

FIELD-EFFECT pH CONTROL IN NANOCHANNELS

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ABSTRACT

We demonstrate a novel capacitive method to change the pH in nanochannels. The device employs metal electrodes outside an insulating channel wall to change the electrical double layer potential by the field effect ('voltage gating'). We demonstrate that this potential change is accompanied by a release or uptake of protons from surface groups, resulting in a pH shift in the nanochannel, and a titration of solution compounds present. This pH actuation method avoids redox reactions and can be very useful as a "soft" way to change the pH in small volumes e.g. in bioassays or cell-based research, but also for detection in separation methods. We demonstrate the detection of 100 attomol of TRIS in the detection volume by titration. Importantly, the proton release mechanism does not rely on double layer overlap.

KEYWORDS: Nanochannel, pH control, nanofluidics, titration, actuation

INTRODUCTION

Glass channel walls have a negative surface charge at pH values above 3, resulting from deprotonation of silanol groups. Recently it was demonstrated that the deprotonation of these groups during capillary filling of nanochannels acidifies the filling solution, titrating dissolved compounds [1]. The surface charge on glass channel walls is normally exclusively determined by the chemical environment of the solution (pH, ionic strength), but can also be modified electrically through the application of an electrical potential difference between an electrode outside the channel wall and the filling solution. This so-called voltage gating process can be used to modify the electroosmotic flow or the ion permselectivity of the channel [2,3]. The change of the double layer potential in theory will be accompanied by a release or uptake of protons from the wall whenever the wall proton buffer capacitance cannot be neglected with respect to the double layer capacitance (figure 1) [4]. From basic electrical circuit theory, the released proton amount equals

$$N_{H^+} = V \cdot C_{ins} \frac{C_{buff}}{C_{buff} + C_{DL}} \quad (1)$$

where N_{H^+} is the released proton amount (C/m^2), V the applied potential (V), C_{ins} the insulator capacitance (F/m^2), C_{buff} the oxide buffer capacitance (F/m^2) and C_{DL} the double layer capacitance (F/m^2). C_{buff} is calculated from the proton buffer capacitance β (groups/ m^2) as $C_{buff} = q^2\beta/2.3kT$, where q is the unit charge (C) and kT/q the thermal voltage [4].

EXPERIMENTAL

Figure 2 schematically shows the device employed, with two gate electrodes insulated from the nanochannel solution by a 360nm thick LPCVD silicon nitride

wall. Devices with 860nm high nanochannels were cleanroom manufactured with the procedure previously published [2]. The channels were filled with a solution of 10mM KCl and 0.1mM fluorescein Na (pH 6.9) and an alternating square wave potential was applied between the gate electrodes of varying amplitude and frequency (typically 20V and 1 Hz).

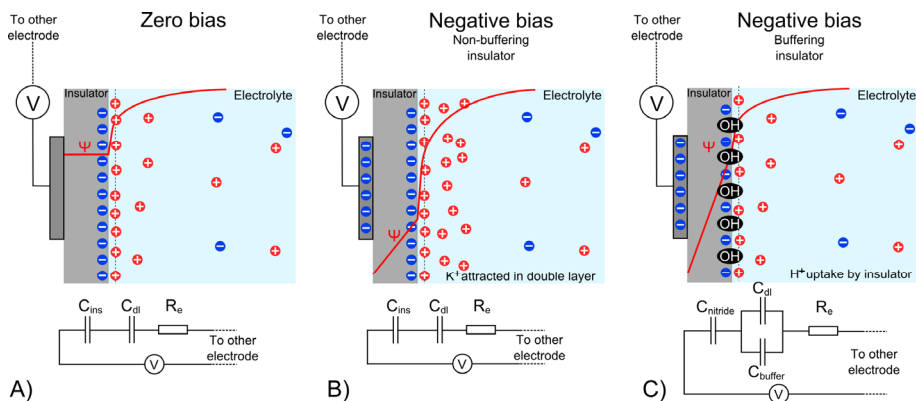


Figure 1. Equivalent electrical circuit of the device. **A)** At zero bias, the surface charge results from surface deprotonation and an equal but opposite charge resides in the solution. **B)** At negative bias and a non proton-buffering insulator surface, extra positive charge is attracted in the electrical double layer. **C)** At a proton-buffering insulator surface, the surface charge decreases because of proton binding, resulting in a proton uptake from solution. For the model see reference [4].

