

UC Irvine

UC Irvine Previously Published Works

Title

Control of ionic transport through gated single conical nanopores

Permalink

<https://escholarship.org/uc/item/61t9w21g>

Journal

Analytical and Bioanalytical Chemistry, 394(2)

ISSN

1618-2650

Authors

Kalman, Eric B.
Sudre, Olivier
Vlassiuk, Ivan
et al.

Publication Date

2009-05-01

DOI

10.1007/s00216-008-2545-3

Peer reviewed

Control of ionic transport through gated single conical nanopores

Eric B. Kalman · Olivier Sudre · Ivan Vlassiuk ·
Zuzanna S. Siwy

Received: 14 October 2008 / Revised: 20 November 2008 / Accepted: 24 November 2008 / Published online: 17 December 2008
© The Author(s) 2008. This article is published with open access at Springerlink.com

Abstract Control of ionic transport through nanoporous systems is a topic of scientific interest for the ability to create new devices that are applicable for ions and molecules in water solutions. We show the preparation of an ionic transistor based on single conical nanopores in polymer films with an insulated gold thin film “gate.” By changing the electric potential applied to the “gate,” the current through the device can be changed from the rectifying behavior of a typical conical nanopore to the almost linear behavior seen in cylindrical nanopores. The mechanism for this change in transport behavior is thought to be the enhancement of concentration polarization induced by the gate.

Keywords Nanotechnology · Electroanalytical methods · Microfluidics/microfabrication

Introduction

Nanopores have attracted the interest of scientists from various fields [1]. Nanopores have a high surface-to-volume ratio; thus, ions and molecules passing through a pore cannot avoid interacting with the pore walls [2, 3]. These interactions

between the transported ions and the pore walls are the basis for the control of transport in nanopores. Nanopores with surface charge on the pore walls, for example, influence ionic transport by electrostatic interactions. This electrostatic control of ions is possible if the diameter of the pore is comparable to the thickness of the electrical double-layer. Ionic filters are the simplest nanoporous devices: a nanopore with negative (positive) surface charges will be filled predominantly with cations (anions) [3–5]. When voltage is applied across the pore, the current will be carried mostly by these counterions. Breaking the symmetry of the electric potential in a nanopore leads to more complex ionic devices, such as ionic diodes and ionic transistors [6–9]. An ionic diode is a system that conducts ions in one direction but does not conduct ions in the other [10–12]. Ionic transistors with electrically addressable gates allow for additional control of the ionic current with the so-called “gate voltage,” leading to ionic switches and amplifiers [13].

Research on transport properties of nanopores provides unique information on interactions on nanoscale. These studies also lead to the development of very important and practically relevant ionic systems for regulating transport of ions and molecules in water solutions. Current electronic devices cannot operate in solutions. The semiconductor transistor for electrons revolutionized the electronic industry, while building an ionic transistor has the potential to revolutionize chemical circuits, sensing devices, and building ionic logic systems with a similar degree of precision as is done with electrons. Ionic diodes and transistors can indeed become components of *ionic* circuits, which would allow for regulating, switching, amplifying, sensing, concentrating, and separating ions and molecules in water-based solutions mimicking similar processes in biological systems. Ionic transport regulating systems could be used in biosensors, drug-delivery, and lab-on-the-chip systems. We

Electronic supplementary material The online version of this article (doi:10.1007/s00216-008-2545-3) contains supplementary material, which is available to authorized users.

E. B. Kalman · I. Vlassiuk · Z. S. Siwy (✉)
Department of Physics and Astronomy, University of California,
Irvine, CA 92697, USA
e-mail: zsiwy@uci.edu

O. Sudre
Teledyne Scientific & Imaging, LLC,
Thousand Oaks, CA 91360, USA

would like ionic transistors to be able to control large currents passing through the device by low, therefore less energy-demanding, voltage gates. Moreover, lower voltage gates allow one to avoid unwanted electrochemical processes, which could interfere with the regulated transport.

