, for which solutions cannot be calculated analytically.

Method

We first validate our model, using Comsol Multiphysics 3.5a®, by simulating a previously experimentally tested gated nanochannel [1].

Gated nanofluidic devices have a geometry that is

Figure 2 Model implementation: the 3 electrokinetic equations are specified with their specific boundary conditions. The site-binding model is recalled and used as the boundary condition for the channel walls.

somewhat similar to that of a MOSFET transistor in which the semiconductor substrate is replaced by an electrolyte (Figure 1 top). The device is composed of a nanochannel connecting two reservoirs of larger size, the source and the drain, in which surface effects can be neglected. A metal gate electrode is imbedded behind the dielectric nanochannel surface, and its electric potential is used to modulate the nanofluidic properties. The nanochannel dimensions are typically in the tens to hundreds of nanometer to allow benefitting from the EDL overlap effect.

Figure 1 (bottom) specifies the specific dimensions of Karnik *et al.*'s device [1], as implemented in the model.

Figure 2 presents the implementation of the electrokinetic equations in the model and specifies the boundary conditions used.

The liquid is modeled as specified in [1], with a 100 mM KCl aqueous electrolyte. Karnik *et al.* do not specify the pH and we therefore simulated for two "extreme" values: pH 7, for DI water, and pH 5.6, for DI water with dissolved CO_2 levels in equilibrium with the atmospheric conditions. The modeled nanochannel wall material is SiO_2 and the surface reaction dissociation constants are taken from two different sources in the literature [14-15].

The correct choice of the boundary conditions is crucial for an adequate modeling of the system. To reduce the model complexity, the source and drain electrode-to-liquid boundaries are simplified and modeled by a fixed potential of the bulk electrolyte in the reservoirs on each side of the nanochannel. The use of an appropriate reference electrode and sufficiently large reservoirs render the consequences of this simplification negligible with respect to the studied effects. This also allows setting the electrolyte concentration equal to the bulk concentration in each reservoir. Additionally, a pressure difference between the source and drain can be defined to account for a forced flow through the nanochannel and to study the streaming potential. In our simulations, the pressure difference was set to zero, as in the experimental conditions [1]. The site-binding model is also illustrated in Figure 2 at the top-right. The surface of most oxides can either be a proton donor, a proton acceptor, or both. The (de)protonation reaction equilibrium is expressed with a dissociation constant K_A or K_B for the acidic and basic reaction respectively. Due to its potential to store and release protons, the surface acts as a capacitor and buffers changes of pH at the surface. In this respect, this reaction should form the cornerstone in any predictive model for the gating of the surface charge, as it opposes the gating effect.

RESULTS

Model validation

Figure 3 compares our model predictions with the experimental data from Karnik *et al.* [1] (Figure 5b in that article) for the channel conductance. We stress here

Figure 3 Validation of the model by comparison with experimental work from Karnik et al. [1] (circles). Left: the model shows a similar trend but with an offset at pH = 7 (dotted line). Right: Close-up of the curves at pH = 5.6 (dashed line), i.e. the typical pH value for non-buffered, CO₂ saturated aqueous solution, showing the good agreement between experiments and simulations. The triangles and the squares refer to different pK values obtained from reference [14] and [15] respectively.

that no fitting is required. All the material characteristics, surface constants and electrolyte properties, were taken from other sources in the literature and the geometry was defined according to the fabrication details in [1].

The range of pH studied in the simulations includes the experimental results of Karnik *et al.*, which confirms the validity of the model (Figure 3, left). It also underlines the importance of pH control for reliable and consistent nanofluidic experiments.

Simulations were also performed with the two different sets of pK constants for SiO₂ found in literature [14, 15]. The results in Figure 3 show a similar trend to the experimental results, albeit with a bias. The bias between the curves corresponding to the different pK values, marked with triangles and squares respectively, is relatively important, which stresses the importance of

the adequate knowledge of the surface pK_a and pK_b.

As a last remark, it can be noted that some discrepancy between experimental and simulated results may stem from unknowns about the exact geometry used by Karnik *et al.*, for example with respect to the distance of the electrode to the entrance of the nanochannel in the reservoir.

Nanochannel-array design

Figure 4 (left) shows the concept and design of a nanochannel-array membrane engineered for gating capability. It is based on a nanoporous anodic alumina (AAO) membrane. Atomic layer deposition (ALD) techniques are suggested to deposit a double layer coating consisting of a metal layer as gate electrode and a dielectric layer as insulator, on the AAO structure. The

Figure 4 Left: Concept and fabrication scheme of the engineered nanochannel-array using an AAO membrane (top-left) and modelled geometry (bottom-right). Right: Behaviour improvement, in terms of tunability of the channel average ionic conductivity, of the array compare to the in-plane Karnik et al. [1] device. The gate voltage is normalized to the dielectric thickness to provide comparable data in terms of applied field strength (x-axis) and the nanochannel average ionic conductivity is normalized to the bulk conductivity (y-axis)

simulated device dimensions are 20 nm for the pore diameters, 1 μ m for the membrane thickness and 5-10 nm for the dielectric layer thickness, as shown in Figure 4 (left). In comparison to the device from Karnik *et al.*, the new design features a 60 times thinner dielectric layer, 120 times shorter channel length and two-third of the channel width. Moreover, the vertical channel geometry allows for a ~ 300 times larger effective cross-sectional area per device footprint, due to a pore density of about 100 pores/ μm^2 compared to ~ 30 channels/100 μm^2 for the planar configuration from Karnik *et al.* [1].

Besides increased throughput, the design promises a much higher ion selectivity and tuning at much lower potentials due to the reduction of the channel diameter, leading to a stronger overlap of the EDL and to that the gating length extends along the entire channel length.

A good measure for the tunability performance of a gated nanochannel is the change of the average channel ionic conductivity per change in gate electrostatic potential. For ease of comparison, the gate voltage is normalized to the gate oxide thickness (x-axis) and expressed in terms of the electrical field strength over the gate oxide. Here, we normalize the average channel ionic conductivity to the bulk ionic conductivity

$$\sigma_{\text{channel}}/\sigma_{\text{bulk}} = \left(\iiint \sigma dV / V_{\text{channel}} \right) / \sigma_{\text{bulk}}.$$

In accordance to the results from Figure 3, all parameters, except for the geometry, were kept unchanged.

The performances of the novel nanochannel-array membrane configuration and of Karnik *et al.*'s design are shown in Figure 4 (right). The model predicts a 37-46 times better tuneability performance compared to Karnik *et al.*'s device, confirming the promises of the new design.

CONCLUSION

We present the first predictive and today's most complete model of an electrostatically gated nanofluidic channel. The model was successfully validated against experimental data. A novel device design is introduced for which a ~ 40 times improvement is predicted in terms of tunability of the ionic conductivity. Our model approach is generic, allowing successful prediction for electrokinetic transport and hydrodynamic flow through nanochannels. It will be used as a base for further refinements by taking into account additional effects such as ion crowding [12] and/or more complex electrochemical interactions [13] such as specific ion adsorption or field-enhanced water dissociation.

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