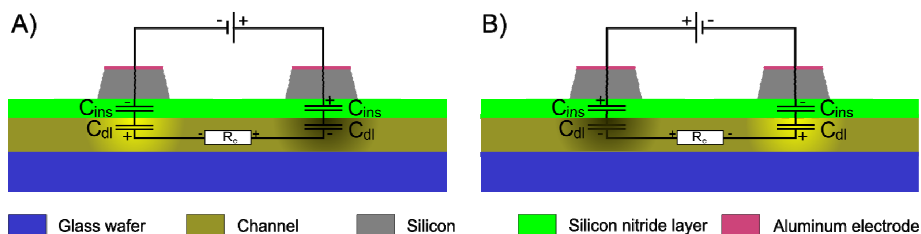


Figure 2. Device cross section and actuation procedure. **A)** In the first actuation phase, proton release occurs under the right electrode, proton uptake under the left electrode. **B)** In the second actuation phase, both processes occur under the opposite electrode.

RESULTS AND DISCUSSION

On application of a square wave potential difference between both electrodes, a fluorescence intensity change was observed under each electrode (figure 3). Since the fluorescence of fluorescein is pH dependent, varying between 10% and 90% from pH=6.2 to pH=7.2, it was concluded that this stems from fluorescein protonation. A possible contribution of redox reactions (Faradaic proton actuation) was excluded in two ways. The maximum leakage current at an applied voltage of -30V was -155pA,

which would only correspond to <5% of the observed signal. Furthermore the change of fluorescence intensity showed a typical RC behavior, stabilizing after 0.5 seconds. Figure 4 shows a linear dependence of observed fluorescence intensity amplitude and applied potential amplitude as predicted by equation (1). Addition of 0.1mM TRIS (100 attomol in the detection volume) could be detected (figure 4).

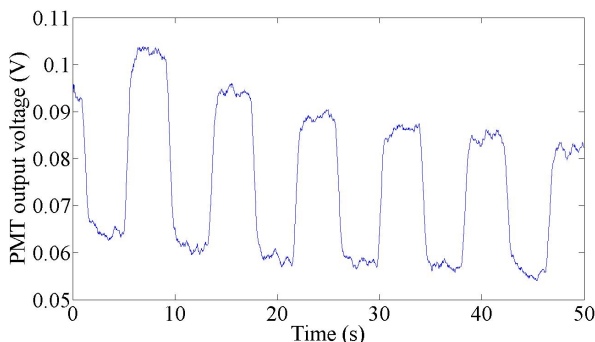


Figure 3. Fluorescence intensity change observed under an electrode. Applied ac-tuation voltage: 20V ampl, 0.25 Hz in 10mM KCl.

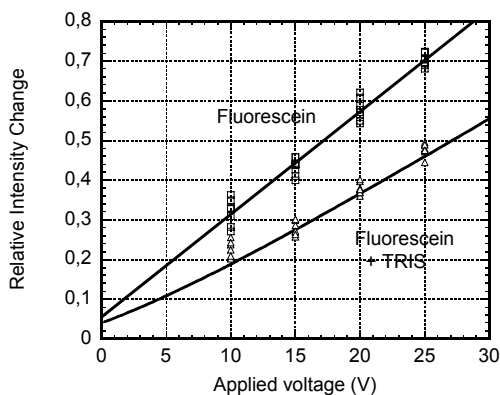


Figure 4. Fluorescence intensity change as a function of applied voltage for solu-tions with (0.1mM fluoresc., 10mM KCl) and (0.1mM fluoresc., 0.1mM TRIS, 10mM KCl). Lines are theoretical predictions for solutions resp. with pH=6.9 and 7.5.

OUTLOOK

The method presented can generally be applied for pH actuation in ultrasmall confined spaces. Since no redox reactions occur and it can be applied at physiological salt conc., it is eminently suitable for pH control in biological systems.

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