Nanoporous ionic transistors prepared thus far are mostly applicable to controlling transport of large ions such as DNA and proteins [14, 15]. In this article, we would like to present a gated ionic device based on single conical nanopores in polymer films and demonstrate its application for controlling the transport of simple inorganic ions such as potassium and chloride ions. The gate of the transistor was introduced in a form of an insulated gold thin film at the narrow opening of the conical nanopores. The nanometer-scale opening of the pores allows one to influence ionic transport with gate voltages lower than 1 V. The gold thin film electrode in this device is an electrically addressable gate in contrast to the device reported by us before, in which the gate potential was changed by means of electrolyte pH [16].

Experimental

Preparation of nanopores Single conically shaped nanopores were prepared in 12 μm thick films of polyethylene terephthalate (PET) by the track-etching technique described before [17]. Briefly, this method entails the irradiation of polymer films with single energetic heavy ions [18] of ~ 2.2 GeV total kinetic energy and the subsequent chemical etching of the resulting ion tracks. The single-ion irradiation was performed at the Gesellschaft fuer Schwerionenforschung (UNILAC) in Darmstadt, Germany. The irradiated foils were subjected to an asymmetric chemical etching in 9 M NaOH performed in a conductivity cell [19]. The etchant was placed only on one side of an irradiated foil, while the other side of the foil was in contact with an acidic stopping solution. A voltage of 1 V was applied across the membrane, which allowed us to monitor the current passing through the foil during the etching process. We used two platinum electrodes and Keithley 6487 picoammeter/voltage source to apply the bias and measure the resultant current. In order to obtain larger pores, the etching continued after the moment of breakthrough (when the process of pore opening is indicated by a finite current) until an etching current of at least ~ 150 pA was measured, which indicates the formation of a pore with a sub-10 nm small opening. When the etching step was completed, the pores were washed with the acidic stopping solution and de-ionized water to neutralize any remaining etchant.

The diameter of the small opening was estimated using the conductivity method described before in [19]: the chambers of the conductivity cell were filled with 1 M

KCl, the platinum electrodes were replaced with Ag/AgCl electrodes, and a current–voltage curve was recorded. The slope of the current–voltage curve at low voltages is a measure of the pore resistance, which is related to the opening diameters of a conical nanopore. The diameter of the big opening D was determined from the so-called bulk-etch rate of the polymer material and the etching duration. For PET that is etched at 20 °C in 9 M NaOH, the bulk etch rate is equal to 2.13 nm/min [19]. The value of the pore diameter D is then determined from the formula: $D = 2 \times 2.13 \times t$ [nm], where t is time of etching in minutes [19]. The validity of this formula was confirmed by scanning electron microscopy studies [20]. The small opening of a conical nanopore is then the only unknown in the formula relating the pore resistance with its geometry. Nanopores used in this study had narrow openings between 5 and 15 nm. We would like to mention that direct scanning electron microscope imaging of nanopores obtained by the track-etching technique was performed only for nanopores with diameters larger than 30 nm [21]. Most probably due to the polymer surface roughness caused by the chemical etching and possible radiolysis by the microscope beam, imaging of smaller pores has not been yet successful. Their diameter is thus determined by the conductivity method, as described above.

It is also important to emphasize that as a result of chemical etching of PET foils performed in NaOH, the surface of the membrane and the pore walls have carboxyl groups at the density of ~ 1 group per square nanometer [22].

Deposition of gold and silica layers Once a pore's diameters were measured, the single-pore polymer foils were removed from the conductivity cell, rinsed in ethanol, and then dried in the air. In the next step, 12.5 nm of titanium, 50 nm of gold, 8 nm of titanium, and then 50 nm of silicon dioxide were deposited on the side of the membrane with the small opening. The metal and silica layers were deposited using the electron beam evaporator (Integrated Nanosystems Research Facility, University of California, Irvine, and Teledyne Scientific & Imaging). The gold film serves as the “gate” electrode used to supply the chosen potential at the surface of the membrane. Several thicknesses of the Au layer between 20 and 50 nm were tested for the device preparation. Although all these devices functioned, we found the thinner layers to be mechanically unstable, and the optimal thickness chosen was 50 nm.

