

Surface-Charge-Governed Ion Transport in Nanofluidic Channels

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A study of ion transport in aqueous-filled silica channels as thin as 70 nm reveals a remarkable degree of conduction at low salt concentrations that departs strongly from bulk behavior: In the dilute limit, the electrical conductances of channels saturate at a value that is independent of both the salt concentration and the channel height. Our data are well described by an electrokinetic model parametrized only by the surface-charge density. Using chemical surface modifications, we further demonstrate that at low salt concentrations, ion transport in nanochannels is governed by the surface charge.

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Nanoscale fluidic channels represent a new regime in the study of ion transport. Recent advances in the fabrication of ultraconfined fluidic systems such as nanoscale “lab-on-a-chip” type devices [1–3] and synthetic nanopores [4–6] raise fundamental questions about the influence of surfaces on ion transport. In particular, surface charges induce electrostatic ion (Debye) screening and electrokinetic effects such as electro-osmosis, streaming potentials, and streaming currents [7–9] that may have large effects on conductance in nanochannels, as suggested by studies of colloidal suspensions [10] and biological protein channels [11]. Here we present experiments that directly probe ion transport in the nanoscale regime, and reveal the role of surface charge in governing conductance at low salt concentrations.

Nanofluidic channels [Fig. 1(a)] were fabricated following a silicate bonding procedure similar to that of Wang *et al.* [12]. Briefly, channels 50 μm wide and 4.5 mm long were patterned between 1.5 mm \times 1.5 mm reservoirs using electron beam lithography on fused silica substrate. A reactive CHF_3/O_2 plasma then etched into the fused silica at a rate of 30 nm/min, and was timed to stop when the desired submicron channel depth was attained. The depth of the resulting channel, h , was measured using an α -stepper profilometer. The channels were sealed by first spinning a 20 nm layer of sodium silicate from 2% solution onto a flat fused silica chip, then pressing the silicate-coated surface to the patterned channel surface, and finally curing the device at 90°C for 2 h.

The channels were filled by introducing distilled, deionized (18 M Ω cm) water into the large fluidic reservoirs, from which point capillary forces were sufficient to draw the water across the channels. The electrical voltage source and IV converter were connected to the fluidic channel with negligible resistive loss via silver wires inserted into the reservoirs [Fig. 1(b)]. The channels were cleaned of ionic contaminants using electrophoretic pumping: The ionic current was observed to decay while 10 V were applied across the channels to drive out ionic impurities. The reservoirs were periodically flushed with fresh solution until the current equilibrated to a mini-

imum, which typically took ~ 20 min. This procedure was also followed to replace different dilutions of 1 M potassium chloride (KCl), 10 mM TRIS, $p\text{H} = 8.0$ aqueous salt solution that were tested in the channels. The KCl concentration is denoted n . The dc conductances of channels were determined by fitting the slope of the ionic current as a function of the applied voltage, which was stepped from -5 to $+5$ V in 1 V intervals every 2 s, in which time current transients were observed to decay.

We have found ionic transport in silica nanochannels to be characterized by a significant enhancement in

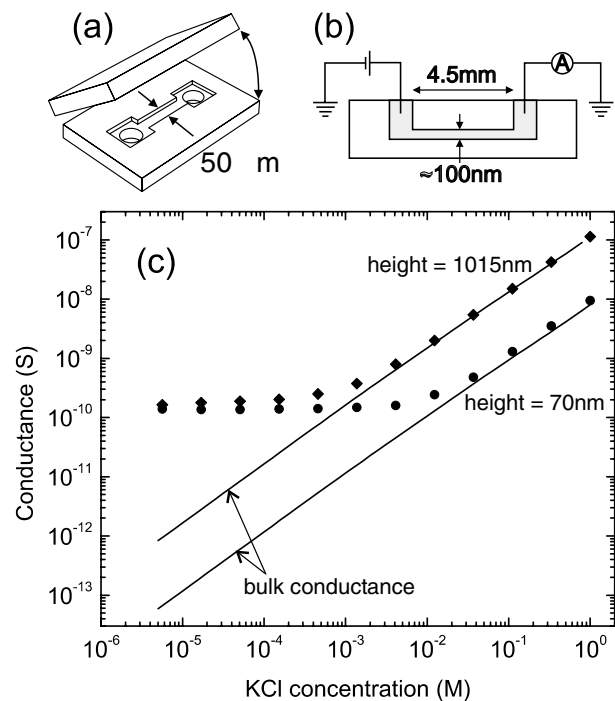


FIG. 1. Illustrations of (a) nanochannel assembly and (b) cross-sectioned side view with the electrical measurement apparatus. (c) Conductance of $h = 1015$ and 70 nm aqueous-filled, fused silica channels as a function of n . The lines depict the conductance expected in each channel from the conductivity of the bulk solution.

conductance relative to the bulk properties of the fluid at low n . Figure 1(c) shows the n dependence of the dc conductances for a 1015 nm high channel and a 70 nm high channel, compared to the expected conductances of idealized, inert channels, that were predicted from the measured channel dimensions and the bulk fluid conductivity [13]. At high n , the measured conductances increased linearly with h and n , following the expected behavior. At low n , however, the measured channel conductances exhibited a striking saturation at a value that was independent of both h and n . The degree of transport in the nanochannels at low n ($\sim 10^{-5}$ M) exceeded that expected in idealized channels by orders of magnitude.

We attribute the low-salt ionic transport behavior in nanochannels to the electrostatic effects of the channel surface charge on the fluid. A charged surface in contact with an ionic solution attracts oppositely charged, mobile counterions while repelling co-ions so as to form a charged layer, called the double layer, that screens the net, immobile surface-charge density, σ [8]. The requirement of charge neutrality suggests that the number of mobile counterions in a channel will exceed the bulk ion contribution and dominate transport when $|\sigma| > enh$. The transport of potassium counterions therefore explains the limiting conductance behavior of our channels at low n . Here we describe the consequences of charged channel surfaces using an extension of the electrokinetic transport model treated analytically by Levine *et al.* [14], and imposing a constant σ as a boundary condition.

The equilibrium electrostatic potential at height y from the channel midplane, $\psi_0(y)$, is described by the mean-field Poisson-Boltzmann equation for a monovalent salt,

$$\frac{d^2\psi_0}{dy^2} = \frac{k_B T \kappa^2}{e} \sinh\left(\frac{e\psi_0(y)}{k_B T}\right), \quad (1)$$

where e is the electron charge, k_B is the Boltzmann constant, T is the temperature, and $1/\kappa$ is the Debye screening length, defined by $\kappa^2 = 2e^2 n / (\epsilon \epsilon_0 k_B T)$, where ϵ_0 is the permittivity of free space and ϵ is the dielectric constant of water. The analytical solution for $\psi_0(y)$ for a symmetrical channel can be expressed as [15]

$$\psi_0(y) = \psi_0(0) + 2 \ln\left(\text{CD}\left(\frac{\kappa y}{2} e^{-\psi_0(0)/2} \left| e^{2\psi_0(0)}\right.\right)\right), \quad (2)$$

where $\text{CD}(u|k)$ is the Jacobian elliptical function with argument u and parameter k . The density of positive and negative ions, n_+ and n_- , are related to the potential by the Boltzmann equation, $n_{\pm}(y) = ne^{\pm e\psi(y)/k_B T}$. A voltage, V , applied across the channel of length, L , generates a parallel electric field, $E = V/L$, that modifies the potential as $\psi = \psi_0 + Ex$, and drives the flow of ions.

The fluid flow induced by and contributing to the transport of ions is described by the Navier-Stokes equation in the absence of a hydrostatic pressure gradient:

$$\eta \frac{d^2 u(y)}{dy^2} - E \epsilon \epsilon_0 \frac{d^2 \psi}{dy^2} = 0, \quad (3)$$

where $u(y)$ is the fluid velocity along the channel at height y , and η is the viscosity. The no-slip boundary condition is imposed at the channel walls, $y = \pm h/2$.