The silicon dioxide serves to electrically isolate the gold from the electrolyte solution. The presence of titanium between the polymer membrane, the gold, and the silicon dioxide is to improve the adhesion of the gold and silica layers. To achieve an area where electrical contact to the gold layer could be made, a region of the membrane was masked after the deposition of gold and before the

deposition of the second layer of titanium and the silica layer. Figure 1 shows a scheme of the device. How much the layer deposition affects the pore geometry and its diameter is still unknown. However, nanopores with initial opening diameters less than 5 nm are typically closed as a result of the deposition. From these measurements, we infer that the deposition leads to reducing the pore diameter by at least several nanometers.

The electrode set-up and measuring ionic current Figure 1a shows the experimental set-up with Keithley 6487 picoam-

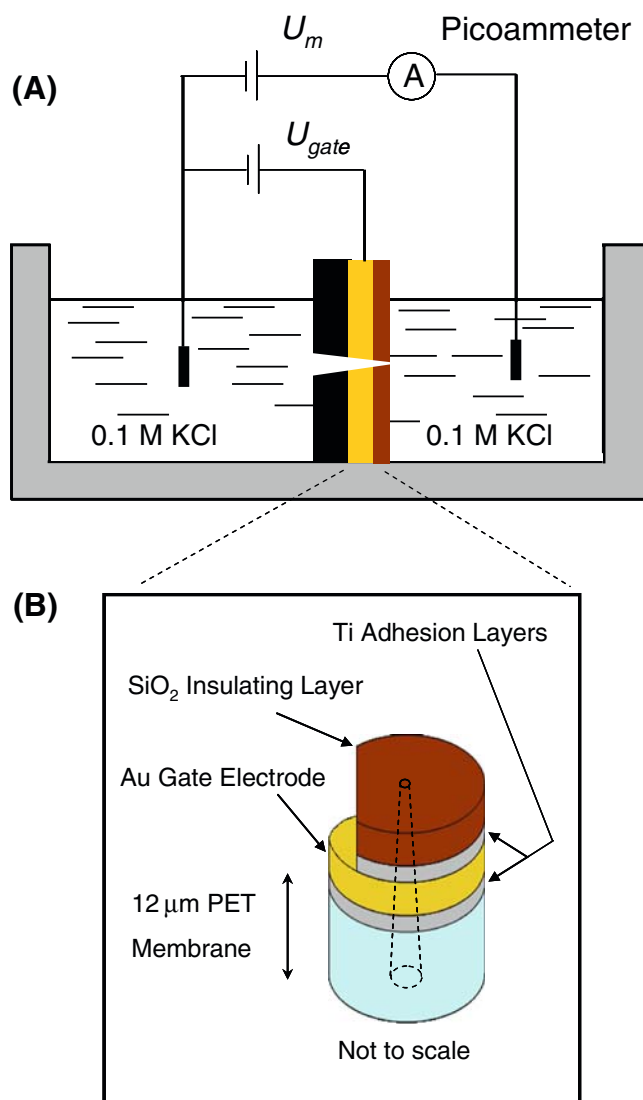


Fig. 1 Experimental set-up used for studying single conical nanopores with a gate. **a** A Tektronix function generator is connected to the gate, while the voltage across the membrane U_m is applied by the voltage source in the 6487 Keithley picoammeter/voltage source unit. The gate voltage U_{gate} is established with respect to the ground electrode, as marked on the scheme. A more detailed electronic circuit is shown in the Electronic Supplementary Material. **b** Scheme of a conical nanopore with metal and silicon dioxide layers

meter/voltage source and the function generator (Tektronix). The Keithley picoammeter provides the voltage across the membrane as well as measuring the current through the nanopore. The polarity of the voltage across the membrane U_m was established with respect to the side with the small pore opening; the ground electrode was inserted on the side of the membrane with the big opening. Thus, the positive voltage indicated that the cations moved from the narrow opening to the wide opening of a conical nanopore. The function generator's output supplies the gate voltage U_{gate} , referenced to the ground electrode. The current–voltage curves are recorded by sweeping the voltage between -2 and $+2$ V with 50 mV steps. Each voltage is applied for a time period of 1 s after which the current measurement is performed.