The ionic current, I , is calculated as the superposition of conductive and convective contributions, $I = ew \int_{-h/2}^{h/2} \{[u(y) + \mu E]n_+(y) - [u(y) - \mu E]n_-(y)\} dy$, where μ is the ion mobility, and w is the channel width. The solution for the channel conductance obtained from Levine *et al.* is [14]

$$I/E = ne\mu h(1 + H), \quad (4)$$

where the correction to the bulk conductivity, H , is

$$H = \cosh\left(\frac{e\psi_0(0)}{k_B T}\right) - 1 + \frac{\mathcal{E}}{4nk_B T h} \left(1 + \frac{4\epsilon \epsilon_0 k_B T}{e\mu \eta}\right), \quad (5)$$

where $\mathcal{E} = \epsilon \epsilon_0 \int_0^{h/2} \left(\frac{d\psi_0(y)}{dy}\right) dy$ is the electrostatic field energy in the channel per unit area.

We introduce a crucial, new element to the electrokinetic model of Levine by imposing a constant σ as a boundary condition. Gauss's law relates σ to the electrostatic potential gradient at both channel walls,

$$\sigma = \mp \epsilon \epsilon_0 \frac{d\psi_0(y)}{dy} \Big|_{y=\pm h/2}. \quad (6)$$

Equations (2)–(6) define transcendental equations for the conductance that must be solved numerically. One already gains physical insight into the predictions of the model by considering the following limiting cases: At high n , where $\kappa h \gg 1$ and $|\sigma| \ll enh$, we recover the inert channel behavior, with $I/E \approx 2ne\mu wh$. At low n , where $\kappa h \ll 1$ and $|\sigma| \gg enh$, the conductance is independent of h and n , behaving as $I/E \approx |\sigma| \mu w (1 + \frac{4\epsilon \epsilon_0 k_B T}{e\mu \eta})$. This corresponds to the electrophoretic transport of counterions, where the second term in the brackets represents the conductance enhancement due to electro-osmosis. The model therefore predicts that σ governs the conductance of nanochannels at low n .

Figure 2 compares the measured n dependence of the conductances of five fused silica channels with h ranging from 70 to 1015 nm to the predictions of our transport model [16]. The model fits the measured conductance values over the full range of h and n tested. The inset of Fig. 2 shows the values obtained for the model's lone fitting parameter, σ , as a function of h . The values of σ are approximately constant as a function of h , and the typical value of ~ 60 mC/m² compares well to the value of ~ 100 mC/m² measured by charge titration for SiO₂ at $n = 1$ mM [17].

The electrokinetic model accurately predicts the conductance saturation observed in silica nanochannels. Further refinements to the model should reconcile the observed, n -independent conductance saturation with the expected reduction in σ with decreasing n and h

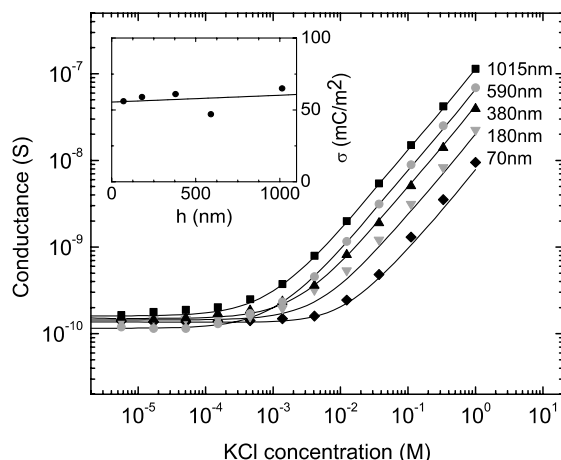


FIG. 2. Channel height dependence of ionic conductance behavior. The conductance of fluidic channels is plotted against n for $h = 1015, 590, 380, 180,$ and 70 nm. The curves represent fits of the data to the electrokinetic model. The inset displays the fit values of σ as a function of h .

due to the chemistry of proton adsorption [15,17,18]. In particular, the sensitivity of conductance measurements to surface protonation will decrease if μ for the counterions nearest the surface is enhanced with their decreasing surface concentration. Also, if the mobility of adsorbed surface protons is finite, their transport will compensate the decreased transport potassium counterions. Such descriptions of double layer transport treated in dynamic Stern layer theories [10] are ignored here, as are such complicating effects as finite ion size [8,19] and ion correlations [19]. Our model nonetheless succeeds in capturing the essential features of ion transport in nanochannels with a single parameter, σ , that is comparable to values measured independently by charge titration. The data and model also suggest observable effects in channels as large as $100 \mu\text{m}$ at $n \sim 10 \mu\text{M}$, emphasizing the general relevance of surface-charge effects to relatively large-scale channels, far from the double layer overlap regime.

In order to test the influence of σ on ionic transport in nanochannels, we directly altered σ by chemical surface modification with octadecyltrichlorosilane (OTS), which self-assembles on silica to form a covalently bound monolayer that reduces $|\sigma|$ because of the neutral CH_3 head group. Nanochannels were filled with toluene containing mM concentrations of OTS, and then flushed with toluene after 1 h. The channels were rinsed in acetone, then isopropanol, and were then blown dry under nitrogen before curing at 120°C for 2 h. Under this treatment, OTS molecules react with the negatively charged silanol surface groups (SiO^-) and each other, resulting in a covalently bound OTS layer that is charge neutral [20]. This OTS treatment rendered channels too hydrophobic to fill with purely aqueous solution; therefore, ion transport in these channels was tested using aqueous salt solution mixed with 50% isopropanol by volume. We expect the

extent of OTS surface coverage, and hence the degree of surface-charge neutralization, to correlate with the OTS concentration used in the treatment.

The effect of OTS surface modification on the conductance properties of 87 nm high fused silica channels is shown in Fig. 3, where the conductance of an untreated channel is compared to channels treated with 1 mM OTS and 3 mM OTS as a function of n . At high n , we observed nearly identical conductance values that scaled with n as we would expect in the bulk. At low n , the conductances of the channels saturated at values that clearly depended on the surface treatment: The untreated channel saturated at the highest conductance, followed by the channel treated with 1 mM OTS, and then the channel treated with 3 mM OTS.

The data were compared to the ion transport model by first fixing the unknown values of μ , η , and ϵ for the water-isopropanol mixture so as to fit the high- n behavior. This three-parameter fit is not unique and therefore excludes numerical predictions of σ . However, since the conductance is linear in σ at low n , it is possible to compare the relative magnitudes of σ between the three channels. Assigning the value σ_0 to the untreated silica channel, we find that σ was reduced to $0.35\sigma_0$ by the 1 mM OTS treatment and to $0.18\sigma_0$ by the 3 mM OTS treatment—a factor of 5 reduction relative to the untreated silica channel.

The role of σ was also tested by varying $p\text{H}$. The negative surface-charge density of fused silica is determined by the density of SiO^- surface groups, and depends on the $p\text{H}$ of the solution [17]. As the H^+ concentration is increased ($p\text{H}$ is lowered) for a given n , SiO^- groups become protonated to become neutral SiOH , reducing $|\sigma|$. As a control, we have also investigated a nanochannel coated with the polymer poly-L-lysine (PLL), whose surface-charge density exhibits the

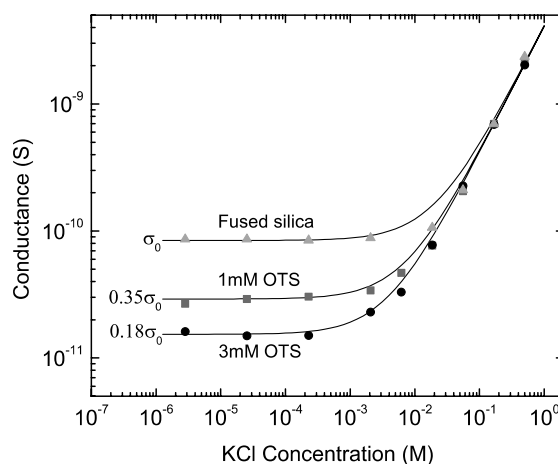


FIG. 3. Effect of surface-charge density on ion transport in 87 nm high fused silica channels. The conductance was measured in a 50%/50% mixture of isopropanol and diluted 1 M KCl, 10 mM TRIS, $p\text{H} = 8.0$ aqueous solution in fused silica channels treated with the indicated concentration of OTS.