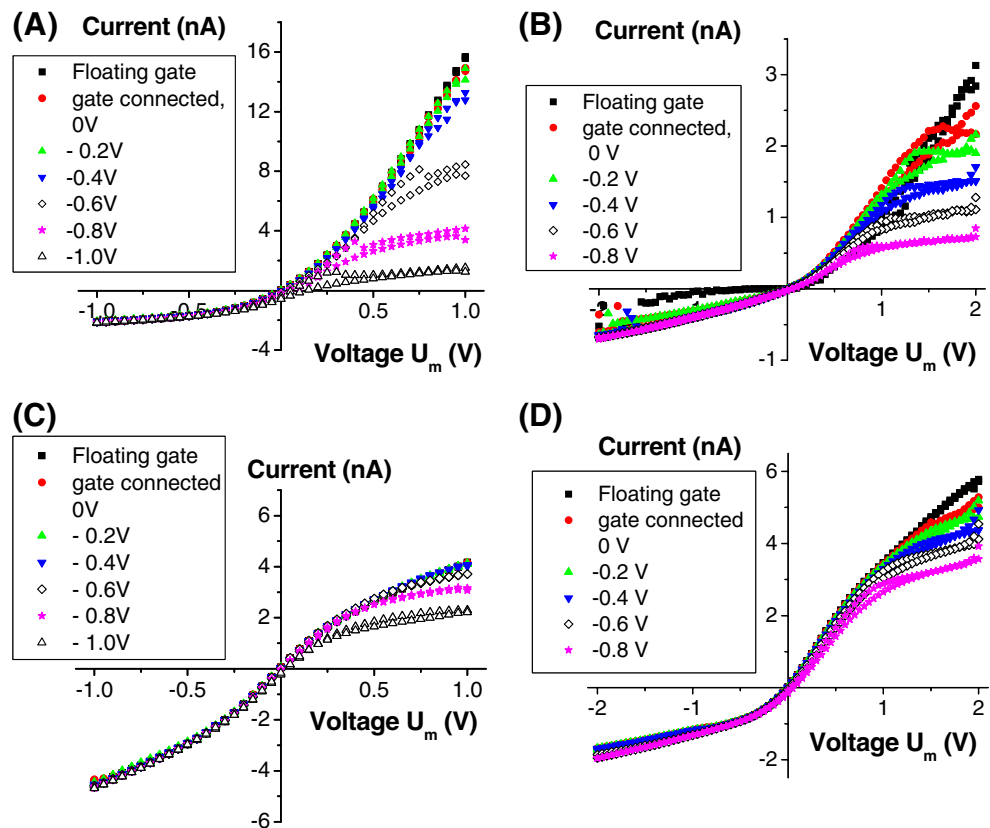
A more detailed electronic circuit is shown in the Electronic Supplementary Material.

Results and discussion

Figure 2 shows a series of current–voltage curves of single conical nanopores with metal and silica layers deposited on the side with the small pore opening. Without the gate, single conical nanopores in pH 8 are cation selective and rectify the current such that the preferential direction of cation flow is from the narrow opening to the wide entrance of the pore [7]. Thus, in our electrode configuration, we have larger currents for positive voltages than currents recorded for negative voltages. Placement of the ground electrode at the big opening of the pore—on the side opposite of the gold layer—assures that any current component must pass through the pore to be recorded, which is not the case with the opposite arrangement, in which any gate leakage current, which does not have to pass through the pore resistance, will dominate. Note that the electrode arrangement used here is reversed compared to the electrode arrangement that we reported in our previous publications (e.g. [7]); the ground electrode was on the narrow entrance of the cone, and the currents were higher for negative voltages.

As expected, for an insulated gold layer, connecting the gate and “applying” gate voltage $U_{gate}=0$ V typically did not change the current–voltage curve, at least in the voltage range between -1 and $+1$ V. Increasing the gate voltage U_{gate} from -200 to -800 mV gradually suppressed the positive currents, and at a certain value of the transmembrane voltage U_m , the currents would saturate. The voltage U_m at which currents started to saturate decreased with the increase of the gate voltage U_{gate} . For the pore shown in Fig. 2a, at $U_{gate}=-600$ mV, the currents saturated at $U_m \approx 0.7$ V, while at $U_{gate}=-1$ V, the currents started to saturate almost immediately. Applying negative gate voltage

Fig. 2 Current–voltage curves of single conical nanopores with a gate placed at the narrow opening of the pores. U_m is the voltage applied across the membrane. In the legend, the gate voltages U_{gate} are given. The devices were based on conical nanopores with the following diameters of the small opening **a** 10 nm, **b** 5 nm, **c** 6 nm, and **d** 12 nm. The diameters were measured before the metal and silica layer deposition. The measurements were performed in 0.1 M KCl, pH 8 (2 mM Tris buffer)



resulted therefore in diminishing the rectification properties of conical nanopores, and almost symmetric current–voltage curves were obtained.

The degree of the current suppression varied for different pores, but in 0.1 M KCl and $U_{gate} \approx -800$ mV, at least 30% reduction of the positive currents was observed at $U_m = 1$ V. Gate voltages larger than -800 mV were generally avoided due to more rapid degradation of the deposited layers most probably due to some electrochemical processes occurring at the surface (if the gold layer even very locally is not covered by silica). In all studied pores, the negative gate voltages did not influence the currents at negative U_m , thus the currents carried by potassium ions from the wide opening towards the small opening of the pores.

We also studied positive gate voltages of up to $+2$ V and found that they did not influence the transmembrane currents for either positive or negative transmembrane potentials U_m . This is because a silica layer is negatively charged when in contact with a solution of pH 8. We would have to apply a very high positive voltage to the gold film to overcome the negative charge in the silica layer (shown before with silica nanochannels [14, 15]).

In order to provide evidence that this current suppression occurred due to the gate, we performed a series of control experiments with a single conical nanopore without the deposited layers. The same electrical connection was made to the membrane surface as was made with the devices with

deposited layers, to which voltage was applied in the same way as in previous experiments. Figure 3 confirms that no effect of this gate voltage was observed, providing evidence that the application of the gate voltage to electron beam evaporated thin films are responsible for the recorded current suppression in the devices shown in Fig. 2.

The influence of possible leakage currents between the gate and the ground electrode on the transmembrane current

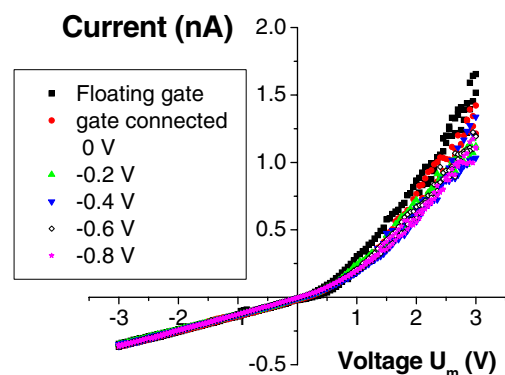


Fig. 3 Current–voltage curves of a single conical nanopore without the gate. The electrical contact to the gate was achieved by copper tape. U_m is the voltage applied across the membrane. In the legend, the gate voltages are given. The measurements were performed in 0.1 M KCl, pH 8 (2 mM Tris buffer). Diameter of the narrow opening of this pore was 3 nm

was also studied. We measured the leakage currents by removing the working electrode and applying voltage to the gate in the range 0 to -800 mV and measuring the current received by the ground electrode placed at the big opening of the pores. Thus, only currents passing through the nanopores were measured. We found that these currents were negative and very small: for the pore shown in Fig. 2b, the leakage currents at -800 mV gate did not exceed 2 pA. In comparison, the change in current from measurement when the gate had no potential applied, and $U_{\text{gate}} = -800$ mV is ~ 250 pA for $U_m = 1$ V. Thus, these leakage currents did not influence the transmembrane transport.