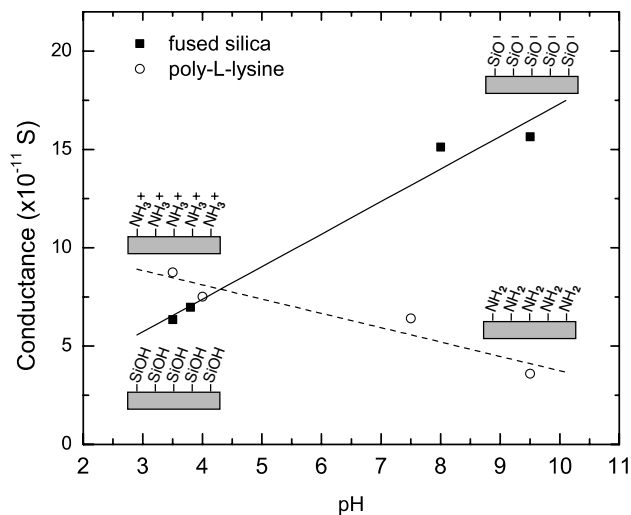


FIG. 4. Effect of pH -adjusted σ on the conductance of a $h = 380$ nm channel at $n = 10^{-4}$ M. A linear fit of the conductance to the pH is consistent with the expected increase in $|\sigma|$ for silica at high pH . That trend was reversed by coating the channel with PLL, whose $|\sigma|$ is expected to decrease with pH .

opposite pH dependence. The reactive groups on the surface of PLL, NH_2 , become positively charged NH_3^+ groups at low pH , increasing $|\sigma|$ for this positively charged surface [21].

Figure 4 shows the conductance of a $h = 380$ nm fused silica channel filled with $n = 10^{-4}$ M aqueous solution as a function of pH that was adjusted by the addition of hydrochloric acid or sodium hydroxide. An increase in conductance was observed with increasing pH . The same channel was then coated with PLL by filling it with 2% solution of PLL by weight, then flushing it with distilled, deionized water after 2 min. The conductance of the channel after the PLL treatment revealed a decreasing trend with increasing pH . The dependences of the conductance on pH for both channel surfaces are in excellent agreement with the expected behavior of $|\sigma|$.

The results of the surface modification experiments, both by OTS treatment and by pH adjustment, confirm the hypothesis of σ -governed ion transport in nanochannels at low n . The OTS treatment reduced $|\sigma|$, and thereby the conductance, in the saturated, low- n regime without affecting the fluid. Adjusting pH raised or lowered $|\sigma|$ without affecting the exposed surface area of silica or PLL. Although n was raised as high as $\sim 3 \times 10^{-4}$ M at $pH = 3.5$ due to the inclusion of sodium ions when the pH was adjusted, we expect the channel to remain in the low- n regime, and the increased conductivity of the fluid cannot explain the decreased conductance observed in the fused silica channel. These results exclude the possibility that a parallel conductance path (through the silica, for example) lead to conductance saturation.

In conclusion, we have shown that the transport of ions in nanofluidic channels under low salt conditions is dominated by the transport of counterions that must accumu-

late near charged channel walls to maintain charge neutrality. The effect is well described by an electrokinetic model that combines the Poisson-Boltzmann distribution of ions with the Navier-Stokes description of the fluid, and imposes a constant σ as a boundary condition.

These results have clear implications for nanofluidic technology. By modifying the surface potential inside a fluidic channel using a gate electrode, others have demonstrated that electro-osmotic flow can be controlled [22] and proposed that ionic flow can be regulated when double layer overlap occurs [23]. Our findings suggest the realization of an electrostatic-gate-controlled ionic current device, analogous to an ionic transistor, with readily manufacturable channel dimensions that do not require double layer overlap.

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