It is, however, important to mention that ion currents measured *outside the pore* in the bulk between the gate electrode and the ground electrode placed in the bulk (~ 0.5 cm away from the gate) were very large, reaching even several hundreds of nA. We think that these currents can be due to (1) charging of the double-layer at the gate or/and (2) electrochemistry at the gate. The latter effect was minimized by using low gate voltages (< 1 V) at which the electrolysis of water and thus electron exchange should not occur. Silica is not a perfect insulator either, and there are reports on the possibility of exchange of holes between silica beads and an electrolyte solution [23]. In our experimental set-up, the ground electrode was always placed at the wide opening of the pores; thus, only transmembrane currents were recorded.

These measurements confirmed that the current modulation that we obtain in a conical nanopore with a metal gate held at a chosen applied potential is not due to currents leaking from the gate into the pore. The current control is rather due to changes of ionic concentrations at the pore entrance induced by the gate.

Performance of the devices was studied in three KCl concentrations: 10 mM, 0.1 M, and 1.0 M KCl. We found that it was much easier to observe the current modulation at lower salt concentrations. At present, it is however still too early to draw conclusions concerning any systematic improvement of the device functioning with the decrease of KCl concentration.

Physical mechanism of the current gating in conical pores with deposited thin films of gold and silica In our original design of the device, we expected that a conical nanopore with an insulated metal layer at the pore opening would function as a field effect transistor. Changes to the gate voltage would thus change the electric potential in a conical nanopore right at the narrow opening. We thought that the asymmetry of the electric potential in the pore would be increased for negative U_{gate} compared to a conical nanopore without the gate [24, 25], resulting in an increased ion current rectification for negative U_{gate} . This is, however, not what we observed experimentally: negative gate voltages at

the narrow opening diminished the rectification properties of the pores.

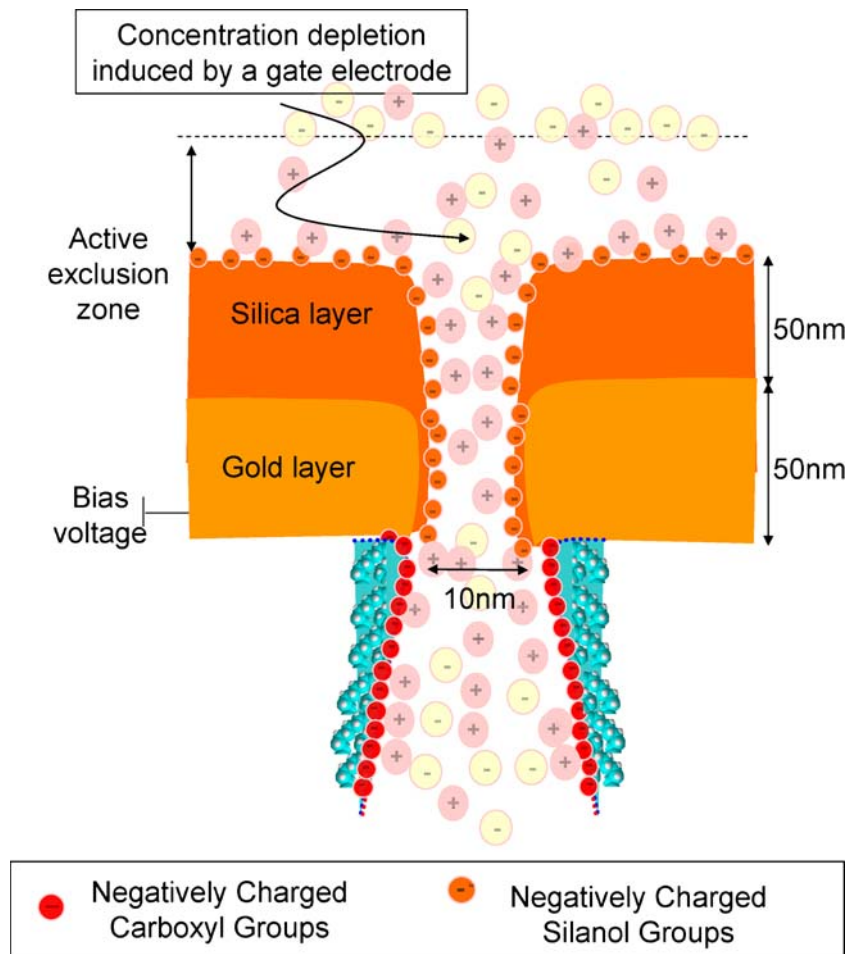
In order to explain the current suppression (Fig. 2), we focused on the ion current saturation, which occurred when negative gate voltages were applied for positive U_m . The current saturation indicates that the device cannot carry more current than a given value, although the voltage across the membrane increases. We think that the ion current saturation results from the concentration polarization at the side of the membrane with the gate, which limits the number of ions available for transport. Figure 4 explains this concept in more detail. For positive voltages across the membrane (U_m), potassium ions move towards the gate and through the pore, while anions are pulled away from the gate. This effect of the gate electrode on the ionic concentrations next to the pore opening is possible since, as we demonstrated, the gate can, in fact, act as an electrode on which charging of the electrical double layer (or electrochemistry) can occur. These processes do not contribute directly to the transmembrane transport by leaking ions into the pore, but they change the ionic concentrations in the proximity of the tip opening. Since the number of anions at the small opening of a pore decreases, the number of cations has to diminish as well so that electroneutrality is fulfilled. The ion current is then saturated when the “demand” for cations by the pore exceeds the number of cations available for the transmembrane transport. Increasing the gate voltage widens the region with depleted number of ions, which in turn decreases even stronger the number of cations that are available for transport. The rate at which cations arrive at the pore mouth to be transported through the pore can also be decreased by the negative gate voltage.

This scenario also explains why the cation currents flowing in the direction from the big opening to the small opening of the pore (those recorded for negative voltages U_m) are not influenced by the gate. Since the pore is cation selective and the number of cations at the big side of the pore is not influenced by the gate, the pore conducts as if the gate was not present.

Unanswered questions and future studies Our experiments show the possibility to control ionic transport through a single conical nanopore by means of gate voltage. We think that the gate voltage in our system induces concentration polarization at one of the pore entrances, which in turn limits the number of ions that are available for transmembrane transport.

There are several observations in our system which need further investigation. One of them is the current saturation that we observe in some devices even in the case with 0 V gate applied (see Fig. 2d for $U_m > 1$ V). We do not know yet how the deposited layers change the geometry of the

Fig. 4 Concentration polarization induced by the metal gate present at the small opening of a conical nanopore. As anions are pulled away from the pore face, electroneutrality demands the concentration of cations near the pore decreases as well



individual pores: pores of similar pore diameters show different levels of current control after the metal and silica deposition. We will investigate the pore geometry by preparing the devices with multi-pore membranes and looking at their cross-sections with the scanning electron microscope.

Our future efforts will be directed towards the preparation of the silica layer in a chemical way, which we expect will improve its stability. We also plan to chemically modify the layer in order to diminish its intrinsic surface charge to see the influence of positive gate voltage. As it was demonstrated with silica nanochannels, it is possible to induce positive potential on such chemically modified silica layers already with low gate voltages of ~ 1 V [15]. Experiments with positive potential on the gate could provide further evidence supporting the concentration polarization hypothesis of the functioning of the device.

Conclusions

We presented a system of single conical nanopores with tunable rectification properties achieved by a metal gate

situated at the narrow entrance of the pores. The gate voltage switches the characteristic of the pores from a rectifier to a symmetric current–voltage curve. This current modulation is obtained with gate voltages lower than 1 V. We think that the mechanism of this current-tuning involves changes in the ionic distributions at the pore entrance so that concentration polarization occurs. Since the system offers a possibility to switch the current rectification on/off, we think it can become the basis for ionic logic devices and ionic amplifiers. We also believe that it can be applied for inducing pumping of ions. By pumping, we mean transport of ions against their concentration gradient. Oscillating positive and negative local electric fields at the gate will cause periodic changes of the ionic concentrations at the pore entrance, which can be the basis for ionic pumping by the flashing ratchet mechanism [26–28].

As the next step, we would like to introduce this layered gating mechanism into the recently prepared ionic diodes [10]. A perfect ionic diode can be considered as a rectifier in which currents can flow only in one direction and do not flow in the other. Such ionic diodes were recently prepared based on nanopores with patterned pore walls so that there was a zone of the pore walls with positive surface charges

in contact with a zone with negative surface charges [10, 11]. These patterned nanopores will be equipped with a metal gate, which we expect will lead to a system that allows for a more complete shutting off of the current.

Acknowledgment This work was supported by the National Science Foundation (CHE 0747237). ZS is an Alfred P. Sloan Research Fellow. The single-ion irradiation was performed at the Gesellschaft fuer Schwerionenforschung, Darmstadt, Germany. We are grateful to Dr. Phan Vu for deposition of metal and silica layers.

Open Access This article is distributed under the terms of the Creative Commons Attribution Noncommercial License which permits any noncommercial use, distribution, and reproduction in any medium, provided the original author(s) and source are credited.

References

1. Dekker C (2007) *Nat Nanotech* 2:209–215
2. Schoch RB, Han J, Renaud P (2008) *Rev Mod Phys* 80:839–883
3. Plecis A, Schoch RB, Renaud P (2005) *Nano Lett* 5:1147–1155
4. Nishizawa M, Menon VP, Martin CR (1995) *Science* 268:700–702
5. Vlassiuk I, Smirnov S, Siwy Z (2008) *Nano Lett* 8:1978–1985
6. Daiguji H, Yang P, Majumdar A (2004) *Nano Lett* 4:137–142
7. Siwy ZS (2006) *Adv Funct Mater* 16:735–746
8. Astumian RD, Hanggi P (2002) *Phys Today* 33–39 (November)
9. Daiguji H, Oka Y, Shirono K (2005) *Nano Lett* 5:2274–2280
10. Vlassiuk I, Siwy ZS (2007) *Nano Lett* 7:552–556
11. Karnik R, Duan C, Castelino K, Daiguji H, Majumdar A (2007) *Nano Lett* 7:547–551
12. Vlassiuk I, Smirnov S, Siwy Z (2008) *ACS Nano* 2:1589–1602
13. Fan R, Yue M, Karnik R, Majumdar A, Yang P (2005) *Phys Rev Lett* 95(1–4):086607
14. Karnik R, Fan R, Yue M, Li D, Yang P, Majumdar A (2005) *Nano Lett* 5:943–948
15. Karnik R, Castelino K, Majumdar A (2006) *Appl Phys Lett* 88(1–3):123114
16. Kalman B, Vlassiuk I, Siwy ZS (2008) *Adv Mater* 20:293–297
17. Fleischer RL, Price PB, Walker RM (1975) *Nuclear tracks in solids. Principles and applications*. University of California, Berkeley, Berkeley
18. Spohr, R. German Patent DE 2 951 376 C2, 1983. b) R. Spohr, US Patent 4369370, 1983
19. Apel PY, Korchev YE, Siwy Z, Spohr R, Yoshida M (2001) *Nucl Instrum Meth B* 184:337–346
20. Wharton JE, Jin P, Sexton LT, Horne LP, Sherill SA, Martin CR (2007) *Small* 3:1424–1430
21. Harrell CC, Choi Y, Horne LP, Baker LA, Siwy ZS, Martin CR (2006) *Langmuir* 22:10837–10843
22. Wolf-Reber A Aufbau eines Rasterionenleitwertmikroskops. Stromfluktuationen in Nanoporen, PhD dissertation, ISBN 3-89825-490-9, dissertation.de, 2002
23. Dimitrijevic NM, Henglein A, Meisel D (1999) *J Phys Chem B* 103:7073–7076
24. Siwy Z, Fulinski A (2002) *Phys Rev Lett* 89(1–4):198103
25. Cervera J, Schiedt B, Ramirez P (2005) *Europhys Lett* 71:35–41
26. Hanggi P, Bartussek R (2006) *Lecture Notes Phys* 476:294–308
27. Astumian RD (2007) *Science* 276:917–922
28. Reimann P, Hanggi P (2002) *Appl Phys A* 75:169–178